An investigation of surface electronic structure and electron-phonon interaction by photoemission spectroscopy

Ph.D. thesis

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Preface

The present thesis is submitted to the Faculty of Science at the University of Aarhus, Denmark, in order to fulfill the requirements for obtaining the Ph.D. degree in physics. The work has been carried out under the supervision of Philip Hofmann in the period from medio 1998 to medio 2001, in the photoemission/surface science group at the Institute for Storage Ring Facilities (ISA), University of Aarhus. The experiments have mostly been conducted at the beamline for angle-resolved photoemission spectroscopy at the storage ring ASTRID in Aarhus. In addition, 6 weeks of beamtime were spent at the synchrotron Elettra in Trieste, Italy.

The subject of the thesis is, as the title reflects, an investigation of surface electronic structure and electron-phonon interaction by photoemission spectroscopy. A significant part of the work carried out during my time as a Ph.D. student is, however, not reflected in the title. When I joined the group, the equipment basically consisted of an empty lab and a hole in the wall for the synchrotron radiation beamline. Today we have a fully operational beamline for state-of-the-art angle-resolved photoemission experiments. Obviously much effort has been devoted to get this far.

Acknowledgements

I owe a debt of gratitude to many people who have been involved in the work leading to the present thesis. First of all, it has been a great pleasure to be a part of the photoemission/surface science group. The helpful and lighthearted spirit made the efforts a lot less strenuous.

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Publications and presentations

The present work has so far resulted in the following publications:


- **Photoemission lineshape at finite temperature**, C. Søndergaard, C. Schultz, P. Hofmann, Elettra highlights 2001


- **Interplay between the electronic structure and the phase transition on α-Ga(010)**, C. Søndergaard, C. Schultz, S. Agergaard, H. Li, S. V. Hoffmann, Z. Li, P. Hofmann, C. Grüttner, J. H. Bilgram, in preparation


- **The electronic structure of α-Ga(010)**, C. Søndergaard, C. Schultz, S. Agergaard, S. V. Hoffmann, Z. Li, P. Hofmann, in preparation


Parts of the work in the thesis have been presented in talks given by the author at the following conferences:

- American Physical Society March Meeting, Minneapolis, USA, March 2000. ‘The direct-transition intensity in photoemission from Al(001)’ [T9.004].

- Danish Physical Society Annual Meeting, Nyborg, Denmark, June 2001. ‘Photoemission lineshape at finite temperature’ [FF10].

- 20th European Conference on Surface Science (ECOSS-20), Krakow, Poland, September 2001. ‘The surface electronic structure of Bi(110)’ [ES-1].
Introduction

Matter in the solid state displays a wide and challenging diversity of phenomena. In order to ease the understanding, we like to classify the solids with respect to their properties. As an example, we may crudely classify solids with respect to electrical conductivity as insulators, semiconductors, or metals. But this classification misses the interesting properties of semimetals, metals on the verge of being semiconductors, and superconductors, materials that abruptly lose electrical resistivity below a certain temperature. Furthermore, the properties may not even be isotropic. In some cases the electrical conductivity depends on the crystallographic directions; in the extreme limit we encounter materials conducting electricity in two-dimensional planes, or even just along one-dimensional lines. In addition, every solid needs to have surfaces, and they have unique properties themselves and may be better/worse conductors than the bulk. The microscopic origin of these macroscopic observables are the interactions between the valence electrons of the constituting atoms. Various theoretical approaches and concepts have been suggested to describe and model matter in the solid state. And the choice of model matters: for instance, in a simple band structure picture NiO will be a metal, but in fact it is a perfect insulator. Positively, this prevalence of not so clear-cut classification schemes, and theoretical models not embracing all observed properties, is a reflection of the diversity and richness of phenomena found in solid state physics. A well-proven fundamental concept, however, is the electronic structure of a material. By the electronic structure we understand the allowed energy states for the electrons involved in the bonding of the material. The electronic structure is the fingerprint of the solid, giving clues about the various properties.

Photoemission spectroscopy (PES) is a much applied experimental technique when it comes to extracting information about the occupied electronic structure of solids and their surfaces. The principle behind PES is the photoelectric effect where an electron is emitted from a solid, molecule, or atom upon the absorption of a photon. Basically, in photoemission spectroscopy the kinetic energy, and to some extent angle-resolved, distribution of the photoemitted electrons is measured. A very basic prerequisite for doing PES (meaningfully) is an answer to the question: How does the PES spectra actually relate to the electronic structure of the material? In the 70s it was realized that peaks in
spectra from angle-resolved ultraviolet photoemission spectroscopy (ARUPS) on crystalline solids could be assigned to states in the bandstructure, if a few simple assumptions were made. In other words: mapping of the electronic structure would be possible with ARUPS. The technical demands for doing such experiments were addressed in the same period of time. Three examples of important instrumental/experimental advances are: First, refinement of ultra-high-vacuum (UHV) techniques and methods for preparing clean and well-defined samples in situ. Second, the development of high resolution, high sensitivity, angle-resolved electrostatic electron spectrometers which allowed measurements in a reasonable time. Third, development of high intensity ultraviolet light sources (e.g. He I radiation from a discharge lamp), and later the advent of synchrotron radiation facilities as a tunable high intensity light sources. Today various implementations of PES have become established methods for investigating the electronic structure of materials in the solid state.

Although the field of photoemission spectroscopy is maturing, we are still far from the closing remarks, and there are still plenty of intriguing questions and challenging technical problems to be solved. As an example, in recent year much effort has been devoted to the measurement and interpretation of the exact lineshapes in ARUPS. The reason is that ARUPS, in principle, directly measures the hole spectral function of the electronic structure of the solid. The hole spectral function is derived from the interactions in the electronic system, and contains information on solid state issues like quasiparticle lifetimes, electron-phonon coupling, and non-Fermi liquid behaviour. Especially highly-correlated electronic systems like high-T\textsubscript{c} superconductors have been the target for these experiments. That ARUPS would play a significant role in elucidating the properties of high-T\textsubscript{c}'s was realized early on, e.g. P. W. Anderson noticed in 1991: ‘If I had my choice of smoking gun, I would ask for . . . better photoemission data, both sample and resolution wise. Angle-resolved photoemission spectroscopy is, for this problem, the experiment that will play the role that tunneling played for BCS.’

This interest in high-T\textsubscript{c}'s pushed the limits of ARUPS investigations. An example is the work from 1990 by Olson et al. on Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8} in the normal state that showed a quasiparticle band crossing the Fermi level[2]. The linewidth Γ\textsubscript{m} of the state was interpreted as being equal to the inverse hole state lifetime Γ\textsubscript{h}, and found to depend linearly on energy with respect the Fermi energy E\textsubscript{F}: Γ\textsubscript{m} \propto (E - E\textsubscript{F}). This result was contrary to the Landau theory of Fermi liquids where a quadratic dependence is expected. However, a general concern about overinterpreting the data was expressed by N. V. Smith a few years later. He wrote: ‘The present degree of control over the execution and analysis of angle-resolved photoemission experiments is not yet sufficiently reliable to make definitive statements on the behaviour of Γ\textsubscript{h} on approaching close to E\textsubscript{F},’ and made the sensible statement that ‘any conclusions on quasiparticle lifetimes on exotic materials should ideally be buttressed by a body of experience on well understood materials’

During the last decade much effort have been devoted to ARUPS experiments on more well understood materials, alongside investigations on high-T\textsubscript{c} materials, and we now have a firmer grip on the behaviour of Γ\textsubscript{h} in the vicinity of E\textsubscript{F}. Instruments have

\\[1\text{Ref. [1], p.60.}\]
\\[2\text{Ref. [3], p. 271.}\]
been built that are compatible with the relevant energy and momentum scales; and our understanding of the hole state decay mechanisms has improved. For instance it has been demonstrated on metals how the electron-phonon coupling affects the hole state lifetime and the electronic structure close to $E_F$.

An important aspect of photoemission spectroscopy, that has made it a standard technique for surface science studies, is the surface sensitive of the technique in the low energy range due to inelastic scattering of the emitted electrons. However, in the context of studying lineshape and spectral functions related to the bulk, this property is to some extent a complicating factor. A way to circumvent this problem is to raise the photon energy. At higher photon energies photoemission is more bulk sensitive due to a longer inelastic mean free path, but new complications arise due to phonon scattering contributing significantly to the photoemission process and the lineshape.

The work I present in this thesis is in many ways a continuation of the efforts outlined above. I have worked on surface electronic structure investigation and the phonon contribution to the photoemission process. An ARUPS facility has been built and a new experimental method has been tested. The remaining part of this introduction is a brief overview of the thesis.

**Instrumentation** A new state-of-the-art ARUPS facility has been built at the storage ring ASTRID in Aarhus, Denmark. Some of the basic features of the instrument are high intensity and resolving power in the energy range 12 eV to 140 eV from a monochromator connected to the undulator section in ASTRID. The electron spectrometer has an efficient multichannel electron detector and high energy- and angular-resolution. The movement of the spectrometer is fully motorised and integrated with the data acquisition software. A closed-cycle He refrigerator allows cooling of the sample to 30 K. The ARUPS instrument is described in Chapter 3 and Ref. [4].

**Surface electronic structure of semimetals** The first application of the new ARUPS instrument in Aarhus has been an investigation of the surface electronic structure of the two semimetals Bi and $\alpha$-Ga. The term semimetal describes solids with a small overlap between the valence and conduction band, which gives rise to a very low bulk density of states at the Fermi level, and broad projected bandgaps about the Fermi level. Prototypical semimetals are the conducting group-V elements As, Sn and Bi, but $\alpha$-Ga may also be considered a semimetal owing to the low density of states at the Fermi level.

Electronic states confined to the surface region, so-called surface states, are effectively a two-dimensional electronic system. Fermi level crossing surface states (metallic surface states) can be regarded as a quasi two-dimensional metal on a semimetal, semiconductor, or insulator. Two-dimensional metals are interesting because new electronic properties are expected in low-dimensional metallic systems owing to the increased importance of exchange and correlation between the charge carriers. This is of fundamental interest in solid state physics, and considered a crucial mechanism behind the properties of layered structures like high-$T_c$ superconductors.

In Chapter 5 and Ref. [5] an investigation on the Bi(110) surface is presented. The surface is found to be more metallic than the bulk due to metallic surface states. The
The $\alpha$-Ga(010) surface is known to undergo a structural surface phase transition, a metallic surface state has been identified, and the electron-phonon coupling is strong. In Chapter 4 and Ref. [6] new results on $\alpha$-Ga(010) is reported, and the driving mechanism behind the phase transition is addressed.

**Final-state phonon scattering in photoemission** The influence of temperature and photon energy on the photoemission process on Al(100) has been studied at the synchrotron Elettra, Italy. There are at least two motivating factors for this study. First, intrinsic excitation/absorption of phonons play an important role in the photoemission process. While the ARUPS spectra at low photon energies and temperatures show distinct direct transition peaks, at high photon energies and/or temperature the angle-resolved spectra resemble the electronic density of states (DOS) of the material. This crossover is due to phonon interaction. Secondly, there is a growing interest in high-resolution photoemission experiments at high energies, owing to the enhanced bulk sensitivity [7].

This work has been done in cooperation with G. Zampieri and coworkers from Centro Atómico Bariloche, Argentina, who have improved the theoretical modelling of the photoemission process to include the phonon interaction in a transparent way. We find that the lineshape of a bulk direct transition is significantly affected by phonon-assisted transitions such that a simple lineshape interpretation is not possible. Furthermore, direct transitions from the surface state are found to be even more stable than bulk direct transitions against phonon scattering. These results concerning the crossover from the direct transition regime to the DOS regime on Al(100) is presented in Chapter 7 and Ref. [8].

**Symmetry resolved density of states** In the beginning of the 90s Osterwalder et al. observed angle-dependent intensity variations in photoemission from the valence band at high photon energies similar to well-known photoelectron diffraction (PED) effects in photoemission from core-levels [9]. This effect is termed valence band photoelectron diffraction (VBPED). The photoelectron diffraction pattern from a core-level depends on the symmetry of the initial state, and evidence of similar dependence has been seen in VBPED data. We have conjectured that it may be possible to decompose the DOS of a material with respect to symmetry by comparing VBPED and PED data from initial states with same symmetry and taken at the same kinetic energy. At medium photon energies, dispersion of direct transitions in the valence band would normally blur the more subtle VBPED effect. However, from the study of the temperature dependence of photoemission on Al(100) it is known that the direct transitions may be effectively quenched by raising the temperature. In Chapter 8 and Ref. [10] VBPED results on Al(100) is presented and a decomposition of the DOS with respect to symmetry is attempted; a preliminary application of the technique to the transition metal oxide NiO, a more complicated system than Al, is also reported.

**First things first** The photoemission process is a pivotal phenomena in this work. Therefore we begin with Chapter 2 on photoemission spectroscopy and the electronic structure of solids and their surfaces.
2.1 Introduction

Photoemission spectroscopy (PES) is a successful and widely used technique for investigating the electronic structure of solids and their surfaces. The properties of the photoemission process, and the characteristics of the observed spectra, depend fundamentally on the photon energy and the solid angle seen by the electron spectrometer. From this point of view different sub-fields of PES may be defined. With respect to the photon energy, the notions UPS or XPS are used for photoemission spectroscopy with ultraviolet (UV) or X-ray light sources, respectively. In the case of angle-resolved PES, the notion ARPES is generally applied, while ARUPS is used for the specific case of angle-resolved photoemission spectroscopy with UV light.

In ARUPS the energy distribution and angular variation of photoemitted electrons is measured, and thus the experimental setup basically consists of a photon source and an angle-resolved electron spectrometer. An illustration of the experiment with all relevant parameters is given in Figure 2.1. Dictated by the scope of the experiment and/or the limitations of the equipment, the experiment will usually be confined to manipulation of a specific subset of the parameters in the figure. The experimental results reported in this thesis have been obtained at three different photoemission facilities. First of all the new ARUPS beamline at the storage ring ASTRID in Aarhus, Denmark (Chapter 3). Secondly the SuperESCA beamline and thirdly the ALOISA beamline; the latter two beamlines at the synchrotron Elettra in Trieste, Italy (Chapter 6).

A photoemission spectrum has to be related to the electronic structure of the crystal before any fundamental knowledge is gained. In the first part of this chapter the photoemission process is considered in a simple picture, where so-called direct transitions from occupied initial states to unoccupied final states will give rise to distinct peaks in the observed spectra. Photoemission spectroscopy of two- and three-dimensional states and mapping of Fermi surfaces are described. In this simple picture the photoemission peaks are delta-functions, while in reality they have finite widths. In the remainder of the chapter, the effects that give rise to the finite width of the photoemission peaks and the spectral shape in general are considered. Initial and final state effects are dis-
Figure 2.1: A fully characterized photoemission experiment involves a set of angles and properties as illustrated in the figure (from Ref. [11]). The incoming photons are characterized by the energy $\hbar \omega$, the polarisation is given by the s and p components and the phaseshift $\Delta$ between them, and the angles of incidence $\theta_p$, $\phi_p$ relative to the normal of the crystal. The orientation and geometry of the crystal should be known. The emitted electrons are specified by the angles $\theta_e$, $\phi_e$ relative to the normal of the surface and the spin-polarisation.

discussed separately. In the initial state scattering with electrons, phonons and impurities determines the lifetime (and hence the linewidth) of the hole state. In the final state inelastic electron scattering gives rise the surface sensitivity of PES, while intrinsic phonon scattering severely influences the direct transitions.

The principles and aspects of angle-resolved photoemission have been reviewed in several cases, see e.g. [12, 13, 14, 11, 15]. A fine general monograph on PES has been written by Hüfner [16], while an introduction from the experimental point of view can be found in [17].

2.2 ARUPS and electronic structure: a simple picture

In the simple picture of photoemission the momentum and energy conservation in the photoemission process is considered as follows. The incoming photon is not carrying enough momentum, such that both energy and momentum can be conserved in the transition, hence the crystal lattice needs to supply additional momentum. In a band
picture of electrons in the valence states of an infinite crystalline solid, the electrons are no longer bound to an individual atom, and only their reduced momentum, or wavevector \( \vec{k} \), is well defined. A change of electron momentum by any reciprocal lattice vector \( \vec{G} \) of the solid is indistinguishable from no change. This means that energy and momentum can be conserved in photoemission of a valence electron from a crystalline solid by the whole solid taking up a recoil momentum of exactly one reciprocal lattice vector \( \vec{G} \). A transition from an occupied initial state (with energy \( E_i \)) to an unoccupied final state (with energy \( E_f \)), where the momentum is conserved in this manner, is termed a direct transition, while a transition where additional momentum is supplied by other scattering mechanisms is termed a non-direct transition. Thus, for a direct transition one has the conservation laws:

\[
E_f = E_i + h\nu \tag{2.1}
\]

\[
\vec{k}_f = \vec{k}_i + \vec{G} \tag{2.2}
\]

where \( h\nu \) is the photon energy; \( \vec{k}_f \) and \( \vec{k}_i \) are the final and initial state momenta inside the crystal expressed in an extended-zone scheme and reduced-zone scheme, respectively. The momentum of the photon, \( \vec{k}_\gamma \), is insignificant at ultraviolet energies while it becomes non-negligible compared to \( \vec{k}_i \) at energies in the XPS range.\(^1\)

When traveling into vacuum and towards the detector, the electrons pass the surface potential barrier before the final state wave vector \( \vec{K}_f \) is observed in vacuum, and generally \( \vec{K}_f \neq \vec{k}_f \). However, the 2D symmetry of the surface imposes conservation of the electron wave vector component parallel to the surface. In other words if \( \vec{K}_f \) is split into components parallel and perpendicular to the surface, \( \vec{K}_f = \vec{K}_{f\parallel} + \vec{K}_{f\perp} \), then:

\[
\vec{K}_{f\parallel} = \vec{k}_{f\parallel} = \vec{k}_{\parallel} + \vec{G}_{\parallel} + \vec{g} \tag{2.3}
\]

where the additional surface reciprocal lattice \( \vec{g} \) is included since momentum may also be exchanged with the surface lattice. Neglecting the surface umklapp, and in the case of small photon energies (\( \vec{G}_{\parallel} = 0 \)), the relationship simply becomes:

\[
\vec{k}_{\parallel} = \vec{K}_{f\parallel} \tag{2.4}
\]

The conservation of the parallel component of the momentum is very important, since it facilitates a very simple analysis of emission from two-dimensional states.

### 2.2.1 Electronic states in two dimensions

In the case of two-dimensional electronic states only the component of the momentum, \( k_\parallel \), parallel to the 2D plane is a relevant quantum number; the perpendicular component, \( k_{\perp} \), of the momentum makes no sense and is not specified. This fact allows a full determination of the initial state dispersion \( (E_i, k_{\parallel}) \) for two-dimensional systems. An example of a two-dimensional electronic system is a surface state on a clean crystalline solid, which is considered below, but also layered compounds (e.g. graphite

\(^1\)The photon momentum is \( k_\gamma = \frac{2\pi/\lambda}{\lambda} = \frac{2\pi E_i}{hc} = \frac{k_\parallel}{|k_\parallel|} = \frac{|k_\parallel|}{E_i} \).
8

[18], transition metal dichalcogenides [19, 20], and to some extend high-$T_c$’s [21], states in layered semiconductor structures [22], states related to adsorbates on surfaces [23], image potential states on metal surfaces [24], or electrons on liquid helium [25] may be considered 2D electronic systems\(^2\).

To be more specific about the analysis: if the angle-resolved electron spectrometer is positioned at an angle $\theta$ with respect to the sample normal, and the kinetic energy $E_{\text{kin}} = \frac{p_i^2}{2m}K_f^2$ of the emitted electrons is measured with respect to the vacuum level, then according to Equation (2.4):

$$k_i = k_f = K_f = K_f \sin \theta = \sqrt{\frac{2mE_{\text{kin}}}{\hbar^2}} \sin \theta \quad (2.5)$$

or in a numerical convenient form:

$$k_i \text{[Å]} = 0.512 \sqrt{E_{\text{kin}}[\text{eV}]} \sin \theta \quad (2.6)$$

The energies of the initial and final state is measured with respect to the Fermi energy, which is a convenient reference point. The kinetic energy is less than the final state energy by the work function $\Theta$ since $E_f = E_{\text{kin}} + \Theta$, and hence the initial state energy is:

$$E_i = E_{\text{kin}} + \Theta - h\nu \quad (2.7)$$

Experimentally the Fermi energy is a convenient reference point because it can be measured with the photoemission setup, and thus a convenient version of Equation (2.7) is $E_i = E_{\text{kin}}(i) - E_{\text{kin}}(\text{Fermi})$. Most often the term ‘binding energy’ is used for the initial state energy\(^3\). Mapping of the surface state dispersion is done by taking series of spectra along a selected direction and subsequently applying Equation (2.5) and (2.7) to determine ($E_i, k_i$).

Surface states on clean crystalline solids are studied in this thesis. A crystal is terminated by surfaces and is not an infinite periodic lattice. For this reason the electronic levels of the bulk crystal may be supplemented by levels, so-called surface states, associated with the two dimensional surface. The concept of surface states was introduced in 1932 when Tamm presented a theoretical study of the semi-infinite crystal in the Kronig-Penney model showing that certain discrete electronic energy levels could exist in the parts of the energy spectrum corresponding to band gaps of the infinite crystal [26]. Surface states are confined to the surface region and the wavefunction decays exponentially into both the bulk and the vacuum. The important fingerprints of a surface state in ARUPS spectra are:

1. The initial state energy of the peak must be independent of the photon energy, $h\nu$, for a fixed $k_i$. If a peak moves as $h\nu$ is changed, then it is due to an initial state which energy depends on $k_{\perp}$. Such a state cannot be a surface state.

\(^2\)The example with electrons on liquid He is not quite like the other examples. In a celebrated experiment from 1979 Grimes and Adams were able to realize the electron crystal, as proposed by Wigner, by depositing electrons on liquid helium. This system belongs to the classical regime where the interactions between the electrons can be described as purely coulombic interactions, since the density of electrons was in the range $10^6$ to $10^9$ cm$^{-2}$ [25].

\(^3\)In this thesis the binding energy is generally considered to be the positive value $E_B = -E_i$. 
2. The energy $E_i$ and parallel momentum $k_i$ of the state must lie in a gap in the projection of the bulk band structure on the surface Brillouin zone. The symmetry of the bulk states must also be considered.

3. Surface states are generally narrower than bulk states because they are less affected by the final state lifetime. We discuss this in detail in Section 2.3.1.

Surface states are not just interesting owing to the fundamental questions related to electronic behaviour in low dimensions. Surface states may also influence physical processes like epitaxial growth, equilibrium crystal shapes, surface catalysis, molecular ordering and sticking on surfaces [27, 28]. The present thesis hinges on photoemission spectroscopy, but also other methods exists by which the surface electronic structure can be investigated. For example scanning tunneling microscopy (STM)\(^4\), reflection anisotropy spectroscopy (RAS)\(^5\), two-photon photoemission (2PPE)\(^6\), inverse photoemission spectroscopy (IPES)\(^7\).

### 2.2.2 Electronic states in three dimensions

For bulk states the conservation of the parallel momentum, Equation (2.5), and the conservation of energy, Equation (2.7), still determine $E_i$ and $k_i$. Unfortunately, there are no trivial relation between the measured perpendicular momentum outside the crystal and the final state momentum inside the crystal. A simple, and quite successful, way to proceed is to assume a free electron dispersion of the final state:

\(^4\)In STM the measured tunnel current is related to the local density of states in the vicinity of the probing tip. Depending on the bias voltage between the tip and the sample this makes it possible to image the spatial distribution of a certain electronic state at the surface. Spectroscopy of the occupied and unoccupied states is achieved by scanning the direction and magnitude of the bias voltage. In a spectroscopy experiment, the width of the tunneling onset is related to the inverse lifetime of the transition. This fact make scanning tunneling spectroscopy an important complimentary technique to photoemission for investigating lifetime effects on surface states. An important distinction between the two techniques is that STM probes the electronic structure in direct space, and is not $k$-resolving like ARUPS. With STM it is possible to investigate the electronic structure in a selected area on the surface, e.g. an area without defects, or the electronic structure in artificially created structures [29, 30, 31]. In addition to this, Friedel-type screening waves which are observed in STM images of steps and defects on metals can be related to the two-dimensional Fermi contour (see Section 2.2.3).

\(^5\)The principle of reflection anisotropy spectroscopy (RAS) is as follows. The complex reflectivity of a sample is compared for two different directions of the polarisation of the incoming light on the surface as a function of photon energy. In case of optically isotropic bulk materials any RAS signal must be related to anisotropies induced by the surface. The RAS technique was demonstrated on metals by Borensztein in 1993, while Hofmann et al. a few years later found that surface states on metals could be observed in the RAS spectra [32, 33, 34]. The use of this technique for surface state investigations has been rather limited.

\(^6\)Two-photon photon photoemission (2PPE) is basically a high-resolution technique for probing unoccupied states in solids. Intense laser radiation is used to populate a normally unoccupied state by absorption of one photon, and then this intermediate state is photoionized by absorption of yet another photon. The technique was demonstrated in 1985 by Giesen with image potential states as intermediate states [35]. It is interesting to notice that it is possible to achieve a high population density of the image-potential state, and in this way create a two-dimensional electron gas in vacuo.

\(^7\)Information about unoccupied surface states and image potential states may also be obtained from so-called inverse photoemission spectroscopy (IPES). In IPES an electron loses a discrete amount of energy and falls from a continuum state to an unoccupied bound state via the emission of a photon (an IPES spectra consists of the photon yield) - in this sense it is the opposite technique of ARUPS. This technique is generally hampered by the fact that the cross-section for the process is very low [36, 37, 38].
\[ E_f = \frac{\hbar^2}{2m^*}k_f^2 - |E_0| \]

where \( m^* \) is the effective mass of the electron and \( E_0 < 0 \) is the bottom of the conduction band. Inside the crystal we have momentum conservation \( k_f = k_i + G \), and let us for simplicity consider normal emission \( (k_i \parallel k_f \parallel 0) \), hence:

\[ k_{f \perp} = k_{i \perp} + nG \perp \]

where \( G \perp \) is the minimum reciprocal lattice vector perpendicular to the surface. To be even more specific we consider normal emission from the \((100)\) surface of a fcc lattice with lattice constant \( a \). In the reciprocal lattice this corresponds to initial states along the \( \Gamma \)-\( X \) direction in the Brillouin zone, and \(^8\) \( G \perp = G_{100} = 4\pi/a \). The final state dispersion is then:

\[ E_f = \frac{\hbar^2}{2m^*}(k_{i \perp} + nG_{100})^2 - |E_0| \]

and the perpendicular component of the momentum in the initial state is found:

\[ k_{i \perp} = \sqrt{\frac{2m^*}{\hbar^2}}\sqrt{E_f + |E_0| - nG_{100}} = \sqrt{\frac{2m^*}{\hbar^2}}\sqrt{\hbar\nu - E_B + |E_0| - nG_{100}} \quad (2.8) \]

In this free electron approximation there are two parameters, \( m^* \) and \( |E_0| \), to be determined in order to map the band structure with Equation (2.8). A good starting point is to assume free electron effective mass, \( m^* = m \), and treat \( |E_0| \) as a free parameter. \( |E_0| \) is chosen such that the observed band structure fits well with either a theoretical band structure, or an observed symmetry (i.e. such that an observed periodicity of the dispersion fits with the appropriate distance to the Brillouin zone boundary).

In Chapter 7 the properties of direct transitions on \( \text{Al}(100) \) in normal emission are investigated. As a preliminary example this situation on \( \text{Al} \) is considered. Aluminium is very well described as a free electron metal. The Fermi energy is 11.2 eV (from the band-structure calculation of Moruzzi, Janak, and Williams [40]; the free electron value is 11.7 eV). In the fcc Brillouin zone the distance to the zone boundary in the \([100]\) direction is \( k_{i \perp} = 2\pi/a \). In Figure 2.2 the free electron bandstructure is shown in the reduced zone scheme. The examples of direct transitions shown in the figure correspond to the experiment reported in Chapter 7. The photon energies where a transition from a specific initial state is possible, like shown on the figure, can easily be found. The transition from the initial state ‘resonates’ whenever \( k_{f \perp} = k_{i \perp} + nG \perp \) is satisfied, or in terms of photon energy:

\[ h\nu = E_f - E_i = \frac{\hbar^2}{2m} [n^2G_{100}^2 + 2nk_{i \perp}G_{100}] \]

\(^8\)Notive that \( G_{100} \) should not be understood as a \([100]\) reciprocal lattice vector in the conventional unit cell, although the index refers to the \([100]\) direction in the conventional unit cell. The minimal vector is a sum of two of the primitive reciprocal lattice vectors, see e.g. [39].
Figure 2.2: Free electron bandstructure of Al in the reduced zone scheme. Selected direct transitions in normal emission on Al(100) are illustrated by vertical lines. The numbers denote the photon energy needed for the transitions (see also Chapter 7). Note that only final states on the solid lines are experimentally available; final states on the dotted lines correspond to electrons going into the sample. The energy scale is such that the Fermi level is at zero.

In Table 2.2.2 photon energies for selected values of $k_i$ are listed, e.g. for $k_{i\perp} = 0.2$ Å$^{-1}$ corresponding to two of the transitions shown on the figure. Emission from the X point, $k_{i\perp} = 1.55$ Å$^{-1}$, is important when emission from the surface state of Al(100) is discussed in Chapter 7.

2.2.3 Fermi surface mapping

The possibility to do bandstructure mapping has been an important motivation in the development of the angle-resolved photoemission technique and equipment. In the recent decade ARUPS has also proven to be a valuable technique for measuring the Fermi surface (FS), a central concept in solid-state physics, of especially low dimensional
Table 2.1: Photon energies (eV) where selected initial states, \( k_{i\perp} \), resonate in normal emission from Al(100).

<table>
<thead>
<tr>
<th>( k_{i\perp} ) (( \text{A}^{-1} ))</th>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma ) ( k_{i\perp} = 0 )</td>
<td></td>
<td>37</td>
<td>147</td>
<td>331</td>
<td>588</td>
<td>918</td>
<td>1322</td>
</tr>
<tr>
<td>( k_{i\perp} = 0.2 )</td>
<td></td>
<td>41</td>
<td>156</td>
<td>345</td>
<td>607</td>
<td>942</td>
<td>1351</td>
</tr>
<tr>
<td>( k_{i\perp} = 1.55 )</td>
<td></td>
<td>73</td>
<td>220</td>
<td>441</td>
<td>735</td>
<td>1102</td>
<td>1542</td>
</tr>
</tbody>
</table>

Table 2.1: Photon energies (eV) where selected initial states, \( k_{i\perp} \), resonate in normal emission from Al(100).

It is worth briefly to consider the Fermi surface concept in a little more detail. In the one-electron model for the electronic structure of metals, corresponding to a system of non-interacting fermions, the Fermi surface is a well-defined concept. In this case the FS is the surface in momentum space that separates occupied single particle states from unoccupied single particle states [39, 41]. Luttinger showed in 1960 that in the case of interacting fermions (and also interacting fermions in a periodic potential, e.g. electrons in a metal) a sharp discontinuity exists in the momentum distribution at absolute zero temperature [42]. This discontinuity is used to define a Fermi surface for a system of interacting fermions [41, 43].

Mapping of the Fermi surface is important since electrons near the Fermi level are coupling to other low energy excitations of the system. This is fundamental to the understanding of phenomena like conventional superconductivity, transport properties, spin- and charge-density-waves. Consequently, it is of interest to know how the Fermi surface develops as a function of temperature, particularly in magnetic metals, spin- and charge-density-wave systems, and other systems that undergo electronic instabilities [41]. The influence of the FS morphology on macroscopic observables will be of greater importance as the dimensionality of the system is reduced to 2D or even 1D, since singularities in momentum- and energy-dependent screening become more severe. In this thesis two experiments is presented where the FS is mapped. The surface phase transition on \( \alpha \)-Ga(010) has been investigated, and it is discussed whether it can driven by the specific morphology of the FS (Chapter 4). Furthermore, the surface Fermi surface of Bi(110) has been investigated and found to be more metallic than the bulk (Chapter 5).

The potential of ARUPS in measuring FSs was realized at an early stage in the development of ARUPS, but as Kevan put it: ’... the application of the technique ... has been slow to develop in part because the measurements are tedious and in part because there are so many other interesting things to do with a photoemission spectrometer’. The development has taken place in the 90s, partly driven by the development of powerful light sources and efficient angle-resolved electron detection schemes, and partly motivated by the application of the technique on high-T\( _c \) superconductors [44].

\( ^9 \)In 1930 de Haas and van Alphen discovered oscillations in the magnetization divided by the magnetic field versus the magnetic field in high fields at low temperatures in a sample of bismuth. In 1952 Onsager was able to explain the effect and relate it to the Fermi surface. This made the de Haas - van Alphen effect the primary probe of the Fermi surface [39].

\( ^{10} \)Ref. [41], p. 176.
In the same way that ARUPS is well suited to investigate two-dimensional electronic structure, the technique is convenient to study surface Fermi surfaces. One way of doing surface FS mapping by ARUPS is to move the angle-resolved electron spectrometer in various directions, and note where the surface states cross the Fermi level. This method was utilized in some of first FS mappings by photoemission [45, 46] but is rather cumbersome. A conceptually and technically simple alternative method is to assume that a state crossing the Fermi level will give rise to an increased intensity at the Fermi level; the experimental procedure is therefore to measure the angular distribution of electrons emitted from the Fermi level. In such a Fermi intensity map, the Fermi level is basically identified with high intensity. This method was demonstrated by Santoni et al. on graphite in 1991. They did the mapping by using a display-type electron spectrometer where a large solid angle of the emitted electrons is imaged on a channelplate electron multiplier [18]. A different method is to sequentially (and preferably motorized) moving an angle-resolved analyser around, and detect the electrons in a narrow energy window at the Fermi level. This technique was developed and applied in several experiments by Aebi, Osterwalder and coworkers [47, 48, 49, 50, 51, 52]. Care should be taken though since an intensity maximum is not necessarily identical with a Fermi level crossing; bands in the vicinity of the Fermi level may also give rise to an increased intensity in the selected energy window. Various alternative methods for analysing the data, and different measuring schemes for determining the Fermi level crossings by ARUPS, have been suggested [43, 53, 54]. Nevertheless, we have successfully applied the simple intensity method in the present work.

As a final point, it is worth to notice that Fourier-transform scanning tunneling microscopy is also a new and promising technique for mapping the surface Fermi surfaces of surface states. Screening of a charged impurity in a metal results in long-range Friedel oscillations in the charge density, due to the abrupt change in density of states at the Fermi level. STM measures a quantity closely resembling the local density of states, and thus Friedel oscillations turn up as wavelike patterns close to steps and adatoms in the images. The periodicity of the oscillations are related to the size of the Fermi surface, and from Fourier-transforms of the images one basically gets the Fermi surface [55, 56, 57, 58, 59].

### 2.3 Spectral shape and lifetime effects

In the simple picture of the photoemission process, and neglecting the instrumental contribution, the photoemission peaks are delta-functions in energy and momentum space. In reality the peaks have a finite width and a specific shape due to many-body interactions in the initial and final states. The fact that information about the interactions in the electronic system is revealed by the lineshape has attracted much interest in photoemission spectroscopy [16, 15, 60, 61].

A helpful method to describe the photoemission process more properly is to introduce quasiparticle states for the hole state left behind and the photoelectron. The interaction effects are included in the spectral functions, or the probabilities of finding an electron/hole with energy $E$ and momentum $k$, of the hole and the electron state. The spectral function can be related to the single-particle Green’s function by:
\[ A(\vec{k}, E) = \frac{1}{\pi} \text{Im} G(\vec{k}, E) \]  

(2.9)

The Green’s function in the case of a non-interacting system with the one-electron energy \( E^0_k \) is:

\[ G_0(\vec{k}, E) = \frac{1}{E - E^0_k - i\epsilon}, \quad \epsilon \text{ is a small number} \]

and according to Equation (2.9) the spectral function is a delta-function, \( A_0(\vec{k}, E) = \delta(E - E^0_k) \), located at \( E^0_k \). In an interacting system the energy gets renormalised by the so-called ‘self-energy’, \( \Sigma(\vec{k}, E) \). The self-energy is a complex number depending on momentum \( \vec{k} \) and energy \( E \):

\[ \Sigma(\vec{k}, E) = \Sigma_1(\vec{k}, E) + i\Sigma_2(\vec{k}, E) \]

The Green’s function in the case of interacting electrons is:

\[ G(\vec{k}, E) = \frac{1}{E - E^0_k - \Sigma(\vec{k}, E)} \]

where \( E^0_k \) is the one-electron energy, and the spectral function becomes:

\[ A(\vec{k}, E) = \frac{1}{\pi} \frac{\Sigma_2(\vec{k}, E)}{[E - E^0_k - \Sigma_1(\vec{k}, E)]^2 + [\Sigma_2(\vec{k}, E)]^2} \]  

(2.10)

Assuming the self-energy is weakly dependent on energy and its imaginary part, \( \Sigma_2 \), is small compared to the binding energy, then \( A(\vec{k}, E) \) is a Lorentzian as a function of energy. The Lorentzian peak is positioned at \( E = E^0_k - \Sigma_1(\vec{k}, E) \) and the width of the peak (FWHM) is \( \Gamma = 2\Sigma_2 \). Furthermore, \( \Sigma_2 = \hbar/2\tau \), and thus the peakwidth is equal to the inverse lifetime:

\[ \Gamma = \frac{\hbar}{\tau} \]  

(2.11)

The photoemission intensity can be written in terms of a convolution of the hole and the photoelectron spectral functions, and only under certain conditions it is possible to access the initial state lifetime. This is the topic of the next section.

2.3.1 The experimental linewidth

Thiery and Smith considered a Lorentzian broadening of the initial and final states, and found the expected measured lineshape to be Lorentzian [3, 62]. The general relationship between the measured linewidth \( \Gamma_m \) (FWHM) and the inverse lifetimes of the hole (\( \Gamma_i \)) and electron (\( \Gamma_e \)) states is:
\[ \Gamma_m = \frac{\Gamma_i}{v_i \parallel} + \frac{\Gamma_f}{v_f \perp} \left[ \frac{1}{v_i \parallel} \left( 1 - \frac{mv_i \sin^2 \theta}{\hbar k_i} \right) - \frac{1}{v_f \perp} \left( 1 - \frac{mv_f \sin^2 \theta}{\hbar k_f} \right) \right] \]  

(2.12)

The subscripts \( i \) and \( f \) refer to the initial and final states (the hole and the electron states), respectively; the subscripts \( \parallel \) and \( \perp \) refer to components parallel and perpendicular to the surface, respectively. The polar emission angle is \( \theta \), \( m \) is the free electron mass, \( k \) is the wave vector, and \( v \) is the group velocity, \( v = \frac{\partial E}{\partial k} \). The separate hole and electron state contributions cannot easily be deduced from Equation (2.12). However, in the limiting cases of emission from quasi-2D or true 2D systems the final state effects vanishes and Equation (2.12) becomes tractable.

A quasi-2D system corresponds to a case where it is valid to assume that the group velocity \( v_i \parallel \) is much smaller than the other velocities. This would be the case for systems with weak coupling and correspondingly weak dispersion of the bands perpendicular to the surface. With this approximation, and in normal emission (\( \theta = 0 \)), Equation (2.12) becomes:

\[ \Gamma_m = \Gamma_i + \left| \frac{v_i \perp}{v_f \perp} \right| \Gamma_f \]  

(2.13)

and in the limit \( v_i \perp \to 0 \) the measured linewidth corresponds to the inverse lifetime of the hole state:

\[ \Gamma_m \approx \Gamma_i \]  

(2.14)

This has been a wide-spread approximation in ARUPS investigations on high-\( T_\text{c} \) materials (they are quasi-2D). However, care should be taken, as was noted in Chapter 1, since it may not be possible to neglect the \( v_i \perp \) term [3].

**2D systems and surface states**

A surface state has no dispersion with respect to \( k \perp \) and is a true 2D system. In this case one has \( v_i \perp = 0 \) and Equation (2.12) reduces to:

\[ \Gamma_m = \frac{\Gamma_i}{1 - \frac{mv_i \sin^2 \theta}{\hbar k_i}} \]  

(2.15)

The final state lifetime contribution has vanished, and this explains why surface states in general appear sharper than bulk states. For a 2D system and normal emission \( (\theta = 0, k_\perp = 0) \), or off-normal emission from a symmetry point \( (v_i \parallel = 0) \), one has the simple relationship\(^{11}\):

\(^{11}\)Notice that the condition \( v_i \perp = 0 \) may also be fulfilled at some points in a 3D-bandstructure. Furthermore, if the parameters in Equation (2.12) at the same time are chosen such that the initial state band has a large negative parallel dispersion, \( v_i \parallel < 0 \), and if \( \theta \) is large, and \( k_i \) is small, then it is even possible to observe \( \Gamma_m \) to be smaller than \( \Gamma_i \). This was demonstrated experimentally by Hansen et al. on an Ag bulk state, and highlights that pitfalls exist in relating the observed bulk state linewidth with the inverse lifetime [63].
and the measured linewidth is identical to the inverse hole state lifetime. This makes surface states a fundamental testing ground for extracting hole state lifetimes from the ARUPS linewidths.

In Chapter 4 investigations on the linewidth of a surface state on α-Ga(010) at a high symmetry point \( \nu_A = 0 \) and in an off-normal geometry \( \theta \neq 0, k \neq 0 \) is reported. In this context it is worth considering the possible additional broadening if the electron spectrometer does not see the right point in \( k \)-space. Assuming a free-electron dispersion for the surface state:

\[
E_i = \frac{\hbar^2}{2m} (k - k')^2 + E_0
\]

where \( k' \) (or \( \theta' \)) is the position of the symmetry point, then \( \nu_i = \frac{\hbar}{m} (k - k') \) and:

\[
\Gamma_m = \frac{\Gamma_i}{|1 - \frac{k - k'}{k'}\sin^2 \theta|}
\]

or if we approximate \( E_i(\theta) \approx E_i(\theta') \):

\[
\Gamma_m = \frac{\Gamma_i}{|1 - (\sin \theta - \sin \theta') \sin \theta|}
\]

In the case of the specific experiment on α-Ga(010) it turns out that even a few degrees misplacement of the analyser only convert into a few percent broadening.

So far, an important contribution to the measured linewidth has been neglected: the instrumental energy- and angular-resolution. The energy-resolution broadens the peak, and is to a good approximation often described as a Gaussian convolution of the spectra. The angular-resolution may cause an asymmetric broadening depending on the dispersion of the state. The instrumental contributions are discussed in Chapter 3.

\section*{2.4 Initial state effects}

In section the initial state effects contributing to the lineshape is considered in detail. This is especially interesting with respect to emission from a surface state since, according to Equation (2.16), the measured lineshape is identical to the hole state spectral function. The different contributions to the linewidth add linearly. In the case of electron-electron \((e-e)\), electron-impurity \((e-i)\), and electron-phonon \((e-ph)\) interactions:

\[
\Gamma = \Gamma_{e-e} + \Gamma_{e-i} + \Gamma_{e-ph}
\]  

Until quite recently the electron-phonon contribution to the lifetime was neglected, and the linewidth of a surface state was regarded as being dominated by the electron-electron interaction plus a constant contribution from defect scattering. However, in
1995 McDougall et al. demonstrated on Cu(111) that the electron-phonon contribution is significant, and actually dominating the temperature dependence of the linewidth [64]. To see why this is the case the McDougall analysis for the surface state on Cu(111) is followed, and the various contributions to Equation (2.17) considered in more detail. A general point to notice is that even though the surface states are 2D and do not mix with the 3D bulk states, the bulk states are available for the surface states to scatter into, and therefore the 3D decay rates are relevant for the lifetime of surface states [64, 31].

The electron-electron contribution \( \Gamma_{e-e} \) is due to Auger decay, which is energy dependent for bulk holes near \( E_F \), and predicted to be:

\[
\Gamma_{e-e} = 2\beta[(\pi kT)^2 + E^2] \tag{2.18}
\]

where the strength of the electron-electron interaction is measured by the \( \beta \) parameter, and \( E \) is the energy with respect to \( E_F \). At zero temperature the linewidth of the state will become infinitely narrow as the Fermi level is approached. The relationship is \( \Gamma_{e-e} \propto E^2 \) and this behaviour is characteristic for a quasiparticle excitation in a Fermi liquid. In the case of Cu the contribution was estimated to \( \Gamma_{e-e} = 5 \text{ meV} \) at the bottom of the surface state band (\( E = 0.4 \text{ eV} \)), and the change with temperature to be less than 1 meV for achievable temperatures [64]. A more recent theoretical analysis has demonstrated that it is insufficient in the case of electron-electron interaction only to consider the 3D decay rate. Kliewer et al. found that the 2D hole state is predominantly filled by 2D surface state electrons rather than electrons from 3D bulk states [31]. This extra decay channel shortens the lifetime of the hole state. On the other hand, the 3D bulk electrons cannot be neglected either since they screen the interactions within the 2D surface state. In the case of Cu(111) Kliewer et al. calculated \( \Gamma_{e-e} = 13.7 \text{ meV} \) at the bottom of the surface state band. This and similar theoretical values for the total linewidth are in good agreement with recent STM and PES data [31, 65]. Nevertheless, the contribution from electron-electron scattering is rather small and the temperature dependence is even smaller.

The impurity contribution, \( \Gamma_{e-i} \), is expected to be proportional to the impurity contribution, but independent of temperature and binding energy:

\[
\Gamma_{e-i} = \text{constant} \tag{2.19}
\]

At sufficiently low temperature impurity scattering will be the dominant decay mechanism for states at the Fermi level.

For the electron-phonon interaction, \( \Gamma_{e-ph} \), it was assumed that [64]:

\[
\Gamma_{e-ph} = 2\pi\hbar \int_0^{\omega_m} d\omega' \alpha^2 F(\omega') [1 - f(\omega - \omega') + 2n(\omega') + f(\omega + \omega')] \tag{2.20}
\]

where \( \alpha^2 F(\omega') \) is the Eliashberg coupling function, \( \omega_m \) is the maximum phonon frequency, \( f(\omega) \) is the Fermi distribution, and \( n(\omega) \) is the Bose-Einstein distribution. The strength of the electron-phonon interaction is measured by the ‘electron-phonon coupling parameter’ \( \lambda \), also called the ‘mass enhancement parameter’. The electron-phonon coupling parameter \( \lambda \) is related to the Eliashberg coupling function:
\[ \lambda = 2 \int_{0}^{\Theta_D} d\omega \alpha^2 F(\omega) / \omega \]

If the temperature is higher than the Debye-temperature, \( T > 1/3\Theta_D \), and the energy is close to the Fermi energy \( E_F \), then a simple linear relationship is valid [64]:

\[ \Gamma_{e-ph} = 2\pi\lambda kT \]  \hspace{1cm} (2.21)

Equation (2.21) is evaluated for \( \lambda = 1 \) in Table 3.1. In order to apply Equation (2.20) in the low temperature case it is convenient to assume the Debye-model for the phonon spectrum. In this case:

\[ \alpha^2 F(\omega) = \lambda (\frac{\omega}{\omega_D})^2, \omega < \omega_D \]  \hspace{1cm} (2.22)

and zero elsewhere. Calculations show that surface effects only give rise to minor correction of the values calculated in this 3D Debye scheme, and the use of the Debye spectrum is furthermore not expected to be a large source of error [31].

McDougall et al. showed that a value of \( \lambda \) could be determined from the temperature dependence of the linewidth of a surface state [64]. The value is denoted \( \lambda_s \) to emphasize that it is specific to the surface electronic structure. This was a noteworthy result that inspired several related studies as we will see below. The superconductivity of a solid depends on \( \lambda \) and it is possible that a higher surface value \( \lambda_s \) might lead to the transition temperature of superconductivity for the surface being well above the bulk value\(^{12}\). McDougall et al. analysed the linewidth of a surface state on Cu(111) according to Equation (2.21) and found \( \lambda_s = 0.14 \pm 0.02 \); in good agreement with the average bulk value of \( \lambda = 0.15 \). Similar kind of experiments have since been reported for the clean surfaces of Be(0001) [67, 68, 69], Be(1010) [70], \( \alpha \)-Ga(010) [71], Mo(110) [72], the layered compound 1T-TiTe2 [20], and for the hydrogen induced surface states on W(110) [23]. We have redone the linewidth versus temperature experiment on \( \alpha \)-Ga(010) by Hofmann et al. [71]; the results are presented in detail in Chapter 4. In addition to the discussion of the Cu(111) experiment by McDougall et al., a brief review of the illustrative Be(0001) case, which reveals a strong electron-phonon coupling spectral function, will be made in the following.

The Fermi level of Be is located in a dip in the electronic density of states. Higher densities are found on the surfaces, e.g. at the (0001) surface the density is about four times larger than in the bulk owing to the appearance of surface states [73]. Large surface core-level shifts [74, 75, 76] and giant Friedel oscillations [57] have been observed, and ascribed to the large ratio between surface and bulk density of states at

\(^{12}\)Superconductivity in 2D, e.g. on surfaces is an interesting concept. The characteristic length scale concerning conventional superconductivity is the ‘coherence length’, i.e., the spatial separation between electrons in a Cooper pair, which is of the order of 1000 Å. Metal films with thickness less than 1000 Å will for this reason be effectively two-dimensional from the point of view of superconductivity. Experimentally, however, it is very difficult to prepare crystalline metal films in this thickness range on a non-conducting substrate. Burns et al. suggested in 1984 a superconductive transition for the Ag/Ge(001) system [66]. Alternative system could be metallic surface states on substrates with a low density of states at the Fermi level. Possible candidates are Be surfaces as discussed later in this section, or Bi surfaces as we will see in Chapter 5.
the Fermi level. Balasubramanian et al. found the electron-phonon coupling parameter of the (0001) surface to be $\lambda_s = 1.15 \pm 0.1$, more than four times the bulk value $\lambda = 0.24$, and discussed the possibility that surface states electrons may pair and superconduct without involving bulk states [67]. The latter conjecture was discarded by Hengsberger et al. who presented new high resolution ARUPS results in 1999. They observed no opening of a gap down to 12 K, and therefore declined any interpretation of the data based on charge density wave (CDW) formation or surface superconductivity [68]. However, they observed something different: a sharp peak emerged at a binding energy around 60 meV as the surface state approached the Fermi level. This was in good agreement with expected spectral functions for a system with strong electron-phonon coupling [77]. The electron-phonon coupling modifies the electronic structure in a characteristic energy region of the order of the phonon bandwidth ($\approx 60$ meV in Be), and a sharp peak is expected to appear near $E_F$ when the energy of the hole becomes comparable to the phonon bandwidth. This quasiparticle excitation corresponds to a hole excitation with a mass enhanced by $(1 + \lambda_s)$. In this way the electron-phonon coupling parameter was determined to be $\lambda_s = 1.18 \pm 0.07$ from the ratio between the dispersion of the surface state and the dispersion of the quasiparticle; in good agreement with the Balasubramanian et al. result. However, LaShell et al. have remeasured the temperature dependence of the linewidth and reanalysed the data of Balasubramanian et al., and they report a somewhat smaller value, $\lambda_s = 0.7 \pm 0.1$, for the electron-phonon coupling strength [69]. The discrepancy between their result and the Balasubramanian et al. result can be ascribed to an error in the data analysis by the latter. Balasubramanian et al. had measured the linewidth in an off-normal geometry, but assumed identity between inverse hole state lifetime and measure linewidth. In other words they had used Equation (2.16) instead of the appropriate off-normal relationship, Equation (2.15).

The Be case is extra interesting because the Be photoemission results by Hengsberger et al. has recently been emphasized in an argument for strong electron-phonon coupling in high-temperature superconductors. Electron-phonon coupling drives the formation of the electron pairs (Cooper pairs) responsible for conventional superconductivity, as explained by the BCS theory, but is generally not thought to play any significant role in high-$T_c$’s. However, Lanzara et al. have systematically investigated three different families of copper oxide superconductors by ARUPS and find spectra similar to the Be case. Therefore they have suggested that electron-phonon coupling may be of importance in high-$T_c$’s [78, 79].

### 2.5 Final state effects

Final state scattering effects determine the lifetime of the electron state. Two relevant effects are picked out here: extrinsic electron scattering and intrinsic phonon scattering, respectively.
2.5.1 The inelastic mean free path

A fundamental phenomenon in photoemission spectroscopy, and similar experimental techniques where electrons are impinged on, or emitted from, a solid surface, is inelastic scattering of the electrons. The average distance between scattering events, the inelastic mean free path (IMFP) $\lambda$, is small for low energy electrons in solids, and this gives rise to surface sensitivity. The dependence of the IMFP on the kinetic energy of the electrons is almost independent of the actual material; the relationship has therefore been termed the ‘universal curve’. The IMFP has a minimum value of 2 to 5 Å at the universal curve for kinetic energies in the 50-100 eV range, and hence the surface sensitivity of photoemission spectroscopy is greatest in this energy range [17, 80]. Calculations and experiments to determine the IMFPs for various materials have a long history, but also notorious difficulties in obtaining reliable data, see e.g. the recent review by Powell and Jablonski [80]. In this section inelastic scattering effects in the photoemission process is considered.

The first thing to notice is that a small IMFP corresponds to a small lifetime of the final state, or a broad final state lineshape function. The inelastic scattering is the most important lifetime limiting effect. The inelastic scattering also affects the sampling of the initial states. The inelastic mean free path of the photoelectrons corresponds to an uncertainty in the component, $\Delta k_\perp$, of the final state wave vector perpendicular to the surface: $\Delta k_\perp = \frac{1}{\lambda}$ [81]. In other words, a small $\lambda$ gives a large $\Delta k_\perp$ in the final state. If more final states are available in the $\Delta k_\perp$ window, then more initial states may take part in direct transitions. This effect is rather small, however, and is counteracted at the lowest kinetic energies because the distance between the backfolded final states is big.

The inelastic loss mechanisms for the electrons are plasmon excitation, excitation of electron-hole pairs, ionisation of core levels, and phonon scattering. The electron-phonon scattering is usually neglected in this context, since most experimental methods to determine the IMFPs are not sensitive to the small energy loss ($\sim 50$ meV) in phonon scattering. Ionisation of core levels has a small cross-section, and correspondingly large IMFP, compared to the other contributions and may also be neglected. The dominating mechanisms for inelastic scattering is therefore excitation of plasmons and electron-hole pairs. At energies below the plasma energy ($E_{\text{kin}} < \hbar \omega_p$) the scattering is solely due to electron-hole pair excitation, while the scattering is dominated (for free electron metals) by plasmon-creation at higher energies ($E_{\text{kin}} > \hbar \omega_p$). An additional complication arises due to elastic scattering of the electrons, since this increases the average path length an electron travels in order to escape the solid13.

In normal emission geometry the intensity $I_0$ from a depth $z$ is reduced14 to $I(z) = I_0 e^{-z/\lambda}$ at the surface due to inelastic scattering. In order to parameterize the surface sensitivity we introduce the depth $d_\alpha$, corresponding to the depth from where $\alpha$ percent of the total intensity is emitted. The total intensity is $I_{\text{tot}} = \lambda I_0$, and the intensity emitted

\[ I_{\text{tot}} = \lambda I_0, \]

13In the presence of inelastic scattering this increases the probability of the electron loosing energy before reaching the surface. From an experimental point of view one may introduce an electron attenuation length to describe the effective loss. The attenuation length can be as much as 30% smaller than the IMFP. The elastic scattering probability is not isotropic, but highly anisotropic and energy dependent. Forward scattering dominates at high energies ($> 500$ eV), while backscattering becomes important at lower energies [38, 82].

14The attenuation length of photons is very long compared to the inelastic scattering length of the photoelectrons, and we may assume the intensity $I_0$ to be independent of the depth.
from within depth \(d\) is \(I_d = I_0\lambda[1 - e^{-\frac{d}{\lambda}}]\), and thus \(d = -\lambda\ln(1 - \alpha)\). Powell and Jablonski have reviewed the published calculations and measurements for the IMFPs of various materials [80]. In the case of Al they recommend \(\lambda\) to be approximated by:

\[
\lambda[\text{Å}^{-1}] = 0.6210E[\text{eV}]^{0.2921} + 0.03164E^{0.9028} \tag{2.23}
\]

Equation (2.23) is a fit to the various calculated IMFP values in the range 50 eV to 2000 eV. A tabulation of the depth from where half the intensity is originating, \(d_{50}\), in Al is presented in Table 2.2. The significant surface contribution is evident.

<table>
<thead>
<tr>
<th>(E_{\text{kin}}) (eV)</th>
<th>50</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda) (Å)</td>
<td>3.0</td>
<td>6.7</td>
<td>10.6</td>
<td>14.2</td>
<td>17.6</td>
<td>24.0</td>
</tr>
<tr>
<td>(d_{50}) (Å)</td>
<td>2.1</td>
<td>4.6</td>
<td>7.3</td>
<td>9.8</td>
<td>12.2</td>
<td>16.6</td>
</tr>
</tbody>
</table>

Table 2.2: The inelastic mean free path, \(\lambda\), and the characteristic depth \(d_{50}\) for Al.

### 2.5.2 Phonon scattering effects

In the previous section the extrinsic electron-electron scattering was considered. A rather different scattering mechanism is intrinsic scattering of phonons in the photoemission process. The consequences of this effect can be realized in a simple picture. Consider interaction with just one phonon. This phonon may get excited or absorbed in the photoemission process. In any case it contributes momentum to the emitted photoelectron, and the parallel momentum conservation rule (2.3) changes to:

\[
\vec{K}_f| = \vec{k}_i + \vec{Q}
\]

where \(\vec{Q}\) is the phonon wave vector, and the − and + signs correspond to the cases of excitation and absorption, respectively. At the same time the energy of the photoemitted electron is almost unaffected because of the very small energy carried by a phonon. A simple consequence of phonon scattering is that various other initial states may be scattered into an observed final state, and that the direct transition initial state may be scattered somewhere else. This situation is schematically illustrated in Figure 2.3.

In the late 70s Shevchik did the first thorough work on the role of phonon scattering in the photoemission process [83, 84, 85]. It is worth briefly to consider the work of Shevchik since it captures the basic physics, and many experiments has been discussed with respect to his results. A simple outcome of Shevchik’s work was that the photoemission intensity is governed by a Debye-Waller factor, \(W(T, h\nu)\), and can be approximated by:

\[
I(E, T, h\nu) = W(T, h\nu)I_{DT}(E) + [1 - W(T, h\nu)]I_{NDT}(E) \tag{2.25}
\]

where \(I_{DT}\) and \(I_{NDT}\) are the intensities of the direct transitions (DT) and the phonon-assisted non-direct transitions (NDT), respectively. \(T\) is the temperature of the sample, \(h\nu\) is the photon energy, and \(E\) is the initial state energy of the electrons. The Debye-Waller factor is:
Figure 2.3: Schematic illustration of how interaction with phonons quenches the direct transition and promotes sampling of all initial states in the Brillouin zone. The dotted polygon is a cut through the fcc Brillouin zone. The Γ-X direction corresponds to normal emission on the (100) surface. \( G \) is the momentum supplied by the lattice in the direct transition from the initial state \( \tilde{k}_i \) and the final state \( \tilde{k}_f \). Momentum supplied by phonon scattering is denoted \( \tilde{Q} \).

\[
W(T, \hbar \nu) = e^{-\Delta k^2(\hbar \nu) \langle u_i^2(T) \rangle}
\]  
(2.26)

where \( \Delta k = |\tilde{k}_f(\hbar \nu) - \tilde{k}_i(\hbar \nu)| \) is the wavevector change in the (scattering) photoemission process, and \( \langle u_i^2(T) \rangle \) is the thermal mean square displacement of the atoms. In the Debye model the thermal mean square displacement of the atoms from the equilibrium positions is given by [15]:

\[
\langle u_i^2(T) \rangle = \frac{3\pi^2}{4MK} \left[ 1 + 4 \left( \frac{T}{\theta_D} \right)^2 \int_0^\infty \frac{z}{e^z - 1} \, dz \right]
\]  
(2.27)

where \( M \) is the atomic mass and \( \theta_D \) is the Debye-temperature.

Owing to the Debye-Waller factor, raising the temperature or the photon energy amounts to the same in this model. The essence of Equation (2.25) is that it predicts
a crossover from a regime where the spectra are dominated by direct transition peaks at low photon energy and/or temperature to a situation where one essentially measures indirect transitions. In the latter case the indirect transitions allow initial states from the entire Brillouin zone to be sampled, and hence the spectra will resemble the DOS of the sample. However, it will not be the DOS proper due to modulations by the photoemission cross-sections [81, 83, 84, 85, 60]. A further simplification of the model, that has often been made, is to assume that the non-direct part of Equation (2.25) contribute only a flat background beneath the distinct direct transition peaks. In this case the intensity of a direct transition peak is expected to be given by a simple exponential function:

\[ I(E, T) = W(T) I_{DT}(E) \]  

(2.28)

Equation (2.28) is a model with no free parameters. In order to compare with the experimental data one may change the point of view and define an effective Debye-Waller factor:

\[ I(E, T) \propto W_{eff}(T, \theta_{D_{eff}}) \]  

(2.29)

where the effective Debye-temperature is to be a fitting parameter. In Chapter 7 the temperature and photon energy dependence of photoemission on Al is investigated, and some limitations of the Shevchik model is pointed out.

In Figure 2.4 (a) the Debye-Waller factor is plotted in the case of Al for relevant values of temperature and momentum transfer. From this figure it is evident how direct transitions will be dominating at low temperatures and low photon energies; this scenario one may call the ‘band structure’ regime of photoemission. In the other limit of high temperature and high photon energy the Debye-Waller factor quenches the direct

\[ I(E, T) = W(T) I_{DT}(E) \]  

(2.28)

Equation (2.28) is a model with no free parameters. In order to compare with the experimental data one may change the point of view and define an effective Debye-Waller factor:

\[ I(E, T) \propto W_{eff}(T, \theta_{D_{eff}}) \]  

(2.29)

where the effective Debye-temperature is to be a fitting parameter. In Chapter 7 the temperature and photon energy dependence of photoemission on Al is investigated, and some limitations of the Shevchik model is pointed out.
transitions and the spectra resembles the DOS of the material; this scenario one may call the 'density-of-states' regime of photoemission. It is important to note that the density-of-states spectra are not strictly equal to the DOS, but the DOS weighted by cross sections depending on the specific initial state. The symmetry of the initial state may thus give rise to angular anisotropic effects; the consequences of this is studied in Chapter 8 on valence band photoelectron diffraction. This crossover is a general phenomena as more schematically illustrated in Figure 2.4 (b). The Figure is similar to the Al results in Figure 2.4 (a), and more generally the Debye-temperature is setting the temperature scale.

From an experimental point of view, the phonon contribution to the photoemission process is in principle an easily accessible parameter; it is just a matter of changing the temperature of the sample, or the photon energy. Temperature effects have, however, mostly been studied in the sense that the sample has been cooled in order to get more pronounced direct transitions. Nevertheless, the photoemission process is significantly temperature dependent, and it is important to understand the actual contributions to the spectra. The promising aspects of detailed lineshape studies have been mentioned. Another example of the relevance of temperature effects is temperature dependent phase transitions. The electronic structure is affected when a material passes through a structural and/or magnetic phase transition (the phase transition can be either a bulk transition or limited to the surface). When applying photoemission spectroscopy to such systems one obviously needs to consider the intrinsic temperature effects when comparing spectra measured above/below the transition temperature. To study the crossover into the DOS-regime as a function of photon energies, the high flux of photons from undulators at 3rd generation synchrotron facilities is well suited since the cross-section for valence band photoemission drops off as the photon energy is increased to X-ray energies.

Finally, there are also other mechanisms giving rise to an increased BZ integration at high energies. The most notable is due to the angular resolution of the electron spectrometer. From Equation (2.6) it is seen that the angular resolution introduces, in a first order approximation, a broadening in the parallel component of the momentum equal to:

\[ \Delta k_{\parallel} = 0.512 \sqrt{E_{\text{kin}}} \cos(\theta) \Delta \theta \]  

(2.30)

This may become an integration over a substantial part of the Brillouin zone at the highest energies. However, the phonon scattering is generally the most important contribution. The angular resolution is also affecting the lineshape in the direct transition regime, as will be demonstrated in the following chapter on the photoemission instrumentation.
The Aarhus ARUPS facility

Recently an ARUPS facility has been set up at the storage ring ASTRID in Aarhus, Denmark. The goal of the project has been to establish a state-of-the-art facility for investigating the electronic structure of complex materials by angle-resolved photoemission spectroscopy in the ultraviolet region. The central features of the facility at the time of writing are:

- High intensity from the ASTRID undulator source, and high energy resolution (approx. 15000) from a monochromator covering the energy range 12-140 eV.
- Rotatable and motorised electron spectrometer with high energy- and angular-resolution and efficient electron detection with multi-channel detector.
- Integrated software controlling data acquisition, analyser position, monochromator energy, exit slit position, and undulator gap.
- Sample cooling to 30 K with a closed cycle He-refrigerator.

In this chapter the facility is described. The central part of the system, the angle-resolved electron spectrometer, was delivered in February 1999, and first light on the sample from the monochromator was obtained in February 2000. The system is now fully operational for doing ARUPS investigations. In the near future a scanning tunnelling microscope (STM) will be added to the system allowing for correlated real-space investigations of the sample.

3.1 ASTRID, undulator, and monochromator

ASTRID is a small storage ring with four 10 m straight sections, and a bending magnet in each corner. An undulator source is installed in one of the straight sections. The electrons are stored at 580 MeV, and the synchrotron radiation is most intense in the low energy X-ray range. The undulator source of ASTRID is characterized by high flux and low divergence of the beam in the (12-140 eV) energy range, and is quite
unique in comparison with contemporary high energy synchrotron radiation facilities. The ARUPS beamline is a branch line on the undulator source, as illustrated in Figure 3.1. ASTRID is unusual in the sense that it is a dual-purpose storage ring. ASTRID is not only used for generating synchrotron radiation, but also used for ion storage. In recent years the time has been equally split between synchrotron radiation and ion storage.

Figure 3.1: A schematic illustration of the ASTRID layout. The ARUPS beamline is ‘SGMIII’ in the upper left corner.

The monochromator (called ‘SGMIII’) is a spherical grating monochromator (SGM) of the Dragon type with three gratings and a movable exit slit. The elements in the beamline (down stream) are: horizontal focusing mirror, vertical focusing mirror, entrance slit, setup with three interchangeable gratings, movable exit slit, and post focusing mirror. The horizontal focusing mirror is rotatable, allowing to switch between the three branch-lines at the undulator section. The exit slit moves over 0.4 m. The three gratings (called LEG, MEG, and HEG) cover the energy range from 8 eV to approx. 160 eV, with a resolving power of approx. 15000 [86].

A gas-cell is mounted in the beamline, between the post focusing mirror and the experimental chamber, for measurements of gas phase photoionisation yields. Photoionisation energies and linewidths of especially noble gases have been carefully tabulated, and are well suited for calibrating the energy scale of the monochromator and optimizing the energy resolution. Figure 3.2 shows a photoionisation spectrum taken on Ne. The resolving power is greater than 15000, and generally the monochromator fulfills the specifications [86]. The medium- and high-energy gratings (MEG and HEG) have, however, not been fabricated as specified, and especially in the HEG case the photon...
flux is severely reduced. For this reason the maximum usable photon energy for the ARUPS experiments has in practice been limited to less than 80 eV. A replacement of the gratings is planned.

The vertical spot size (from ray tracing) in the experimental chamber is generally less than 0.5 mm. The horizontal spot size is below 1 mm over most of the energy range, except in the range 8-30 eV where it varies from 1.5 mm to 1 mm [86].

![Figure 3.2: Gas phase photoionisation spectrum of Ne taken with second order light from the SMMIII monochromator.](image)

### 3.2 The ARUPS setup

The end station consists of two connected UHV-chambers: a big main chamber, with the electron spectrometer, and a smaller chamber for sample preparation. Two loadlocks allow the sample to be inserted into either the main chamber or the preparation chamber without breaking the vacuum. In the main chamber the sample-holder is mounted on a manipulator with four degrees of freedom: x, y, z, and rotation around the manipulator axis. In the preparation chamber the manipulator has an additional degree of freedom: rotation around the sample normal. The transfer of the sample between the two chambers is done by moving the preparation chamber manipulator into the main chamber. In the main chamber the sample can be grabbed by a wobble-stick, and transferred between the sample-holders on the two manipulators.

In addition to the electron spectrometer the main chamber is equipped with a LEED apparatus and a gas discharge lamp. The gas discharge lamp is used as source of He I/II radiation whenever synchrotron radiation is not available. An ion gun for sputtering the sample with noble gas ions (sample preparation) is also mounted in the chamber. A
ceramic spacer secures electrical insulation between the chamber and the beamline to avoid ground loop problems. Two diode-lasers are mounted on windows in the central plane. This setup makes it possible to position the sample in the center of the chamber.

The manipulator in the main chamber is equipped with a closed cycle He-refrigerator. This allows cooling of the sample to 30 K. The temperature of the sample is measured via a K-type thermocouple spot-welded on the back of the sample. Heating of the sample is achieved by using radiating heat from a filament mounted behind the sample. A feedback system, where the temperature of the sample controls the current through the filament, allows a fixed temperature to be set. The temperature may be controlled from the analyser software. This allows two different measuring schemes: either current is passed through the filament constantly while measuring, or the current may be pulsed and emission from the sample is detected in current free periods. The pulsed mode is intended to avoid possible influence of magnetic fields and stray electrons from the filament. So far, small differences in resolution between the two measuring schemes have only been detected at very low temperatures, and for very sharp spectral features. Therefore the spectra have in general been measured in the constant current mode, since this is faster and the temperature is more exactly fixed.

In the preparation chamber there is an ion gun for sputtering the sample with noble gas ions and several flanges available for mounting equipment like alkali-sources etc. In this chamber there is also a garage for storing samples. The planned STM will also be mounted on the preparation chamber.

### 3.3 Electron spectrometer

The VG-ARUPS10 electron spectrometer is illustrated in Figure 3.3. The mean radius of the hemispheres is 75 mm, and the entrance slit to the hemispheres is 0.5 mm. A lens system in front of the hemispheres allows different focus and angular resolution properties. The electrons that pass through the hemispherical energy analyser are detected by a multi-channel detector.

The spectrometer is rotatable on a two-axis goniometer. An important upgrade of the Aarhus spectrometer compared to the commercial setup is motorisation of the spectrometer movements. Normally the position is set by moving the spectrometer by hand. Here these movements are achieved with two stepper motors connected to the motional feedthroughs by belts. The control of the stepper motors driving the spectrometer is integrated with the data acquisition software. This allows for very efficient measuring schemes. For instance, the system can be programmed to take spectra along a selected direction of the surface Brillouin zone, or most notably spectra can be taken in selected areas of the surface Brillouin zone. This way Fermi surface intensity maps can be measured. Note that the polarisation vector of the light is fixed with respect to the surface during these measurements, since it is the spectrometer that is being moved. In other systems the analyser is fixed and the sample is rotated when Fermi surface maps are measured. The movement of the spectrometer is for mechanical reasons limited to half of the hemisphere above the sample surface. Hence some symmetrization is generally needed to obtain full Fermi intensity maps. The motors are electrically insulated from the chamber and the electron analyser by teflon gaskets and insulating belts.
Two central parameters characterizing an electron spectrometer are the angular- and energy-resolution. These parameters have been specified, e.g. by gas phase measurements, by the manufacturer for the specific instrument. However, it is also worth considering how to determine actual values from a solid state photoemission experiment. This is discussed in the sections below.

### 3.3.1 Energy-resolution

The energy-resolution of a photoemission instrument is determined by the energy spread of the photon beam, and the properties of the electron spectrometer. The various contributions are generally well approximated by Gaussians, hence the total instrumental convolution function is also well approximated by a Gaussian. The instrumental energy-resolution function is therefore:

\[
D_I = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{E^2}{2\sigma^2}\right), \quad \sigma = \frac{\Delta E_I}{2.35488}
\]  

where $\Delta E_I$ is the energy resolution (FWHM). If one separately considers the contributions from the photon beam ($h\nu$) and the electron spectrometer (EEA) then:

\[
\Delta E_I = (\Delta E_{h\nu}^2 + \Delta E_{EEA}^2)^{1/2}
\]  

Similarly, to a first approximation, the measured linewidth $\Delta E_m$ of a peak with Lorentzian width (FWHM) $\Gamma$ is:

\[
\Delta E_m = (\Delta E_I^2 + \Gamma^2)^{1/2}
\]
For most bulk photoemission features $\Gamma > 100$ meV, while $\Delta E_I < 100$ meV is easily obtained, and hence the energy-resolution will be negligible. This is not always the case, however. For surface states inverse lifetime widths less than 10 meV have been observed\(^1\).

The energy-resolution $\Delta E_{\nu}$ of the SGMIII monochromator is typically better than 10 meV for the whole energy range, and much better for low photon energies. Therefore the dominating contribution to Equation (3.2) is from the electron spectrometer. The energy-resolution of the electron spectrometer may be split into two contributions: a constant intrinsic broadening $\Delta E_0$ due to the stability of the electronics and the precision of the mechanical parts, and a contribution $\Delta E_{\text{pass}}$ proportional to the pass energy.

\[
\Delta E_{\text{EEA}} = \left( \Delta E_0^2 + \Delta E_{\text{pass}}^2 \right)^{1/2}
\]  
(3.4)

The VG-ARUPS10 analyser is specified to $\Delta E_{\text{EEA}} = 15$ meV at the smallest pass energy, and $\Delta E_{\text{EEA}} = 13$ meV was demonstrated in a gasphase factory test.

In order to determine $\Delta E_I$ a signal with a negligible, or at least well known, line-shape is needed. The Fermi edge of a cold metallic solid is a good testing ground. The Fermi-Dirac distribution gives the fractional distribution of levels at a finite temperature:

\[
f_{\text{FD}}(E) = \frac{1}{1 + \exp \left( \frac{E - E_F}{kT} \right)}
\]  
(3.5)

where $E_F$ is the Fermi energy, $T$ the temperature and $k$ is the Boltzmann constant. Only electrons in the energy range of the order of $kT$ at the Fermi level that may be thermally excited. The width of the Fermi-Dirac distribution, measured as the width between 12% and 88% of the step height is $\Delta E_{\text{FD}} = 4kT$. The convolution of a Fermi-Dirac distribution with a Gaussian with width $\Delta E_I$ results in a Fermi-Dirac-like function with width:

\[
\Delta E_{\text{FD}}^* = \sqrt{\Delta E_{\text{FD}}^2 + \Delta E_I^2}
\]  
(3.6)

In the case of $4kT \ll \Delta E_I$ the 12%-88% width of the Fermi-Dirac distribution is equal to the instrumental energy-resolution, and the determination on the instrumental energy-resolution simple. However, in this case $\Delta E_I < 20$ meV is pursued, and then $\Delta E_I \approx \Delta E_{\text{FD}}$ (see Table 3.1 for actual values), at least for the temperatures that can be reached with this instrument. A more proper determination the energy-resolution involves fitting a Fermi-edge convoluted with a Gaussian to the data. In this context one should

\(^1\)Recently impressive experimental results have been presented by the Hüfner group for surface states on the (111) surface of Cu, Au, Ag [87, 65], and the superconducting gap on the conventional superconductor V$_3$Si [88]. For the surface state on Ag(111) measured in normal emission and at $T=30$ K they found the linewidth to be $\Gamma_m = 9.5 \pm 0.5$ meV. The instrumental energy resolution function was known to be a Gaussian with FWHM $= 3.7$ meV and from these facts the hole state lineshape could be determined as a Lorentzian with $\Gamma_s = 6.2$ meV. This value and the linewidths for Au and Cu agree well with new theoretical predictions and STM results by Kliever et al. [31]. This was a bit surprising since it has generally been accepted that photoemission measures too short lifetimes due to the sampling of large surface areas, say $1 \times 1$ mm$^2$, including an unknown number of defects and impurities, which give rise to additional scattering and a corresponding reduction in lifetime. In comparison STM is a local probe and it is possible to select an atomically smooth area for the measurements [31].
notice that an ARUPS investigation on a crystalline sample is not a trivial setup for measuring the Fermi-Dirac distribution. Kröger et al. has recently shown in a systematic study on Ni that the Fermi edge can be severely distorted in this situation. The distortion is due to electronic levels crossing the Fermi level [89]. The best way to avoid these problems is to measure the Fermi edge on a polycrystalline sample, where all the direct transitions are averaged. From measurements on polycrystalline Au films the energy resolution at the pass-energies used for most of the measurements in the present work is determined to be 30-50 meV. These values are not quite as low as the values achieved in gas phase factory test. The reason is probably related to grounding problems, and several improvements of the electrical wiring will be implemented.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>T (°C)</th>
<th>kT (meV)</th>
<th>4kT (meV)</th>
<th>2πkT (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-263</td>
<td>1</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
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<td>300</td>
<td>27</td>
<td>26</td>
<td>103</td>
<td>162</td>
</tr>
</tbody>
</table>

Table 3.1: Characteristic energies with respect to temperature the T. k is the Boltzmann constant. 4kT is equal to the 88% - 12% width of the Fermi edge. 2πkT is equal to the expected linewidth due to electron-phonon coupling with λ = 1 (in the linear approximation, Equation (2.21), valid for T > 1/3ΘD).

3.3.2 Angular-resolution

The importance of angular resolution was realized quite early in the development of PES for bandstructure mapping; see e.g. [90]. The angular resolution affects the lineshape of the observed peaks. In the case of a low angular-resolution, transitions from a significant range of initial states become possible. High angular-resolution |Δθ| < 1° is needed if detailed information of the initial state is to be gained from the analysis of the observed lineshapes. However, there is a price to pay for improving the angular-resolution: the smaller solid angle the analyser sees, the less electrons are detected. Assuming the intensity, I, to be proportional to the solid angle, Ω, then:

\[ I \approx \Omega = 2\pi(1 - \cos\Delta\theta) \approx \pi\Delta\theta^2 \]

In other words, an quadratic reduction in intensity is the price to pay for a linear improvement in resolution. In this section it is discussed how the angular resolution
influences the lineshape of the well-known Shockley surface state on Cu(111), and to what extent the actual angular resolution can be determined from the analysis of experimental data. An alternative direct method to determine the angular resolution is to scan a well-defined electron beam across the analyser entrance.

Several careful photoelectron spectroscopy experiments of the Shockley surface state on Cu(111) have been done to study the lineshape and the dispersion of the state. The state has a binding energy of ~400 meV, and disperses upward to cross the Fermi edge at a parallel momentum $k_\parallel = 0.2$ Å, as shown in Figure 3.4. The following analysis is inspired by the work of Matzdorf [15].

![Figure 3.4: Figure showing dispersion of the Shockley surface state on Cu(111) and the related energy broadening (from Ref. [15]). Experimental data are shown as filled circles and the solid line is a parabolic fit. Contributions to the linewidth for various angular resolutions and emission angles are schematically illustrated on the right hand side.](image)

The parallel component of the momentum, Equation (2.6), of an electron emitted with kinetic energy $E_{\text{kin}}$ in an off-normal emission angle $\theta$ is:

$$k_\parallel^0 = 0.512 \sqrt{E_{\text{kin}}} \sin(\theta)$$

where $E_{\text{kin}}$ is measured in eV and $k_\parallel$ in Å$^{-1}$. The related uncertainty due to the angular resolution, Equation (2.30), is:

$$\Delta k_\parallel^0 = 0.512 \sqrt{E_{\text{kin}}} \cos(\theta) \Delta \theta$$

Owing to the dispersion of the state with respect to $k_\parallel$ this $\Delta k_\parallel$ uncertainty give rise to contributions to the spectra from an extended energy range; this can be seen quite easily from Figure 3.4.

Explicitly, the measured intensity distribution is expected to be given by:
\[ I(E_{\text{kin}}, k_1) \propto \int \int D_k(\vec{k}_1 - \vec{k}_1') A_h(E', \vec{k}_1') D_l(E' + \Theta - h\nu - E_i(\vec{k}_1')) d\vec{k}_1' dE' \quad (3.7) \]

\( D_k \) is the instrumental \( k \)-space acceptance function due to the angular resolution; \( A_h \) is the hole state spectral function; \( D_l \) is the instrumental energy resolution function; \( h\nu \) is the photon energy and \( \Theta \) is the workfunction.

A simple acceptance function for \( D_k \) is assumed:

\[ D_k(\vec{k}_1) = D(\vec{k}_1) = \begin{cases} 1, & \frac{k_0^\theta - \Delta k_1}{\Delta k} \leq k_1 \leq \frac{k_0^\theta + \Delta k_1}{\Delta k} \\ 0, & \text{else} \end{cases} \quad (3.8) \]

A Lorentzian lineshape is assumed, see Equation (2.10), for \( A_h \):

\[ A_h(E, k_1) = \frac{1}{2\pi} \frac{\Gamma}{(E - E_i(k_1))^2 + \left(\frac{\Gamma}{2}\right)^2} \quad (3.9) \]

In normal emission and room temperature McDougall measured \( \Gamma = 55 \text{ meV} \) \[64\]. So far it has been tacitly assumed that \( \Gamma \) is a constant independent of the initial state energy. However this is not true, e.g. the electron-electron scattering contribution to \( \Gamma \) depends on the energy, and gets smaller as the Fermi-level is approached (see section 2.3). However, in most cases \( \Gamma \) is observed to increase as the Fermi level is approached, presumably due to electron-impurity scattering; various scenarios are tested below.

The surface state has a parabolic dispersion around the \( \bar{\Gamma} \)-point in the surface Brillouin zone:

\[ E_i(k_1) \left[ \text{eV} \right] = -0.390 + 9.38 k_1^2 \left[ \text{Å}^{-1} \right] \quad (3.10) \]

In this case the Fermi level crossing is at \( k_F = 0.2039 \text{Å}^{-1} \). For \( D_l \) a Gaussian lineshape, Equation (3.1) is assumed. The photon energy is fixed by the experiment. The workfunction of Cu(111) is \( \Theta = 4.88 \text{ eV} \), but it is allowed to vary freely in the fitting process to accommodate for any offset of the energy scale. In case of negligible energy resolution:

\[ I(E_{\text{kin}}, k_1) \propto \int_{\frac{k_0^\theta - \Delta k_1}{\Delta k}}^{k_0^\theta + \Delta k_1} A_h(E_{\text{kin}}, k_1') d\vec{k}_1' \quad (3.11) \]

\[ = \int_{\frac{k_0^\theta - \Delta k_1}{\Delta k}}^{k_0^\theta + \Delta k_1} \frac{\Gamma}{2\pi (E_{\text{kin}} - E_i(k_1'))^2 + \left(\frac{\Gamma}{2}\right)^2} d\vec{k}_1' \quad (3.12) \]

In many cases it is possible to use an energy-resolution which is high enough to justify using Equation (3.12). This is also preferable from a computational point of view, since the energy resolution of analyser broadens the lineshape due to an additional convolution with the energy resolution function. This extra convolution severely increases the computational time needed to fit the experimental data. Furthermore, the energy broadening effect due to the energy resolution will make the energy broadening effect due to the angular resolution harder to separate out.
Results

In Figure 3.5 is shown simulated spectra without energy broadening according to Equation (3.12). Spectra for two different angular resolutions, and three different scenarios for the Lorentzian width, are compared for different emission angles. A Fermi edge, Equation (3.5), is included in the calculations, and the photon energy is chosen to be 24.2 eV.

![Simulated Spectra](image)

**Figure 3.5**: Effect of a limited angular resolution on the measured lineshape of the Cu(111) surface state. Simulated spectra is shown in (a), (b), and (c). Different Lorentzian linewidth in each panel (see text). Two different angular resolutions $\Delta \theta = 0.1$ (solid line), $\Delta \theta = 1$ (dashed line) are compared for three different emission angles. Data and fits to the lineshape function is shown in (d). The energy scale is chosen such that the Fermi level is at the photon energy (24.2 eV).

In Figure 3.5 (a) and (b) the simulation assumes a Lorentzian width of 55 meV and 95 meV, respectively. In (c) the effect of increasing the Lorentzian width (from 95 meV to 150 meV) as the hole state approach the Fermi level is tested. From these
simulations several points may be stressed. First, the peak broadens asymmetrically towards the Fermi level (this would be in the opposite direction in case of a state with negative effective mass). Second, in the case of normal emission the contribution from the angular resolution is very small. Third, effects due to the angular resolution is most easily seen if the Lorentzian width is small. Fourth, the angular resolution and the Lorentzian width are highly correlated parameters. This fact will complicate the lineshape analysis since the energy dependence of the Lorentzian width is uncertain. Obviously, a very good angular resolution is needed for a precise analysis of surface state lineshape.

Figure 3.5 (d) shows experimental data and fits to Equation (3.12). Included in the fit is a Fermi function, and a smooth function describing the background intensity. The photon energy is 24.2 eV, and the analyser is moved in the plane of polarisation. Immediately, a good qualitative agreement between the data and the trends from the simulation is seen. The surface state is asymmetric towards the Fermi energy, and the asymmetry increases with increasing off-normal angle. Likewise, a reasonable quantitative agreement is found when fitting the lineshape function, Equation (3.12), to the data. However, it is not trivial to fit the spectra since many of the free parameters affect the lineshape in a similar manner. For the data set shown in (d) the best agreement is found if the inverse hole state lifetime is assumed to depend on the energy as simulated in (c). In this case the angular resolution is found to be $\Delta \theta = 0.7$. This is also the lens mode of the VG-ARUPS10 analyser used for the results in the present thesis. In general it is found that it is possible to determine the angular resolution of a electron spectrometer from analysis of experimental lineshape data. To obtain robust results it is preferable if i) one analyses spectra from several emission angles ii) the energy broadening due to the analyzer/photon-source can be neglected iii) the Lorentzian width is small, and preferably independent of energy.
CHAPTER
FOUR

Surface phase transition: $\alpha$-Ga(010)

4.1 Introduction

The stable phase of gallium at room temperature and low pressure, $\alpha$-Ga, is a semimetal containing both metallic and covalent bonds. The basic building blocks of $\alpha$-Ga are assumed to be covalently bonded Ga$_2$ dimers interacting with neighbouring dimers through weaker metallic bonds. This predominantly covalent character of $\alpha$-Ga is reflected in peculiar physical properties. The Fermi surface is anisotropic and the thermal and electrical conductivities are likewise highly anisotropic, being lowest for the direction almost parallel to the orientation of the dimers.

The dual covalent-metallic character has attracted much theoretical and experimental interest in recent years. An interesting question is how the electronic properties are affected when a surface is created. In metals this generally leads to an inward relaxation of a surface layer with bulk terminated structure. On the other hand, semiconductor surfaces often reconstruct in order to saturate broken bonds, so-called dangling bonds, if they arise in a bulk terminated structure. On $\alpha$-Ga especially the very stable (010) surface has been studied, and while the actual geometric structure is a complicate issue, it is generally agreed that the surface is more metallic than the bulk.

The properties of $\alpha$-Ga(010) surfaces\(^1\) have so far been studied by optical techniques [91], STM [94, 95], X-ray diffraction [92], LEED [98], SPA-LEED [99], ARUPS [71], and first principles calculations [100, 101, 97]. The LEED experiments have revealed that the surface undergoes a reversible phase transition upon cooling below 220 K. We have reinvestigated the surface electronic properties of $\alpha$-Ga(010) at the new ARUPS facility at ASTRID in order to study the interplay between this phase transition and the electronic structure. In this chapter the results are presented and the driving mechanism behind the surface phase transition is discussed.

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\(^1\)Note that there are different conventions in use for the crystallographic directions in $\alpha$-Ga. In accordance with [91, 71, 92], the crystallographic convention (Cmma symmetry) [93] is followed here, while [94, 95, 96, 97] follow the historic (pseudotetragonal) convention. In the latter case the $b$ and $\bar{c}$ axes are reversed, and the structure has the non-standard Mbab symmetry. The (010) surface in the present case corresponds to the (001) surface in the latter case.
4.1.1 Structure and surface phase transition

The crystal structure of gallium at atmospheric pressure (the $\alpha$-phase) can be described as an orthorhombic lattice with a basis of 8 atoms (space group $Cmca$, Strukturbericht A11); two of the axes are very nearly equal in length. The lattice constants are (at room temperature): $a = 4.5192 \, \text{Å}$, $b = 7.6586 \, \text{Å}$, and $c = 4.5258 \, \text{Å}$. A gallium atom has seven neighbors: one at a distance of 2.465 Å, two at 2.700 Å, two at 2.735 Å, and two at 2.792 Å [93]. For this reason the structure has often been viewed as consisting of singly bonded Ga$_2$ dimers, with each Ga atom weakly bound to six other atoms. In Figure 4.1 (a) the structure is illustrated with the Ga$_2$ dimers emphasized. The dimers are oriented almost perpendicular to the (010) surface plane, and alternatingly tilted by $\pm 16.9^\circ$ with respect to the [010] axis.

![Figure 4.1](image)

**Figure 4.1:** (a) The $\alpha$-Ga crystal structure with the Ga$_2$ dimers emphasized. (b) The bulk truncated (010) surface terminations A and B. (c) A charge density plot of surface C which is a (1 x 1) reconstruction resembling an $\alpha$-Ga(010) surface covered by two layers of GaIII. All Figures from [96], but the indexing is changed.

Three different surface structures have been considered for the (010) surface. First (surface A), a structure where the crystal is cleaved without cutting the inter-dimer bonds. Second (surface B), a structure where the crystal is cleaved cutting the inter-dimer bonds, creating dangling bonds at the surface and a metallic surface state. Third (surface C), a GaIII termination suggested by Bernasconi, Chiarotti and Tosatti (BCT) [97]. GaIII is a high pressure polymorph. All three terminations are illustrated in Figure 4.1 (b) and (c), while top views of the corresponding surface terminations are shown in Figure 4.2. The three surfaces are identical with respect to the top layer: the unit cell is rectangular (and almost square) containing two atoms, one at the corners and one slightly moved off the center.

The (010) surface has the highest packing density and is faceting spontaneously on $\alpha$-gallium crystals; hence, high structural stability is expected for this surface. Indeed, the (010) surface is found to be atomically flat and exceptionally stable. Note that the melting point of Ga is very low: $T_m = 303 \, \text{K}$. Züger and Dürig studied the surface at room temperature (near the melting point) with scanning tunneling microscopy (STM) and saw (010) terraces extending over several 1000 Å. The terraces were separated
Figure 4.2: (a) top view of α-Ga(010). This geometry is identical for all three terminations in Figure 4.1. (b) Surface Brillouin zone of α-Ga(010). The marker (○) between $\bar{\Gamma}$ and $\bar{C}$ indicates the $k$ point where the data in Figure 4.13 were taken.

by irregularly oriented steps. Remarkably, no surface defects were found due to the sputtering, and no surface diffusion was observed up to the bulk melting point. The crystal even seemed to melt from within the sample. The observed surface structure was in good agreement with the expected termination in Figure 4.2, but STM is not depth-sensitive and cannot distinguish between surface A, B, and C. However, only steps with a height of $b/2 = 3.8$ Å were found in the step distribution, indicating that Ga$_2$ dimers are the building blocks of gallium, and that only one surface termination is prevailing [94, 95].

The STM data also indicated a possible surface reconstruction in which the atom near the center is moved slightly towards one of the corner atoms. Such a reconstruction is consistent with the fact that Züger and Dürrig observed a $(1 \times 1)$ LEED pattern with no missing spots. For any of the three terminations in Figure 4.2, a LEED pattern with every odd-integer spot in the [100] direction missing would be expected because of the glide plane symmetry of bulk α-Ga which is preserved in the surface structure\(^2\). This observation is, however, not supported by other LEED investigations [71, 99, 98], and also in the present work missing spots is observed. The reason for the discrepancy in the case of Züger and Dürrig’s work could be that their LEED apparatus was not aligned exactly at normal incidence, or stray magnetic fields could play a role. In both cases the symmetry is broken and the missing spots will appear. The LEED pattern at room temperature is therefore regarded to be $(1 \times 1)$ with every odd-integer spot in the [100] direction missing.

Structural LEED and surface X-ray diffraction [92] investigations find a B termination of the surface. In particular, LEED [98] and SPA-LEED [99] patterns from a well-aligned surface near the melting temperature reveal the missing spots expected

\(^2\)A glide plane symmetry is a reflection plus a displacement parallel to the reflection plane. In normal incidence LEED this symmetry element introduces missing odd-integer beams along the glide plane [38].
for the glide plane symmetry. The LEED structural analysis has been performed using this symmetry constraint. However, in the surface X-ray analysis a broken glide plane symmetry is found, and it is not quite clear why these data are contrary to the LEED results. Further evidence for the B termination is found in the ARUPS investigation from 1998 by Hofmann, Cai, Grütter and Bilgram (HCGB). HCGB measured an electronic structure which resembled the theoretical result of the B termination by BCT. A predicted surface state was found at the $\bar{C}$ point of the surface Brillouin zone (SBZ) and surface states in the lower lying gaps, which are predicted only for the A and C terminations, were not observed. There were, however, two noteworthy points of disagreement. First, the theory predicts an almost circular surface Fermi surface around $\bar{C}$, what did not seem to be the case in the experiment. Second, a predicted surface state at $\bar{\Gamma}$ was not observed. In the present work, among other observations, the latter surface state has been identified. All in all, the experiments so far seem to agree upon the B termination of the surface near the melting point.

A phase transition at about 220 K was observed by HCGB with LEED. In the phase transition, the LEED pattern changes reversibly from the $(1 \times 1)$ pattern to a $c(2 \times 2)$, or $(\sqrt{2} \times \sqrt{2})R45^\circ$, pattern and spots could be observed at all integer positions. In other words, the glide plane symmetry is lost in the phase transition. Later, additional spots have been found in the low temperature LEED pattern. These spots were very weak and only observable in a small energy range. However, it turns out that the correct description of the low temperature LEED pattern is $(2\sqrt{2} \times \sqrt{2})R45^\circ$. To make matters even more complicated, SPA-LEED has shown that the overstructure spots in the low temperature phase are actually split along the direction of the glide plane by a very small amount corresponding to a real-space distance 18 times larger than the $(1 \times 1)$ unit cell [99].

Structure determination of both the high (HT) and low (LT) temperature phases from LEED I(V) analysis have recently been obtained [98]. Their main results are briefly stated since knowing the actual structure of both phases is important for a discussion of the phase transition. As mentioned above, the HT phase is a relaxed form of the B-termination. Good agreement between experiment and simulated I(V)-curves could only be achieved by assuming a very small surface Debye temperature, indicating thermal vibrations of large amplitude, or the prevalence of other types of disorder. The LT phase has been analysed using two structural models: the originally proposed $(\sqrt{2} \times \sqrt{2})R45^\circ$ structure as well as the $(2\sqrt{2} \times \sqrt{2})R45^\circ$. An analysis in terms of the very big, and possibly incommensurable unit cell indicated by the spot-splitting in SPA-LEED, is far beyond the possibilities of quantitative LEED analysis, and has not been attempted. Both structures are rather similar and give good reliability factors, with the $(2\sqrt{2} \times \sqrt{2})R45^\circ$ being the best. The structure shows a certain degree of dimerisation, likely to remove some of the dangling bonds of the B terminated $(1 \times 1)$ structure. As for the HT phase, a low Debye temperature had to be assumed in order to achieve a good agreement between measured and simulated I(V)-curves.

**Surface phase transition**

The aim of this ARUPS re-investigation of the $\alpha$-Ga(010) surface is to study in detail the interplay between the electronic structure and the phase transition, and possibly to
find the driving mechanism behind the reconstruction. In the following, surface phase transitions, and some of the work done on related systems, are briefly introduced in order to set the stage for the present work.

Phase transitions are fundamental and important phenomena in solid state physics. A phase transition is characterized by a transition temperature, \( T_c \), where the system changes between two phases. Surface phase transitions are interesting due to the two-dimensionality of the system \([102, 103]\). A solid surface may undergo various phase transitions, e.g. reconstruction, roughening\(^3\), melting. The most obvious is the melting transition, where the long range order is lost and the solid becomes a liquid. In the present context the interest is the reconstructive transition where the in-plane arrangement of the surface atoms is changed. Surface reconstructions have been observed on many clean surfaces, and are very often induced by adsorbates. Clean surface reconstruction is the rule rather than the exception in the case of surfaces on the covalently bonded semiconductors, while many metals have surface structures closely resembling a termination of the bulk structure. Phase transitions involving reconstruction are either classified as order-disorder or displacive (order-order) transitions. In the order-disorder transition the atoms occupy several equivalent sites, which are preserved through the transition, even though the long range order is lost. In the displacive transition the atoms move gradually towards the high temperature positions as the temperature is raised.

A simple explanation for the driving mechanism behind the surface phase transition on \( \alpha \)-Ga(010) is not very likely considering the complicated structural transition. Nevertheless, a fact which suggests a simple mechanism is the broken dangling bonds in the B terminated high temperature structure, which leaves the surface metallic with a high density of states at the Fermi level. Energetically this is not a very favorable situation, and one may expect the surface to reorganize in order to saturate the dangling bonds in a metal-insulator transition.

Related to the metal-insulator transition is the formation of a charge density wave (CDW); a phenomenon which has attracted considerably attention recently. While this type of instability is most likely to occur in one dimensional systems \([104]\), where it is called a Peirls distortion, it has also been observed in transition metal dichalcogenides \([19]\) and constrained to surfaces \([105, 106]\). The latter case is denoted a surface charge density wave. The most likely candidates for surface CDWs are W(100), Mo(100), H on W(110) and Mo(110) \([106, 107]\) as well as Pb \([108]\) and Sb \([109]\) on Ge(111). A charge density wave arises as follows: One introduces a periodic lattice distortion in a normal metal. This distortion will give rise to a new Brillouin zone with gaps in the band structure opening at the zone boundaries. If the new zone boundaries coincide with large parallel segments (nesting) of the original Fermi surface, the energy of many electrons will decrease upon opening of the gaps. If this electronic energy gain is larger than the energy needed to set up the lattice distortion, then a CDW will be created. The CDW mechanism is delocalised and the reconstructed structure need not be commensurate with the bulk lattice. A CDW transition should in principle be easily recognizable in PES experiments: In the high temperature metallic phase it should

\(^3\)The roughening transition happens at a characteristic temperature where long wavelength fluctuations in the local height of the surface are allowed, and the surface becomes rough and rounded rather than faceted.
be possible to observe a nested Fermi surface which in the low temperature phase disappears upon opening of a gap.

A celebrated and much studied temperature dependent reconstructions on a clean metal surface is the \((\sqrt{2} \times \sqrt{2}R\frac{45}{4}\)) reconstruction on W(100) (see [107], and references therein). The \((\sqrt{2} \times \sqrt{2}R\frac{45}{4}\)) \(\leftrightarrow (1 \times 1)\) transition on W(100), at a critical temperature \(T_c=210\) K, was the first clean surface phase transition to be characterized. In 1977 two groups (Debe, King and Felter, Barker, Estrup) reported the transition, and it was realized that the low temperature phase consisted of a zig-zag distortion along a diagonal direction of the \((1 \times 1)\) lattice. These observations generated widespread interest in the W(100) and W(100)/adsorbate systems. Many experiments have been carried out to characterize the two phases and the transition, especially in order to answer the central question: What is the driving mechanism behind the phase transition? Explanations have been approached from two opposite point of views: a charge-density wave driven periodic lattice distortion versus local bonding of surface orbitals.

The CDW scenario was suggested in the original report on the phase transition on W(100) and further elaborated by Tosatti in the following year [110]. Shortly after the CDW scenario was introduced, a local bonding picture was suggested, where the transition was suggested to be driven by Jahn-Teller like instabilities. This was inspired by the first PES experiments where the Fermi surface was mapped, and no significant nesting of states near the Fermi level were found. The local bonding picture generally favors a commensurate structure. The CDW scenario regained strength when new PES measurements found a surface state near \(E_F\) over a large portion of the surface Brillouin zone, that could participate in a CDW transition for a variety of phonon vectors. Furthermore, in 1986 Woods and Erskine were the first to report the existence of a phonon related to the reconstruction, and later a soft phonon mode was observed in the clean surface phase transition by Ernst, Hulpke and Toennies. These results suggested that the CDWs explanation could not easily be dismissed [107].

The scenario is more complicated though, and the PES evidence have been scarce. One of the reasons is that the CDW is not always purely electronic as considered above, but the lattice vibrations play an active role. A surface phonon may get frozen below the transition temperature because of an electronic instability involving surface states, and the electronic energy gain does not have to originate (only) from a nested Fermi surface [111]. In fact, the electronic states can be changed in a large fraction of the SBZ, and the gap can be much larger than in a CDW which is driven purely by electrons. Tosatti has called this scenario for a ‘strong coupling’ CDW [106]. Another complication is the nature of the transition from the ordered low temperature CDW phase to the high temperature phase. Just above the transition temperature the long range order is lost, but short range order of similar nature may still be present and lead to confusing photoemission results. In particular, it may not be possible to observed a clear-cut Fermi surface [106].

The work presented here is in many aspects a continuation of the work by HCGB using a more sophisticated apparatus. Compared to the HCGB experiment the data are taken with much higher energy resolution and additionally the sample can be cooled to lower temperatures. Last but not least, the option to automatically scan the analyser angles, and map the Fermi surface, is a conceptually important difference.

The remaining part of this chapter is structured as follows: First the experiment
is discussed and a brief overview of the observed electronic structure is given. This is followed by a detailed description of the temperature dependence of the various surface states and the entire two-dimensional Fermi surface. The driving mechanism behind the surface phase transition is discussed, and finally the main conclusions are summarized.

4.2 The experiment

The ARUPS investigation was done at the new ARUPS facility at storage ring ASTRID in Aarhus. See Chapter 3 for a detailed description of the instrumentation.

The α-Ga(010) sample was cut from a bulk single crystal, and was mechanically polished to a perfect mirror finish. Obviously care needed to be taken to avoid melting of the sample during the polishing process. This was achieved by cycles of cooling the sample to −20°C in a freezer, followed by polishing for while. The sample was inserted into the vacuum chamber via the load-lock system. The cleaning and preparation of the surface was done by the standard method of ion sputtering (Ne⁺) followed by annealing. However, in the case of Ga the annealing is a bit unusual due to the very low bulk melting point (~room temperature). The initial cleaning cycles consisted of sputtering at 2 kV for about 20 min at T = 253 − 273 K, followed by ‘annealing’ at the same temperature for a similar amount of time. A clean and well ordered surface at room temperature was evidenced by a sharp (1×1) LEED diffraction pattern with missing spots in the [100] direction, and characteristic photoemission spectra. In the initial states of the cleaning cycles oxygen related peaks were clearly seen in the valence band. Once an almost clean surface was obtained, the surface state at Ĉ turned out to be rather sensitive to the surface quality. The clean surface was maintained by sputtering at 2 kV for 8 min at 253 K, followed by ‘annealing’ for 17 min at 253 K.

The maintaining procedure was optimized in order to both clean the surface and in the same time heat the cryostat as little as possible, allowing a fast successive cooling of the sample. Some spread in the linewidth at a certain temperature was found with respect to the previous cleaning cycle, although the sample position was reproduced with high accuracy. This was ascribed to the preparation history, though a systematic pattern has not been identified.

Temperature scans were performed using two different approaches. The first was to clean the sample at 253 K and let it cool down while taking spectra at the desired temperatures. Cooling from 253 K to 30 K takes about one hour plus the time needed to collect the data (~30 min). The second approach was to clean the sample at 253 K and remove it from the cryostat by grabbing it with a wobble stick. An hour later, when the cryostat was cooled down, the sample was reinserted into the sample holder where it cooled to 30 K within a few minutes. The temperature scans were then taken while warming up the sample.

Above 80 K the surface is rather insensitive towards contamination. At the lowest temperatures the surface was found to be more reactive against contamination: the surface state at Ĉ degraded fast and new peaks appeared in the valence band. This low temperature contamination is illustrated in Figure 4.3. Two options for doing measurements of long duration at the lowest temperatures were then: either flash the sample to
Figure 4.3: Adsorption at a cold α-Ga(010) surface. Normal emission and photon energy $h\nu = 31$ eV. Spectrum (A) show two peaks at binding energies 11.5 eV and 7.7 eV, respectively, developed after the sample has been kept for almost two hours at $T = 35$ K. The peaks are gone after cleaning the sample at room temperature and re-cooling to $T = 35$ K (B). One hour later the peaks are visible again (C). Heating the sample to $T = 78$ K removes the peaks (D), but after re-cooling and keeping the sample at $T = 35$ K the peaks re-emerges (E). Again, reheating to $T = 78$ K removes the peaks (F). The pressure during these measurements was in the mid $10^{-11}$ mbar region.

80 K every one hour, or just keep the sample at 80 K. The latter strategy was chosen for the low temperature Fermi surface mappings.

In this experiment the total energy resolution was around 40 meV and the angular resolution was circa $\pm 0.7^\circ$. The pressure during measurements with the synchrotron radiation was in the $10^{-11}$ mbar range. For the photoemission measurements the sample was positioned such that the angle between the surface normal and the incident light was 40 degrees with synchrotron radiation, and 60 degrees with the discharge lamp. The azimuthal orientation was chosen such that the polarization vector was oriented along the $\bar{\Gamma}$-$\bar{\Sigma}$ direction of the SBZ. All spectra taken with synchrotron radiation were normalized to the photoemission current of the last focusing mirror in the beamline. The method appears to work well, especially if the spectra are taken within the same electron-filling of the storage ring, and allow us to compare absolute count rates for the temperature scans.
4.3 Results

In the previous ARUPS investigation by HCGB, and in the present work, the surface electronic structure is found to closely resemble the theoretical result by BCT for the relaxed B termination - in good agreement with recent structural studies. BCT's theoretical results for the A and C terminations predicted surface states in the lower lying projected bandgaps, between 6 and 9 eV binding energy, which have not been observed so far, neither by HCGB nor in this investigation.

A central feature is the surface state in the projected bandgap around $\bar{\Gamma}$ in the SBZ. We denote this state $S_H$ in the following. The experimental binding energy of this state at $\bar{\Gamma}$ is around 1.1 eV, and somewhat larger than the calculated value of 0.5 eV. This surface state is a dangling bond state which arises due to the cutting of the dimers. It is doubly degenerate since each of the two surface atoms supports such a state. The dispersion, Fermi surface and temperature dependence of this state will be discussed in details below. A second surface-related feature is found at $\bar{\Gamma}$ very close to the Fermi energy in the low temperature phase. This low binding energy state is denoted $S_L$ in the following. HCGB had already observed this state but only as weak shoulder; a well defined structure is found. Such a state was not predicted by BCT for any of the considered surface terminations.

Finally, BCT did also predict a surface state at the $\bar{\Gamma}$ point of the SBZ for all three terminations. This state was not observed by HCGM but has been found in the present work, as shown in Figure 4.4. The binding energy of the state is 0.5 eV in good agreement with the BCT prediction. The state has been identified according to the common traits discussed in Section 2.2.1: it is located in a projected band gap and shows no dispersion with change of $k_\perp$. The state is always barely visible and owing to its weak cross-section not very well suited for detailed line shape studies. The reason why the state was not identified by HCGB is probably the fact that it can only be seen at higher photon energies than used in that study.

4.3.1 The two surface states at $\bar{\Gamma}$

Two surface states can be found at $\bar{\Gamma}$. The first is the dangling bond state $S_H$ with a binding energy of around 1.1 eV, which can be observed at all temperatures. At low temperatures the additional state $S_L$ is found very close to the Fermi level. Spectra of the electronic structure at $\bar{\Gamma}$ taken at two different photon energies are shown in Figure 4.5, illustrating the independence of the features from $k_\perp$. Both spectra have been taken such that the $S_H$ surface state is exactly at $\bar{\Gamma}$ and the $S_L$ state is not. Moving the analyser a few degrees to the position where the $S_L$ state is exactly at $\bar{\Gamma}$ leads to an increase in the intensity of the peak. Note that this state was only observed as a weak shoulder by HCGB; in this case it is a well resolved peak. It is very difficult to make further statements about the binding energy and line width of the $S_L$ state since it appears to be cut off by the Fermi level. At the lowest temperatures the $S_L$ state also appears to be rather sensitive to contamination.

The temperature-dependence of the surface state linewidth can be used to extract information about the strength of the electron-phonon mass enhancement parameter for the surface $\lambda_s$. We reviewed the assumptions and the formalism in Section 2.4.
Figure 4.4: Spectrum taken in normal emission at T=78 K and $h\nu = 39$ eV. The small feature at about 0.5 eV binding energy is the surface state at the $\Gamma$ point in the surface Brillouin zone.

Figure 4.5: Spectra taken at low temperature and for two different photon energies with the $S_H$ surface state at $\bar{C}$. The $S_L$ surface state is only approximately at $\bar{C}$. 

The maximum phonon energy in bulk α-Ga is $E_{\text{max}} = 40$ meV [112]. HCGB reported an electron-phonon coupling parameter $\lambda_s = 1.4 \pm 0.10$, derived from the temperature dependence of the width of the surface state. This value is higher than the bulk value $\lambda = 0.98$ showing a strong electron-phonon coupling on the surface. An unexpectedly high background intensity in the projected bulk band gap was seen as a further indication of a breakdown of the quasiparticle picture [71].

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{spectra.png}
\caption{Temperature dependence of the surface electronic structure at $\bar{C}$ for $h\nu = 15.5$ eV. The spectra have been normalized by the photon flux and are plotted with a constant offset. The temperature is changed by $\Delta T = 20$ K between the spectra.}
\end{figure}

Figure 4.6 shows a typical set of spectra taken at the $\bar{C}$ point as a function of temperature. One clearly observes the narrowing of the $S_H$ peak, and the evolution of the $S_L$ peak as the temperature is lowered. An interesting spectral feature is the high background intensity between the surface state and the Fermi level. From the gap in the projected bulk band structure one would actually expect the spectral intensity to be zero or at least very low. Finite intensities can be created by scattering events which does not, or only very little, change the electron energy; this does notably take place by phonon or impurity scattering. At least at the lowest temperatures phonon scattering is unimportant. On the other hand, it is also inconceivable to assume a high amount of defects for this surface since the methods of preparation used here are known to lead to highly ordered surfaces with very large terraces [95, 99].
Figure 4.7: The surface state is fitted with an asymmetric Lorentzian and a linear background in order to extract the linewidth. This is shown for a high and a low temperature spectrum in the figure.

For a quantitative analysis of the lineshape, a Lorentzian-like lineshape is fit to the peak in order to obtain the inverse lifetime of the hole state; this is illustrated in Figure 4.7. The peak is slightly asymmetric and not purely Lorentzian due to the the angular resolution of the analyser (and any other $k_f$ integrating mechanism). However, the high-binding energy side of the peak ought not to be broadened, and for this reason the peakshape is approximated with a lineshape consisting of two ‘half’ Lorentzians. The part of the peak below the binding energy is a Lorentzian with width $\Gamma_<$ while the other part has width $\Gamma_>$. The FWHM of the peak is then $\Gamma = 1/2 \cdot (\Gamma_<> + \Gamma_>)$. The $\Gamma_<$ value is used as the best measure of the inverse hole state lifetime. Note that this way of fitting allows the asymmetry, $(\Gamma_> - \Gamma_<)/(\Gamma_<> + \Gamma_<)$, to be quantified; in this manner the conservation of $k_f$ can be investigated. In addition, a linear background is included. As indicated in the figure, the fit is performed only over a restricted region [1.45, 0.70] eV. The objective of this procedure is to fit all the spectra in a consistent way, and at the same time to avoid problems with the different backgrounds on both sides of the peak. The above-described fitting procedure yields consistent fits for all temperatures and various photon energies. The absolute values for the widths depend on the specific choice of the lineshape function and the energy range to be fitted. However, the
qualitative behaviour of the lineshape versus temperature reported below is a robust
and inherent feature independent of the fitting procedure. Note that this approach to
data analysis is different from the one pursued by HCGB. In that case the fitting of the
peaks was done with a Voigt lineshape, assuming a certain energy resolution. In the
present case the energy resolution is much smaller than the peak width such that only a
fit with a Lorentzian is required, i.e. the Gaussian broadening is neglected. In this way
the large uncertainties associated with a fitting procedure in which the resolution and
the linewidth to be determined are of the same order of magnitude is avoided.

![Linewidth as a function of temperature for the $S_H$ state at $\hbar\nu = 15.5$ eV](image)

**Figure 4.8:** Linewidth as a function of temperature for the $S_H$ state at $\hbar\nu = 15.5$
eV. The data set consists of 11 independent series; the sample was cleaned before
each series. The error bars represent the uncertainties resulting from the fitting of an
asymmetric Lorentzian to the data.

The resulting linewidth for several measurements performed at 15.5 eV photon
energy is shown in Figure 4.8. the sample was cleaned in between each set of data.
From the included error bars one sees that the spread in data is somewhat larger than
the uncertainty in the individual fits. This difference is most likely to be dependent of
the preparation history, e.g. the amount of surface defects. It is also noteworthy that the
relative spread is bigger in the HT phase. Otherwise the data are rather reproducible.
The most important observation to be made in the figure is the almost sudden increase of linewidth at the temperature of the phase transition. The linewidth changes by about 60 meV in a temperature region of about 10 K. Below the phase transition the linewidth appears not to be a linear function of the linewidth. Rather, it is flattening out at the lowest temperatures. This behavior can be expected from Equation (2.20) even in a simple Debye model, Equation (2.22). However, it has seemingly only recently been observed [20].

Figure 4.9: The data from Figure 4.8 together with three different fits within the Debye model; the fixed parameter is underlined. The fits have been restricted to the data taken below 220 K. The transition temperature $T_c = 231$ K and the melting point $T_m = 303$ K are marked by vertical lines.

Figure 4.9 shows selected fits to the linewidth data below the phase transition using Equation (2.20) in the Debye-model, Equation (2.22), and including a constant term $\Gamma_0$ taking into account the temperature independent contribution from electron and impurity scattering. The phase transition cannot be explained by the model, and this region is excluded from the fit. Above the phase transition the temperature range is too short to permit a meaningful fit. It turned out that the three free parameters $\lambda_s, \omega_D, \Gamma_0$ in the fitting function are highly correlated in the low temperature region. One of the
parameters was therefore fixed. First, the sample Debye temperature was fixed to the bulk value of α-Ga (ω₀ = 28 meV). Second, λₚ was fixed to the averaged bulk value λ = 0.98. Third, motivated by recent calculations Γ₀ = 56 meV was chosen [113]. The correlation of the parameters can immediately be seen from the similarity of the three fits in the figure. From the fit with the fixed bulk Debye temperature we find an energy-independent offset Γ₀ = 92 meV and a value of λₚ = 1.06. The position of the phase transition has been precisely determined by fitting a step-like function to a region around Tₚ. In this case Tₚ = 231 K and the width of the transition is about 10 K.

The resulting fit parameters have to be considered with respect to the observed preparation-dependence of the linewidth, and keeping in mind that a different fitting region for the determination of the Lorentzian width also leads to slightly different results. This is mostly affecting the temperature-independent offset, and the absolute value of the Γ₀ parameter has to be treated with care. The value of λₚ determined here is similar to the result of HCGB, although the absolute linewidth values in that work were smaller, and the fit was performed with the unlikely assumption of no temperature-independent broadening. These differences are ascribed to the poor energy resolution in the work of HCGB which required an indirect determination of the linewidth.

![Figure 4.10:](image)

**Figure 4.10:** (a) Spectra from the series shown in Figure 4.6, but plotted without vertical offset and in ∆T = 10 K steps. A sudden change in the spectral shape at the temperature of the phase transition is easily recognizable. (b) A comparison between a high temperature spectrum and a very cold spectrum for the Sₐ surface state at C. Also shown is a cold spectrum with the Sₐ surface state at C. Note how the Sₐ state increases the density of states at the Fermi level around C.

In order to learn more about the spectral changes at the phase transition, it is very instructive to plot a set of spectra taken at C in the vicinity of the phase transition.
without a vertical offset. This is done in Figure 4.10. Again one observes the narrowing of the \( S_H \) state upon decreasing the temperature. More importantly, an apparently discontinuous change of the spectral shape in a broad energy range from the Fermi level and below is observed at the phase transition. Above the transition temperature a round Fermi edge is present. Just below a small peak due to the \( S_L \) state is seen near the Fermi level, leading to an enhancement of spectral intensity there. Between the \( S_L \) state and the \( S_H \) state there is a considerable loss of spectral intensity. Note that this loss is intimately related to the sudden decrease of surface state linewidth observed when cooling through the phase transition (see Figure 4.8). The spectral intensity at binding energies higher than \( \sim 1.5 \) eV does not seem to be affected much by the phase transition.

To summarize the main findings of this section: a re-investigation of the temperature dependence of the \( S_H \) state confirms the presence of strong electron-phonon coupling as already reported by HCGB [71]. In a small temperature range around the phase transition a quasi-discontinuous change of spectral shape is observed; especially the phase transition is accompanied by a change in the linewidth of the \( S_H \) state. The \( S_L \) state is observed immediately below the transition temperature and seems to be characteristic for the LT phase, being completely absent above the transition temperature.

### 4.3.2 The electronic structure away from \( \bar{\mathbf{C}} \)

When moving away from the \( \bar{\mathbf{C}} \) point, the \( S_H \) state shows a parabolic dispersion with an effective mass of 1.3 electron masses. The dispersion along two high-symmetry lines (\( \bar{\mathbf{C}} \rightarrow \bar{\mathbf{X}} \) and \( \bar{\mathbf{C}} \rightarrow \bar{\mathbf{W}} \)) and along the \( \bar{\mathbf{C}} \rightarrow \bar{\mathbf{\Gamma}} \) line is shown in Figure 4.11 for two temperatures, 253 K and 78 K. For the \( \bar{\mathbf{C}} \rightarrow \bar{\mathbf{X}} \) direction, HCGB have observed a Fermi level crossing of the quasiparticle peak in the HT phase. This crossing was removed in the LT phase. This simple scenario cannot be confirmed here. The intensity plots shows clearly the presence of a strongly dispersing bulk feature which mixes with the surface state at about 0.5 eV binding energy. At lower binding energies, both features cannot be distinguished anymore. Close to the Fermi energy, both states form a broad peak which may have some spectral weight above the Fermi energy but does not show a clear crossing. At 78 K the state is sharper, and the spectral weight at the Fermi level therefore smaller, but the qualitative dispersion in this region is similar. For the \( \bar{\mathbf{C}} \rightarrow \bar{\mathbf{W}} \) direction the strongly dispersing feature is also seen but it is unclear whether or not it mixes with the surface state. In both directions no clear Fermi level crossing is observed in the HT phase, but the surface state, in this case more correctly termed a surface resonance, closely approaches the Fermi level. In the \( \bar{\mathbf{C}} \rightarrow \bar{\mathbf{\Gamma}} \) direction the situation is clearer. Here the surface state dispersion clearly ends in the bulk continuum about 200 meV below the Fermi level.

The \( S_L \) state is barely visible in the low temperature data of Figure 4.11, mainly because its intensity with respect to \( S_H \) is relatively low; additionally the state is only present in a narrow range around \( \bar{\mathbf{C}} \), as is clearly seen in Figure 4.12. When moving the emission angle away from \( \bar{\mathbf{C}} \), the \( S_L \) state appears to either cross the Fermi level or to loose its intensity and disappear. What actually is happening cannot be decided on the basis of these data. It is interesting, however, to speculate about the origin of the \( S_L \) state. When viewing the reconstruction as “almost” \( (\sqrt{2} \times \sqrt{2})R45^\circ \) one could expect
Figure 4.11: A grey-scale intensity plot of the dispersion of the $S_H$ state along selected high symmetry directions away from the $\bar{C}$ point. Dark areas correspond high intensity. The data are taken for two temperatures: above and below the phase transition temperature, respectively. Note that the data are taken with both the discharge lamp (21.2 eV) and synchrotron radiation (24.5 eV).

an umklapp process which folds the states from the $\Gamma$ point into the $C$ point, and the $S_L$ state could be the same as the surface state at $\bar{\Gamma}$ shown in Figure 4.4. This origin of the $S_L$ state can, however, be excluded because it is much closer to the Fermi level than the state at $\bar{\Gamma}$.

Figure 4.13 shows a set of spectra in the vicinity of the phase transition taken at an arbitrary point away from $\bar{C}$ in the SBZ (the point is indicated in Figure 4.2). An observation similar to that in Figure 4.10 is made: at the phase transition the spectral shape changes discontinuously. Away from $\bar{C}$, the $S_L$ state is not present and consequently one finds a decrease of spectral intensity from the Fermi level down to the $S_H$ state. It
Figure 4.12: Dispersion of the $S_L$ state in the vicinity of $\bar{C}$, along the $\bar{C}$ - $\bar{X}$ direction at $T=78$ K and $h\nu = 15.5$ eV.

has to pointed out that there is nothing special about this $k$ point. We have performed similar measurements at many other points in the projected band gap around $\bar{C}$ and made similar observations. A more systematic approach to this is described in the next subsection.

Figure 4.13: Temperature dependent ($\Delta T = 10$ K) spectra taken away from the $\bar{C}$ point on the $k_{\parallel}$ point indicated in Figure 4.2 (b). At the temperature of the phase transition a sudden loss of spectral intensity is observed between the Fermi level and circa 1.5 eV binding energy.
4.3.3 The two-dimensional Fermi surface

A discussion of the phase transition in terms of a CDW or, more general, a metal insulator transition requires the experimental determination of the surface Fermi surface above and below the transition temperature. In the previous sections we have already seen that the phase transition leads to a quasi-discontinuous change of photoemission intensity at the Fermi level, at least at some point of the SBZ. The surface state dispersions shown in Figure 4.11 do not reveal any clear-cut Fermi surface in the directions considered, but there may be some spectral intensity at $E_F$ from the $S_H$ state, or a surface resonance derived from this state, in both the $\bar{C} - \bar{X}$ and $\bar{C} - \bar{W}$ directions. In order to obtain more complete information about the surface Fermi surface in the entire SBZ, the photoemission intensity at the Fermi level was measured for two photon energies (15.5 eV and 17 eV) and at two temperatures (273 K and 83 K). The measurements for each photon energy where performed right after each other, within the period of one electron filling of the storage ring, and thus the absolute count rates normalized by the last mirror photoemission current should be well comparable at each photon energy. The intensity at the Fermi level was determined by integrating over a 50 meV energy window centered on the Fermi level. A background correction was performed by subtracting the averaged intensity of a 50 meV energy window well above the Fermi level. The mapping was only done in one irreducible quarter of the SBZ. The rest of the plots is obtained by symmetry. The resulting Fermi level intensity maps are shown in Figure 4.14. The color scale at each photon energy is chosen such that the same scaling applies to the HT and LT scan. The difference between the HT and LT intensity plots is calculated as $(I_{LT} - I_{HT})/I_{HT}$.

Before moving to an interpretation of the maps some remarks of caution is worth restating. In Section 2.2.3 it was noted that identifying the photoemission intensity at the Fermi level with an image of the (surface) Fermi surface is not without problems. A minor issue with respect to this experiment, is the fact that the determination of the Fermi surface position by this technique suffers from small systematic errors [53]. The bigger problem is that it might result in a qualitatively misleading or wrong picture. While the approach seems to work well in cases where bulk and surface Fermi surface are simple and well separated from each other such as on Cu [49] or Bi [5], if can fail to reproduce certain features of the Fermi surface in the case of narrow band systems or Fermi surface segments which are very close to each other [43].

We now come back to the interpretation of the results presented in Figure 4.14. The strongest features in the maps of the Fermi level intensity are the half-circles close to $\bar{\Gamma}$ in the $\bar{C} - \bar{X}$ direction, the two vertical features at the sides of the $\bar{X}$ point, and the point-like feature at $\bar{W}$. All these are interpreted as bulk-related. The peak at $\bar{W}$ must be a bulk feature, or at least a surface resonance, because there is no projected bulk band gap at $\bar{W}$ [97]. All the other features are immediately identified as bulk related because one can see their form change with photon-energy, demonstrating a sensitivity towards a change of $k_\perp$ which would not be expected for a surface state.

For the HT phase, a clear-cut surface Fermi surface, caused by the Fermi level crossing of the quasiparticle peak from the $S_H$ state at any point of the SBZ, is not observed. Instead, a relatively high intensity at the Fermi level is found in almost all of the projected bulk band gap around the $\bar{C}$ point. This intensity is much lower in the
Figure 4.14: Maps of the integrated Fermi level intensity at two different photon energies, and temperatures above/below the surface phase transition. Data was only obtained in irreducible quarter of the SBZ, the rest of the image was generated by symmetry. The two maps in the bottom row show the difference (see text) between the low temperature and the high temperature maps.
LT phase, consistent with Figure 4.13. One can characterize this as the opening of a pseudogap over large fractions of the SBZ.

In the LT data the $S_L$ state is visible as a relative maximum in intensity around the $\bar{C}$, as expected. We do, however, also observe an increase of Fermi level intensity in a broader region around $\bar{C}$ in the HT data, suggesting that the $S_L$ state is still present to some degree, but smeared out in momentum space. This seems surprising, especially when considering the data in Figure 4.10 where the $S_L$ state is vanishing abruptly at the phase transition.

### 4.3.4 Core levels

Signs of the surface phase transition were also found in the shape of the Ga 3$d$ core level lines. The temperature-dependence$^4$ of the core level spectra is shown in Figure 4.15. Just as in the valence band, a sudden change of the core level lineshape is observed at the transition temperature. In the low-temperature phase the spin-orbit split components of the 3$d$ line are apparently broadening as well as slightly shifting in energy position. The lineshape change has some minor dependence on the emission angle as shown in Figure 4.15.

![Figure 4.15](image)

Figure 4.15: Temperature dependence of Ga 3$d$ for two different emission angles ($\theta$). The photon energy was $h\nu = 52$ eV. The spectra are taken in temperature steps of $\Delta T = 10$ K with $T = 253, 243, 233$ K above the phase transition temperature ($T_c$) and $T = 223, 213, 203$ K below.

These changes related to the surface phase transition must obviously originate in

$^4$The main concern in the present thesis is photoemission from the valence band, but one should note that there are similar temperature effects in photoemission from core levels [114, 115].
a surface contribution to the 3d signal. The core level binding energies of atoms in the surface layer may be different, by the so-called surface core level shift (SCLS), from the bulk values. This effect is due to the reduced coordination of the atoms in the surface. One could now imagine the SCLS to be different for the two phases, giving rise to the observed abrupt change in lineshape. Unfortunately, it has not been possible to clearly identify SCLS components of the Ga 3d lines. In fact, spectra of the 3d line for various emission angles and photon energies are generally quite well fitted with two Gaussian broadened Doniach-Sunjic lineshapes. Notice that the Gaussian broadening is an intrinsic effect due to phonon scattering of the core hole, and significantly greater than the instrumental broadening. The fact that any SCLS components cannot be resolved does not rule out this explanation of the lineshape change. The angular dependence seen in Figure 4.15 is most likely due to different photoelectron diffraction effects for the surface and the bulk components.

Related to the SCLS difference between the surface and bulk, one may consider whether the Ga 3d states show some band structure behavior. The 3d states are shallow and may not be fully localized. If this is the case, the surface 3d band structure would be expected to be different from that of the bulk. The observation could then be explained by a change in the 3d surface band structure at the phase transition. The possibility of band dispersion in the 3d states has been investigated by looking at the angular dependence of the lineshape. Unfortunately, the small lineshape dependence on emission angle and photon energy makes it impossible to decide whether the SCLS or the bandstructure picture is the best description.

### 4.4 Discussion

Several ingredients seem to be important in the phase transition: an at least partial dimerization of the surface atoms [98], the opening of pseudogap at the Fermi level, the absence of a clear-cut nested Fermi surface from the $S_H$ quasiparticle peak, remaining short range order and thermal fluctuations in the HT phase, and probably also the strong electron-phonon coupling. All these points suggest the transition to be interpreted as an order-disorder transition which is very likely to be close to the ‘strong coupling CDW’ scenario discussed by Tosatti [106]. In the following a detailed discussion of the findings is given in the light of this picture.

The present study has confirmed that the electron-phonon coupling is very strong on $\alpha$-Ga(010), a fact that would favor the type of phonon softening transition considered. The sudden increase of the linewidth at the phase transition temperature cannot readily be explained in the usual picture of the electron-phonon coupling. A likely explanation for the increase is that a new efficient decay channel for the hole state, which does not have to be phonon related, is opened at the phase transition. Such a channel could be an excitation which corresponds to fluctuations shifting the domain walls between areas of short range order still present at the surface.

The presence of large thermal fluctuations in the HT phase agrees well with an increased surface disorder above the phase transition as observed with SPA-LEED [99], and with the fact that good agreement between simulated and measured LEED I(V) curves for the HT phase can only be achieved assuming a very low surface Debye
temperature in the simulations [98]. The concept of a surface Debye temperature in quantitative LEED analysis is intended to describe the enhanced thermal vibrations at the surface, however, other kinds of disorder will also lead to a low surface Debye temperature. On the other hand, we need to note that the LEED I(V) analysis of the LT data also requires the assumption of a low Debye temperature. So maybe the surface vibrational amplitudes are indeed very large, weakening the argument.

The LEED structure determination suggests, in agreement with naive intuition, that a dimerization in the surface does at least play some role in driving the phase transition. Such a dimerization should remove the dangling bonds and decrease the metallicity of the surface. In other words, one should observe a partly removal of the surface Fermi surface, or at least a decrease in the density of states at the Fermi level in the LT phase.

In the following the possibility of Fermi surface nesting and related issues is discussed. It is useful to have two limiting cases of the surface structure in mind. The first is to view the reconstruction, crudely simplified, as \((\sqrt{2} \times \sqrt{2})R45^\circ\). In this case one would have to look for a Fermi surface with a nesting vector corresponding to the \(\bar{\Gamma} - \bar{C}\) vector. The \(S_H\) surface state would in fact be a good candidate to set up such a nesting scenario. It would have to have Fermi level crossings half-way along the \(\bar{\Gamma} - \bar{C}\) line. In addition to this, the Fermi surface should continue as straight lines perpendicular to the \(\bar{\Gamma} - \bar{C}\) line. The other limiting case is the complicated real structure which is not only \((2\sqrt{2} \times \sqrt{2})R45^\circ\) but also show split spots in SPA-LEED which indicate a periodicity about 18 times the lattice constant in the direction of the glide plane. In this structure, Fermi surface nesting could happen almost over the entire \((1 \times 1)\) Brillouin zone where the \(S_H\) state crosses the Fermi level.

If the electronic dispersions in Figure 4.11 and the Fermi level intensity scans in Figure 4.14 is considered little evidence is found to support the simple Fermi surface nesting scenario which would explain the \((\sqrt{2} \times \sqrt{2})R45^\circ\) structure. Indeed, according to Figure 4.11 the surface state does not cross the Fermi level in the \(\bar{\Gamma} - \bar{C}\) direction but runs into the bulk bands. This happens so far below the Fermi level (at around 400 meV binding energy) that even the spectral intensity due to the finite width of the peak is small at the Fermi level. Moreover, the Fermi intensity map does not show a clear Fermi line in the region of interest. It reveals rather a smeared out Fermi level intensity in the HT phase which is disappearing in the LT phase not only along \(\bar{\Gamma} - \bar{C}\) but in a large fraction of the projected bulk band gap around \(\bar{C}\). Also for the other structural model, \((2\sqrt{2} \times \sqrt{2})R45^\circ\) with and additional elongation of the unit cell along the glide plane, one would at least require the observation of a clear Fermi surface in the HT phase in order to claim nesting.

The absence of a well defined Fermi surface in the data for the HT phase is particularly striking when comparing the data to the theory of BCT for the B termination, which is assumed to be the correct structure for the HT phase. According to BCT, the \(S_H\) surface state should have an almost circular surface Fermi surface around \(\bar{C}\), and a maximum binding energy of 0.5 eV. No clear Fermi surface and a maximum binding energy of 1.1 eV is found this work. One could be tempted to argue that the absence of a Fermi surface is due to the higher binding energy of the \(S_H\) surface state, which shifts the surface state band down and causes the band to end up in the bulk continuum rather than crossing the Fermi surface. The situation cannot be this simple, however, since the \(S_H\) state on the B termination is a dangling bond state, and thus only partly
occupied. This means that the $S_H$ state needs to have a Fermi surface. A missing Fermi surface apparently leads to a contradiction with the structural data which indicate a B termination.

This apparent problem may be solved by considering the importance of fluctuations in the HT phase. It has been emphasized by Tosatti [106] that these fluctuations will necessarily lead to a situation where the information gathered in photoemission spectroscopy is unclear. In simple terms this is due to the fact $k_{\parallel}$ is no longer a good quantum number, and thus one cannot expect to measure a well defined two-dimensional Fermi surface. The observations of spectral changes near the Fermi level which accompany the phase transition fit very well into this picture: a considerable change in spectral intensity near the Fermi level at the phase transition temperature is observed, as seen in Figure 4.10, 4.13, 4.14. In most regions of the SBZ this change is a loss of spectral intensity, corresponding to the opening of a pseudogap. Directly at $\bar{C}$ this is not the case because of the emergence of the $S_L$ peak in the LT phase. The spectral change is not restricted to the immediate vicinity of the Fermi level. In fact, Figure 4.10 shows a loss of spectral intensity over a broad energy range. The entire behaviour can be interpreted as the removal of an ill-defined Fermi surface by the opening of pseudogap, as expected following Tosatti’s argument. Note that the spectroscopic signatures of the phase transition are very similar to the findings of Dardel et al. for the incommensurate to quasi-commensurate transition on 1T-TaS$_2$ [116, 117]. In that system they have observed a sudden opening of a pseudogap together with spectral changes over an energy range much larger than the $kT$ associated with the phase transition.

The fact that $k_{\parallel}$ ceases to be a good quantum number in the HT phase has obviously consequences beyond the Fermi surface. In fact, it provides a good alternative explanation for the jump in surface state linewidth at the transition temperature. The transition from the LT to the HT phase is accompanied by a loss of clearly defined $k_{\parallel}$. This leads to a broadening of the surface state not because of a new decay channel for the hole state, but simply because the initial state is not longer well-defined. However, in this case one would also expect the surface state to broaden asymmetrically, what does not seem to be the case.

It has to be mentioned that these considerations do also apply, to a smaller degree, to the LT phase since at finite temperatures, a CDW is not perfectly ordered either. An interaction between the excitations of the CDW will at least contribute to the finite intensity at the Fermi level which we do observe for all temperatures in the gap around $\bar{C}$. This view is supported by the fact that the Fermi level intensity decreases as the temperature is lowered even below the phase transition, a behaviour which would not be expected in the case of defect scattering. This effect also has to be kept in mind when interpreting the temperature dependence of the surface state linewidth entirely in terms of the electron-phonon coupling. A change in the degree of the $k_{\parallel}$ smearing will also have an influence on the linewidth.

It is well established that the appearance of the pronounced $S_L$ peak at $\bar{C}$ is closely related to the phase transition. The Fermi level intensity scans show, however, that a higher but smeared out Fermi level intensity around $\bar{C}$, can also be found above the transition temperature. This finding can be explained by the fact that the phase transition does not entirely destroy the LT phase, just its long range order. Indeed a smearing out in momentum space of the spectral features related to the LT phase is
exactly what one expects in the HT phase. The problem is that only little is known of the significance of the \( S_L \) state in the first place, since theoretical calculations of the surface electronic structure in the LT phase are lacking. One possibility is that the \( S_L \) state is simply a state which lies above the Fermi level for the HT phase and is pulled down by the reconstruction. This seems rather unlikely, however. When the LT phase is viewed as a slight distortion of the HT phase, a state above the Fermi level at \( \bar{C} \) should be found in the calculations for electronic structure of the B termination, but this is not the case. It is more likely that the \( S_L \) state has a more complicate many-body nature which is linked to the CDW state. Electronic correlations could also play a role. They may at least be of some importance for the bulk electronic structure where the \( Ga_2 \) dimers lead to very flat bands in the [010] direction [96]. More theoretical work is needed to resolve this issue.

In connection with the discussion of CDW phenomena it is interesting to point out that bulk \( \alpha \)-Ga can be viewed, in a certain sense, as a layered material where metallic planes, the so-called buckled planes, are separated by covalent bonds. This point of view agrees with the very anisotropic Fermi surface and transport properties of \( \alpha \)-Ga. In this picture, a B terminated (010) surface can be viewed as a quasi two-dimensional metal. It should be even more metallic than the corresponding bulk layers due to the dangling bonds. It is a curious fact that this increased metallicity apparently leads to an unstable situation and a phase transition which is not observed in the bulk buckled planes.

### 4.5 Conclusions

The interplay between the surface phase transition and the electronic structure on \( \alpha \)-Ga(010) has been studied and evidence found for an interpretation in terms of a surface charge density wave. This interpretation of the phase transition is corroborated by the fact that i) a pseudo-gap opens in a large fraction of the surface Brillouin zone, ii) the electron-phonon coupling is strong, iii) the presence of disorder in the high temperature phase. The disorder is most likely due to loss of long range order in the high temperature phase, while the short-range surface structure is supposed to resemble the structure in the low temperature phase.

There are still unsettled questions that call for further experiments and calculations. Most importantly, a temperature-dependent measurement of the surface vibrational structure (phonon spectrum) by EELS or He-scattering would be very important. Further investigations of the long-range low temperature structure are also a needed, and especially low temperature STM seems to be a good option. From scanning tunneling spectroscopy it may also be possible to see observe the inverse lifetime of the surface state at \( \bar{C} \).

Last but not least, first-principle calculations for the low temperature structure, the \((\sqrt{2} \times \sqrt{2})R45^\circ\) or even the \((2\sqrt{2} \times \sqrt{2})R45^\circ\) phase, are needed in order to understand the properties and the differences compared to the high temperature phase. Especially the LT surface state feature at the \( \bar{C} \) point and close to the Fermi level, which is not well understood so far, is intriguing.
Bi(110): metallic surface on a semimetal

5.1 Introduction

Throughout this century experimentalists have discovered many new solid state phenomena when scrutinizing the electronic properties of the semimetal bismuth. The de Haas - van Alphen effect and quantum confinement are among the highlights\(^1\). Semimetals are similar to metals but with a carrier density several orders of magnitude lower. The prototypical semimetals are the rhombohedral group-V elements As, Sn, Bi, but also graphite, HgTe, HgSe, α-Ga, and Be may be considered semimetallic due to a low density of states at the Fermi level. Bi has a small overlap between the valence and conduction band. The conduction band minima at the L point in the Brillouin zone lie 40 meV lower than the valence band maxima at the T point, hence electrons spill over such that hole pockets and electron pockets are created at the T and L points, respectively. Therefore Bi has a band gap over most of the Brillouin zone and is almost an semiconductor, or at least close to the limiting case of a narrow-bandgap semiconductor (or a zero-gap material) [118].

The density of electrons and holes is small \((3 \cdot 10^{17} \text{ cm}^{-3})\), and the carriers have small effective masses; for electrons along the trigonal axis in the rhombohedral structure \(m^* \approx 0.003 \cdot m_0\). Therefore the Fermi energies with respect to the extrema of the electron and hole pockets are small, \(E_F = 27.2 \text{ meV}\) for the electrons and \(E_F = 10.8 \text{ meV}\) for the holes, and the Fermi surface is small. The corresponding de Broglie wavelength of the carriers is very long (300-400 Å). Furthermore the mobility is high and the mean free path long \((\sim \mu\text{m})\) in Bi. These features make Bi the ideal material for investigating quantum transport behavior, and are the reason why the de Haas - van Alphen effect, quantum confinement and other solid state electronic phenomena were first realized in bismuth [119, 120].

Quantum confinement, or quantum size effects, arise when the wavelength of the carriers is comparable to the dimensions of the electronic conductor [121, 122, 22]. The first observations of quantum size effects in thin films were reported in 1966 by

\(^1\)See Section 2.2.3 for the de Haas - van Alphen effect.
Ogrin, Lutskii and Elinson. They studied thin Bi films and observed oscillations in the resistivity, the Hall constant, the magnetoresistance, and the Hall mobility as a function of the film thickness [124]; see Figure 5.1.

Figure 5.1: (left) Oscillations in the transport parameters of thin Bi films: the resistivity ($\rho$), the Hall constant ($RH$), the magnetoresistance ($\Delta\rho/\rho$), and the Hall mobility ($\mu = RH/\rho$). Figure from Ref. [124]. (right) Conductivity in granular thin films of Bi clusters versus temperature. The mean cluster size is $L = 3.8$ nm. The transition temperature depends on the gas matrix in which the clusters are embedded. Figure from Ref. [125].

In the mid 60s a consequence of quantum confinement was pointed out by Lutskii and Sandormirskii. They noticed that quantum confinement may convert bismuth into a semiconductor by inducing a slight shift in energy of the electronic bands. Numerous experiments have since been conducted to reveal the predicted semimetal-to-semiconductor transition in bismuth thin films, but as Yang et al. wrote: ‘...the availability of high quality Bi thin films has been a major hindrance for these pursuits.’

Another experimental problem is the fact that the carrier density rises significantly as the film thickness decreases due to band bending and increased importance of surface states [123, 127]. A confirmatory report on the semimetal-to-semiconductor transition was presented in 1993 by Hoffman et al., who studied thin films on CdTe and got results in good agreement with theory, e.g. they found the critical thickness to be on the order of 300 Å. However, this interpretation has been questioned [128], and it is fair to say that this issue is still controversial [127].

These quantum confinement experiments have been performed on [111] oriented thin films since this is the direction along which the quantum confinement is largest due

---

2The work by Ogrin et al. have been characterized as ‘...the forerunner to all subsequent research into the physics of heterostructure quantum wells.’ (Ref. [123], p. 11431.)

3Ref. [126], p. 3328.
the small effective mass of the electrons. Various growth strategies have been studied, and it has turned out that semimetal-semiconductor superlattices like Bi/CdTe(111), Bi/PbTe(111), or Sb/GaSb(111) are interesting as indirect narrow-gap heterostructures with potentially attractive properties for optical and electro-optical devices [129, 130]. Very large magnetoresistance, also an technologically interesting property, has recently been observed by Yang et al. in high quality single crystal Bi thin films grown by electrodeposition [126, 131]. The (111) surface is also the natural cleavage plane of Bi, and as we will see later, all photoemission experiments so far on single crystal surfaces have been done on the (111) surface.

The delicate balance between being a metal or a semiconductor is closely related to the geometrical structure. Shick et al. have shown that by slightly changing the structure it will be possible to control a semimetal-to-semiconductor transition in Bi [132]. The transport properties of thin films under pressure have been studied, though a semimetal-to-semiconductor transition could not be identified [127]. The surface is obviously a sever change in the structure of the crystal. In Chapter 4 it was discussed how the breaking of covalent bonds may influence the surface electronic structure on α-Ga, and possibly drives a surface reconstruction. The (110) surface of Bi studied here is also obtained by breaking covalent bonds. If the surface does not reconstruct and become semimetallic (or semiconducting) these surface states will constitute a metallic two-dimensional (2D) electronic system on top of a semimetallic substrate. Such a system will be interesting for investigating the properties of electronic interactions in 2D, e.g. correlation, screening, exchange, quasiparticle excitation, superconductivity. Examples of semimetals where metallic surface states have been found are Be [73, 75], α-Ga (Chapter 4).

A related inspiring experimental work on bismuth was presented by Weitzel and Micklitz in 1991 [125]. They studied granular Bi thin films built from well-defined Bi clusters with rhombohedral bulk structure, and found the films to be superconducting, while bulk Bi is not a superconductor down to 50 mK. The superconducting transition temperature $T_c$ was dependent on cluster size, e.g., $T_c = 4.3$ K for a mean cluster size of $L = 5$ nm; see Figure 5.1. They proposed that the surface of the clusters could support surface states giving rise to increased density of states at the Fermi level, $N(E_F)$, and leading to surface superconductivity. Motivated by this finding, Patthey, Schneider and Micklitz studied the (111) surface by ARUPS, but found no evident sign of surface metallicity [133]. They wrote: ‘The question how the specific electronic structure of the Bi(111) surface is involved in the formation of the superconducting state of Bi clusters, however, must await the answer of further experiments.’

The remaining part of this chapter is structured as follows: first is given a rather detailed description of the geometry of the bismuth structure and the (110) surface. Then follows a short discussion of the band structure calculations, and especially the projection on the (110) surface, including a comment on previous photoemission experiments. Then the present ARUPS investigation on the (110) surface is presented and discussed. The results have recently been published [5].
5.2 The bismuth structure

The electronic properties and the geometrical structure of a solid are closely related phenomena. A full understanding of the electronic structure demands a full understanding of the geometrical structure and vice versa. The crystal structure of Bi is unusual and only one previous study of the (110) surface exists [134]. Therefore the properties of the real and reciprocal space structure of Bi in general, and the (110) surface in particular, will be discussed in some detail in the following.

![The bismuth crystal. The solid lines illustrate the strong bonding between nearest neighbors.](image)

The crystal structure of bismuth, see Figure 5.2, has a rhombohedral symmetry (space group R̅3m, Strukturbericht A7, arsenic structure) with two atoms per unit cell. The A7 structure is typical of the group V elements. As, Sb and Bi crystallize in this structure under common conditions while it can be obtained in black phosphorus under pressure\(^5\) [93].

Each atom has three equidistant nearest neighbors, and three equidistant next-nearest neighbors at a slightly larger distance. This gives rise to puckered layers of atoms, perpendicular to the [111] direction, within which each atom forms three pyramidal bonds to its nearest neighbors. The next nearest neighbors lie in the adjacent layer. The bonding to the nearest neighbors is strongly covalent, while the bonding to the next-nearest neighbours is relatively weaker. When crystals of Bi are cleaved it is the weak inter-layer bonds that are broken [134]. This structure is in good agreement with the fact that the group-V elements preferentially form three bonds. The bonding angles are close to 90 degrees, suggesting that they are predominantly of p-bonding orbitals [134, 135].

The relationship between structure and properties of the group-V semimetals has been highlighted in two recent theoretical calculations. Needs et al. performed total-energy calculations of the A7 structure versus the simple cubic structure in the case of arsenic, and found A7 to be the stable structure, with parameters close to experimental values [135]. Likewise, relativistic total energy LDA calculations by Shick et al. have shown good agreement for the structural parameters in the case of Bi. They

\(^5\) Under normal conditions black phosphorus is a narrow-gap semiconductor with orthorhombic crystal structure [93].
suggested that by varying the trigonal shear it would be possible to control a semimetal-to-semiconductor transition in Bi [132].

Very little is known of the surface structure. A pioneering LEED study on the (111), (110) and (101) surfaces of Bi and Sb was presented by Jona in 1967 [134]. Jona found (1 × 1) patterns for the (111) and (110) surfaces, which therefore were assumed to have the bulk truncated structures. A (2 × 10) reconstructed pattern was observed for the (101) surface. STM investigations [136, 137, 138, 139] on the (111) surface supported the bulk truncated surfaces structure description.

5.2.1 Indexing

First, a possible source of confusion needs to be resolved: the indexing of the crystal structure. In the literature the indices are referring to either the rhombohedral unit cell, the hexagonal unit cell, or the pseudo-cubic unit cell (face centered rhombohedral unit cell) [93]. Unambiguous identification requires the rhombohedral indexing, which is therefore used in this work.

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<td>3m</td>
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<td>(101)</td>
<td>(1120)</td>
<td>(110)</td>
<td>2</td>
<td>2×10</td>
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Table 5.1: Indexing, symmetry elements, and observed LEED pattern of selected low-index surfaces on Bi. The indexing is with respect the rhombohedral (Rhombo.), hexagonal (Hex), and the pseudo-cubic (Pseudo.) lattices. The LEED structure for the (100) surface is an unpublished result [140].

Table 5.1 summarizes the indexing related to the different lattices, the symmetry of the surface and the experimentally known LEED pattern. The lattice systems are described below together with equations for transforming lattice constants and indices.

Rhombohedral Bravais lattice with 2 atomic basis

The rhombohedral lattice is generated by three primitive vectors \( \vec{a}_1, \vec{a}_2, \vec{a}_3 \) of equal magnitude \( a \) [39]. The angle between any pair of the primitive vectors is \( \alpha \). The two basis vectors are \( \pm u(\vec{a}_1 + \vec{a}_2 + \vec{a}_3) \), and thus the crystal structure is completely described by \( a, \alpha, u \). These parameters are summarized in Table 5.2, while Figure 5.3 illustrates the rhombohedral lattice together with the symmetry axes.

A fundamental property of a certain crystal structure is the symmetry. The basic symmetry elements of the bismuth structure are [141]:

6Interestingly, Edelman reported stripes to arise when the crystals were cleaved at liquid nitrogen temperature, and that the stripes ‘cause considerable changes in the electron properties of the sample surface by forming one-dimensional surface conductors with an electron density different from that of the rest of the surface.’ (Ref. [138], p. 108.).
Figure 5.3: The rhombohedral lattice vectors and symmetry elements with respect to a cartesian coordinate system.

- The trigonal axis ($C_3$). The axis between the rhombohedral vectors has 3-fold symmetry. This is the [111] direction.
- The binary axis ($C_2$). The axis is perpendicular to ($C_3$).
- The bisectrix axis ($C_1$). The axis is perpendicular to ($C_3$) and ($C_2$).
- The mirror plane. The plane suspended by the trigonal and the bisectrix axes is a mirror plane.
- Inversion symmetry

The symmetry elements are indicated on Figure 5.3. Note that since the trigonal axis has three-fold symmetry, and the binary and bisectrix axes will exist three times. The inversion symmetry is broken at the surface, and the consequences of this for the surface electronic structure is discussed in a later section.

**Hexagonal Bravais lattice with 6 atomic basis**

Alternatively, one can describe the crystal structure as a hexagonal lattice generated by three primitive vectors ($\vec{a}_1, \vec{a}_2, \vec{c}$) and a 6 atomic basis. The basis vectors are $\pm u\vec{c}$ and the hexagonal cell contains 6 atoms at the positions: $(0,0,u), (0,0,-u), \left(\frac{1}{3}, \frac{2}{3}, \frac{2}{3} - u\right), \left(\frac{2}{3}, \frac{1}{3}, \frac{1}{3} + u\right), \left(\frac{2}{3}, \frac{1}{3}, \frac{1}{3} - u\right)$. In this case the crystal structure is completely described by $a_1, c, u$. See Table 5.2 for specific values.

In the [111] (rhombohedral) direction the structure consists of puckered planes stacked in pairs. Considering the hexagonal representation of the crystal it is seen that planes are given by the following coordinates along the $\vec{c}$-direction (in units of $c$): $\ldots, \frac{1}{3} - u, u, \frac{1}{3} - u, \frac{1}{3} + u, 1 - u, \frac{1}{3} + u, \ldots$. The nearest neighbours are in the adjacent planes of a pair of planes which are separated by a distance $w$:

$$w = \left(\frac{1}{3} + u\right)c - \left(\frac{2}{3} - u\right)c = \left(2u - \frac{1}{3}\right)c$$
while the pairs of planes are separated by a larger distance \( v \):

\[
v = (\frac{2}{3} - u)c - uc = (\frac{2}{3} - 2u)c
\]

The nearest neighbour distance \( a_{nn} \) is given by [135]:

\[
a_{nn} = \frac{a_h}{\sqrt{3}}[1 + \frac{1}{3}(6u - 1)^2(c/a_h)^2]^{1/2}
\]

In the case of bismuth (at 4.2 K), the distances are \( w = 1.5903 \) Å, \( v = 2.3420 \) Å and \( a_{nn} = 3.0589 \) Å.

**Rhombohedral system in cartesian coordinates**

To calculate the bulk truncated structure, the Brillouin zone and the surface Brillouin zone, we generate the lattice in a cartesian coordinate system. Obviously this can be done in many different ways, but a natural choice is to let the cartesian coordinate system coincide with the symmetry axes such that, e.g. \( x = C_2 \), \( y = C_1 \), \( z = C_3 \). This is the case illustrated in Figure 5.3. By introducing the angle \( \theta \) between the primitive vectors and the \( z \)-axis we find the components:

\[
\begin{align*}
\hat{a}_1 &= (-\frac{\sqrt{3}}{2}a \sin \theta, -\frac{1}{2}a \sin \theta, a \cos \theta) \\
\hat{a}_2 &= (\frac{\sqrt{3}}{2}a \sin \theta, -\frac{1}{2}a \sin \theta, a \cos \theta) \\
\hat{a}_3 &= (0, a \sin \theta, a \cos \theta)
\end{align*}
\]

The relationship between \( \theta \), the angle between the rhombohedral axes and the trigonal axis, and the rhombohedral angle \( \alpha \) is:

\[
\sin \theta = \sqrt{\frac{2}{3}(1 - \cos \alpha)}
\]

In the case of bismuth at 4.2 K, \( \theta = 33.6468^\circ \). Equation (5.1) can be rewritten in terms of the hexagonal lattice parameters if we realize that (see Equation (5.5) below):

\[
\begin{align*}
a_h &= \sqrt{3}a \sin \theta \\
c &= \frac{1}{2}a \cos \theta
\end{align*}
\]

and thus

<table>
<thead>
<tr>
<th>Rhombohedral lattice</th>
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<tr>
<td>( a )</td>
<td>( a_h )</td>
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<td>( \alpha )</td>
<td>( c )</td>
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<td>( u )</td>
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Table 5.2: Crystal structure parameters of bismuth at 4.2 K [130].
\[
\begin{align*}
\bar{a}_1 &= \left(-\frac{1}{2}a_h, -\frac{\sqrt{3}}{2}a_h, \frac{1}{2}c\right) \\
\bar{a}_2 &= \left(\omega a_h, -\frac{\sqrt{3}}{2}a_h, \frac{1}{2}c\right) \\
\bar{a}_3 &= \left(0, \frac{\sqrt{3}}{2}a_h, \frac{1}{2}c\right)
\end{align*}
\]

(5.3)

The corresponding reciprocal lattice is generated by:

\[
\begin{align*}
\bar{b}_1 &= \left(-1, -\frac{\sqrt{3}}{3}, b\right)g \\
\bar{b}_2 &= \left(1, -\frac{\sqrt{3}}{3}, b\right)g \\
\bar{b}_3 &= \left(0, \frac{\sqrt{3}}{3}, b\right)g
\end{align*}
\]

(5.4)

where \(g = 2\pi/a_h\) and \(b = a_k/c\). The reciprocal lattice vector basis (5.4) is chosen in a tight-binding calculation by Liu and Allen [130], which have been reproduced in the present work in order to calculated the projected band structure on the (110) surface.

From rhombohedral indices to hexagonal indices

When describing the hexagonal structure a set of 4 indices \((hkl)\) is normally used, though the structure is totally specified by the three indices that refers to the generating lattice vectors. Simplicity is gained by using the set of 4 indices, since equivalent surfaces are then given by permutations of the first three indices. The index \(i\) is related to \(h\) and \(k\) by:

\[i = -(h + k)\]

and for this reason a truncated notation \((hk \bullet l)\) is sometimes used.

The relationship between indices referring to the rhombohedral axes and the indices referring to the hexagonal axes depends on the choice of their relative orientation. In the 'obverse relationship' the hexagonal vector \(\bar{a}_{h1}\) is taken parallel to the line joining the terminus of the rhombohedral vector \(\bar{a}_3\) to the terminus of \(\bar{a}_1\), and vector \(\bar{a}_{h2}\) is taken parallel to the line joining the terminus of \(\bar{a}_1\) to the terminus of \(\bar{a}_3\), and vector \(\bar{a}_{h3}\) is taken parallel to the line joining the terminus of \(\bar{a}_2\) to the terminus of \(\bar{a}_1\) [142]. If \(\bar{c}\) is the hexagonal vector perpendicular to \(\bar{a}_{h1}\) and \(\bar{a}_{h2}\) (and \(\bar{a}_{h3}\)) then the relationship is:

\[
\begin{align*}
\bar{a}_{h1} &= \bar{a}_2 - \bar{a}_3 \\
\bar{a}_{h2} &= \bar{a}_3 - \bar{a}_1 \\
\bar{c} &= \bar{a}_1 + \bar{a}_2 + \bar{a}_3
\end{align*}
\]

(5.5)

If the rhombohedral indices are \((nmp)\) and the hexagonal are \((hk \bullet l)\) then the indices are related by:

\[
\begin{align*}
h &= n - p \\
k &= -m + p \\
l &= m + n + p
\end{align*}
\]

(5.6)

When adding the three equations we find: \(-h + k + l = 3p\), a number divisible by 3. This restriction reflects the fact that not all \(hkl\) values correspond to planes of atoms.
**Pseudo-cubic lattice**

Finally, the pseudo-cubic unit cell, or more properly the face centered rhombohedral unit cell, of the crystal structure will be described. The relationship between the rhombohedral lattice and the cubic lattice is illustrated in Figure 5.4. The lattice is not exactly cubic since the rhombohedral angle $\alpha$ is not $60^\circ$, and for this reason the lattice is termed *pseudo-cubic*. If $\alpha$ was $60^\circ$ then the lattice would be the face centered cubic lattice (fcc). With the rhombohedral lattice vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ in the y-z, x-z, x-y planes respectively, as chosen in Figure 5.4, the cubic vectors $\vec{x}, \vec{y}, \vec{z}$ can be written:

$$
\begin{align*}
\vec{x} &= -\vec{a}_1 + \vec{a}_2 + \vec{a}_3 \\
\vec{y} &= \vec{a}_1 - \vec{a}_2 + \vec{a}_3 \\
\vec{z} &= \vec{a}_1 + \vec{a}_2 - \vec{a}_3
\end{align*}
\tag{5.7}
$$

and the relationship between the indices are:

$$
\begin{align*}
h &= -m + n + p \\
kh &= m - n + p \\
k &= m + n + p
\end{align*}
\tag{5.8}
$$

The angle $\nu$ between the cubic lattice vectors can be calculated from Equation (5.7) and (5.1):

$$
\cos \nu = \frac{-1 + 2 \cos \alpha}{3 - 2 \cos \alpha}
$$

Likewise the pseudo-cubic lattice distance is found to be:

$$
x = a\sqrt{3 \sin^2 \theta + 1} = a\sqrt{3 - 2 \cos \alpha}
$$

In case of bismuth at 4.2 K, $\nu = 87.64^\circ$ and $x = 6.5469 \text{ Å}^{-1}$. 

![Figure 5.4: The pseudo-cubic lattice versus the rhombohedral lattice](image)
5.2.2 The (110) surface

The structure of the Bi(110) surface is shown in Figure 5.5. The surface structure is assumed to be identical to the bulk truncated structure. Perpendicular to the surface one finds double layers separated by almost the nearest neighbor distance $a_{nn} = 3.06$ Å. The layers are identical but slightly displaced along the mirrorplane. The distance (perpendicular to the surface) between the two different kinds of atoms in one layer is 0.17 Å.

![Figure 5.5](image)

**Figure 5.5:** (a) Top view of the (110) surface lattice and (b) top view of the second layer; (c) and (d) show projections on the planes perpendicular to the mirror plane $m$ and parallel to $m$, respectively. The dashed lines on every second atom in the surface represent the dangling bonds. The puckered layers perpendicular to the [111] direction are clearly seen in (d).

Figure 5.6 shows the bulk Brillouin zone (BZ) of Bi and the (110) surface Brillouin zone (SBZ). The usual notation for symmetry points have been used for the BZ [141].

The reciprocal lattice and Brillouin zone for the (110) surface is shown in Figure 5.7. The points at the side of the SBZ is called $\bar{X}$, and the points at the corners are called $\bar{M}$. The low symmetry of the SBZ with only a mirrorplane is reflected in the electronic structure. For example, the $\bar{X}_2$ and $\bar{X}_2'$ points correspond to $k_\perp$ rods along...
Figure 5.6: The bulk Brillouin zone of Bi and the (110) surface Brillouin zone. The hole pockets at T and and the electron pockets at L are indicated (not to scale).

the T-L-T line of the bulk BZ, while the $\bar{X}_1$ points correspond to a $k_\perp$ rod along the L-L-L line. This means that the projection of the bulk electronic structure on $\bar{X}_2$ and $\bar{X}_1'$ is different from the projection on $\bar{X}_1$. The bulk BZ in Figure 5.6 also contain a sketch of the bulk Fermi surface consisting of electron pockets at the $L$ points and hole pockets at the $T$ points. We see that the bulk Fermi surface projected on the (110) surface only gives rise to features in the vicinity of the four $X$ points.

The two surface lattice vectors turn out to be equal to a rhombohedral unit vector $\vec{a}$ in the mirrorplane and a hexagonal unit vector $\vec{a}_h$ perpendicular to the mirrorplane. The surface has a very low symmetry with only one mirror plane, as indicated in the figure. From the direct surface lattice it can be seen that the reciprocal surface lattice is generated by two perpendicular vectors $\vec{g}_{1}, \vec{g}_{2}$ of length:

$$|\vec{g}_{1}| = \frac{2\pi}{a_h} = 1.3855 \text{Å}^{-1}$$

$$|\vec{g}_{2}| = \frac{2\pi}{a} = 1.3239 \text{Å}^{-1}$$

The presence of only one mirrorplane in the SBZ may tempt one to expect that the dispersion of electronic surface states in the ‘left’ section of the SBZ in Figure 5.7 will be different from the dispersion in the ‘right’ section. This turns out not to be the case, however, because of time-reversal symmetry. For a two-dimensional system
the time-reversal symmetry give rise to a symmetry in the dispersion of the electronics states:

\[ E(k_\uparrow) = E(-k_\downarrow) \]  \hspace{1cm} (5.9)

This means that if one considers a surface state at \( k_\uparrow \) with energy \( E \) and a spin \( \uparrow \), then there must also be a surface state at \( -k_\downarrow \) with the same energy but opposite spin \( \downarrow \). For example, if one of the \( \bar{M}_1 \) points in Figure 5.7 is considered, then the opposite \( \bar{M}_2 \) point will be equivalent. In combination with the mirrorplane all the \( \bar{M} \) points become equivalent. This corresponds to an effective mirrorline \( m_2 \) perpendicular to \( m \), as illustrated in Figure 5.7. In a non-spin-resolved investigation of the surface electronic structure, as in the case of our ARUPS experiment, it will be sufficient to measure in a quarter of the SBZ\(^7\).

### 5.3 Electronic structure

Experiments on bismuth have revealed outstanding electronic properties, as mentioned in the introduction, and obviously a considerable amount of theoretical work has been

\(^7\)Domains may also give rise to an effective extra mirrorplane if domains exist that are rotated by 180 degrees with respect to each other. This is not the case on the (110) surface since different domains will be oriented similarly. Hengsberger et al. studied the (111) Fermi surface by ARUPS, and found the expected three-fold symmetry, but also a weaker Fermi surface rotated by 180 degrees around the trigonal axis. They explained the latter observation as being due to sampling of different oriented domains [143]. In the (111) case the time-reversal mechanism will, however, also give rise to an extra mirrorplane and an effective six-fold symmetry.
Shoenberg carried out the first studies of quantum oscillations in the susceptibility of bismuth in 1939, and suggested a parabolic ellipsoidal model of the conduction band, in which the electrons occupy six sets of ellipsoidal energy surfaces. An early theoretical investigation of the band structure was a tight-binding calculation performed by Mase in the late 50s. Mase correctly determined the location and symmetries of the free carriers, but not very properly the actual band structure [130].

The general picture of the band structure was first presented in 1968 by Golin, who calculated the band structure by adjusting the parameters in a pseudopotential model to experimental results [144]. More recent calculations of the electronic properties of Bi are an *ab initio* calculation by Gonze et al. [145], and a tight-binding calculation by Xu et al. [129]. Xu et al. obtained the tight-binding parameters by fitting to pseudopotential results (e.g. [144]) and the ab initio result by Gonze et al. In 1995 Liu and Allen presented an improved tight-binding model by fitting the bands to experimental data in the vicinity of the Fermi energy, including band overlaps, effective masses of electrons and holes, shape of the Fermi surface at the electron and hole pockets, and small energy gaps [130]. In this calculation the properties of the electronic structure in the vicinity of the Fermi level is expected to be well reproduced. For this reason we have implemented the calculation in order to project the band structure on the (110) surface. The band structure calculated by Liu and Allen is shown in Figure 5.8.
We will have a little closer look at the band structure. The electronic configuration of Bi is \( s^2p^3 \) plus a complete \( d \) shell. The \( d \)-electrons are not contributing to bonding and only the \( s \) and \( p \) levels are considered valence electrons. The binding energies of the 5\( d \) core levels are \( 5d_{3/2} = 26.94 \text{ eV} \) and \( 5d_{5/2} = 23.90 \text{ eV} \) [146]. In the occupied band structure two low lying \( s \) bands (\( \sim 12 \text{ eV} \)) are seen, and three \( p \) bands between 5 eV and the Fermi level. These 5 bands are filled with 10 electrons, 5 from each atom of the unit cell. Two distinct bands are generated from the atomic \( s \) levels, each being doubly degenerate with respect to spin. They can be denoted as ‘bonding’ and ‘anti-bonding’ levels [145]. The strength of the spin-orbit coupling (1.5 eV) of the \( p \) levels has a significant effect on the band structure and split the \( p \)-levels. Each \( p \)-band is doubly degenerate owing to the inversion symmetry of the Bi structure [147].

The inversion symmetry, \( E(\hat{k}, \uparrow) = E(-\hat{k}, \uparrow) \), together with time reversal symmetry, \( E(\hat{k}, \uparrow) = E(-\hat{k}, \downarrow) \), correspond to:

\[
E(\hat{k}, \uparrow) = E(-\hat{k}, \downarrow)
\]

Therefore splitting of the bands due to spin-orbit interaction is not possible. For an illustrative comparison between Bi and the fictional Bi without spin-orbit coupling see the calculations by Gonze et al. [145]. The central feature of bismuth is the small number of carriers owing to the overlap between the highest valence band and the lowest conduction band, which creates small and equal numbers of free electrons at point L and free holes at point T. The conduction band minimum lies 40 meV lower than the valence band maximum [130]. This small overlap is highly dependent on the strength of the spin-orbit coupling.

The (111) surface and the (100) surface are very similar in the Bi structure; this fact is also reflected in the band structure. The \( \Gamma \)-T direction is normal to the (111) surface in the BZ, while the \( \Gamma \)-L direction is normal to the (100) surface in the BZ, and the similarity of the bands is obvious from the band structure in Figure 5.8. If the possibilities for metallic surface states is considered, then in the \( \Gamma \)-T and the \( \Gamma \)-L directions there are no projected band gap at the Fermi level, and thus these surfaces can not support a surface state crossing the Fermi level at the center of the surface Brillouin zone. The \( \Gamma \)-X direction is normal to the (110) surface, and here a projected band gap is found at the Fermi level, and hence there is a possibility of a surface state crossing the Fermi level in the vicinity of the surface Brillouin zone center.

### 5.3.1 Projected band structure on Bi(110)

In order to project the bulk band structure onto the (110) surface, a cartesian coordinate system \((o, p, n)\) is introduced on the surface, with \( \hat{n} \) perpendicular to the surface, and \( \hat{o}, \hat{p} \) in the (110) plane. According to the definition of Miller indices of a surface, the normal to a surface \((hkl)\) is the \([hkl]\) reciprocal lattice vector. In the case of the (110) surface of Bi therefore \( \hat{n} \approx \vec{b}_1 + \vec{b}_2 \). Knowing \( \hat{n} \) one can find two mutually perpendicular vectors, \( \hat{o} \) and \( \hat{p} \), in the (110) plane. A convenient choice is to take \( \hat{o} \) perpendicular to the mirrorplane and \( \hat{p} \) along the mirrorplane. From Figure 5.3 it is seen that a possible choice of unit vectors are:
By projecting the lattice and the reciprocal lattice on the \((o, p, n)\) axes one may calculate the surface structure in Figure 5.5 and the SBZ in Figure 5.7, respectively.

The band structure is projected as follows. The point \(\vec{k}_1\) in the SBZ, where the band structure is to be projected on, is specified by a set of numbers \((m_1, m_2)\) according to:

\[
\vec{k}_1 = m_1 \hat{o} + m_2 \hat{p}
\]

The \(k\)-points on the rod normal to the surface can be written \(\vec{k} = \vec{k}_1 + \vec{k}_\perp\) where:

\[
\vec{k}_\perp = m_3 \hat{n}
\]

Explicitly,

\[
\vec{k} = m_1 \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + m_2 \begin{pmatrix} 0 \\ a_{3y} \\ a_{3z} \end{pmatrix} \frac{1}{|d_3|} + m_3 \begin{pmatrix} 0 \\ -a_{3z} \\ a_{3y} \end{pmatrix} \frac{1}{|d_3|}
\]

By varying \(m_3\) one can choose an appropriate number of \(k\)-vectors in the bulk BZ and along the projection rod, and for each \(k\) solve the tight-binding Hamiltonian and find the 16 energy eigen values. For the projection shown in Figure 5.9 \(m_3=60\) and 100 \(\vec{k}_1\) points along each segment in the SBZ (141 points for the diagonal segments \(\bar{X}_2 - \bar{X}_1\) and \(\bar{\Gamma} - \bar{M}_1\)) have been chosen. From the figure one notices that there is a projected bulk band gap at the Fermi level spanning most of the surface Brillouin zone. Only at the \(\bar{X}\)-points there are small areas of projected bulk Fermi surface. In this sense the \((110)\) surface is well suited for supporting Fermi level crossing surface states.

Previous PES results

Several photoelectron spectroscopic studies of bismuth either as a melt, polycrystal or single crystal have been reported during the last 30 years. However, the number of experiments is modest compared to, say, the intensively studied simple metals or noble metals. The development of photoemission spectroscopy on Bi reflects very well the trends in photoemission as a technique during the same period in time. A development from angle integrated spectra of polycrystalline samples at room temperature to highly angle- and energy-resolved spectra of well-defined single crystals at very low temperatures. The photoemission investigation on Bi\((110)\) presented here is considered to be the first of its kind on this surface.

The first PES experiments studied amorphous crystals, single crystals, melts, oxidation of polycrystalline thin films [146, 148, 149, 150]. The liquid was found to be
more metallic than the solid phase, but otherwise the electronic structure (density-of-states) for the two phases is rather similar. This indicated that the electronic structure was dominated by short range interactions. In the valence band a 6s peak at about 12 eV with a weak doublet structure, and a split 6p level with peaks at about 3.5 eV and 1 eV was observed. These data are in good agreement with the expected band structure.

At least six ARUPS experiments on the (111) surface have been conducted since 1986. These experiments are quite similar, also concerning conclusions, and differ mainly in the performance of the photon source and electron spectrometer. One of the studies is on thin film [151, 152], while the others are on single crystal surfaces [153, 133, 154, 155, 143].

In 1986 Jezequel, Petroff, and Pinchaux investigated the (111) surface to see whether a surface state could be found in a spin-orbit gap. For this purpose the (111) surface of Bi is a good choice, since it does not reconstruct and the spin-orbit coupling of Bi is large [153]. A state was found with a binding energy of 0.3 eV at $\bar{\Gamma}$, and a surface related peak was also found at 3 eV. In 1997 Jezequel et al. reported similar results obtained under similar experimental conditions as in their 1986 study, but with a more extensive discussion [154]. The results by Thomas, Jezequel and Pollini recently published are also much the same concerning resolution and data [155]. Inspired by the results of Weitzel and Micklitz on superconductivity in granular Bi thin films, as mentioned in the introduction, Patthey, Schneider and Micklitz conducted an ARUPS investigation of the Bi(111) surface in 1994. They used a better performing ARUPS instrument compared to the previous work, and three peaks close to the Fermi level

---

\[\text{Figure 5.9:} \text{ Projection of the bulk band structure on the (110) surface of Bi. Tight-binding calculation with parameters by Liu and Allen [130].}\]
were resolved compared to the one peak known. Patthey et al. confirmed the existence of the surface state near $E_F$ at $\Gamma$. Moreover, they found a bulk derived band to cross the Fermi level and contribute to an enhanced density of states at this surface [133]. Recently high-resolution data\(^{10}\) from the (111) surface were presented by Hengsberger et al. [143]. They investigated the electronic structure close to the Fermi level and found differences with respect to the bulk band structure. The Fermi surface observed for the electron and hole bands resembled those of antimony, the next group-V element, probably due to surface relaxation. This surface electronic structure renders the surface more metallic than the bulk.

Generally, the previous PES/ARUPS results on Bi are in good agreement with the expected bulk electronic structure, but deviations are found in the vicinity of the Fermi level. Surface states have been found on the (111) surface but none of these, however, are crossing the Fermi level. Anyway, the (110) surface is a much better candidate for finding a metallic surface state since the truncated bulk structure features dangling bonds and the surface does not appear to reconstruct. Indeed, metallic surface states are found on this surface, as will be reported in the remaining part of the chapter.

5.4 The experiment

The present investigation of the electronic structure of Bi(110) was performed at the ARUPS facility at the storage ring ASTRID. See Chapter 3 for a detailed description of the instrumentation.

The Bi crystal was mechanically polished to within 0.5° of the (110) direction. The orientation of the mirror plane with respect to the sample was determined by Laue diffraction such that the orientation of the SBZ was known beforehand in the photoemission experiment. It is not easy to determine the orientation of the SBZ from either LEED or photoemission due to the almost square SBZ and the symmetry of the dispersion. After insertion into the vacuum system, the surface was cleaned by cycles of Ne\(^+\) and Ar\(^+\) sputtering at room temperature and annealing of the sample. In the first stages of cleaning, the annealing temperature was chosen to be 200 °C, later 50 °C was found to be sufficient, consistent with the fact that Bi has a very low Debye temperature (119 K [156]). Note that the bulk melting temperature of Bi is 271 °C. The surface order was checked by LEED and a reasonable (1 x 1) pattern, in agreement with the results of Jona [134], was observed. The cleanliness was judged from the quality of the valence band spectra.

The geometry of the ARUPS measurements was such that the light was incident in an angle of 50° with respect to the surface normal, with the polarisation vector of the light coinciding with the mirror plane of the crystal. The total energy resolution used in this experiment was better than 30 meV for the surface state dispersion measurements, and around 50 meV for the Fermi surface mapping. The angular resolution was ±0.7°. The sample temperature was around 30 K, and the pressure was in the 10\(^{-11}\) mbar range.

\(^{10}\)The energy and angular resolution of the spectrometer were set to 5 meV and ±0.5°. The sample was cooled down to 12 K. The exciting source was monochromatised and polarised HeI (21.2 eV)
5.5 Results

Two different sets of data have been measured for the Bi(110) surface. The first set of data consists of spectra showing the dispersion of electronic states along selected symmetry directions in the lower half of the SBZ (see Figure 5.7), and in the vicinity of the Fermi energy. In Section 5.2.2 we considered the consequences of symmetry on the surface and found that any surface electronic structure ought to be symmetric with respect to the $m_2$ line in Figure 5.7. This was also found to be case in the experiment, and thus for convenience of presentation of the data, the electronic dispersion is only reported for a quarter of the SBZ in the following. The second set of data is a mapping of the Fermi level intensity in the SBZ.

The central result of the present work, the dispersion of electronic states along selected symmetry directions in the SBZ, is shown as an intensity plot in Figure 5.10 together with the projected band structure. The spectra are measured at a photon energy of 16 eV and at 30 K. The series of spectra taken along the $\bar{\Gamma} - \bar{M}_1$ direction is shown in Figure 5.11. The projected band structure was calculated using the tight-binding parameters determined by Liu and Allan, as described in Section 5.3.1.

Several surface states (A, B, C, D, E) can clearly be identified in Figure 5.10. The surface states are identified by the fact that they appear as sharp peaks in projected bulk band gaps and show no dispersion upon changing $k_z$ via the photon energy (see also Section 2.2.1). All of the identified surface states, except E, give rise to a Fermi surface. The states A and B form hole pockets around the $\bar{\Gamma}$ and $\bar{M}_1$ points, respectively. The effective mass of both states is estimated to be of the order of one electron mass, in
sharp contrast to the very small effective masses of the carriers for most directions in bulk Bi. The small effective masses in the bulk are part of the reason why Bi has a low density of states at the Fermi level. The state C forms an electron pocket around the \( \bar{M}_1-\bar{X}_1 \) line. For the state D the situation is less clear since it seems to cross the Fermi level only at one line in the \( \bar{X}_1-\bar{\Gamma} \) direction.

Supplementary information is supplied by measuring the intensity at the Fermi level as a function of \( k \) in order to map the Fermi surface. This method was discussed in Section 2.2.3, and demonstrated on \( \alpha \)-Ga(010) in Chapter 4. Figure 5.12 shows the result of such a mapping for a photon energy of 16 eV at a temperature of 30 K. Similar images, except variations in the ratio between the intensities of the surface states, were observed for other photon energies, in accordance with the 2D character of the surface states. The intensities in Figure 5.12 are integrated in an energy window of 50 meV centered on the Fermi level (and normalized to the current on the last mirror). The hole pockets created by the state A and B in Figure 5.10 are clearly visible, and so is the small electron pocket from state C. The state D merely give rise to a weak intensity along the \( \bar{X}_1-\bar{\Gamma} \) line. In addition to these surface related features, an intensity maximum is found close to \( \bar{X}_2' \), which is probably related to a bulk Fermi level crossing smeared out in \( k_\perp \).

### 5.6 Discussion

The experimental evidence reveal the central result of the present work: Bi(110) is very different from bulk Bi. It has a complex Fermi surface consisting of two hole pockets.
Figure 5.12: Integrated Fermi-level intensity for $h\nu = 16$ eV. The data have been taken in a quarter of the surface Brillouin zone, the rest of the image is generated by symmetry. The features A, B, C and D correspond to the surface states in Figure 5.10.

around $\bar{\Gamma}$ and $\bar{M}_1$, respectively, an electron pocket along the $\bar{M}_1-\bar{X}_1$ line, and a feature close to the $\bar{X}_1-\bar{\Gamma}$ line. The effective mass for the carriers in the two hole pockets is in the order of a free electron mass, much higher than that of the bulk carriers. For these reasons, we conclude that the surface must be a better metal than the bulk.

Surface states and surface electronic structure are closely related to the geometric structure. In the case of Bi(110) this interesting relationship is difficult to discuss, since the available structural knowledge is rather limited. In fact one basically knows that the LEED pattern is $(1 \times 1)$. Nevertheless, it seems quite likely that the surface states are related to the dangling bond located on one of the two atoms in the unit cell, as discussed by Jona [134] and illustrated in Figure 5.5. The (111) has no dangling bonds and is not reconstructed, while the (10\bar{1}) surface has dangling bonds on every atom and is reconstructed [134]. On the (110) surface the density of dangling bonds is in between these cases and seemingly not sufficient to induce a reconstruction. Note that since there are two atoms per surface unit cell, it is possible to have rearrangements of the structure without destroying the $(1 \times 1)$ LEED pattern. For instance, the atoms with the dangling bonds (the ‘white’ atoms in Figure 5.5) can get displaced within the surface unit cell without changing the periodicity of the surface lattice. A quantitative LEED study to answer this question would be most welcome.

Another noteworthy point to consider is the possibility that the surface state bands are completely non-degenerate, i.e. that for every $k_1$ point only one electron can be found in a band. This is caused by the combination of spin-orbit coupling and the loss of bulk symmetry at the surface. In bulk Bi the spin-orbit coupling has a considerable
effect on the band structure, as we have seen, but the two-fold degeneracy of the $p$-bands remains because of the inversion symmetry in the bulk structure. At the surface the bulk inversion symmetry is broken, and a complete lifting of the degeneracy can be expected for surface electronic states. Spin-orbit split surface states have in fact already been observed on Au(111) [157, 65], Mo(110) [158], W(110) [158]. In the case of Bi one may expect the spin-orbit splitting to be so large that only one of the split bands is observable. Alternatively, it is also possible that the pairs of states which are observed at several points in the SBZ (e.g. B and C or A and D) correspond to the same states separated by the spin-orbit splitting. The splitting of the surface state band should scale with the magnitude of the spin-orbit parameter. For the three similar semimetals As, Sb and Bi the parameters are 0.36 eV, 0.6 eV, and 1.5 eV, respectively [145]. It would therefore be interesting to perform the same kind of measurements on As and Sb, and possibly follow the splitting of the surface band.

A spin non-degeneracy of the surface state bands has interesting consequences. Consider, for example, the hole pocket around the $\bar{\Gamma}$ point. If one takes an electronic state on this Fermi surface with a wave-vector $k_\parallel$ and a certain spin, then will be an electron at $-k_\parallel$ with a spin in the opposite direction, according to Equation (5.9). This will affect the screening properties of the electronic system. In a normal, free-electron like system a point defect on the surface would be screened by the interference of incoming and scattered Bloch waves. This changes the electronic density in the immediate vicinity of the defects, and gives rise to long range Friedel oscillations. In the case of non-degenerate states the wave vector $k_\parallel$ can not be backscattered into the state $-k_\parallel$, at least not without flipping the spin. These speculations could be checked by STM since the Friedel oscillations, which are caused by the scattering of the surface state electrons are directly visible, and can be related to the Fermi surface (see Section 2.2.3). For a spin non-degenerate Fermi surface, certain Friedel oscillations should not be observable [159].

In the introduction to this chapter, the results concerning superconductivity found in granular films build from well-defined rhombohedral Bi clusters were mentioned as a motivation. At this point it is worth to consider the relevance of the present results in this context. Weitzel and Micklitz initially suggested an enhanced density of states at $E_F$, due to surface states, on the surface on the clusters as the origin of the superconductivity. In this picture a cluster is to be considered as a semimetallic core covered by a metallic layer. None of the ARUPS investigations on the (111) surface have revealed any metallic surface states, though it seems that the electronic structure close to the surface is modified and more metallic than the bulk [133, 143]. This picture of rhombohedral clusters with metallic surfaces has been challenged in an experiment by Vosloh, Holdenried, and Micklitz, who studied the Hall coefficient and the magnetic-field dependence of $T_c$ for the granular Bi films. They did not find the results to support the ‘surface superconductivity’ conjecture. Instead they found the electronic structure to be size-dependent but homogeneous for a given cluster size. Furthermore, the clusters seemed to undergo a structural phase transition from the rhombohedral bulk structure (at $L > 4$ nm) to an amorphous Bi structure with decreasing cluster size [160]. Here one should note that many different crystallographic bulk phases of Bi exists that are superconducting, e.g. amorphous Bi is superconducting with $T_c = 6$ K [125]. On the other hand, transmission electron microscopy (TEM) investigations of small Bi clus-
ters have found the clusters to be predominantly covered by (110) and (111) facets [161]. Additionally, the TEM investigation found the clusters smaller than \( L = 8.4 \) nm to have the rhombic structure, while larger clusters transformed to cubic-like structures surrounded by crystalline shells of rhombic structure. The conclusion must be that the actual structure of small Bi clusters is an open question, let alone the question of the corresponding electronic structure. Yet a point to remember is the observation that the carrier density in thin film increases as the film thickness decreases [123, 127].

In the present work the (110) surface, which is also present on the clusters [161], has been found to be a good metal. This supports the enhanced density of states explanation. Unfortunately, it is not trivial to relate this observation to the actual electronic structure of the clusters. The surface states are found in a narrow gap, and their linewidth are relatively large, what is consistent with a large penetration length of the surface state into the bulk. From the latter fact one may question the relevance of the distinction between surface and bulk electronic properties for the small clusters at all. Even the comparison between a single crystal and a facet on a cluster is problematic. Note that the length of a (110) facet on a cluster of a few nm is only of the order of 10 lattice constants and that, moreover, strong structural fluctuations may be present on these small clusters. In conclusion it seems likely that the explanation for superconductivity in the granular films of Bi is more complex than being a matter of metallic facets on a semimetallic core. An interesting possibility, however, is to change the point of view, and speculate whether the Bi(110) surface is superconducting.

5.7 Conclusions

In summary, the (110) surface of Bi has been investigated by high-resolution ARUPS. The electronic structure along various symmetry directions in the surface Brillouin zone and the surface Fermi surface have been mapped. Surface state have been identified in the projected band gap close to the Fermi edge over a broad range of the surface Brillouin zone. These states cross the Fermi level and have effective masses which are much higher than those of the bulk carriers in bulk Bi. From this it is concluded that the surface is effectively a metallic layer on top of the semimetallic bulk. It is likely that the surface states are related to the dangling bonds in the assumed terminated bulk structure, though the actual surface structure is not known. It is also interesting to speculate whether the large spin-orbit interaction in Bi, combined with the loss of bulk inversion symmetry at the surface, leads to a surface band structure and surface Fermi surface which is non spin-degenerate. This should lead to some peculiar screening properties which could be observed by STM. Likewise, ARUPS investigations of the (110) surface of the related semimetals As, Sb could be carried out to investigate the effect of spin-orbit coupling on surface band splitting. Progress along two lines will be needed to gain a better understanding of the properties of Bi(110). First, more structural information is needed, and second, it would be interesting to have first-principles calculations of the electronic and geometric structure.
Beamlines at Elettra

We have done experiments concerning temperature dependence of direct transitions and valence band photoelectron diffraction at the SuperESCA and ALOISA beamlines at the third generation synchrotron radiation source Elettra in Trieste, Italy\(^1\). The results are presented in Chapter 7 and 8, while the technical details of the beamlines are briefly summarized in following two sections.

6.1 SuperESCA

SuperESCA is a high-performance photoemission spectroscopy beamline for experiments on surfaces, especially designed for high energy resolution and time resolved XPS [162, 163].

The beamline uses an undulator section covering a 90-1500 eV photon energy range at a ring energy of 2 GeV (120-2100 eV at a ring energy of 2.4 GeV). A stigmatic SX700 monochromator covers the whole photon energy range with a single plane grating (a modification of the standard version of the plane grating SX700 monochromator). The resolving power of the monochromator is \(\sim 10000\) [162].

The experimental station consists of an UHV-chamber equipped with an angle-resolved double pass hemispherical electron energy analyser with a multi-channel detector (96 channels). The electron analyser is mounted 40\(^\circ\) away of the incoming light, in the plane of polarization.

The sample is mounted on a nitrogen cooled manipulator allowing temperatures down to 130 K. Heating of the sample is done by a filament mounted behind the sample. Accurate sample positioning is possible owing to five (motorised) degrees of freedom of the manipulator: \(x, y, z, \phi\) (rotation around sample normal), \(\theta\) (rotation around the vertical manipulator axis).

\(^1\)Much information about Elettra and the beamlines are to be found at the web-site of the facility: http://www.elettra.trieste.it

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6.2 ALOISA

ALOISA is a multipurpose beamline for surface science studies. The beamline uses an undulator-wiggler insertion device covering the 0.2-8 keV energy range and is designed to facilitate a broad range of experimental techniques like surface X-ray diffraction and reflectivity, photoemission spectroscopy, photoelectron diffraction, and \( e^- \)-Auger coincidence spectroscopy [164, 165, 166].

To monochromatize the radiation in the wide energy range a design with two interchangable dispersive systems has been chosen (similar to the Hunter monochromator). For energies above 3 keV a channel-cut Si crystal is used for dispersing the radiation, while at energies below 2 keV a plane mirror, plane grating system (similar to the SX-700 monochromator) is used. Two gratings cover the 0.2-2 keV range [164].

The experimental chamber hosts seven hemispherical electron analysers and three X-ray detectors. The sample is mounted on a manipulator with 6 degrees of freedom. The photon beam is passing through the manipulator along the rotational axis of the manipulator, and impinges on the sample surface at a grazing angle. Two of the electron analysers are mounted on a rotating frame which, together with the possibility to rotate the entire experimental chamber around the beam axis, allow the electron analysers to be positioned in any emission direction from the surface, for any orientation of the surface. This setup makes the experimental station well suited for diffraction studies [165, 166].

Preparation of the sample is done in a separate preparation chamber, where the surface preparation, surface quality, and film growth can be monitored by a RHEED system².

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²Reflection high energy electron diffraction (RHEED) is a simple experimental technique that is very suitable for monitoring growth on surfaces. The principles of RHEED is very similar to low energy electron diffraction (LEED). In a RHEED experiment a high energy (\( \sim 30-100 \) keV) electron beam impinges on the surface in grazing incidence. At such high energies the elastic scattering is strongly peaked in the forward direction and the inelastic mean free path is very long (\( \sim 100-1000 \) Å). Therefore grazing incidence is needed to achieve surface sensitivity, and also needed to allow observation of the diffraction pattern [38].
Final state phonon scattering effects in photoemission

7.1 Introduction

Well defined initial states are probed in photoemission experiments conducted at low photon energies, low temperatures, and good angular resolution. This is the direct transition regime where the experiments reported in Chapter 4 on α-Ga(010) and Chapter 5 on Bi(110) belong. In the other limit of high photon energy and high temperature the spectra resemble the density-of-states (DOS) of the material. In Chapter 2 the crossover between these two regimes was discussed, and it was emphasized that phonons play a central role. In this chapter an investigation of the crossover on Al(100), especially with focus on the temperature dependence, is presented. The experimental results are compared to a model developed by G. Zampieri and coworkers from Centro Atomico Bariloche, Argentina. A substantial contribution of phonon-assisted non-direct transitions to the apparent direct transitions in the spectra, and good agreement between the suggested model and the experimental data, is found. The properties of the surface state has also been investigated and found to be more stable against high temperature and/or high photon energy than the bulk direct transition. This was rather unexpected and not like previously thought [167]. The bulk state results have recently been published [8].

Temperature effects have been studied since the early days of photoemission spectroscopy. Lapeyre, Huen and Wooten reported a PES experiment on single crystals of bismuth in 1970, in which they observed the characteristic temperature related effects: the features in the valence band spectra get narrower at low temperature, and may also depend in magnitude on the temperature. Lapeyre et al. suggested phonon scattering and electronic structure effects as mechanisms for the temperature dependence [168]. In the late 70s Shevchik presented the first thorough theoretical study of temperature effects in the photoemission process. Shevchik found that phonon-assisted non-direct transitions contribute appreciably at high temperatures and/or high energies [83, 84, 85]. The Shevchik model was already presented in detail in Chapter 2. Several experiments were conducted in the 80s, e.g. results were reported for Cu(100) [169, 170], Cu(100) [171, 172, 173], Cu(111) [174, 175, 167], Ag(100) [176], Pb(110) [156], W(100) [177, 178], W(110) [178]. The effect of temperature on photoemission
experiments have been reviewed by Goldmann and Matzdorf [167], while discussions are also found in more general photoemission reviews like [15], and the monograph by and Hufner [16]. A short review of the theoretical approaches up to the late 80s is presented in [175].

This chapter is organized as follows: The remaining part of this section contains more details on the Shevchik model and previous experiments. Then the present experiment is described and the results discussed. The discussion is split into three parts. First, the experimental lineshape for the bulk direct transition is qualitatively compared with the theoretical model. Second, the quantitative agreement between model and data for the bulk direct transition is compared. Third, emission from the surface state is discussed. Finally, the findings are summarized.

In conjunction with the work of Shevchik, Williams et al. confirmed the consequences of the model in an experimental study of Cu(110) at $h\nu = 45$ eV [171]. As the temperature was raised from room temperature to 800 °C, the direct transition peak disappeared and the spectra converged towards a spectrum resembling that of polycrystalline copper at the same photon energy. Williams et al. compared the intensity of the direct transition peak with an exponential model, Equation (2.29), and found the effective Debye-temperature to be lower than the bulk value. They explained the latter observation by the surface contribution to the spectra. The vibrational amplitude of the surface atoms is bigger (corresponding to a lower Debye-temperature) than for bulk atoms, and due to the short inelastic mean free path of the photoelectrons one gets a significant contribution to the spectra from the surface.

To be more specific about this argument, Al is considered as an example. The root-mean-square vibrational amplitudes for atoms in the bulk and the three utmost layers were reported in a recent LEED study of the clean Al(100) surface [179]. The data and the corresponding Debye temperatures $\theta_D$ calculated according to Equation (2.27) are summarized in Table 7.1.

<table>
<thead>
<tr>
<th>layer</th>
<th>$U_z$ (Å)</th>
<th>$U_z^2$ (Å²)</th>
<th>$\theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.17±0.02</td>
<td>0.0289</td>
<td>140</td>
</tr>
<tr>
<td>2</td>
<td>0.14±0.02</td>
<td>0.0196</td>
<td>172</td>
</tr>
<tr>
<td>3</td>
<td>0.10±0.02</td>
<td>0.0100</td>
<td>251</td>
</tr>
<tr>
<td>bulk</td>
<td>0.08±0.02</td>
<td>0.0064</td>
<td>327</td>
</tr>
</tbody>
</table>

Table 7.1: Thermal mean square vibration amplitudes for the bulk and the utmost three layers of Al(100). The $U_z$ data are from [179], while the $\theta_D$ values are deduced from Equation (2.27).

As evident from Table 7.1, the surface layers have a lower Debye-temperature than the bulk. Furthermore, in Section 2.5.1 it was found that the utmost layers contribute a considerable part of the intensity. Hence, it is very reasonable if one measures effective Debye temperatures less than the bulk value. Jezequel et al. studied the temperature dependent emission of Pb(110), and found improved agreement between a calculated effective Debye-Waller factor and the effective Debye-Waller factor from the experimental data [156]. They calculated the effective Debye-Waller factor by weighting the layer-dependent Debye temperatures (not from experimental results, but by scaling the
mean square vibrations according to the calculation by Wallis et al. for a fcc-lattice [180]. A similar strategy is followed in the present work.

Apart from the value of the effective Debye-temperature, other fundamental discrepancies were observed. Mårtensson et al. reported in the beginning of the 80s results from a number of experiments on various samples, e.g. Cu(110) and Ag(100) [172, 172, 173, 176]. They studied the behaviour of emission from different initial states on the same sample. Their main result was that the temperature behaviour was dependent on the specific initial state, which is not in agreement with the simple theory by Shevchik, Equation (2.25). In some cases they even found the intensity of the emission to increase with temperature, which is clearly not in agreement with the exponential model (2.29). Goldman and Matzdorf drew the following conclusion concerning the direct transition intensities: ‘it is not possible to describe the temperature dependence of a photoelectron spectrum by a single exponential’.

So far emission in bulk direct transitions has been considered, but emission from a surface state will also be affected by phonon scattering. Emission from surface states have generally been thought to decay faster than emission from bulk states, for the simple reason that atoms in the surface are vibrating more than atoms in the bulk. On the other hand the experimental evidence for this claim has been sparse, and in the case of Al(100) the contrary result is found: emission from the surface state is more stable against raising the temperature than emission from the bulk states.

### 7.2 The experiment

Basically the experiment is quite simple: clean the Al sample and take spectra of the valence band for various temperatures and photon energies. The valence band photoemission cross-section gets smaller as the photon energy is increased into the X-ray range. Therefore a photoemission spectroscopy beamline with high photon flux, like the SuperEsca beamline at Elettra in Trieste where this experiment has been conducted, is required. See Chapter 6 for a detailed description of the instrumentation.

The Al(100) surface was cleaned by standard methods: cycles of i) sputtering at room temperature with Ar ions at 1 keV, ii) sputtering at 400 °C temperature with Ar ions at 0.5 keV and iii) annealing of the sample at 460 °C. The first sputtering cycles after the sample is introduced into the chamber need to be at higher energies, 2 keV, to get rid of the aluminium oxide. The cleanliness of the surface was checked by XPS (e.g. no trace of oxygen) and the long range order by LEED (sharp (1x1) pattern). A good sign of the clean surface is the Al 2p surface core level shift in the XPS spectra [181].

Count rate rather than energy resolution is a critical parameter in this experiment. From the width of the Fermi edge the total instrumental resolution (beamline and analyser) is estimated to change from about 0.5 eV at 165 eV photon energy to 1 eV at 940 eV photon energy. The angular resolution is not known exactly but estimated to be around one degree. This is an educated guess made from the the width of the surface state in a similar was as explained in Chapter 3. All spectra are normalized to the beam  

1Ref. [167], p. 342
current. The flux of photons from the beamline drops off significantly at higher photon energies, and the measuring time cannot be increased by a similar factor. Thus the noise level in the spectra is increasing with photon energy.

7.3 Results: lineshape

Spectra of photoelectrons emitted from the valence band of Al(100) along the surface normal were collected over a wide range of photon energies (165 eV - 940 eV) and sample temperatures (133 K to 673 K). Figure 7.1 shows the sets of spectra acquired at $h\nu = 165$ eV and 567 eV. The main feature in these spectra is the peak at around 11 eV binding energy. This is the direct transition from an occupied state along the $\Gamma-X$ direction of the Brillouin zone to a photoemitted final state along the surface normal.

![Figure 7.1: Spectra of electrons emitted from Al(100) along the surface normal at $h\nu = 165$ eV and $h\nu = 567$ eV, and at several temperatures in the range 133-673 K. The first temperature step is 40 K from 133 K to 173 K; all the following steps are 50 K.](image)

This is the situation illustrated on Figure 2.2 in Section 2.2.2. Notice that the direct transition is originating from the same initial state in both cases ($\vec{k}_i$ is equal to $-\vec{k}_f$). The peak at $\sim 2.8$ eV, best seen in the spectra acquired at $h\nu = 165$ eV, is the surface state first observed by Gartland and Slagsvold [182, 183, 184]. This is a Shockley-type surface state existing in the gap at the X point of the Brillouin zone. The surface state is located very close to the band-edge, and thus very close to a peak in the density of states [185]. The spectra clearly show a decay of the direct transition peaks as temperature is increased. It can also be seen that the decay rate increases with the photon energy: at $h\nu = 165$ eV the direct transition peak does not disappear even at the highest temperature,
while at $h\nu = 567$ eV it disappears at around 423 K. At the highest photon energies and temperatures the spectra resemble the parabolic density of state of Al. The same behavior is also observed in the rest of the data set which is not shown here. These observation are in good qualitative agreement with the Shevchik model. Note that the direct transition peak also broadens and shifts while decaying. This latter observation is, however, not in agreement with the Shevchik model.

### 7.3.1 The photoemission model

The experimental work on Al(100) is compare to a refined model of the photoemission process including the phonon contribution. The model originates in studies of similar crossovers found in related branches of electron spectroscopy. In X-ray photoelectron diffraction (XPD) and Auger electron diffraction (AED), maxima of intensity is observed at energies above 500 eV along main crystallographic directions due to the forward focusing effect of electrons. Below 500 eV there is a different regime dominated by multiple scattering. Similarly, scattering of electrons at low energy (LEED) show intensity in distinct Bragg directions, while scattering of electrons at medium energy (MEED) resembles XPD/AED patterns. The model applied here is developed from the work of Vicente Alvarez, Ascolani, and Zampieri who successfully were able to explain the LEED to MEED transition in terms of phonon scattering [186].

An important feature of the model is that it allows to calculate separately the contributions to the intensity of the photoemission transitions in which $m$ phonons have been excited and/or absorbed ($m = 0, 1, 2, \ldots$). The initial state of the electron is composed of two Bloch waves, one propagating towards the surface and one reflected back at the surface, and the final state is the time-reversed LEED wave function. This time-reversed LEED wave function is written in the cluster approximation, i.e. as a plane wave plus the single-scattering waves emanating from each atomic site, plus the double-scattering waves, etc. In other words multiple scattering is included. The lattice vibrations are treated within the Debye model. The larger vibrational amplitudes at the surface have been taken into account by defining an effective Debye-temperature. This is done by weighting the layer-dependent Debye-temperatures summarized in Table 7.1 with exponentials $\exp(-z/\lambda)$, where $\lambda$ is the inelastic mean free path and $z$ is the distance from the surface. The inelastic scattering is discussed in Section 2.5.1 and values of $\lambda$ are found in Table 2.2. The photoemission transition probability per unit time including the vibrational degrees of freedom of the lattice in a golden rule expression is the starting point of the model. More details about the model can be found in the original work by Vicente Alvarez et al. [186, 187].

Figure 7.2 shows calculated photoemission spectra (at $h\nu = 180$ eV) in the region of the direct transition peak, at two different temperatures and decomposed into the direct ($m = 0$) and non-direct (sum over $m \geq 1$) contributions. The calculations correspond to the experimental situation with emission along the surface normal, i.e. initial states along the $\Gamma-X$ line of the bulk Brillouin zone. Several features are to be noted in these spectra. First, the relative strengths of the direct and non-direct contributions interchange with the temperature. Second, the direct contribution has a sharp peak when $\Delta k_x = 2G_{100}$, which is known as the “third” Laue condition. Third, and most importantly, the non-direct contribution also has a peak close to the initial state energy


**Figure 7.2:** Calculated spectra corresponding to photoemission from Al(100) along the surface normal at $h\nu = 180$ eV, $T = 133$ K, and $T = 423$ K. The spectra are presented decomposed into the direct (dotted lines) and non-direct (dashed lines) contributions. The upper scale shows the electron wave vector change in units of the minimum reciprocal lattice vector.

for which the third Laue condition is fulfilled. Note that the peak in the non-direct contribution causes the lineshape of the peak at 423 K to be severely different from the direct lineshape: scattering with phonons do not simply create a flat non-direct background under the direct peak. Furthermore, the non-direct peak may explain the observed apparent broadening and shift in energy of the direct transition peak.

To get a better insight into which non-direct transitions contribute to the broad non-direct peak, the first four contributions to this peak has been plotted in Figure 7.3. It is seen that: i) the temperature hardly changes the form of the contributions, only their relative strengths, and ii) the broad peak is formed essentially by the $m = 1$ and $m = 2$ contributions; all the contributions with $m \geq 3$ are rather flat in the region of interest and, therefore, contribute mainly to form the background under the peak. Thus it is concluded that the peak in the calculated spectra in the region of the experimental direct transition peak is formed not only by the $m = 0$ or direct contribution, but also by the $m = 1$ and $m = 2$ contributions to the non-direct intensity. Qualitatively, the agreement between the model and data is good.
\[ m = 4 \]
\[ m = 3 \]
\[ m = 2 \]
\[ m = 1 \]

\[ 0.0 \]
\[ 0.2 \]
\[ 0.4 \]
\[ 0.6 \]
\[ 0.8 \]
\[ 1.0 \]

\[ T = 133 \text{ K} \]

\[ T = 423 \text{ K} \]

\[ \Delta k / G_{100} \]

\[ \text{Intensity (arb. units)} \]

\[ \text{Binding energy (eV)} \]

\[ \Delta \kappa / G_{100} \]

\[ \text{Binding energy (eV)} \]

\[ \text{Intensity (arb. units)} \]

\[ \text{Binding energy (eV)} \]

**Figure 7.3:** First four contribution to the non-direct spectra of Figure 7.2. \( m \) is the number of phonons that have been excited and/or absorbed during the photoemission transition. The small negative intensities are caused by the cutoff in the sum over the multiple scattering waves in the final state.

### 7.4 Results: bulk states

The next step is to make a more quantitative comparison with the measured peak intensities. In Figure 7.4 the area of the direct transition peaks in the experimental spectra is plotted together with the areas under the calculated peaks for the \( m = 0, 1, 2 \) contributions, as well as the sum of these three contributions. The data have been normalized such that this sum and the experimental peak area have a value of unity at the lowest temperature.

It is seen that the direct contribution falls continuously in all the cases, whereas the \( m = 1 \) and \( m = 2 \) contributions in many cases first increase with the temperature and have a broad maximum. It can be shown that each \( m \)-contribution must reach its maximum strength when \( |\Delta \kappa|^2 < \langle U_z^2 \rangle \approx m \), where \( \Delta \kappa \) is the electron wave vector change during the photoemission transition, and \( \langle U_z^2 \rangle \) is the mean square amplitude of vibration of the atoms. This simple formula predicts correctly that the maximum of the \( m = 1 \) contribution should occur at \( T \approx 180 \text{ K} \) when \( h\nu = 165 \text{ eV} \), and below 100 K at the other photon energies; while that of the \( m = 2 \) contribution should occur at \( T \approx 365 \text{ K} \) when \( h\nu = 165 \text{ eV} \), around 160 K when \( h\nu = 317 \) and 345 eV, and below 100 K at the other photon energies.

The main feature to be noted in this figure, however, is that the pure direct con-
Figure 7.4: Plot of the areas of the peaks as a function of temperature. The solid circles correspond to the experimental direct transition peaks while the other curves are the results of the theoretical calculations.
tribution (dashed line) decays in all cases faster than the experimental intensity, while the sum of the \( m = 0, 1, 2 \) contributions (thick solid line) describes the experimental data rather well. This is consistent with Figure 7.2 and Figure 7.3, and proves that the experimental peak contains considerable contributions from the photoemission events with excitation/absorption of 1 and 2 phonons.

The above findings can be explained by the fact that the probability of exciting/absorbing phonons goes inversely with the modulus of the phonon wave vectors [83, 84, 85]. Thus, the photoemission events with excitation and/or absorption of only one or two phonons involve on average a total phonon wave vector small enough for the conservation rules of the electron wave vector to remain valid to a high degree. As the number of phonons exchanged with the lattice increases so does the average total phonon wave vector, and the conservation rules for the electron wave vector gradually relax. Therefore, the \( m = 1, 2 \) contributions to the non-direct intensity have structures in both the energy and angular distributions similar to those of the \( m = 0 \) contribution, while the contributions with \( m \geq 3 \) simply add up to form a featureless background under the peak.

In brief, it is found that there are a significant amount of phonon-assisted non-direct transitions in the so-called direct transition peaks in photoemission spectroscopy, and that this fact may affect the lineshape. Retrospectively, it is perhaps not so surprising that the phonon scattering has such a large contribution to the photoemission signal when keeping in mind that even the direct transitions can only be achieved by an umklapp process or, in other words, by the scattering with a phonon of zero energy.

### 7.5 Results: surface state

Finally, photoemission from the surface state at the \( \bar{\Gamma} \) point in the surface Brillouin zone of Al(100) is discussed. Generally, it has been considered that photoemission from surface states would be quenched faster than for bulk states as a function of increasing temperature and/or photon energy. Nevertheless, the surface state on Al(100) is found to be more stable towards an increase of the sample temperature than the direct transitions from the bulk. At the highest photon energies only the surface state is observed, while the bulk direct transitions are almost gone.

The intensity plots in figure 7.5 show a series of spectra taken at photon energies between 125 eV and 760 eV, in normal emission, and at room temperature. The upper part of the figure shows the photoemission intensity as a function of photon energy and binding energy; each vertical line corresponds to a spectrum taken at a fixed photon energy. The spectra have been normalized in the energy window \([14, 14.2]\) eV. The lower part of the figure shows an interpolation of these data such that the photoemission intensity is displayed as a function of binding energy at a constant final state momentum. This is essentially the bandstructure along \( \Gamma-X \) in the repeated zone scheme [39]. Notice the simple parabolic dispersion in Al. The final state momentum is calculated in the free electron approximation (see Section 2.2.2).

Several features can be identified in the figure. The sharp edge at a binding energy of 0 eV is due to the Fermi distribution. The dispersing band between 0 eV and 11 eV binding energy is caused by the direct transition from the band in the \( \Gamma-X \) direction of
the Brillouin zone (BZ). In the band gap at the BZ boundary (the X point) the Al(100) surface state is located. In these plots the surface state is seen as a horizontal line with considerably intensity variation at about 2.8 eV binding energy.

A closer inspection of the figure reveals several interesting details. First, the surface state intensity resonates whenever the final state momentum gets close to the X point. This phenomenon is discussed below. Second, weaker ‘twin images’ of the main dispersing band can be seen. These are also accompanied by a resonance in the surface state intensity when they get close to the X point. The most pronounced of these resonances can be found at $k_f/\theta$ values around 6 and 9 Å$^{-1}$. The ‘twin image’ responsible for this resonance is caused by a surface umklapp process. Third, one also notices that at higher energies the bands appear increasingly blurred. This illustrates the consequences of the simple Shevchik model, Equation (2.25). The direct transition peaks decay upon raising the photon energy, while the indirect transition intensity, which leads to a DOS-like spectra, is increasing.

Resonances in the cross-section for photoexcitation of a surface state were first demonstrated and explained on Cu by Louie et al. in 1980 [188]. A maximum is found whenever the photon energy is correct to excite the surface state into a final bulk band with a value of $\vec{k}$ corresponding to a band extremum. In the case of normal emission on Al(100) one therefore expects a maximum in the emitted intensity whenever a final state at the X point is reached. When this is the case, the initial state of the bulk direct transition will also be close to the X point. In Figure 7.5 it is clearly seen how the surface state intensity resonates whenever the dispersing bands get close to the surface state and the X point. In Table 2.2.2 the appropriate photon energies were listed, and the agreement is good. On Al(100) these oscillations were first observed and discussed by Levinson et al. [184].

The most surprising observation in Figure 7.5, however, is the fact that the surface state is observed at rather high photon energies. One should expect it to be strongly suppressed by two mechanisms. First, the mean free path increases by a factor of two or more over the energy range investigated here (see Table 2.2), which corresponds to a decrease in surface sensitivity. Second, the Debye temperature of the surface is known (by LEED) to be considerably lower than in the bulk (see Table 7.1), corresponding to a smaller Debye-Waller factor. An even more clear illustration of the surface state’s stability with respect to raising the temperature and/or the photon energy is given in Figure 7.6 and Figure 7.7.

Figure 7.6 shows a few spectra taken in normal emission and with photon energies between 1000 eV and 1100 eV. While the signal to noise ratio is rather poor due to the combination of a small photon flux and a small cross-section, one is indeed still able to identify the surface state resonating on top of a DOS-like background from the bulk in the spectrum taken at 1050 eV. The energy range is slightly below the next X point where the surface state intensity is expected to resonate. There are only a weak trace of a bulk direct transition seen in the 1080 eV spectra.

Similar to the analysis done for bulk direct transition, Figure 7.7 shows spectra, and the integrated surface state intensity at $h\nu = 425$ eV as a function of temperature. At this photon energy the surface state emission resonates. An exponential fit to the intensity yields a surface Debye temperatures of about 330 K. This value is similar to the bulk Debye temperatures obtained from LEED [179] and bigger than the bulk
Figure 7.5: (top) Intensity plot of spectra from Al(100) as a function of photon energy; normal emission and room temperature. In the range 125 eV to 590 eV the spectra were taken in 5 eV steps, while steps of 10 eV were used in the range 590 eV to 760 eV. The spectra have been normalized in the energy window [14,14.2] eV. (bottom) The same data transformed and interpolated such that the photoemission intensity is plotted as a function of final state momentum. The (long dash) line indicates the direct transition, while the (short dash) line indicates an umklapp transition. Notice the simple parabolic dispersion in the Al bandstructure.
Debye temperatures obtained from the bulk direct transitions in the previous sections. Also shown in the Figure is a theoretical calculation similar to the bulk state results; in this case the model has been modified to simulate the photoemission from a surface state with excitation/absorption of phonons.

The quantitative agreement is not as good as in the case of photoemission from the bulk state, but it is evident that the phonon contribution is crucial. This is preliminary theoretical results, and work is done to improve the simulation of photoemission from a surface state within the model. However, the stability of the surface state can basically be understood from the following simple explanation of the behaviour. The direct transition intensity, whether from a bulk state or the surface state, is originating from a volume of coherently emitting atoms. In the bulk, atoms inside a sphere with radius \( r \) have to emit coherently in order to produce a direct transition peak. At the surface, however, only atoms within a disk with radius \( r \) have to emit coherently in order to produce a direct transition peak. In other words, it takes less coherently emitting atoms to produce a direct transition peak from a surface state, and therefore the surface state is rather stable against elevated temperatures.

### 7.6 Conclusions

The dependence of photoemission from Al(100) on temperature and photon energy has been investigated by both photoemission spectroscopy experiments and theoretical modelling. The difference between emission from a bulk state and a surface state has been discussed. There are two important conclusions of this work.
First, it has been shown that emission/absorption of phonons during the photoemission event can lead to a severe change of the photoemission lineshape. This has consequences for interpretation of lineshape data in terms of a spectral function. This effect is going to be especially important when the experimental data are taken at high temperature and/or high photon energies, or when the sample has a low Debye temperature. The lineshape is affected because transitions involving phonons do not give a featureless contribution to the spectra, but a peak at almost the same energy position as the direct transition peak. The theoretical calculations show that scattering events involving one or two phonons are the dominating contributions to the peak in the non-direct transition intensity. This change of lineshape also explains an observed apparent shift and broadening of the direct transition peak when raising the temperature. Good agreement between the calculated total intensities and the observed intensities substantiates the modelling and the interpretation.

Second, contrary to common expectations, the surface state on Al(100) is observed to be more stable against increased temperatures and/or photon energy than the direct transition from bulk states. A simple explanation was propose based on the number of emitters that have to emit coherently in order to produce a surface state peak compared to the number of emitters involved in coherent emission from a bulk state. However, the phenomena could also be simulated by proper modifications to the theoretical model for the bulk transitions.
CHAPTER EIGHT

Valence band photoelectron diffraction

8.1 Introduction

In solid state physics we are confronted with a huge and seemingly ever growing diversity of materials. Understanding interesting properties like magnetoresistance, high-$T_c$ superconductivity, and metal-insulator transitions in new and complex materials is a major challenge. Various measures of the electronic properties can be determined from a broad range of experimental techniques. For example, information on the density of states (DOS) of a material can be obtained from X-ray emission spectroscopy. This technique offers access to the chemically-resolved and symmetry-restricted partial density of states (PDOS) if a suitable core level is available [189, 190]. We have studied valence band photoelectron diffraction as an alternative method for investigating the PDOS; a method which potentially combines higher spectral resolution with stringent symmetry restrictions. In this chapter the method, and the experimental results are presented and discussed. Al is investigated as a test case, and the DOS has been decomposed into the $s$ and $p$ contributions. Aluminium is obviously not a new and complex material, and as a outlook results of a preliminary investigation on the correlated electron material NiO is also reported. NiO and other first-row transition metal monoxides have been a challenge to the solid state physics community since the 1930s when the controversial electronic and magnetic properties were first recognized. In general, the field of transition metal oxides drew a lot more attention after 1986, when Bednorz and Müller reported the discovery of high-temperature superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, since it was believed that an understanding of the electronic structure of transition metal oxides would fertilize an understanding of high-temperature superconductivity.

Photoemission spectra resemble the DOS of the material in the limit of high temperature and high photon energy, while at low temperature and low photon energy the spectra are dominated by direct transitions. This dependence on temperature and temperature and photon energy was introduced in Chapter 2, and investigated experimentally in Chapter 7. However, a single spectrum of the valence band at high temperature and high photon energy is not readily interpreted in terms of either the chemically-
or symmetry-resolved PDOS. In this chapter it is investigated whether observed angular variations in the photoemission intensity, and some inspiration from photoelectron diffraction, may be helpful in determining the symmetry-resolved PDOS.

Photoelectron diffraction (PED) is angle- and energy-dependent intensity variations in X-ray photoemission from core levels. The origin of the phenomenon is interference between the directly emitted photoelectron wave and the elastically multiple-scattered waves from the neighbouring atoms. Modulations of the photoemission intensity are measured as a function of emission angle or kinetic energy. PED is an established technique for determining the local geometry of the emitter [191, 14, 192, 193, 194].

Similar modulations was observed in photoemission from the valence band of Al by Osterwalder [9], and the effect was termed valence band photoelectron diffraction (VBPED). Valence band electrons are not localized like core levels, and the origin of the diffraction effect is not so obvious in this case. The origin is thought to be an effective localization which could either be real [9], or caused by an integration over all initial states in momentum space [195, 196, 197, 187]. Nevertheless, Stuck et al. demonstrated that the VBPED data could be applied for deducing the chemically resolved partial density of states of the alloy Cu3Au [198, 199]. This was done by comparing the VBPED pattern with diffraction patterns of the Au 4f and Cu 3p levels. The idea behind the present investigation is to compare the VBPED pattern with PED patterns from core levels of the same initial state symmetry.

Evidence for influence of the initial state symmetry on the diffraction pattern has been reported [197, 200, 201], but a systematic decomposition has not been attempted. Using VBPED to determine the symmetry-resolved PDOS will be more difficult than deducing the chemically-resolved PDOS, since the initial state symmetry has only a small effect on the diffraction pattern. Al is investigated in the present work, and the s and p contributions to the DOS is determined by directly comparing energy-resolved VBPED modulations to PED modulations of the Al 2s and Al 2p core levels taken at the same kinetic energy. This is done to assure similar scattering conditions for the outgoing electrons. Al is good test because the electronic structure of Al is well known, and Al samples are simple to handle in a PES experiment. Additionally, Al is also to some extend a ‘worst case’ example owing to the quasi-free electron character. If the decomposition method works on Al it may very likely also work in cases with more localized bonding.

8.2 The Al experiment

The experiment on Al was conducted on a (100) oriented crystal at the SuperEsca beamline at the synchrotron radiation source Elettra. Refer to Chapter 3 for a description of the instrument, and to Chapter 7 for the sample preparation. The data were taken as ‘azimuthal scans’, whereby the the polar emission angle, \( \theta \), of the analyser was fixed and the azimuthal emission angle, \( \phi \), was swept by rotation of the sample around its normal. The zero of the azimuthal scale is defined in Figure 8.1. Note that the azimuthal scans should be symmetric around \( \phi = 0^\circ \) because of the mirrorplane in the crystal structure. Two data sets in different scattering geometries were measured. A data set consists of one valence band azimuthal scan and three core level azimuthal
scans. The core levels are taken at slightly different kinetic energies covering the more than 10 eV broad valence band of Al. The first data set (set I) was taken at a kinetic energy of about 400 eV and polar angle $\theta = 35^\circ$, while the second data set (set II) was taken at a kinetic energy about 350 eV and polar angle $\theta = 56^\circ$.

From the results in Chapter 7 it is known that at these intermediate photon energies, and if the experiment is done at low temperature, photoemission from the valence band of Al will contain a significant amount of direct $k$-conserving transitions [8]. In an azimuthal scan the direct transitions will move forth and back, and blur the subtle diffraction effects. A convenient remedy to avoid direct transitions is phonon scattering and therefore the spectra have been measured at a sample temperature of 673 K. For the purpose of illustration an azimuthal scan at low temperature, where the influence of the direct transitions is easily seen, will also be shown.

8.3 Results

The intensity of the Al 2$s$ and 2$p$ levels versus the azimuthal angle is shown in Figure 8.1 for both data sets. For the sake of comparison the curves have been multiplied by an arbitrary factor. In a first inspection of data set I, two main features are observed in the data: peaks at $\phi = 45^\circ$ and a peak at $\phi = 0^\circ$. The peaks at $\phi = 45^\circ$ are the tails of the pronounced forward scattering peaks which appear in the [101] directions of the fcc structure, i.e. in directions like $\theta = \phi = 45^\circ$. The peak at $\phi = 0^\circ$ is close to the bulk [112] direction. Note, however, that in this medium energy range multiple scattering is important and the PED patterns cannot simply be interpreted in terms of crystallographic directions. The most important observation for this experiment is the difference between the $s$ and the $p$ level. The modulation curves are rather similar, but small and well-reproducible differences are found. The most significant is the stronger modulation of the $s$ core level. Another difference is the smaller relative intensities of the shoulders on the $\phi = 0^\circ$ peak for the $s$ level. Figure 8.1 also shows the modulation curves for the dataset II. Again the modulations for the $s$ and $p$ levels are similar, but small differences are found. The $s$ component shows a stronger degree of modulation, and smaller relative intensity around the center of the scan. For both data sets, similar differences between $s$ and $p$ can be found in simulated data obtained using the MSCD package [202].

The corresponding azimuthal scans of the valence band are shown in Figure 8.2. The left hand side of the figure shows the raw data. Every column of the displayed matrix corresponds to a spectrum. The black area at the top is due to the cut-off by the Fermi-function. Below the Fermi edge the intensity is decreasing until the bottom of the valence band is reached. At the lowest kinetic energies the intensity increases again owing to plasmon excitations associated with the photoemitted valence electrons.

The VBPED effect is already visible in the raw data, but it is far more clearly seen in the modulation functions shown in right hand side of Figure 8.2. For each row of kinetic energy in the raw data, a modulation function is calculated according to:

$$\xi(\phi) = \frac{I(\phi) - I_0(\phi)}{I_0(\phi)}$$

(8.1)
where $I_0(\phi)$ is a smoothly varying function through the data; in this case $I_0$ is the average. Above the Fermi level this normalization gives rise to random and relative intense noise since $I_0$ is close to zero. In the valence band data of data set I one readily recognizes the three main peaks seen in the core level data in Figure 8.1 (a). A closer inspection reveals variations depending on photon energy: at the bottom of the valence band, in the binding energy range 6 to 11 eV, the modulations are stronger and the shoulders on the sides of the $\phi = 0$ peak are more pronounced. Furthermore, the peaks around $\phi = 40$ are more narrow at the bottom of the band. When comparing these observations with the the core level data in Figure 8.1 they qualitatively suggest that the bottom of the valence band is more $s$-like than the top. This is in good qualitative agreement with the actual symmetry-resolved PDOS of Al.

**Figure 8.1**: (a) Integrated intensity of the Al 2s (dashed) and 2p core levels for an azimuthal scan 35$^\circ$ off-normal with a kinetic energy of about 400 eV. The curves have been multiplied by an arbitrary factor in order to permit a better comparison. (b) Similar, but for 56$^\circ$ off-normal and a kinetic energy of about 350 eV. Insert: definition of the azimuthal angle scale.
Figure 8.2: (a) Photoemission intensity from a valence band azimuthal scan corresponding to Figure 8.1 (a). The lowest values are black, the highest white. Left: Raw data. Right: Modulation function \( \frac{I(\phi) - I_0}{I_0} \) calculated for each kinetic energy. (b) Similar, but corresponding to Figure 8.1 (b).

8.3.1 Decomposition of the DOS

For a more quantitative analysis it is necessary to consider the intensities of the valence band and the core levels rather than the modulation functions. The procedure outlined by Stuck et al. for the decomposition of \( \text{Cu}_3\text{Au} \) into the copper and gold contributions
is followed [199]. The basic assumption is that the final state diffraction of the $s$ and $p$ valence band levels are exactly the same as for the corresponding core levels. In this case one may write the energy-resolved valence band intensity $I^{VB}(\phi, E)$ as a sum over integrated core level intensities $S^\text{core}_i(\phi)$ and $S^\text{core}_p(\phi)$:

$$I^{VB}(\phi, E) = \sum_{i=s,p} S^\text{core}_i(\phi) c_i d_i^{VB}(E)$$  \hspace{1cm} (8.2)

The factors $c_i$ contain cross sections, which are assumed to be independent of $\phi$ and $E$ as well as the number of electrons in the $s$ and $p$ levels. The $d_i^{VB}$ factors are the PDOS. In practice the decomposition is achieved by finding the factors $c_i d_i^{VB}$ such that the right hand side of the equation represents the best fit to the left hand side for every kinetic energy. The $c_i$ factors are unknown and there is no way to determine these independently from the data. Therefore the outcome of the fitting procedure is more precisely the PDOS on an arbitrary scale. The valence band is rather broad and the scattering conditions may change throughout the energy range. Therefore three $s$ and $p$ core level scans, spanning the kinetic energy range of the valence band, have been measured; spectra for energies in between have been interpolated. The energy dependence is very small, however. Like in the case of the core levels, a Shirley-type background has been subtracted from the valence band spectra.

The result of the decomposition is given in Figure 8.3. The resulting PDOS components for both data sets are plotted together with a calculated PDOS cut off by a Fermi function. Each set is normalized such that the area under the experimental curve is the same as under the calculated curve. The theoretical density of states functions were obtained by means of ab initio density functional calculations using the local density approximation (LDA). The self-consistent solution of the one-electron Schrödinger-like equation was obtained by means of the Linear Muffin Tin Orbital (LMTO) method in the so-called Atomic Spheres Approximation (ASA) [203, 204]. Apart from the $s$ and $p$ components, the calculation also yield a small $d$ component in the upper part of the valence band, and a very small $f$ component. The relative contributions of these two are small enough to be of little interest in the present case. The valence band is split into two regions: the bottom of the band is more $s$-like, while the top of the band is more $p$-like. This is in accordance with the qualitative inspection of Figure 8.1 and 8.2. This ordering is also in reasonable agreement with the calculated PDOS contributions, though the experimental contributions are narrower. In a sense the experimental data look more ‘atomic-like’. It is noteworthy that the results are very similar for the two datasets, even though they are obtained under rather different scattering conditions. There is a sharp spike in $s$-contribution from dataset II, which can also be observed in Figure 8.1, caused by the strong modulation at this binding energy. The physical origin of this is unclear.

### 8.4 Discussion

Before discussing possible physical mechanisms behind the discrepancy between theory and experiment, a closer look at the possible sources of error in the data analysis is given. The first thing is purely statistical: the difference between the $s$ and $p$ core
Figure 8.3: Partial $s$ and $p$ density of states for Al obtained from comparing the valence band data in Figure 8.2 (a) and (b) to the corresponding core level data. Crosses: result form the scans taken at 35° off-normal with a kinetic energy of about 400 eV (dataset I); open circles: scans taken at 56° off-normal with a kinetic energy of about 350 eV (dataset II); solid lines: calculated PDOS according to Ref. [203] convoluted with a Fermi distribution.

levels is clear and reproducible, but also very small. In the case of a very flexible experimental setup it may even be possible to decompose the valence band by measuring in a geometry where emission from the $s$-state is suppressed. This experiment has, however, been limited to cases with rather small differences, like shown in Figure 8.1. This difference depends on the scattering conditions and experimental geometry. However, the fact similar decompositions are obtained under rather different conditions indicates that statistical fluctuations are of minor importance, and that one should rather consider systematic errors.

The first point to raise is whether any residual direct transitions are influencing the
spectra. The quenching of direct transitions has been studied carefully, see Chapter 7, and it was found that direct transitions are effectively suppressed under these experimental conditions. Direct transitions will also show up as sharp features in plots like Figure 8.2, and would easily be recognized. To illustrate this an azimuthal scan of the valence band at polar angle $\theta = 45^\circ$ off-normal, a kinetic energy of about 194 eV, and a temperature of 128 K has been measured. These energy and temperature conditions will obviously emphasize the direct transitions, and this is also clearly seen in Figure 8.4. Direct transitions are therefore excluded as a significant source of systematic errors.

![Figure 8.4: Azimuthal scan of the valence band taken at 45\(^\circ\) off-normal, a kinetic energy of about 194 eV and a temperature of 128 K. Left: Raw data. Right: Modulation function. The direct transitions are easily visible as narrow and strongly dispersing features.](image)

The next possible source of error is the background in the valence band data. The background might show modulations similar to the actual photoemission intensities, depending on its nature (intrinsic or extrinsic). It is well-established that such modulations are present in the losses from core level data [205], and modulations are also evident in Figure 8.2 in the region of the plasmon loss below the bottom of the band. Note that the subtraction of the Shirley-background from each spectrum in the valence band data does, to some extent, take care of this problem.

Another questionable point is the assumption that the initial state dependent modulations of the valence band are exactly the same as those of the corresponding core levels. A possible problem in this context is the fact that the initial state symmetry of a fully occupied core level is different from a partially-filled valence band state, and this might lead to different diffraction effects [201, 206]. It is not thought that this will be
a severe problem in present case due to the high symmetry of the crystal.

Finally, the $d_{i}^{\ell}(E)$ factor has been identified directly with the PDOS. This is only approximately correct since the $d_{i}^{\ell}(E)$ might have a directional dependence [198]. First of all, the possible transitions may to some extent be dependent on the available initial and final states, although this condition will be relaxed by the interaction with phonons. A more severe reason for the directional dependence could be the fact that the ratio between the contribution of surface and bulk PDOS to the measured signal will change strongly as a function of the polar emission angle. This point is discussed below.

After these words of caution we can now come back to the question why there are differences between this experimental DOS and the theoretical prediction. Two possible explanations are suggested. The first is that the measured PDOS is a superposition of surface and bulk PDOS. There will be a difference between the two owing to band-narrowing and re-hybridization at the surface. These effects render the surface PDOS more atomic-like and this could explain our results. One could, however, expect this effect to be stronger for data set I than for data set II because of the higher polar emission angle and the lower photon energy. A more likely reason lies in the measurement itself. Consider a picture where, for whatever reason, the electrons which give rise to the VBPED effect can be viewed as locally emitted from near the atom cores. In such a case the VBPED experiment would primarily probe the wave functions near the core, and the resulting PDOS would probably be more atomic-like than the total PDOS. It is clear that this ‘artificial’ band-narrowing would be stronger on our free-electron metal Al than on $d$ and $f$-systems where the initial state is already rather localized.

Nevertheless, the ordering of the symmetry resolved PDOS is correct, and an improved understanding of the VBPED process may make the quantitative agreement better. In the solid state physics community there is obviously more interest in knowing the symmetry resolved DOS of more complicated materials than Al. We have conducted a preliminary investigation on NiO in order to try the VBPED technique under more realistic conditions. These results are presented in the next section.

### 8.5 Introduction to NiO

It is worth considering the possibilities of actually observing VBPED, and to what extent it may be possible to perform the decomposition on NiO, before the experimental results are presented. One notices immediately that the situation is different from the Al experiment. First, it will be difficult to quench the direct transitions due to the high Debye temperature of NiO ($\Theta_{D} = 595$ K [207]). Secondly, it will be difficult to decompose the DOS of NiO, since proper core levels are lacking for comparison with the O $2p$ and Ni $3d$ states in the valence band. Thirdly, from the atomic photoionisation cross-section ratio (Table 8.1) between Ni $3d$ and O $2p$ levels it seems likely that Ni $3d$ will be dominating in valence band photoemission, at least at the highest photon energies. Obviously, there are challenging experimental problems to be faced, but this is also a situation were the limitations of the method can be tested.

To be more specific about the direct transition problem, the Debye-Waller factor of NiO is shown in Figure 8.5, and compare also to Figure 2.4 for Al; it is readily seen
that it will be difficult to suppress the direct transitions. In the experiment on Al it was demonstrated that quenching of direct transitions is an essential experimental requisite for measuring VBPED. On the other hand, the problem may not be that severe in the case of NiO, since the band structure description is inadequate, and the electronic levels expected to be rather localized. The lack of proper core levels obviously rules out the kind of decomposition of the DOS that was done on Al. This is a general problem for all first-row transition metal oxides, and many other interesting materials. Nevertheless, if it turns out to be possible to measure a VBPED effect one may consider resorting to calculated modulation functions in order to do the symmetry resolved decomposition.

The experimental results on NiO to be presented here are not as conclusive, and painstakingly analyzed, as the Al results. However, they illustrate very well the issue of studying VBPED on more complicated systems. For this reason, some more details on the structure, electronic structure of NiO, and the growth of NiO thin films are given below. The huge number of transition metal oxides, and their broad range of interesting properties, have stimulated a significant amount of research, and a correspondingly huge amount of literature. Two reviews from a photoemission point of view are the pre-high-Tc work by Davis [209], and the post-high-Tc work by Shen and Dessau [21]. As a general introduction to the field the book by P. A. Cox [210] is highly recommendable.

Figure 8.5: Debye-Waller factor for NiO as a function of momentum transfer and temperature.
Table 8.1: Atomic subshell photoionization cross-sections (in Mb) for selected elements and soft x-ray energies [208]. The second column is the calculated binding energy of the levels (eV). Cross-section ratios between selected subshells are shown in the lower part.

<table>
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<th>Level</th>
<th>$E_B$</th>
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<tr>
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</tr>
<tr>
<td>Ni 4s</td>
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<tr>
<td>O 2p</td>
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</tr>
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<td>Al 3p</td>
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<td>22.27</td>
<td>0.48</td>
<td>16.90</td>
<td>8.06</td>
</tr>
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</table>

Structure

The geometric structure of NiO is closely related to the magnetic properties. NiO is paramagnetic at high temperatures and antiferromagnetically ordered at low temperatures. The transition temperature, the Néel temperature, is $T_N = 523$ K (250 °C). Above $T_N$ the NiO crystals adopt the rock salt (sodium chloride) structure. Below $T_N$ the structure undergoes a slight rhombohedral distortion. The distortion is the bigger the lower the temperature [211]. However, the distortion is so small that it is barely noticeable in, for example, the X-ray powder diffraction pattern of NiO [212].

If the fcc (or fcc-like) structure is viewed along one of the four equivalent [111] directions, parallel to the body diagonals of the fcc unit cell, alternate layers of Ni$^{2+}$ and O$^{2-}$ ions are found. In the antiferromagnetically ordered phase the spins of all the Ni$^{2+}$ ions within a given layer are aligned parallel, while in adjacent layers they are all aligned antiparallel. This corresponds to a magnetic superstructure, or a spin superlattice, that can be treated as a cubic cell with dimensions twice as big as the high temperature paramagnetic structure. The translational spin symmetry of the spin system on the (100) surfaces is (2x1) with respect to the chemical unit mesh.

The (100) surface is by far the most studied surface of NiO since: "Cleavage on (001) planes is easily achieved and this results in a relatively flat and defect free surface. . . one can therefore regard the geometry of the (001) face as a near perfect bulk termination." For this reason many studies have been done on NiO crystals cleaved in situ. Generally the (100) surface is reported to be stable and staying clean for several days, e.g. Sawatsky et al. wrote: "The surface remained unchanged during . . . [the]
measurements and remained free of any detectable changes for several days after the measurements.\(^4\)

Rather than cleaving bulk NiO crystals it is possible to grow crystalline thin films. In the present case the VBPED experiment was conducted on crystalline films of NiO grown with (100) orientation on an Ag(100) substrate. The growth of NiO films is discussed separately below. The \textit{in situ} growth of NiO enables us to regenerate the surface when it degenerates. Thin films also reduce charging of the sample in photoemission experiments. NiO is an insulator, and one needs to worry about charging of the sample in photoemission spectroscopy. Thin films of insulators on metallic substrates are known to charge less in PES experiments than their bulk counterparts, and are therefore a suitable alternative. Also scanning tunneling microscope (STM) experiments are troubled by the insulating gap, and may similarly benefit from thin films on metallic substrates\(^5\) Noteworthily, several groups have done PES on cleaved crystals at room temperature without significant problems: e.g. Steiner et al. commented: ‘For the bulk NiO(100) single crystals sometimes sample charging of a few tenth of an eV was observed …\(^6\), while Shen et al. similarly observed: ‘No charging effects was observed in the photoemission spectra, and the experiments were performed at room temperature.’\(^7\)

\textbf{Electronic structure}

NiO is an ionic solid and a very good insulator with a band gap of 4.3 eV. From a naive band structure point of view this is a contradiction since the partially filled 3\textit{d} levels of the Ni ions ought to become partially filled bands in the solid, and therefore become metallic. The reason for the breakdown of the simple band theory description is the neglect of repulsion between the electrons which tends to keep the electrons localized on individual atoms. This picture of the electronic properties of NiO was captured by R. E. Peirls already in 1937. Peirls pointed out that the repulsive energy between two Ni\textsuperscript{++} \textit{d} electrons was larger than the kinetic energy which might be gained by allowing the \textit{d} electrons to form a band. Therefore the \textit{d}-shell occupancy of every site would remain \textit{d}\textsuperscript{8}Ni\textsuperscript{++}, and NiO remaining insulating even though the occupancy does not correspond to a filled band. Mott and Hubbard elaborated this description for NiO and similar materials which became known as ‘Mott’ insulators. For 3\textit{d} transition-metal compound they suggested that charge fluctuations of the type:

\(^4\)Ref. [214], p. 2339.
\(^5\)STM results concerning thin NiO films grown on metal crystal substrates were first presented by Bertrams et al. [215]; more recent results are [216, 217]. The first STM study on cleaved NiO crystal surfaces was presented by Castell et al. [213]. Problems with charging had been avoided by heating of the sample (as had also been done in several photoemission experiments). Castell et al. wrote: ‘The NiO crystals were heated … [to] 200 °C during the STM experiments. This heating resulted in an order of magnitude decrease in resistivity … STM imaging was attempted at RT, but was not successful’ ([213], p. 7860). From the experiment Castell et al. concluded: ‘The nickel sites are seen in empty-states images and the oxygen sites are seen in filled-states images. These results provide experimental evidence that NiO is a charge-transfer insulator with strongly correlated electrons and not a Mott-Hubbard insulator’ ([213], p. 7862).
\(^6\)Ref. [218], p. 156.
\(^7\)Ref. [219], p. 624.
where $i$ and $j$ labels transition metal sites, would be strongly suppressed owing to the high energy $U$ involved arising from coulomb and exchange interactions between the $d$ electrons.

Despite the success of the Mott-Hubbard theory there has been much controversy regarding the proper theoretical description of the electronic properties of NiO and related materials. It is an immense amount of work, both experimentally and theoretically, that have been devoted to NiO during the last 70 years. The controversy has mainly been hinging on a resistance to reject the band theory motivated by its general success in solid state physics. The several attempts on band structure calculations often predicted gaps which were order of magnitudes smaller than the experimentally observed, or even metallic ground states [220, 221, 222, 223].

The Mott-Hubbard description was revised in the mid 80s by the work of Fujimori and Minami [224], and Zaanen, Sawatsky and Allen [220]. The Mott-Hubbard theory implies that the band gap is a $d$-$d$ gap which did not always seem to be the case, e.g. for Ni compounds the gap seemed to be directly related to the electronegativity of the anion. This observation suggested that the Ni compounds are rather so-called charge transfer materials. It was pointed out that in addition to the $d$-$d$ charge fluctuations involving the energy $U$, the $p$-$d$ charge transfer involving the energy $\Delta$ needed to transfer an electron from an oxygen ligand to the Ni site had to be considered [220, 225, 226]:

$$d_i^n d_j^n \leftrightarrow d_i^{n-1} d_j^{n+1},$$

where $L$ denotes a hole in the anion (ligand) valence band. If $\Delta < U$ then $\Delta$ becomes the characteristic energy and the material is called a charge-transfer insulator. This is the case of NiO where the on-site Coulomb interaction among two $d$ electrons is larger ($U \sim 9$ eV) than the energy required to transfer an electron from an oxygen ligand to the Ni site. This change the orbital character of the top-filled band from Ni $3d$ to O $2p$. NiO is thus regarded as a charge-transfer insulator, which is also supported by the experimental results.

### 8.5.1 Growth of NiO thin films

Thin ordered films of NiO is important in the study of the properties of bulk NiO since they reduce the effects of charging in electron spectroscopy methods. Thin oxide films are also important for studies of oxide surface properties, for example with respect to catalysis where a typical system consists of metal nanoparticles on an oxide substrate. Two growth strategies have been pursued to obtain surfaces with (100) orientation:

**Oxidation of clean Ni(100) surfaces** The oxidation is done at moderate temperatures (600 K), followed by annealing to 1000 K. The resulting thin films ($\sim 4$ ML) of NiO(100) are mostly rather imperfect due to the large lattice mismatch of nearly 20% between NiO and Ni. This approach was studied by Bäumer et al. in 1991 [227], and has also been used in a photoemission study of NiO [228].
Evaporation of Ni in an O$_2$ atmosphere onto an Ag(100) surface  Well ordered and smooth surfaces can be obtained this way. The reason for the more perfect growth, than in the case of oxidation of clean Ni surfaces, is the small lattice mismatch of only 2% between NiO and Ag. This approach was introduced by Marre and Neddermeyer [229], who also applied the same strategy to grow (111) orientated NiO films on an Au(111) substrate.

Obviously, as perfect as possible films are needed for a VBPED study. Furthermore, one needs to be able to grow the films sufficiently thick, in order to avoid contributions from electrons photoemitted from the substrate. For this reason, in the present study thin films of NiO have been grown according to the method of evaporating Ni in an O$_2$ atmosphere onto an Ag(100) surface. Marre, Neddermeyer, and collaborators have applied this method in several studies, and the general procedure has been the following [229, 216, 217]:

1. The Ag(100) crystal was cleaned by cycles of Ar$^+$ sputtering and annealing to 750 K (= 480°C) until LEED showed the expected pattern with fourfold symmetry.

2. Ni was deposited onto the substrate by using a water-cooled Knudsen-type effusion cell with aluminum crucible. The deposition rate was measured by means of a quartz film thickness monitor, and was 0.3 ± 0.1 monolayer per minute.

3. The best growth conditions for the NiO layers were found at an O$_2$ partial pressure of 10$^{-6}$ mbar, the substrates being at room temperature. This means that an O$_2$ excess is present during the NiO film growth.

Growth of thick films is facilitated by heating the sample. The thicker films, in particular those obtained after moderate annealing (450-500 K), or by deposition on a slightly heated substrate (450-500 K), showed the pattern of the oxide with fourfold symmetry along the surface normal. Müller et al. wrote: ‘The film thickness was estimated from XPS line intensities, and thicknesses up to 30-50 NiO layers could easily be prepared. The sharpest LEED spots, especially for thicknesses above 10 layers, were obtained by post annealing of the samples . . . up to 600-700 K.’

The thin film surfaces grown this way seem to be as stable as the cleaved surfaces. A brief comment on what constitutes a sufficiently thick film. Atomic photoionization cross-sections for relevant levels of Ni, O, and the substrate material Ag are listed in Table 8.1. From the Ni 2$d$ to Ag 3$d$ ratio one sees that care should be taken about the film thickness, especially at high photon energies. Experimentally, a simple way to assure that the Ag 3$d$ contribution is suppressed is to monitor the Ag 3$d$ level by photoemission spectroscopy in between sequentially growing the film. The films in the

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8The lattice parameters are $a_{\text{Ni}} = 3.52$ Å, $a_{\text{Ag}} = 4.09$ Å [39], and $a_{\text{NiO}} = 4.20$ Å [211].

9It is also possible to grow ultrathin (111) oriented films (<4 ML) of NiO on ultrathin films of V$_2$O$_3$ on Cu(100) [230].

10Ref. [231], p. 489.

11Note that Al has also been suggested and tested as a substrate because of the convenient Ni 3$d$ to Al 3$s$ ratio [232].
The NiO films were grown under the following conditions:

- Oxygen pressure: \( P_{O_2} = 2.5 \cdot 10^{-7} \) mbar
- Ni source temperature: \( T_{\text{source}} = 1423^\circ C \)
- Exposure time = 60 min
- Annealing in \( O_2 \) until temperature below 250 \( ^\circ C \)

The pressure in the experimental chamber during the measurements was better than \( 1 \cdot 10^{-10} \) mbar, and the NiO(100) surface was found to be very inert and staying clean for several days. Nevertheless, the surface needed to be annealed in an oxygen atmosphere every day due to beam induced degradation of the surface. This was done by:

- Annealing for 10 min at 370 \( ^\circ C \) in an \( O_2 \) atmosphere of \( P_{O_2} \sim 2 \cdot 10^{-7} \) mbar

The degradation of the surface can be monitored by the O 1s level. A shoulder (at 531.5 eV, shifted by 1.8 eV) on the O 1s peak from NiO films grown on Ni low-index surfaces was observed and examined by Norton et al. [233]. The additional peak could be assigned to structural disorder in the films. The absence of this peak was used by Sawatsky et al. to judge the quality of the cleaved NiO surface [214]. The ‘loss-of-oxygen’ interpretation has been challenged by Makay and Henrich, who in 1985 reported a PES study concerning the influence of defects on adsorption of oxygen and water on NiO [234]. They found that oxygen vacancies (created by preferential sputtering of oxygen) in the surface layers made the O 1s peak asymmetric, but they did not see a new peak. The asymmetry was well explained by the increased density of states at the Fermi-level due to the defects (Donjiach-Sunjic lineshape). On the other hand they observed a new peak, shifted with 1.8 eV towards higher binding energy, after exposure of oxygen to the defect surface. They associated this peak with the adsorbed oxygen. Furthermore they argue that oxygen vacancies are not likely to create a new peak, since the remaining anions (oxygen) remain their five-fold ligand environment. In any case emergence of a shoulder on the O 1s peak is a sure sign that the surface quality is not perfect.

### 8.6 The NiO experiment and results

The NiO VBPED experiments was conducted at the ALOISA beamline (see Section 6.2) at the synchrotron Elettra. The NiO films were grown by evaporating Ni in an \( O_2 \) atmosphere onto an Ag(100) surface as reported in the previous section.

The VBPED data were taken in a different mode compared to the Al experiment at the SuperESCA beamline. In the Al experiment, the series of spectra were measured as a function of the azimuthal angle for a specific polar angle, and this was done for two different polar angles. In the NiO experiment, the spectra of the valence band were measured in a 90 degrees azimuthal slice of the hemisphere around the sample normal,
and for a whole range of polar angles. The angles was chosen such that they would constitute an evenly distributed grid in a stereographic projection (i.e., less azimuthal scans close to normal emission). The measuring procedure was: first, place the electron spectrometer in the proper polar angle; second, scan the azimuthal angle by rotating the sample around its normal in an appropriate number of steps. In this experiment, the maximum polar angle was 56°. The time needed for each spectrum was about 5 min, and the entire dataset was measured in a few days. The photon energy was about 180 eV for the valence band spectra, and the sample was at room temperature.

VBPED data for the O 1s core level were measured for comparison with the O 2s level just below the valence band. There are no suitable core levels for comparison with the Ni 3d and O 2p levels constituting the valence band. The O 1s data were measured in a slightly differently scheme than the valence band. An automatic set up allows the full hemispherical slice to be measured in one experiment. In this mode an azimuthal angle is selected, then the polar angle is scanned, then the next azimuthal angle is selected, etc. This mode is very convenient, but it only maps an evenly distributed grid of angles, and therefore many more spectra are needed to cover the hemispherical slice. For this reason this mode was not suitable for the time consuming valence band spectra. In this experiment, the maximum polar angle was 78°. The binding energy of the O 2s level is about 21 eV, and hence the photon energy was selected such that the kinetic energy of the O 1s electrons was 159 eV.

The data were analysed in a similar manner for both the core level, and the valence band data. Each azimuthal series of spectra was converted into a modulation function according to Equation (8.1), and the angle positions were converted into a stereographic projection. A full hemispherical projection of the modulation functions was created by symmetry from the measured 90 degrees slice. The data are presented by plotting the stereographic modulation function for the intensity integrated in a certain energy range of the valence band (or the intensity of the core level, in the case of the O 1s data).

### 8.7 Results

Figure 8.6 shows the various kinds of data obtained on NiO. The valence band spectrum at the top is taken in normal emission. The characteristic energy regions marked by O 2s, O 2p, and Ni 3d are shown as the stereographic modulation function plots marked in the same way. The assignments of the O 2p and Ni 3d regions are very crude: actually, the O 2p level covers most of the valence band, and Ni 3d satellite features are also found. Finally, the stereographic modulation function plot for the O 1s level is shown in the lower left corner of the figure. It is clearly seen that the O 1s data cover a larger polar range, and has been measured in a different mode, than the valence band modulation function plots.

There are several qualitative observations to make in Figure 8.6. First of all, one notices that angular variations are seen in the valence band photoemission, and that the specific modulation depends on the energy position in the valence band. Like in the case of Al, modulation differences are minor compared to the overall diffraction pattern. Significant dispersion of the features in the valence band has not been observed, and therefore the angular variations are ascribed to VBPED effects. The fact that dif-
Figure 8.6: NiO data. The spectrum at the top shows the valence band region taken in normal emission. The three stereographic modulation function plots marked by O 2s, O 2p, and Ni 3d are calculated from the integrated intensity of the correspondingly marked areas in the spectrum. The stereographic modulation function plot marked O 1s, in the lower left corner, is a similar plot for the intensity of the O 1s core level.

Differences in the VBPED effect with respect to energy are observed is promising for any attempt to decompose the DOS of NiO. The lack of suitable core levels rule out the kind
of decomposition performed on Al. However, it is still interesting to look at the O 1s modulation function plot, and see how it resembles the results for the VB region. The dominating diffraction pattern is similar, and the O 1s plot has common features with the O 2s plot. This observation gives confidence that these kind of measurements on the ALOISA beamline to some extend may be useful for investigating VBPED effects.

8.8 Conclusions and outlook

The intensity of electrons photoemitted from the valence band of crystalline solids at X-ray energies shows angular variations. This reasonably newly observed phenomenon has been termed valence band photoelectron diffraction (VBPED). At X-ray energies photoemission from the valence band resembles the density of states (DOS) of the material. In the present thesis it has been investigated whether it would be possible to use VBPED data to decompose the DOS of a material into partial contributions (PDOS) from the different initial state angular momenta (symmetry). The origin of this conjecture is the resemblance of the VBPED data to core level photoelectron diffraction (PED) data, and the fact that PED data is dependent on the initial state symmetry.

It has been shown for the free-electron like metal Al that the VBPED data can be used to decompose the DOS with respect to symmetry. The decomposition was achieved by comparing to photoelectron diffraction data from core levels of the same symmetry and taken at the same kinetic energy. Data sets obtained under different scattering conditions show a similar ordering of the s and p contributions to the PDOS. However, the quantitative agreement with the calculated PDOS is not very satisfying. It is most likely that the discrepancy is related to the interpretation of the data rather than the experiment. It is important to notice that the basic understanding of the VBPED process is still deficient. Nevertheless, the performance of technique was also tested on a more complex material. The preliminary investigations on NiO has revealed experimental challenges that will be difficult to overcome for many materials. For instance it may be difficult to avoid direct transitions in the valence band, and appropriate core levels may not be available or unreachable. In the latter case one could alternatively resort to calculated symmetry resolved modulation functions.

However, there is no superior experimental technique for determining the symmetry resolved DOS and therefore it is interesting to pursue VBPED as a supplementary method. Notice that the technique in principle should also work in the case of spin-resolved photoemission spectroscopy.
The electronic structure of a solid is a telltale fingerprint because the properties of a solid are intimately related to interactions in the electronic system. A successful method to determine the electronic structure is photoemission spectroscopy, a technique based on the photoelectric effect where an electron is emitted upon the absorption of a photon. Photoemission spectroscopy has been in the tool box of solid state physics for almost 30 years, and the progress in terms of development of equipment and theoretical framework has been immense. This does not imply, however, that the field has reached a standstill. On the contrary, the development in photoemission spectroscopy has allowed new and intriguing questions to be addressed. An example is the advent of synchrotron radiation sources, and efficient electron spectrometers that have made new detection schemes possible, e.g. mapping of the surface Fermi surface.

The present thesis is concerned with investigation of surface electronic structure and the role of electron-phonon interaction by photoemission spectroscopy. The experimental work has mainly been carried out at the new facility for angle-resolved photoemission spectroscopy (ARUPS) at the storage ring ASTRID in Aarhus, Denmark. This instrument is characterized by high photon flux in the energy range 12 eV to 140 eV from a monochromator on the undulator section of ASTRID, high energy- and angle-resolution of the electron spectrometer, motorised movement of the electron spectrometer integrated with the data acquisition software, and cooling to 30 K of the sample with a closed-cycle He-refrigerator. The instrument has been set up as a part of the present work, and is now operational. Several experiments have been conducted at the instrument already, and two studies of the surface electronic structure of Bi(110) and α-Ga(010) are presented in this thesis. Experiments at higher photon energies have been conducted at the synchrotron Elettra in Trieste, Italy. In this thesis studies of final-state phonon scattering, and valence band diffraction effects in the photoemission process on Al(100) are presented. More details on the results are summarized in the following sections.
Surface electronic structure of $\alpha$-Ga(010) and Bi(110)

Angle-resolved photoemission from a two-dimensional electronic state is directly related to the hole state spectra function, while photoemission from the bulk electronic structure includes a convolution of the hole and electron spectral functions. Therefore ARUPS is well suited to address questions concerning the interactions in two-dimensional electronic systems. The electron-phonon coupling is known to dominate the temperature dependence of the hole state lifetime, and this is studied for the surface state at $\bar{C}$ in the surface Brillouin zone of $\alpha$-Ga(010). Additionally, the $\alpha$-Ga(010) surface undergo a surface phase transition at $T = 231$ K, and it is investigated how this affects the surface electronic structure. Notably, an abrupt change in the surface state linewidth, and the emergence of a new surface state in close vicinity of the Fermi level are observed. The driving mechanism behind the phase transition is a challenging question. Evidence for an interpretation in terms of a surface charge density wave scenario are presented. The observations that corroborate this interpretation are i) a pseudo-gap is opening in a large fraction of the surface Brillouin zone, ii) the electron-phonon coupling is strong, iii) disorder is present in the high temperature phase. The disorder is most likely due to loss of long range order in the high temperature phase, while the short-range surface structure is supposed to resemble the structure in the low temperature phase.

Metallic surface states on a semimetal would constitute a two-dimensional metal on a semimetallic substrate. Two-dimensional metals are interesting because the electronic properties of a metallic system is expected to be modified by reduced dimensionality. The Bi(110) surface is reported to support several metallic surface states in the projected bulk band gap, rendering the surface more metallic than the bulk. It is speculated whether the large spin-orbit interaction in Bi, combined with the loss of bulk inversion symmetry at the surface, leads to a surface band structure and surface Fermi surface which is non spin-degenerate. The latter scenario may have interesting consequences for the screening properties.

Final state phonon scattering and valence band photoelectron diffraction

Intrinsic phonon scattering in the photoemission emission process affects the the spectral function of the photoemitted electron. This process is increasingly important at high temperature and high photon energy. The dependence of photoemission from Al(100) on temperature and photon energy is investigated by photoemission spectroscopy, and compared to new theoretical modelling of the process. Results are presented showing that emission/absorption of phonons during the photoemission event can lead to a severe change of the photoemission lineshape. This has consequences for interpretation of lineshape data in terms of a spectral function. Good agreement between the calculated total intensities and the observed intensities substantiates the modelling of the process, and the interpretation of the data.

Contrary to common expectations, the surface state on Al(100) is reported to be more stable against increased temperatures and/or photon energy than direct transitions from bulk states. However, this can be understood in terms of the presented model.

The intensity of electrons photoemitted from the valence band of crystalline solids
at X-ray energies shows angular variations; a phenomenon termed valence band photoelectron diffraction (VBPED). At X-ray energies photoemission from the valence band resembles the density of states (DOS) of the material, because the intrinsic phonon scattering allows all initial states in the bulk Brillouin zone to be sampled. It is conjectured that it may be possible to use VBPED data to decompose the DOS of a material into partial contributions from the different initial state angular momenta. The VBPED effect is investigated on Al, and the DOS is decomposed into the \( s \) and \( p \) contributions, demonstrating the feasibility of the technique. However, discrepancies with respect to the theoretical partial densities of states are found. The possibilities and limitations of the technique for these kind of investigations is discussed, and highlighted by a preliminary investigation on the transition metal oxide NiO.


[99] S. Lizzit, A. Baraldi, P. Hofmann, C. Grütter, and J. Bilgram. to be published.


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