Adatoms, Quasiparticles & Photons

The Multifaceted World of Photoelectron Spectroscopy

MARTIN MÅNSSON

Doctoral Thesis in Materials Physics
Stockholm, Sweden 2007
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Cover illustration:

Charge density of copper at a binding energy of 5 eV, as extracted from angle-resolved photoelectron spectroscopy.

N.B.: The strange looking “Q” in the title of the cover is not a typo! This is merely a perk of the official font that is used at KTH.

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Nothing shocks me. I’m a scientist.
Harrison Ford (1942-), as Indiana Jones

ABSTRACT

The experimental work presented in this thesis is based on a wide assortment of very advanced and highly sophisticated photoelectron spectroscopy (PES) techniques. The objective of the present study has been to reveal and understand the electronic structure and electron dynamics in a broad spectrum of materials, ranging from wide band gap oxides, via semiconductors along with metals, and finally high-temperature superconductors.

The first part of the thesis concerns laser-based pump-and-probe PES. This unique experimental technique has permitted a study of the excited electronic structure and the electron dynamics of several semiconductor surfaces. An insight into details of the adatom to restatom charge-transfer of the Ge(111)c(2x8) surface is presented, as well as an estimate for the timescale in which the dynamic adatoms of the Ge(111):Sn(\sqrt{3}\times\sqrt{3})R30° surface operate. Further results comprise a novel unoccupied surface state at the GaSb(001) surface as well as a time-resolved study of the charge accumulation layer at the InAs(111)A/B surfaces.

In the second part, high-resolution synchrotron based angle-resolved PES (ARPES) data from the cuprate high-temperature superconductor La_{2-x}Sr_xCuO_4 (LSCO) is presented. This extensive study, reveals detailed information about how the Fermi surface and electronic excitations evolve with doping in the superconducting state. The results comprise support for a connection between high- and low-energy electronic responses, the characteristics of the superconducting gap, and indication of a quantum phase transition between two different superconducting phases.

In the third group of experiments we move away from the two-dimensional systems and concentrate on fully three-dimensional compounds. By the use of soft x-ray ARPES it is possible to extract the three-dimensional electronic structure in a straightforward manner with increased \(k_{||}\)-resolution. As a result the first high-quality ARPES data from Cu_{2}O is presented, as well as a novel method for extracting the (real space) electron density by ARPES. These experiments clearly display the advantages of using soft x-ray ARPES. If the material and type of experiment is chosen wisely, the benefit of the increased \(k_{||}\)-window and the free electron final state, surpass the drawbacks of decreased count-rate and inferior energy resolution. Finally we return to the high-temperature superconductors (NCCO & Nd-LSCO) and make use of the increased bulk-sensitivity. From an evident change in the shape of the Fermi surface when moving from low to high photon energies, the surface to bulk difference in electronic structure is highlighted.

Keywords: angle-resolved photoelectron spectroscopy, electronic structure, electron dynamics, semiconductor surfaces, oxides, high-temperature superconductors.
Vacuum: a large empty space where the Pope lives

(Quote taken from an 11-year-old student's science exam)
In the beginning the Universe was created.
This has made a lot of people very angry
and been widely regarded as a bad move.
Douglas Adams (1952-2001)

PREFACE

The experimental work presented in this thesis was performed at:

- The fs-laser lab, Materials Physics section, KTH, Stockholm, Sweden (Time- and angle-resolved photoelectron spectroscopy, TARPES)
- The SIS-beamline of the Swiss Light Source (SLS), Paul Sherrer Institut (PSI), Villigen, Switzerland (high-resolution ARPES)
- The ID08 beamline of the European Synchrotron radiation Facility (ESRF), Grenoble, France (soft x-ray ARPES)
- The BL25SU beamline of the SPring-8 Synchrotron, Hyogo, Japan (soft x-ray ARPES)

The thesis is divided into two parts. The first part will set the framework of the presented work and also gives a brief introduction to the scientific area, experimental methods and studied samples. In the second part the appended articles are presented. The following articles, to which I have made a large contribution, are included in this thesis:

I. **Electronic structure and electron dynamics of delocalized adatom states at the Ge(111)c(2 x 8) surface**
   *submitted for publication*

II. **Ultrafast electron dynamics and recombination at the Ge(111):Sn(\sqrt{3}\times\sqrt{3})R30° surface**
    M. Månsson, O. Tjernberg, M. Göthelid, M.A. Grishin, T. Claesson, and U.O. Karlsson
    *submitted for publication*

III. **Anisotropy of electron structure at InAs(111) surfaces by laser pump-and-probe photoemission spectroscopy**
    M.A. Grishin, M. Månsson, O. Tjernberg, H.S. Karlsson, and U.O. Karlsson
    *Surface Science, 574, 89 (2005)*
IV. **Electron structure and electron dynamics at the GaSb(001) surface studied by femtosecond pump-and-probe pulsed laser photoemission spectroscopy**  
Martin Månsson, M.A. Grishin, O. Tjernberg, T. Claesson, H.S. Karlsson, and U.O. Karlsson  

V. **Revealing the charge density in solids**  
M. Månsson, T. Claesson, M. Finazzi, C. Dallera, C. De Nadaï, N.B. Brookes, and O. Tjernberg  
*manuscript*

VI. **Probing the valence band structure of Cu$_2$O using high-energy angle-resolved photoelectron spectroscopy**  

VII. **On-board sample cleaver**  

VIII. **When low- and high-energy electronic responses meet in cuprate superconductors**  

IX. **Anisotropic scattering in slightly underdoped to optimally doped La$_{2-x}$Sr$_x$CuO$_4$**  
*arXiv:0708.2782v1 [cond-mat.supr-con]*

X. **Experimental evidence of a quantum phase transition in La$_{2-x}$Sr$_x$CuO$_4$**  
*manuscript*
XI. **The coherent d-wave superconducting gap in underdoped La$_{1.855}$Sr$_{0.145}$CuO$_4$ as studied by angle-resolved photoemission**
*arXiv:0708.2333v1 [cond-mat.supr-con]*

XII. **Angle Resolved Photoemission from Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ using High Energy Photons: A Fermi Surface Investigation**
T. Claesson, M. Månsson, C. Dallera, F. Venturini, C. De Nadaï, N.B. Brookes, and O. Tjernberg

XIII. **The electronic structure of La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$ probed by high- and low-energy angle-resolved photoelectron spectroscopy: evolution with probing depth**
*submitted for publication*

The subsequent articles, to which I have also made a contribution, are not included in the thesis:

XIV. **Electronic structure and electron dynamics at the Ge(111)c(2 x 8) surface studied by femtosecond pump-and-probe laser photoemission spectroscopy**
M. Månsson, O. Tjernberg, M. Göthelid, M.A. Grishin, T. Claesson, and U.O. Karlsson
*manuscript*

XV. **Transfer of spectral weight across the magnetic transition in CoO: novel results from high-energy angle-resolved photoelectron spectroscopy**
T. Claesson, M. Månsson, M. Finazzi, C. Dallera, J. Cezar, N.B. Brookes and O. Tjernberg
*manuscript*
XVI. **Band bending and structure dependent HOMO energy at the ZnO(0 0 0 1)-titanyl phthalocyanine interface**
P. Palmgren, T. Claesson, A. Önsten, B. Agnarsson, M. Månsson, O. Tjernberg and M. Göthelid  
*Surface Science, 601, 4222 (2007)*

XVII. **Charge transfer and band alignment at the InSb(111)B-TiOPc Interface**
M. Göthelid, P. Palmgren, Shun Yu, B. Agnarsson, A. Önsten, M. Månsson, and B. Brena  
*manuscript*

XVIII. **Oxygen structures on Fe(110)**
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*Surface Science, 527, 163 (2003)*

XIX. **Electron structure and electron dynamics at InSb(111) 2 × 2 semiconductor surface**
M.A. Grishin, H.S. Karlsson, M. Månsson, and U.O. Karlsson  
*Applied Physics A, A76, 299 (2003)*

XX. **The importance of surface quality of cuprate superconductors in angle-resolved photoemission experiments**
*manuscript*
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First of all I would like to express my gratitude to my supervisor Prof. Ulf O. Karlsson for giving me the grand opportunity and total freedom to develop my interest in materials physics and surface science. Thank you for believing in me when I needed and for asking those tough questions at the correct points in time.

I am in great debt to my supervisor in practice, Docent Oscar Tjernberg, who has been a constant source of knowledge, support and guidance. Even do I have probably forced you into a chronically stage of synchrotronification you have always been happy to answer my endless list of “det måste vara nåt’ med nåt’ questions. Even though we never got to measure on those Unobtainium samples or try out the choco-hooks, I still hope we someday will realize at least one of our modest ideas.

Mats Göthelid, your pedagogical approach and experimental expertise have in numerous ways helped me through this ὄδυσσεια*. In addition, your extraordinary melodic mix of opera and holy psalms is a vital ingredient for creating that pleasant matphys-atmosphere.

Thomas “hjälmen” Claesson, my brother in arms with whom I have shared so many months of beamtime, endless lines of Matlab scripts and serious headaches in the “istället för fysik förvirring”-course. I think the only way to show you my appreciation is to reward you with an “all-you-can-eat-coupon” for squid-pasta at the ESRF cantina. Enjoy my friend… enjoy!

Michael Grishin, I will never overlook the 5 months of TARPES measurements in the old bomb-shelter fs-lab of KTH. We performed great things together! In this context I would also like to give credit to Prof. Guy Le Lay who helped me with the Ge-paper, along with Henrik Karlsson who designed and built the TARPES system.

To all my room-mates during the years: Jonas Weissenrieder, Torbjörn Åkermark, Mohammed Goshtasbi Rad, and of course Thomas again. Thank you all for

---

* The epic poem, ascribed to Homer, illustrating the journey of Odysseus after the fall of Troy. In the English language as well as many others, the word odyssey has come to refer to a long-winded and rambling voyage.
rewarding discussions about everything as well as nothing, and for always creating such an inspiring and easy going climate.

Of course also ett stort tack to the whole matphys society including Anneli who did a great job at SPring-8 and who always comes up with new perspectives to approach a problem. Also a big hand to my fellow Bergsman, Palp-fiction, who introduced me to the fantastic devil burger of Gloria’s and moreover gave me someone to bother during the thesis writing.

Eine herzlichen dank/merci beaucoup to the excellent Swiss team of PSI/SLS/LNS, including: Joël Mesot, Stéphane Pailhés, Ming Shi, Johan Chang, Luc Patthey, Yasmine Sassa, Azzedine Bendounan, and Pomelo-san. It has been a real treat to work with you all and hopefully this will be possible also in the future. During our experiments we have been privileged to have access to very high quality samples and I would like to acknowledge the fantastic work of Naoki Momono, Migaku Oda and Masayuki Ido, of the Hokkaido University, Japan.

I send many thanks to the ID08 beamline of the ESRF where Nicholas Brookes, Céline De Nadaï, Júlio Cezar, Federica Venturini, Gilles Retout, and Raymond Barrett, have supported us in a fantastic way during our numerous beamtimes. I would also like to take this opportunity to acknowledge the valuable contribution of the late Kenneth Larsson.

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Final words of reflection (a.k.a. "The Synchrotronification Effect") ....... →∞

xiv
The discovery of a fairly large, clearly visible atom

Well, my colleagues, that destroys all the work that's ever been done in the field of physics!

(Copyright and courtesy of: http://www.wulffmorgenthaler.com/)
> Only in quiet waters do things mirror themselves undistorted.
> Only in a quiet mind is adequate perception of the world.
> Hans Margolius (1902-1984)

### Abbreviations & Useful Lingo

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ARPES</td>
<td>angle-resolved photoelectron spectroscopy</td>
</tr>
<tr>
<td>BCC</td>
<td>body centered cubic</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>EDC</td>
<td>energy distribution curve</td>
</tr>
<tr>
<td>ExS</td>
<td>excited state</td>
</tr>
<tr>
<td>ESRF</td>
<td>European Synchrotron Radiation Facility</td>
</tr>
<tr>
<td>FCC</td>
<td>face centered cubic</td>
</tr>
<tr>
<td>FEFA</td>
<td>free-electron final state approximation</td>
</tr>
<tr>
<td>FS</td>
<td>Fermi surface</td>
</tr>
<tr>
<td>HWHM</td>
<td>half width at half maximum</td>
</tr>
<tr>
<td>HTSC</td>
<td>high-temperature superconductor</td>
</tr>
<tr>
<td>LEED</td>
<td>low-energy electron diffraction</td>
</tr>
<tr>
<td>LDA</td>
<td>local density approximation</td>
</tr>
<tr>
<td>LSCO</td>
<td>( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 )</td>
</tr>
<tr>
<td>MDC</td>
<td>momentum distribution curve</td>
</tr>
<tr>
<td>NCCO</td>
<td>( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 )</td>
</tr>
<tr>
<td>PE</td>
<td>photoelectric effect</td>
</tr>
<tr>
<td>PES</td>
<td>photoelectron spectroscopy</td>
</tr>
<tr>
<td>QCP</td>
<td>quantum critical point</td>
</tr>
<tr>
<td>QP</td>
<td>quasiparticle</td>
</tr>
<tr>
<td>QPT</td>
<td>quantum phase transition</td>
</tr>
<tr>
<td>SBZ</td>
<td>surface Brillouin zone</td>
</tr>
<tr>
<td>SC</td>
<td>superconductor/superconductivity</td>
</tr>
<tr>
<td>SHG</td>
<td>second harmonic generation</td>
</tr>
<tr>
<td>SLS</td>
<td>Swiss Light Source</td>
</tr>
<tr>
<td>STS</td>
<td>scanning tunneling spectroscopy</td>
</tr>
<tr>
<td>SX-ARPES</td>
<td>soft x-ray ARPES</td>
</tr>
<tr>
<td>TARPES</td>
<td>time- and angle-resolved photoelectron spectroscopy</td>
</tr>
<tr>
<td>THG</td>
<td>third harmonic generation</td>
</tr>
<tr>
<td>ToF</td>
<td>time-of-flight</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra-high vacuum</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
</tbody>
</table>
Chapter 1.
PHOTOELECTRON SPECTROSCOPY

The experimental data presented in the appended articles are acquired using several different variations of photoelectron spectroscopy (PES) that are chosen explicitly for each experiment. Hence, given both the title and contents of this thesis, the natural starting point is evidently an introduction to PES.

1.1 Historical Recapitulation

The basis for PES is the well-known photoelectric effect (PE) which states that a material emits electrons when subjected to radiation with sufficient energy. The PE was first discovered by Heinrich Hertz in 1887 [1], though in order to fully understand the effect, W. K. Röntgen first had to discover x-rays [2] and J. J. Thomson the electron [3]. It was also Thomson who in 1899 proved that it is really electrons that are emitted in the PE [4]. Finally in 1905, in his famous paper “On a heuristic point of view concerning the production and transformation of light” [5], Einstein presented the explanation of the PE on the form

$$E_{\text{kin}} = \frac{R}{N} \beta \nu - P$$  

(Eq. 1.1)

Here $E_{\text{kin}}$ is the “kinetic energy of the electron directly located on the surface and excited perpendicular to it”, $R\beta \nu / N$ is nowadays written as $h\nu$ and $P$ is the work function of the sample, $\Phi_{\text{sample}}$. In this description the PE is not in itself the most interesting part. Instead the most intriguing ingredient was the fact that the $h\nu$ term stated that the incoming radiation delivers energy to the electrons in packages of $h\nu$ and not continuously as previously assumed.

PES is the realization of PE as an experimental tool to investigate the electronic structure of a wide range of compounds. During the following decades an intense development began in the field of photon sources (mainly photocathodes), ultra-high
vacuum (UHV) technique and electron analyzers. In fact it took more than 50 years until Kai Siegbahn in 1956 recorded the “first photoelectron spectrum with extremely sharp lines” from a newly cleaved NaCl crystal [6]. Finally in the middle of the 1960s the technique made its breakthrough [7, 8] as a powerful non-destructive analysis technique both in physics (XPS) and chemistry (ESCA).

A principal set-up of a PES experiment is presented in Fig. 1.1. The main parts are (i) the sample, (ii) a light source, (iii) the electron detector connected to a computer, and (iv) the photoelectron spectrum that hopefully will result in (v) a published paper. By measuring the intensity of emitted electrons at a specific kinetic energy and then scanning the observed energy window, it is possible to acquire a spectral intensity $I(k, \omega)$. Here $k$ is the electron momentum and $\omega$ is the binding energy. When the binding energy corresponds to an occupied electronic state in the material ($E_1$-$E_4$ below) a peak in the photoelectron spectrum is observed (see Fig. 1.1).

---

* This also puts focus on the need for high surface quality in PES.
1.2 Angle-Resolved Photoelectron Spectroscopy

In the world of condensed matter physics, PES is in its simplest form described by extending Einstein’s equation (Eq. 1.1)* into

\[ E_{\text{kin}} = h\nu - \omega - \Phi_{\text{sample}} \]  
(Eq. 1.2)

Here \( \omega \) is the binding energy of e.g. a valence band electron and \( \Phi_{\text{sample}} \) the work function (= \( E_{\text{vacuum}} - E_F \)) of the sample. The basic idea is to subject a sample to light of well-defined photon energy and detect the kinetic energy distribution of the emitted electrons. If not only the energy distribution but also the escape angle of the photoemitted electrons is measured (see Fig. 1.2) the experimental technique is called angle-resolved photoelectron spectroscopy (ARPES). All data presented in this thesis is collected using this technique.

In quantum mechanics the photoemission of an electron is a one step process where the electron is moved from its ground state within the material and set down onto the detector. In practice this process is usually describe in the so-called “three-step model” [9]†:

1. Photo-excitation of the electron from an initial (ground) state \( \varepsilon_i(\mathbf{k}_i) \) into a final state, \( \varepsilon_f(\mathbf{k}_f) \), inside the crystal
2. Transportation through the solid to the crystal surface
3. If the kinetic energy is large enough to overcome the work function of the material, the electron escapes through the surface into vacuum \( \varepsilon_f(\mathbf{k}_f) \Rightarrow E_{\text{kin}}(K) \)

During the first stage the absorbed photon energy, \( h\nu \), is transmitted to a single electron having a binding energy, \( \omega \), below the Fermi level (\( E_F \)). In this process both the energy and crystal momentum are conserved. Further, since the photon momentum is usually insignificant, \( \mathbf{k}_i \) and \( \mathbf{k}_f \) will be equal modulo a reciprocal lattice vector \( \mathbf{G} \). The conservation of energy and momentum can be described by the expressions:

\[ \varepsilon_f = \varepsilon_i + h\nu \]  
(Eq. 1.3)
\[ \mathbf{k}_f = \mathbf{k}_i + \mathbf{G} \]  
(Eq. 1.4)

* The original equation is only valid for the maximum electron kinetic energy.
† However it is actually presented as “a two-step process” in the first sentence of Ref. 9.
In the second stage the excited electrons are easily subjected to inelastic scattering and hereby generate secondary electrons on their way to the surface. Since energy and wave-vector are not conserved (inelastic), these electrons will lose all information about their initial stage and are merely seen as a secondary background in the photoemission spectrum.

**Fig. 1.2:** Basic principle of ARPES showing some of the key geometrical parameters involved: polar and azimuth angle ($\theta$ and $\phi$) of the incoming photon ($p$) and outgoing electron ($e$), polarization ($P$) of the light, and kinetic energy ($E_{\text{kin}}$) of the photoelectron. The inset to the right schematically shows how the parallel component of the electron momentum ($k_{||}$) is conserved while the perpendicular component ($k_{\perp}$) is not.

The probability for an excited electron to be inelastically scattered depends on its kinetic energy. Hence the depth into the sample, from which valuable information about the electronic structure can be achieved, strongly depends on the photon energy and also the binding energy of the electrons that are being studied. The parameter most commonly used to describe the energy dependence of this escape depth is the inelastic mean free path, $\lambda_{\text{mfp}}$, which is empirically quantified by the curve in **Fig. 1.3**.
This curve is usually referred to as the “universal curve” due to the fact that $\lambda_{\text{mfp}}(E_{\text{kin}})$ has been found to behave in a similar way for most solids \cite{11,12}. Nevertheless, the curve should be considered more as a band of values that depend slightly on the selected material, especially for low energies ($E_{\text{kin}} \lesssim 10 \text{ eV}$). The shape of this curve is in principle related to the cross-sections for electron-electron scattering and collective excitations e.g. plasmons. For high kinetic energies, above approximately 100 eV, the cross-section for electron scattering by plasmons decreases linearly and consequently $\lambda_{\text{mfp}}$ increases linearly \cite{13} with $E_{\text{kin}}$. When the energy is lowered, $\lambda_{\text{mfp}}$ is decreased until the plasmon cut-off energy \cite{14} is passed ($E_{\text{kin}} \approx 40 \text{ eV}$). Here the escape depth displays a minimum of approximately 4 Å, which corresponds to the topmost atomic layer(s) of the sample. This clearly shows that PES can be a very surface sensitive technique. For even lower energies the mean free path increases again caused by the reduction of possible excitations with decreasing $E_{\text{kin}}$ and the absence of plasmons.

In the final and third step the electron can escape out from the material into the vacuum if its kinetic energy is greater than the work function of the sample (see Fig. 1.4). In reality the sample and analyzer are in electrical contact, hence their Fermi
levels are aligned. As a consequence the “effective” work function of the measurement

\[ \Phi_{\text{eff}} = \Phi_{\text{sample}} - (\Phi_{\text{sample}} - \Phi_{\text{analyzer}}) = \Phi_{\text{analyzer}} \]  

(Eq. 1.5)

is the work function of the analyzer and not the sample. Consequently what is measured in a PES experiment is \( E_{\text{kin}}^{\text{analyzer}} \) as shown in Fig. 1.4. Hence in order to extract the parameter of interest, \( \omega \), from the experiment, a very precise knowledge about the value for \( \Phi_{\text{analyzer}} \) is required. This calibration problem is usually solved by measuring, with the same photon energy, both the spectrum of interest and a Fermi edge spectrum of the sample or a metallic reference in electrical contact with the sample. By evaluating the difference between the two obtained kinetic energies all unknown factors are canceled out and \( \omega \) is obtained.

![Fig. 1.4: Schematic energy diagram for the photoemission process from a semiconductor in electrical contact with the electron analyzer.](image)

When the electron escapes the sample into the vacuum the Bloch wave of the electron is matched to a free-electron wave outside the sample. Since the surface of the sample has two-dimensional translation symmetry, a transmission of an electron
through the surface into the vacuum requires conservation of the wave vector component parallel to the surface \((k_\parallel)\) modulo a reciprocal surface lattice vector \(G_{s\parallel}\):

\[
K_\parallel = k_\parallel + G_{s\parallel}
\]  
(Eq. 1.6)

Here \(k\) is the wave vector inside the sample and \(K\) the wave vector in the vacuum (see also the inset to the right in Fig. 1.2 above). However, the perpendicular wave vector component \(k_\perp\) is not conserved in the transmission through the surface due to the potential step, \(V_0\), in this direction. Outside the sample the kinetic energy \(E_{\text{kin}}(K)\) is given by:

\[
E_{\text{kin}}(K) = \frac{\hbar^2 K^2}{2m_e} = \frac{\hbar^2 (K_\perp^2 + K_\parallel^2)}{2m_e} = \varepsilon_f(k) - E_{\text{vacuum}}
\]  
(Eq. 1.7)

\(K_\perp\) and to \(K_\parallel\) are related to each other through the escape polar angle \(\theta_e\) of the photoemitted electron (see right panel of Fig. 1.2). Combining this with Eq. 1.7 leads to:

\[
||K|| = \sqrt{ \frac{2m_e}{\hbar^2} E_{\text{kin}} \cdot \sin \theta_e } = |k_|| \Rightarrow
\]

(Eq. 1.8)

\[
|k_|| [\text{Å}] = 0.5123 \cdot \sqrt{E_{\text{kin}}[\text{eV}] \sin \theta_e}
\]

Consequently, it is possible to straightforwardly extract the wave vector component parallel to the surface inside the sample \((k_\parallel)\) by simultaneously measuring the kinetic energy, \((E_{\text{kin}})\) and the emission angle \(\theta_e\). For the perpendicular component we have the expression:

\[
|K_\perp| = \sqrt{ \frac{2m_e}{\hbar^2} E_{\text{kin}} \cdot \cos \theta_e }
\]  
(Eq. 1.9)

But since there is no relation similar to Eq. 1.6 that can connect \(K_\perp\) and \(k_\perp\) to each other, there is no straightforward approach to extract \(k_\perp\). However if the final state

* Compare Eq. 1.4
\( \varepsilon_r(k_f) \) is known, Eq. 1.7 can be used to calculate \( k_\perp \). The easiest, and most frequently used approach, is to assume a free-electron final state:

\[
\varepsilon_f(k_f) = \frac{\hbar^2 k_f^2}{2m_e^*} - V_0 \quad \text{(Eq. 1.10)}
\]

Since the excitation occurs in the presence of the periodic potential of the lattice, this is only an approximation. Depending on which material and photon energy is used this approximation is more or less valid. At low photon energies (10-100 eV) the free-electron final state approximation (FEFA) works satisfactory for e.g. valence band (VB) ARPES of metals. However, when considering measurements of the VB in strongly correlated materials (e.g. CoO) the approximation breaks down. All experiments presented in this thesis concerning materials that have three-dimensional electron structure* are performed at high (soft x-rays, \( h\nu \approx 500-1500 \) eV) photon energies. Since the effect of the crystal potential decreases with increased kinetic energy of the electron, for \( h\nu \geq 400 \) eV, the FEFA is valid also for VB spectroscopy of strongly correlated materials. However, even if the FEFA can be motivated, in order to extract \( k_\perp \), a precise knowledge of the inner potential \( (V_0) \) and the effective electron mass \( (m_e^*) \) is needed. This is generally not the case and when performing an actual experiment, the process of finding the correct value for \( k_\perp \) is more of a pragmatic approach. First a “qualified guess” of \( m_e^* \) and \( V_0 \) is made. Hence a starting value, usually for a \( \Gamma \)-point and corresponding photon energy is achieved. Several ARPES spectra for that and nearby photon energies are then acquired. From the symmetry in \( k_\perp \)-dispersion of the bands, a photon energy corresponding to the \( \Gamma \)-point is extracted. For verification the next instance of a \( \Gamma \)-point (higher or lower photon energy) is calculated as well as probed, and the shape and symmetry of the bands should then evidently match the previously acquired spectrum.

Finally it should be pointed out that in materials that have energy bands that do not depend on \( k_\perp \) e.g. semiconductor surface states (Paper I-IV) and layered materials like cuprate high-temperature superconductors† (Paper VIII-XIII), the dispersion is fully determined by Eq. 1.8.

* Hence information concerning \( k_\perp \) is desired.

† As will be mentioned below and presented in paper XII-XIII, caution regarding this matter is needed.
According to an old English system of time units, a moment is one and a half minutes. Consequently, our laser produces pulses that are $1.6$ femto-moments long.

Chapter 2.
THE TARPES TECHNIQUE

By using a pulsed laser as light source, a new dimension of ARPES is possible, time- and angle-resolved PES (TARPES). The time resolution in this technique originates from the fact that one utilizes so-called pump-and-probe laser photoemission (see Fig. 2.1). The energy required to lift the electrons above the vacuum level ($E_{\text{vacuum}}$) is divided into two separate laser pulses. The first pulse (pump) lifts up the electrons to a normally unoccupied excited state (ExS), but below $E_{\text{vacuum}}$, i.e. an electron-hole pair is produced. The second pulse (probe) then ejects photoelectrons into vacuum and their kinetic energy can be detected. By tuning the time between the pump and probe pulse while monitoring the ExS an insight into the electron dynamics and lifetime of the ExS is achieved.

Fig. 2.1: Pump-and-Probe laser photoemission
The probe pulse in the current system has a wavelength of ~130 nm, which corresponds to a photon energy of 9.6 eV. This is for some semiconductors larger than their $E_{\text{vacuum}}$ and we can therefore create photoelectrons from both the VB as well as from an ExS is the conduction band. This makes it possible to obtain the ordinary photoelectron spectrum separated from the excited states by the bandgap (see Fig. 2.1) in one single measurement.

2.1 The TARPES System [15]

2.1.1 The laser pulse generating system

As the source for ~100 fs laser pulses a regeneratively amplified femtosecond Ti:S laser system (See Fig. 2.2) is used. It consists of a self-mode-locked Ti:S oscillator that is continuously pumped by a small frame Ar-Ion laser, and a regenerative Ti:S amplifier that is pumped by a 1 kHz Q-switched and frequency doubled (532 nm) Nd:YAG laser.

A pulse train comprising $10^8$ pulses per second with a pulse width shorter than 100 fs is produced in the self-mode-locked oscillator. These are directed into the so called Faraday Router, which acts as a directional device. With the help of a Faraday rotator and two thin film polarizers, it guides the pulse to different parts of the laser system depending on the direction and polarization of the pulse. From these $10^8$ pulses, only every $10^5$ is picked out and amplified by a three-step process called Chirped Pulse Amplification (CPA). In order to keep the peak power down and thereby preventing damage to optical components in the amplifier, the pulse is elongated in the Pulse Stretcher to about 100 ps before entering the Amplifier. In the amplifier, a Pockels cell picks out pulses at a rate of 1 kHz and locks it in the amplifier cavity for about 10 roundtrips, amplifying it by a factor of approximately $10^6$. The synchronization of the amplification processes is controlled by the Pockels cell driver, utilizing a fast photodiode that monitors the mode-locked train from the oscillator. The photodiode response is used to produce trigger signals, sent to the Q-switched device in the Nd:YAG laser and to the Pockels cell in the cavity of the amplifier. After amplification the pulse is directed via the faraday router into the Pulse Compressor, where the pulse width is decreased to just above* the original 100 fs. The pulse leaving the laser system typically has a width of 120 fs with a pulse energy >600 µJ, corresponding to a peak power of ≈ 5 GW, at a repetition rate of 1 kHz. A schematic overview of the pulse path and the laser system’s most important parts are shown below in Fig. 2.2 with an additional table of explanation.

* Due to bandwidth limitations of optical components (mainly gratings) in the stretcher and the compressor.
**Fig. 2.2:** Schematic overview of the femtosecond laser system.
See also descriptive table below.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti-sapphire Oscillator&lt;br&gt;M1-M2-M3: Laser Cavity Mirrors&lt;br&gt;C1: Ti-Sapphire Crystal&lt;br&gt;P1, P2: Prisms&lt;br&gt;110 fs pulse at 100 kHz (average power ~60 mW)</td>
</tr>
<tr>
<td>2</td>
<td>Faraday Router&lt;br&gt;PD1: Photodiode&lt;br&gt;FR: Faraday Rotator&lt;br&gt;TFP1, TFP2: Thin Film Polarizers&lt;br&gt;Utilizing the Faraday Rotator and the thin film polarizers, this box is the route chopper for the laser pulse.</td>
</tr>
<tr>
<td>3</td>
<td>Pulse Stretcher&lt;br&gt;G1: Grating&lt;br&gt;Stretches the pulse to ~100 ps so that the peak power should not be too high in the amplifier. So called 'Chirped-Pulse-Amplification'.</td>
</tr>
<tr>
<td>4</td>
<td>Amplifier&lt;br&gt;C2: Ti-Sapphire Crystal&lt;br&gt;PD2: Photodiode&lt;br&gt;PC: Pockels Cell&lt;br&gt;TFP3: Thin Film Polarizer&lt;br&gt;M1, M2: Cavity&lt;br&gt;M3: Mirrors&lt;br&gt;A Nd-Yag laser pumped Ti-Sapphire crystal increases the energy in the pulse about 100 times, resulting in an average power ~400 mW at 1 kHz.</td>
</tr>
<tr>
<td>5</td>
<td>Pulse Compressor&lt;br&gt;L: J/2-Pulse&lt;br&gt;G2, G3: Gratings&lt;br&gt;PD3: Photodiode&lt;br&gt;Compresses the amplified pulse to ~120 fs giving a pulse energy larger than 600 µJ, peak power ~50 kW.</td>
</tr>
<tr>
<td>6</td>
<td>Other&lt;br&gt;BS: Beamsplitter&lt;br&gt;Single Shot Autocorrelator (SSA)&lt;br&gt;The beamsplitter reflects ~4% of the light into the SSA, and the remaining passes through to the rest of the TAPPE system. The SSA does us the possibility to monitor the pulse characteristics (length and mode) after the compression stage.</td>
</tr>
</tbody>
</table>
From the fs-laser system the beam continues to the second part of the TARPES system (see Fig. 2.3). The most important parts are:

- BBO Crystal for frequency doubling
- Dicroich Beamsplitter
- Optical Delay Stage
- Berek Compensators
- Gas Cell for frequency tripling
- Grating Monochromator
- The Vacuum System, including the ToF Photoelectron Detector

\[ \lambda = 800 \text{ nm} \quad \lambda = 400 \text{ nm} \quad \lambda = 133 \text{ nm} \]

Fig. 2.3: Overview of the TARPES experimental Setup (Courtesy of Dr. Henrik S. Karlsson [15])

2.1.2 SHG & the beamsplitter

The pulse leaving the laser system is <120 fs long and has a wavelength of approximately 800 nm. First of all this pulse will be frequency doubled by a process called Second Harmonic Generation (SHG) (see chapter 2.2 below). This is performed by guiding the pulse through a 1-mm-thick β-BaB₂O₄ (BBO) non-linear crystal. When leaving the BBO crystal the pulse is a combination of two different wavelengths, the original 800 nm and the frequency doubled 400 nm. By passing the pulse through a dichroic beamsplitter, these two wavelengths can be separated into

* Polarization compensator devices. By using them both the pump and probe pulse can individually be set to either s- or p-type polarization.
two individual pulses of different wavelengths. Hence, after the dichroic beamsplitter one has to keep track of two separate laser pulses with different characteristics and separate beam-paths.

2.1.3 The probe pulse

The 400 nm probe pulse is directed via a Berek compensator, into a Third Harmonic Generation (THG) stage. This consists of a static gas cell filled with xenon gas at a pressure of about 10 mbar. The light is focused into the gas by a 150 mm focal length ultraviolet (UV) grade fused silica lens, producing an intensity of $\approx 10^{14}$ W/cm$^2$ in the focus. Due to the high intensity, the gas displays nonlinear effects and produces odd (isotropic media) harmonics. This means that in addition to the doubled wavelength ($\lambda=400$ nm), radiation with the wavelengths $\lambda/3$, $\lambda/5$, $\lambda/7$,... will appear from the focus. The intensity of the doubled wavelength is undoubtedly supreme, while the intensity of the higher harmonics decreases quickly with increasing order. The static gas cell has an output window of LiF in order to prevent the gas from entering the vacuum system. Owing to the fact that LiF becomes opaque at wavelengths below $\approx 110$ nm, the only harmonic to leave the gas cell is the frequency tripled ($\lambda/3 \approx 133$ nm), which corresponds to a photon energy of approximately 9.6 eV*. The two (400 and 133 nm) transmitted wavelengths expand collinearly in a vacuum beam line towards a spherical grating placed in the Grating Chamber (see below). This grating is used to separate the wavelengths and focus the Vacuum Ultraviolet (VUV) radiation onto the sample inside the analysis chamber (see below).

2.1.4 The pump pulse

The pulse with the fundamental 800 nm wavelength will act as the pump pulse. A wavelength of 800 nm equals a photon energy of $\approx 1.6$ eV, sufficient to excite electrons, but not enough to lift them above $E_{\text{vacuum}}$. In order to tune the delay between the two pulses, the pump pulse passes through a delay stage. This is simply 4 mirrors placed onto a motorized and computer controlled translation stage on top of a manual one. Both of the translation stages have a travel range of 25 mm and micrometer precision. Because the pulse travels the delay distance both back and forth, the pulse path length can be prolonged by 100 mm, corresponding to a maximum delay time $t_D \approx 333$ ps between the pump and the probe pulse. Hereafter the pump pulse travels via a Berek compensator into the Grating Chamber where it is reflected by a 5-mm-diameter dielectric mirror onto the sample surface.

* An useful relation is: $h \nu [\text{eV}] = \frac{1242}{\lambda [\text{nm}]}$
2.1.5 The vacuum system

Due to three facts, (1) VUV radiation is used, (2) PES is a surface sensitive technique, and (3) contamination of the sample surface should be minimized, the measuring process should be carried out under UHV conditions. The vacuum system consists of two main parts:

- **The grating chamber**   Enclosing the dispersive grating for the probe pulse and the pump pulse mirror ($P \sim 5 \times 10^{-10}$ torr)
- **The analysis chamber**   Enclosing the sample, sample manipulation and the detector parts ($P < 1 \times 10^{-10}$ torr)

The two chambers are connected by the diaphragm tube in an angle of 70.5° as shown above in Fig. 2.3. This specific setup-angle is called the Seya-Namioka monochromator configuration. The actual tube contains four sequential circular diaphragms in a decreasing sequence of 25, 15, 5, and 2 mm. The purpose of these diaphragms is to hinder any other radiation than that reflected from the pump pulse mirror and the wavelength selected by the grating from reaching the sample surface. The main analysis chamber is equipped with a μ-metal shield to prevent external magnetic filed from interfering with the motion of the photoelectrons. Attached to this chamber is also the electron energy time-of-flight analyzer.

2.1.6 Electron energy detection

There are several methods of analyzing the kinetic energy distribution of the emitted photoelectrons, e.g. Retarding Field Analyzers (RFA), Concentric Hemispherical Analyzers (CHA) or Cylindrical Mirror Analyzers (CMA). All of these methods are constructed as an energy band pass filter where they are set to detect photoelectrons in a pre-set energy window. The spectrum is then obtained by scanning this energy window. A technique that does not restrict the energy detection to a certain energy interval is the
Time-of-Flight (ToF) technique. In this method the kinetic energy of the photoelectron is extracted from the drift time from the sample to the detector according to:

\[
E_{\text{kin}} = \frac{m_e \cdot v^2}{2} = \frac{m_e \cdot l^2}{2 \cdot t^2}
\]  
(Eq. 2.1)

Here, \( t \) is the drift time, \( l \) is the well-defined distance between the sample and the detector, and \( m_e \) is the electron mass. This technique could be compared with a stopwatch where the probe pulse pushes the START button when it is detected by the photodiode (PD2 in Fig. 2.2) inside the amplifier. When a photoemitted electron later hit the detector, it pushes the STOP button. The analog pulse from the photodiode is converted to a digital fast NIM pulse in a Constant Fraction Discriminator (CFD) before being used as START in the data acquisition system.

The electrons leaving the sample drift in a field-free, \( \mu \)-metal shielded, tube towards the detector. This is mounted on an 8" ConFlat flange and consists of a grounded metal grid, a chevron-mounted pair of 40-mm-diameter micro-channel plates (MCP), and a single detection anode (see Fig. 2.4).

* This is why the ToF technique is restricted to pulsed photon sources

† Nuclear Instrumentation Module
When an electron is photoemitted from the sample and hits the inner wall of a MCP channel it produces secondary electrons. By applying a high-voltage over the MCP these secondary electrons are accelerated and produce more secondary electrons. Through this scheme an amplification of the photoelectron signal is accomplished. The channel bias angles are typically $8^\circ/8^\circ$, giving sufficiently high probability for the incident electron to hit the channel walls several times before passing and thereby generating a large amount of secondary electrons. By this design only two or three plates are needed in order to reach sufficient amplification of the signal, leading to a much smaller device, in comparison with the straight electron multiplier. When the electrons leave the second plate they fall upon the metal anode, producing a negative output signal (i.e. one electron hit is counted and also acts as the STOP pulse mentioned above).

### 2.2 Basic Non-linear Optics

When speaking of optics, it most commonly refers to the linear part of the field i.e. when the polarization, $P$, depends linearly on the electric field strength $E$, according to:

$$P = \varepsilon_0 \chi \cdot E$$  \hspace{1cm} (Eq. 2.2)

Here $\varepsilon_0$ is the permittivity in vacuum* and $\chi$ is the (linear) susceptibility†. When dealing with relatively weak electric fields, this is basically all that one needs to know. Though when working with light having very high peak power, e.g. a femtosecond laser, it is necessary to return to basic physics and mathematics in order to explain the effects that start to occur in the lab [16].

A unit volume of a transparent dielectric medium is basically an assembly of charged particles joined together by coulomb forces. So what is present is the light, negatively charged electrons and heavier, positively charged nuclei. In the presence of an oscillating electric field, the particles move. Electrons move in the opposite direction of the electric field vector, and the nucleus move in the same direction. These movements induce an electric-dipole moment, i.e. the electromagnetic wave induces a polarization of the dielectric medium (see Fig. 2.6).

---

* $\varepsilon_0 = 8.85 \times 10^{-12}$ C$^2$/kgm$^3$

† A material-specific constant
If the electric field varies sinusoidally, the charged particles of the dielectric medium will form oscillating dipoles. This motion can be described by a simple mechanical analogy with two particles connected by a spring. Here the mass of the nucleus is much bigger than the mass of the electron. Hence, the problem could be simplified to a one-particle system, where the nucleus is fixed in space and only the electron is oscillating. The position of the electron varies in response to the electric field $E(t)$ and is described by the simple equation of motion for an oscillator:

$$
\begin{align*}
    m \frac{d^2 x}{dt^2} + 2 \Gamma \frac{dx}{dt} + \omega^2 x - \left( \xi^{(2)} x^2 + \xi^{(3)} x^3 + \ldots \right) & = -eE(t) \\
\end{align*}
$$

(Eq. 2.3)

Here $x$ is the displacement from mean position, $\omega$ is the resonance frequency, and $\Gamma$ is a damping constant. Usually the anharmonic terms $\xi^{(2)} x^2 + \xi^{(3)} x^3 + \ldots$ are neglected and only the harmonic part is solved. If the anharmonic parts are included, no exact solution is found and Eq. 2.3 has to be solved to successive orders of approximation by expressing $x$ as a power series in $E$. Equivalently, the polarization $P$ in the applied electric field can be expanded according to:

$$
P = \varepsilon_0 \left( \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right) \quad \text{(Eq. 2.4)}
$$

Here $\chi^{(1)}$ is the linear susceptibility known from above (Eq. 2.2) while $\chi^{(2)}$ and $\chi^{(3)}$ are the so called nonlinear (quadratic and cubic respectively) susceptibilities of the
medium. Since the latter two generally are much smaller than $\chi^{(1)}$, strong electrical fields ($\sim 3 \cdot 10^{10} \text{ V/m} \leftrightarrow 10^{14} \text{ W/cm}^2$) are needed in order to gain non-linear effects. If an incident monochromatic electric field:

$$E(t) = E_0 \cos(\omega t) = \frac{1}{2} E_0 [\exp(-i\omega t) + \exp(i\omega t)]$$  \hspace{1cm} (Eq. 2.5)

is inserted in Eq. 2.4, it is easy to see that the induced polarization $P$, in addition to oscillating at the same frequency ($\omega$) as the incident field, also contains components that oscillate at frequencies $2\omega, 3\omega, \ldots$, as well as a static component. Consequently, the interaction between a strong oscillating electrical field and a non-linear optical material can be utilized to produce radiation at new frequencies (remember that oscillating dipoles emit radiation at the frequency of oscillation). This process is known as \textit{Harmonic Generation}. The frequency doubled ($2\omega$) and tripled ($3\omega$) radiation is derived from the quadric and cubic terms of Eq. 2.4, and the related processes are called \textit{Second Harmonic Generation} (SHG) and \textit{Third Harmonic Generation} (THG), respectively. A joint name for the higher order frequency generating processes is \textit{Higher Harmonic Generation} (HHG). It should be noted that in materials with inversion symmetry, there can be no even powers in the non-linear expansion of $P$ in Eq. 2.4. Accordingly, the lowest order non-linearity in isotropic media such as glasses, liquids and gases is the cubic term.
Synchrotron radiation is created when a charged particle (e.g., an electron or a positron) is accelerated. The first observation of artificial synchrotron light was made over 60 years ago (April 24, 1947) at the General Electric Research Laboratory in Schenectady, New York [17] (Fig. 3.1). However, natural synchrotron radiation from charged particles spiraling around magnetic field lines in space is as old as the stars e.g., the light seen from the Crab Nebula.

The first generation synchrotron-radiation facilities are often called parasitic facilities because the accelerators were built and operated primarily for high-energy or nuclear physics. Parasitic operation meant a severely limited output of synchrotron radiation.
By the development of electron storage rings the basis for all of today’s synchrotron sources were set and in the early 1980’s the first dedicated (second-generation) sources started to produce light.

With time, users started to understand that not only the photon flux but also the spectral brilliance (the flux per unit area of the radiation source per unit solid angle of the radiation cone per unit spectral bandwidth\(^*\)) is important for many experiments. In the third-generation synchrotrons (e.g. SLS, ESRF, SPring-8) the ring is optimized for high brightness, low emittance\(^†\) and long straight sections dedicated to insertion devices (see below). This brings us up to the synchrotron radiation facilities used in today’s modern experiments. The most promising candidate for a fourth-generation source is the hard x-ray (\(\lambda \leq 1\AA\)) free electron lasers (FEL), which unfortunately lie beyond the scope of this thesis.

### 3.1 Basic Principles

When an electron is moving in a circular orbit at a non-relativistic speed (\(v << c\)) the angular distribution of the emitted synchrotron radiation is that of an oscillating dipole [18] shown in Fig. 3.2(a). At a relativistic speed (\(v \approx c\)) the emission is subject to a Lorentz transformation. As a result, the angular distribution will be strongly distorted into a narrow cone, Fig. 3.2(b), in the tangential direction, and the emitted spectrum will in addition be severely Doppler-shifted [19], Fig. 3.2(c-d).

Practically a synchrotron radiation source is built around an electron (or positron) storage ring (Fig. 3.3). The heart of the synchrotron is the electron gun and linear particle accelerator (LINAC) that creates the electrons. In modern synchrotrons the electrons are then furthered accelerated in a booster synchrotron before being released into the storage ring in well defined bunches. While circling the storage ring some electrons are scattered and the ring current slowly decreases i.e. the ring current has a finite lifetime. Hence the ring needs to be refilled, usually a couple of times a day, during which it is not possible to perform experiments. Modern synchrotrons, however, have a so-called top-up mode where the electron beam is not dumped before refill, but instead gently refilled in a “continuous” manner. As a result, the ring current (and hence photon flux) remains more or less constant and there is no down-time i.e. experiments can be performed without interruption.

\(^*\) Often measured in units of [photons s\(^-1\) m\(^2\) r\(^-2\) mm\(^2\) (0.1% bandwidth\(^-1\)]

\(^†\) \(\varepsilon = \) product of beam size and divergence
Fig. 3.2: Geometrical shape of the radiation emitted by electrons moving in a circular trajectory having (a) $v << c$ (b) $v \approx c$. (c-d) Corresponding Doppler shift. Also shown are some useful relations where $E_e$ is the electron energy and $\lambda$ the wavelength. (From Refs. 19 & 20)

Fig. 3.3: Example of a third generation synchrotron facility, SOLEIL, France (Courtesy: SOLEIL [21])
The high-energetic (e.g. $E_e = 8$ GeV at SPring-8) electrons are kept circulating in an UHV environment by an elaborate construction of hexapoles, quadropoles and bending magnets. Every time the electrons are turned by a bending magnet synchrotron radiation is emitted. The spectral distribution of the emitted light obtained from a bending magnet displays a continuous spectrum, as shown in Fig. 3.4. Here is also a very useful relation shown, from which it is evident that the maximum photon flux is obtained at a critical wavelength $\lambda_C$. This wavelength is uniquely selected by the kinetic energy of the electrons $E_e$ and the radius $R$ of the storage ring*.

![Fig. 3.4: Spectral distribution from an electron moving in a curved trajectory i.e. from a bending magnet. Maximum photon flux is obtained at a critical wavelength $\lambda_C$. This wavelength is determined by the kinetic energy of the electrons ($E_e$) and the bending radius ($R$). (From Ref. 19)](image)

There are several intrinsic properties of synchrotron radiation that during the years have made this light-source so dominant in the field of photoelectron spectroscopy (and also other fields):

- Selectable photon energy (broad spectrum of emitted light)
- High photon flux and high brilliance
- Linear polarization in the plane of orbit
- Clean environment (UHV conditions)
- Pulsed time structure in the picosecond range
- High repetition rate (almost continuous)

However, there are also some drawbacks of this light source, e.g. low accessibility and high running costs.

* The radius around which the electrons are bent
3.2 Undulators

As mentioned above, in the quest for higher photon-flux and brilliance new techniques have been developed, so-called insertion devices. In the experiments described in this thesis all work has been performed at third-generation synchrotrons and at beamlines equipped with one or two undulators. An undulator is a periodic magnetic construction (Fig. 3.5) that is placed in a straight section of the storage ring. The longer straight section, the longer undulator is possible. As first suggested by Ginzburg [22] in 1947, it is possible to generate radiation when electrons are moving in a periodic electromagnetic structure.

![Schematic view of an undulator](image.png)

**Fig. 3.5:** Schematic view of an undulator. (Courtesy of Prof. David T. Attwood [20])

In a planar undulator (Fig. 3.5) the electrons are forced to oscillate transversally in a given plane and the angular deflection ($\alpha$) is kept smaller than the natural radiation divergence angle of the synchrotron radiation ($\theta = 1/\gamma$). All released radiation is emitted along the axis of the undulator and since this is a periodic device the amplitudes of the field radiated in each period can consequently interfere creating a periodic radiation field [23]. Hence a typical undulator spectrum displays a periodic structure with a strong first order peak and several weaker higher order peaks (see Fig. 3.6).
The wavelength of the undulator radiation is determined by several parameters according to:

\[ \lambda = \frac{\lambda_u}{2\gamma^2} \left( 1 + \frac{K^2}{2} + \gamma^2 \theta^2 \right) \]  
(Eq. 3.1)

Here \( \lambda_u \) is the periodicity of the undulator (see Fig. 3.5), \( \theta \) the angular divergence and \( K \) a dimensionless parameter that can be expressed as:

\[ K = \frac{eB_0\lambda_u}{2\pi mc} = 0.934 \cdot \lambda_u [\text{cm}] \cdot B_0 [\text{T}] \]  
(Eq. 3.2)

This makes it possible to alter the characteristic wavelength emitted by the undulator first in the design by choosing a desired \( \lambda_u \) and second by changing the magnetic field strength \( B_0 \). However, by studying Eq. 3.1 and Eq. 3.2 it is evident that the emitted wavelength primarily depends on \( \lambda_u \) (and the electron energy through \( \gamma \)). Hence, once \( \lambda_u \) is selected, the magnetic field is primarily thought of as a tuning possibility within a relatively narrow photon energy range.

In most conventional undulators tuning of the magnetic field strength is achieved by varying the gap between the upper and lower parts of the magnetic structure. However, in the quest for even higher brilliance, better energy resolution and more versatile beamlines, many novel undulator concepts have been developed. Most new undulators are moving away from the idea to alter the magnetic field by simply changing the gap. Instead the magnetic structures are made more complex and the
character of the magnetic field is tuned by also sliding the top and bottom part relative to each other along the axis of the undulator (e.g. at the ID08 [25] beamline of the ESRF). This has the advantage that it adds the possibility of freely selecting the polarization of the light (linear horizontal, linear vertical, circular). A variation of this concept has recently been installed at the ADRESS [26] beamline of the SLS. In this construction the gap tuning is removed completely (world’s first fixed-gap undulator, Fig. 3.7). Instead a composite magnetic structure is used where all four parts can be individually slid along the axis of the undulator. If the parts are moved parallel, Fig. 3.7(b) an energy shift is created, and if they are moved diagonally, Fig. 3.7(c), a polarization shift is obtained.

![Fig. 3.7](image)

**Fig. 3.7:** (a) Photograph of the new fixed-gap undulator of the ADRESS beamline of the SLS. Also shown is a schematic view of how the individual parts of the undulator are moved to generate (a) an energy shift, (b) a polarization shift. (Courtesy of Dr. V. N. Strocov [26])

Among many desirable features, this construction is mechanically very rigid and simple (only four motors are needed). It is also possible to freely choose the polarization of the light whilst the flux as a function of photon energy remains uniform. The only drawback of this construction is that the undulator movements for energy and polarization shifts are coupled. Hence very elaborate mathematical models have to be used in order to be able to change energy without altering the polarization and vice versa.
Other developments include e.g. the undulator for the NIM beamline at the MAX III synchrotron in Lund, Sweden. This beamline is optimized for very high energy resolution at 10-40 eV photon energies. So as to realize the desired energy resolution of 500 μeV, contamination from higher order light in the undulator spectrum has to be suppressed. This is achieved by deliberately making the magnetic structure of the undulator slightly aperiodic.

### 3.3 Beamlines & End Stations

When the radiation leaves the undulator it enters the beamline (see Fig. 3.3) that guides the light to the experimental end station. One of the most important parts of the beamline is the monochromator. There are many configurations, into which I shall not go into detail, but one common set-up consists of a plane grating and an exit slit (Fig. 3.8). By tilting the grating and scanning the exit slit it is possible to select a desired wavelength from the synchrotron light. The bandwidth, $\Delta \lambda$, of the outgoing light is determined by both the number of lines in the grating $N$ (see relation in Fig. 3.8) and the size of the exit slit. However, the important thing to remember is that the narrower bandwidth that is selected (i.e. higher energy resolution in the end) the less number of photons will pass the monochromator. Generally, the problem is not how to select a narrow bandwidth of the radiated spectrum, but rather how to do so without loosing too many photons in the process. This is especially true for soft x-ray beamlines.

After leaving the monochromator, the light is guided into the experimental chamber and onto the sample. The synchrotron-based work presented in this thesis is performed at three different synchrotrons (ESRF, SLS and SPring-8). However, the end stations of these three locations have more or less the same fundamental set-up (see Fig. 3.9) and desirable properties*.

The most vital part of the end station is naturally the electron analyzer, which in all three cases is a Scienta SES-2002/200 imaging analyzer. The advantage of these analyzers is that they make it possible to extract several EDC along a line in momentum space (i.e. angle-resolved) in a single measurement. In addition the energy and momentum resolution is very high, which is crucial for many of the experiments presented in this thesis. For instance, to perform a Fermi surface mapping collecting each single EDC individually would in theory be possible, but in reality unfeasible. Every time the sample is moved or turned a non-negligible uncertainty is added to the probed $k$-point. In addition, the task of orienting yourself in momentum space would in itself be a commendable experiment.

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* Disregarding minor differences and photon energy ranges.
Fig. 3.8: Schematic view of a plane grating monochromator and some useful equations. $N$ equals the number of lines in the grating [20].

Fig. 3.9: Schematic representation of an ARPES experiment performed at a synchrotron radiation facility.
There are several other key properties of the end stations that are all essential for the experiments presented in this thesis:

- **Low sample temperature (< 30 K)**  
  To facilitate measurements below $T_c$ and to minimize thermal broadening

- **Motorized high-precision manipulator**  
  Allowing versatile and high-resolution $k$-space mapping

- **Excellent UHV conditions**  
  Very important, especially the HTSC that degrade very fast in bad vacuum

- **Possibility to freely select the polarization of the light**  
  To assure that the matrix element will not be zero and also to facilitate a method for aligning the sample by circular dichroism.

Even though not shown in **Fig. 3.9** it is also worth mentioning that all end stations mentioned above have a set-up with a main analysis chamber and a separate preparation chamber. In addition the main heating stage for annealing samples is separate and located inside the preparation chamber, *i.e.* detached from the main manipulator. The reason for this is that the combination of both high- and low-temperature abilities of the manipulator is extremely hard to facilitate. There have been attempts, but in most cases the final product will not excel in either temperature region. In most cases, and certainly in the work presented here, there is no desire to perform ARPES measurements at elevated temperatures (well above room-temperature). This finds its natural explanation in the systems that are investigated (*e.g.* HTSC), but also in the fact that the thermal broadening already at room-temperature is approximately 100 meV ($\approx 4k_BT$).

### 3.4 Selecting Photon Energy

In order to obtain the desired and accurate data from an ARPES experiment, it is very important to choose the proper photon energy. Modern light sources used in PES ranges from approximately 10-8000 eV (see *The Electromagnetic Spectrum* to the right) and are usually divided into three different branches:

1. **Vacuum Ultraviolet (VUV)**  
   $\nu = 10$-100 eV  
   (fs-lab at KTH & SIS beamline at SLS)

2. **Soft x-rays (SX)**  
   $\nu = 200$-2000 eV  
   (ID08 at ESRF & BL25SU at SPring-8)

3. **Hard x-rays**  
   $\nu = 2$-6 keV  
   (VOLPE project at ESRF) *

* N.B.: Only PES, not angle-resolved PES!
THE ELECTROMAGNETIC SPECTRUM

WAVELENGTH (in meters)

10^3, 10^2, 10^1, 1, 10^-1, 10^-2, 10^-3, 10^-4, 10^-5, 10^-6, 10^-7, 10^-8, 10^-9, 10^-10, 10^-11, 10^-12

COMMON NAME

RADIO WAVES, ULTRAVIOLET, INFRARED, MICROWAVES, TERAHERTZ, "SOFT" X RAYS, "HARD" X RAYS, GAMMA RAYS, "HARD" X RAYS

ACCELERATOR-BASED LIGHT SOURCES

Synchrotron PES

COMMON SOURCES

Radioactive Elements, X-ray Machines, Light Bulb, People, Radar, Microwave Oven, AM Radio, FM Radio

FREQUENCY (waves per second)

10^6, 10^7, 10^8, 10^9, 10^10, 10^11, 10^12, 10^13, 10^14, 10^15, 10^16, 10^17, 10^18, 10^19, 10^20

ENERGY OF ONE PHOTON (electron volts)

10^9, 10^8, 10^7, 10^6, 10^5, 10^4, 10^3, 10^2, 10^1, 1, 10^-1, 10^-2, 10^-3, 10^-4, 10^-5, 10^-6, 10^-7, 10^-8, 10^-9, 10^-10, 10^-11, 10^-12

(Courtesy: Advanced Light Source)
In this thesis, the work has been performed using the first two branches. In principle all presented data concern the low binding energy electronic structure (within 10 eV from the Fermi level), hence the reason for using SX might not be so obvious. As mentioned in the previous sub chapters, today’s modern analyzers and modern synchrotrons allow ARPES measurements using VUV radiation at very high energy and momentum ($k_\parallel$) resolution. In this context there is absolutely no point in going to SX. With present technology the energy resolution will be an order of magnitude better when using VUV. In addition, the photoionization cross-section [27] for most electronic states in the VB is much higher for VUV than for SX. Hence will SX-ARPES be a much more time-consuming approach.

Nevertheless, as will be presented in Paper V-VI & XII-XIII, one big advantage of going to high photon energies is that the inelastic mean free path will increase from approximately 5 Å to 15 Å. Hence, SX-ARPES will reveal a more bulk-like electronic structure. In addition, the increased $\lambda_{\text{mfp}}$ will also result in an improved $k_\perp$-resolution ($\Delta k_\perp \approx 1/\lambda_{\text{mfp}}$) as well as (according to Eq. 1.8) a wider accessible $k_\parallel$-window (using the same emission angles). However, the latter has the drawback that the $k_\parallel$-resolution will be poorer (same angle resolution of the detector but larger $k_\parallel$-window). Consequently, the $k_\parallel$-resolution is also more sensitive to imperfections in the crystal structure and surface of the sample.

![Fig. 3.10: Schematic illustration of how the curvature of the probed momentum slice changes when moving from VUV to soft x-rays. When an equal range in $k_\parallel$ is probed, the deviation in $k_\perp$ is evidently large for VUV (blue region) and negligible for soft x-rays (red region).](image)

(Courtesy of Dr. Oscar Tjernberg)

Another aspect is that if data covering an entire Brillouin zone is required, the total emission angle needed for VUV is very much larger than for SX, as shown in Fig. 3.10. As a result, the resultant line in momentum space will be significantly curved. Hence, to acquire data along a specific (high-symmetry) direction will be very hard.
using VUV, in the case of a material with 3D electronic structure \( \text{i.e.} \) dispersion in \( k_\perp \).

As clearly seen in Fig. 3.10 the curved line will result in a big deviation of \( k_\perp \) for different emission angles. Hence, in order to extract the band dispersion along a specific line in momentum space using VUV, the \( k \)-dispersion of the final state \( k_f \) is needed. Further, given that \( k_f \) is known, in order to acquire a straight line in \( k \)-space using VUV, the deviation in \( k_\perp \) have to be compensated by changing the photon energy along with the emission angle. This is a tedious task that also will add a vast amount of uncertainty to the acquired results. Here a third benefit of using SX ARPES appears. At these high energies the emission angle needed to cover the Brillouin zone of most compounds will be only a few degrees. Consequently, the deviation in \( k_\perp \) will be negligible and the task of acquiring a straight line in \( k \) will be straightforward and the \( k_\perp \)-dispersion of the final state is irrelevant*.

If the \( k_f \) is not known (usually the case) a final state approximation is required. The most common approach is to approximate the final state with a free-electron parabola (Eq. 1.10). For VUV this approximation is not valid for all compounds (e.g. strongly correlated materials). Here the fourth advantage of SX is manifested. As mentioned in Chapter 1.2, at high enough kinetic energy of the photoemitted electron \( \text{i.e.} \) SX, the free-electron final state approximation (FEFA) is valid also for strongly correlated compounds.

In summary the advantages and drawbacks of SX ARPES is presented in Table 4.1. Hence VUV should be used when the surface electronic structure is required for compounds without \( k_\perp \)-dispersion and/or when very high energy and \( k_{||} \)-resolution is needed. SX-ARPES is better suited when mapping the bulk electronic structure of compounds having both \( k_{||} \) and \( k_\perp \)-dependence and the need for high resolution is not crucial.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk sensitive probe</td>
<td>Low valence band cross-section</td>
</tr>
<tr>
<td>Improved ( k_\perp )-resolution</td>
<td>Inferior energy resolution</td>
</tr>
<tr>
<td>Easy to acquire a straight line in ( k )-space</td>
<td>Low ( k_{</td>
</tr>
<tr>
<td>FEFA is valid</td>
<td>Very flat/uniform samples are needed</td>
</tr>
</tbody>
</table>

* Information about final state is still needed in order to extract the absolute value of \( k_\perp \).
Chapter 4.

**STUDIED SAMPLES & PERFORMED EXPERIMENTS**

The work presented in this thesis covers a wide range of different compounds. Among the studied samples, representatives from four different groups of materials are found:

- **Semiconductors**: Ge, GaSb, InAs
- **Metals**: Cu
- **Oxides**: Cu$_2$O
- **Superconductors**: La$_{2-x}$Sr$_x$CuO$_4$ (LSCO), La$_{2-x}$Sr$_x$CuO$_4$ (NCCO)

In the following subchapters the studied samples along with background and justification for the performed experiments will be presented.

### 4.1 Sample Preparation Techniques (*Paper VII*)

As mentioned above, PES can be a very surface sensitive technique. Hence in order to acquire high-quality data the sample surface needs to be very clean. When dealing with ARPES the surface is also required to be very flat not to loose the momentum resolution. In the present work two main surface preparation techniques have been applied to the samples:

1. **Ion-bombardment and subsequent annealing** (Ge, InAs, GaSb, Cu, Cu$_2$O)
2. **In situ sample-cleaving** (LSCO, Nd-LSCO, NCCO)

Sputtering with Ar$^+$ ions and annealing is primarily used on monoatomic or chemically and structurally simple materials [28]. When applied to polyatomic materials there is always risk for selective sputtering and depletion of the lightest atomic species causing non-stoichiometry of e.g. the oxide or semiconductor surface. Hence for the Cu$_2$O sample in *Paper VI*, only very few and gentle sputtering cycles were performed in order to avoid depletion of oxygen from the surface.
For the more complex HTSC, the samples are instead cleaved in situ to expose a clean surface. Two different approaches have been used. For the NCCO samples a so called post-cleaving method, Fig. 4.1(a), is employed, where a small metal rod is glued to the sample surface. The metal rod is then in situ pushed by a wobble-stick and the sample is cleaved (or broken). This method works reasonably well for yielding, layered and rather small samples. For the more rigid LSCO samples (Paper VIII-XI) a special on-board sample cleaver, Fig. 4.1(b), has been developed (presented in Paper VII) in order to achieve good cleaves. With this arrangement it is possible to mount the sample and align the desired cleavage plan to the blade ex situ using e.g. Laue x-ray diffraction. Consequently, better surfaces and alignments can be realized, which considerably simplifies and improves the experiments.

![Fig. 4.1: (a) Post-cleaving method (b) The on-board sample cleaver](image)

(Courtesy of Dr. Ray Barrett @ ESRF)

4.2 Semiconductor Surfaces (Paper I-IV)

Semiconductors built from group IV (Si, Ge) or from group III (Ga, In) and group V (As, Sb) atoms, are based on atomic bonds that are formed from linear combinations of valence s- and p-orbitals. These are by definition called $sp^3$ hybrids, which results in four highly directional bonds pointing towards the corners of a regular tetrahedron (see Fig. 4.2). This is the reason that an atom in these semiconductors has four nearest neighbors, i.e. a coordination number of four. Owing to this, the two most common crystal structures encountered in semiconductors are the diamond structure and the zinc-blende structure. By studying Fig. 4.2 below one could realize that the locations of the atoms are exactly the same in both structures. The only difference is that in diamond structure all atoms are of the same species, while the zinc-blende structure consist of equal amounts of two
different atomic species (note that the atoms in the corners only are counted as 1/8 of an atom and the ones on the face of the cube as 1/2 of an atom). The bonds are covalent for the group IV semiconductors, while the difference in electronegativity between the atoms in III-V gives a partly ionic bonding character.

Fig. 4.2: (a) The zinc-blende/diamond-structure (b) View along the (111) direction. (c) View along the (100) direction (d) View along the (110) direction. N.B.: For zinc-blende red and blue atoms are of different species and for diamond structure they are the same.

In these experiments the goal was to study not only the surface electronic structure but also the electron dynamics for some highly debated semiconductor surfaces. The first study was concentrated on Germanium, or more accurately on its (111) surface that after relaxation display a stable c(2×8) reconstruction [29] (see Fig. 4.3(a-b)). This surface, together with the Si(111) (7×7) surface, are two of the most investigated and debated systems in the field of surface physics. When cleaving a Ge-crystal along the (111) plane, Fig. 4.2(b), every surface atom will have one half-filled dangling bond. The c(2×8) is a so-called adatom-restatom reconstruction where 3/4 of the surface atoms are saturated by the adatoms, Fig 4.3(a-b). Through charge transfer [30] from the adatoms (A1 and A2) to the restatoms (R1 and R2) all remaining dangling bonds are either completely filled or empty, and the surface is stable.
The filled restatoms have been investigated by normal PES but the electronic structure of the empty adatom states have been overlooked, much due to limitations of experimental equipment. It is only in recent years where scanning tunneling spectroscopy (STS) has been able to resolve the two different unoccupied adatom states\[^{31}\] that have been previously predicted in surface density of states (SDOS) calculations\[^{32}\]. However, the momentum dependence and electron dynamics of the unoccupied adatom states where completely unexplored and made this surface a perfect candidate for TARPES. The results from these experiments are presented in Paper I.

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**Fig. 4.3:** (a) Topview and (b) sideview of the atomic model of the c(2×8) surface. (c) Surface Brillouin zone of the c(2×8) reconstruction for one domain. (d) Same as (c) but for three domains.
By obtaining an increased understanding of the clean Ge(111)c(2×8) surface, the aim was also to cast new light on the even more debated Ge(111):Sn(√3×√3)R30° adsorption system. The (√3×√3)R30° Sn adatom reconstruction is obtained when 1/3 of a monolayer (ML) of Sn is evaporated onto the Ge(111)c(2×8) substrate. A large difference between the Sn adsorbate surface and the clean Ge surface is that the Sn adatoms states are not empty but instead approximately half-filled. As first discovered and suggested by Mats Göthelid et al. [33, 34], the electrons of the Sn adatoms inherit dynamic properties. Through a vast amount of experimental and theoretical studies [35, 36] the nature of this dynamics has been more or less resolved. The main idea is that the Sn adatom electrons are “shared among all” adatom dangling bonds by a rapid oscillation of the adatoms and a constant redistribution of charge. Hence the dangling bonds can momentarily be either completely filled or completely empty at room-temperature. When performing time-integrated measurements, e.g. STM, the surface is on average found to have a (√3×√3)R30° symmetry due to the constant flipping (up and down) of the adatoms. When cooling the surface, adatom switching stops. In STM this is seen as a (3×3) reconstruction of the surface where the adatoms has “frozen” in an up or down position. From this it is evident that the fluctuations found at room-temperature must be driven by phonons [37].

The main purpose of this study was to use time-resolved PES to study the Ge:Sn surface and if possible extract information regarding the dynamics (i.e. at room-temperature) of the adatom electrons.

In addition to the investigation of fundamental semiconductors a study of some III-V semiconductor surfaces has also been performed as an extension of a beforehand started project. Many cleavage surfaces in this group of compounds had already been investigated with TARPES [38, 39, 15]. In order to better distinguish between intrinsic properties and surface effects, the InAs(111) and GaSb(001) surfaces have been investigated using TARPES.

* One adatom in a raised position and two adatoms in a lowered position, or vice versa.
4.3 Cu Charge Density: a proof of principle (Paper V)

One of the main advantages of ARPES is that the measured intensity, \( I(k, \omega) \), more or less directly probes the spectral function \( A(k, \omega) \):

\[
A(k, \omega) \propto I(k, \omega) \quad \text{(Eq. 4.1)}
\]

However, effects from optical matrix elements (cross-section, resolution function etc.) need to be considered. In the experiments presented in Paper V (as well as in Paper VI, XII, and XIII) these effects have been “minimized” by the use of higher (soft x-ray) photon energies. As a result the optical matrix elements are approximately constant due to the small emission angles and an energy range that is small compared to the kinetic energy.

The goal of this experiment was to prove that if enough information is gathered about the spectral function (momentum space) the data tell you everything you need to now in order to extract all single particle properties of the investigated material. More concrete, the aim was to show that it is possible to extract the electron density (real space) from ARPES spectra collected at \( k \)-points sampling the whole BZ, Fig. 4.4(b). By definition, the spectral function is in fact the imaginary part of the single-particle Green function (whereas the real part, \( \text{Re}(G) \), can be extracted by a Kramers-Kronig transformation):

\[
G(k, \omega) = i \cdot A(k, \omega) + \text{Re}(G) \quad \text{(Eq. 4.2)}
\]

The sought charge density can be extracted from the real space Green function in a straightforward manner. However, to transform the available momentum-space Green function to real space is not a trivial step. In the case of free electrons this operation is a basic Fourier transform. In the experiment presented in Paper V electrons of the copper valence band reside in a periodic potential and cannot be considered free and the Fourier like transformation should include the eigenfunctions \( \langle \Psi \rangle \):

\[
\rho(r, \omega) = i \cdot G(r, \omega) = \int_{\text{BZ}} \Psi^* \cdot G(k, \omega) \cdot \Psi \, d^3k \quad \text{(Eq. 4.3)}
\]

Consequently, if the transformation should be performed correctly, information regarding the eigenfunctions of the system is needed. Further, \( G(k, \omega) \), and hence \( A(k, \omega) \), should be recorded for the complete integration range \( i.e. \) the entire BZ.
Since the exact eigenfunctions are not known, an approximate bases set is constructed. For this experiment plain Cu was chosen as a model system (for many reasons mentioned below). The Cu valence band measured using SX-ARPES is heavily dominated by spectral weight from Cu-3\textit{d} bands. Given these conditions, it is assumed that the system can be well described by tight-binding functions constructed from Cu-3\textit{d} orbital functions:

\[ \varphi_{\mu}(\mathbf{r}) = f_{n\ell\mu}(\mathbf{r}) = R_n(\mathbf{r}) \cdot Y_{\ell\mu}(\theta, \phi) \]  \hspace{1cm} (Eq. 4.4)

These are built up from spherical harmonics (\(Y_{l\mu}\)) and Herman-Skillman radial functions \([41]\) (\(R_n\)) with \(n = 3, 1 = 2\) (\(d\)), and \(\mu = 1...5\) (\(xy, yz, xz, z^2\) and \(x^2-y^2\)), that are then summed over the twelve nearest neighbors (\(R\), see Fig. 4.4(a)) according to:

\[ \varphi_{\mu}^{i}(\mathbf{r}, \mathbf{k}) = C \cdot \sum_{\mathbf{R}} \varphi_{\mu}(\mathbf{r} - \mathbf{R}) \cdot e^{i(\mathbf{k} \cdot \mathbf{R})} \]  \hspace{1cm} (Eq. 4.5)

Tight-binding functions can then be constructed from linear combinations of Eq. 4.5:

\[ \Psi_{m}(\mathbf{r}, \mathbf{k}) = C_{m1}(\mathbf{k}) \cdot \varphi_{1}^{i}(\mathbf{r}, \mathbf{k}) + ... + C_{m5}(\mathbf{k}) \cdot \varphi_{5}^{i}(\mathbf{r}, \mathbf{k}) \]  \hspace{1cm} (Eq. 4.6)

where the constants \(C_{m1}...C_{m5}\) should be determined by solving the corresponding eigenvalue equations. However, in the present context the exact values of these coefficients have turned out to be of minor importance.

Fig. 4.4: (a) Crystal structure of Cu (FCC) showing a central atom and twelve nearest neighbors. (b) The bulk Brillouin zone of FCC including the irreducible wedge into which all probed \(k\)-points can be folded.
As mentioned above this experiment was chosen to be performed on a copper single crystal. The reasons for selecting copper were many:

- Monoatomic material with simple FCC crystal structure
- Conducting (no charging effects)
- Easy to buy high quality (flat) single crystals
- Easy to clean (prepare a good surface) in UHV
- Strong photoemission signal originating from the filled d-bands
- LDA calculations are expected to give an accurate description of the electronic structure.

The last fact permits a straightforward comparison between theoretical and experimental charge densities. This was a very important point since the experiment itself was a proof of principle and the result needed to be easily verified.

As stated above, in order for the transformation to be accurate a complete momentum-space sampling is required. With today’s modern synchrotrons and analyzers, the best approach to acquire k-resolved electronic structure from three-dimensional systems is to use SX-ARPES. First of all the high energy allow access to a wide k∥-space window at moderate emission angles (see Eq. 1.8). In most compounds this window (or slice) is big enough to cover a complete Brillouin zone* without changing the polar angle of the sample. In addition, the moderate emission angles that are needed will also result in an insignificant deviation from a straight line in momentum space. In addition, the increased λ_{mfp} will also result in an improved k⊥-resolution (Δk⊥ ≈ 1/λ_{mfp}). Hence the task of acquiring the spectral function for a complete three-dimensional set of k-points is uncomplicated. Given these conditions the ID08 beamline of the European Synchrotron Radiation Facility (ESRF) was the ideal location. With access to photon energies in the 400-600 eV range, liquid helium-cooled sample, a Scienta SES-2002 analyzer, and motorized manipulator, this experiment was a fairly simple yet time-consuming task. In total 121 two-dimensional ARPES spectra were collected corresponding to 4840 individual energy distribution curves (EDC) i.e. k-points.

* If the data is collected from the VB the kinetic energy of the electrons is close to that of the photons. For a Scienta SES-2002 analyzer the angular acceptance is ±6°, resulting in a k∥ window of approximately ±1.2 Å⁻¹ when using 500 eV photons. The new Scienta R-4000 has in fact an angular acceptance of ±15° → ±3 Å⁻¹.
4.4 Cu₂O (Paper VI)

Cuprous oxide*, Cu₂O, has attracted significant attention for the last five decades. During recent years this p-type wide bandgap (direct \( E_g = 2.17 \) eV) material have been in the center of attention for applications regarding e.g. solar energy conversion [42] and catalysis [43]. Cu₂O has a simple cubic structure where oxygen atoms form a BCC lattice and every oxygen atom is surrounded by a tetrahedron of copper atoms (see Fig. 4.5). Each copper atom thus binds to two oxygen atoms in an unusual linear fashion, a type of bonding that is also present in the CuO₂ planes of high-temperature superconductors (HTSC) [44]. One of the long-term objectives for this opening study of the electronic structure of Cu₂O was in fact to obtain an increased understanding of the HTSC and related phenomena observed in more complex cuprate materials (e.g. \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \), see below).

![Crystal structure of Cu₂O](image)

**Fig. 4.5**: (a) Crystal structure of Cu₂O. Big red spheres are oxygen atoms and small copper colored spheres are copper atoms. (b) Brillouin zone and high symmetry points

As already mentioned this oxide has been thoroughly studied, also with photoemission. However, until now the only ARPES study found in the literature was performed using low-energy ARPES [45]. The quality of the data found in Ref. 45 was severely hampered by the limitations of investigating a three-dimensional electron structure using low-energy ARPES. The first aim for our experiment was to acquire data from a symmetry direction not reachable in previous measurements. Further, by means of SX-ARPES the quality of the data could be highly improved and the results presented in Paper VI will show that this approach was very successful. The experiment was a straightforward task where the strength of SX-ARPES is manifested in the fact that only two 2D ARPES spectra at two different photon energies were needed and that the sample never had to be moved at all during the entire measurement. The data were collected at the BL25SU beamline of the SPring-8 synchrotron radiation facility in Japan.

* Also known as cuprite.
4.5 High-Temperature Superconductors (Paper VIII-XIII)

In 1911 Kamerlingh-Onnes [46] first discovered superconductivity (SC) in Hg below a critical temperature $T_c = 4.2$ K. With the discovery of the isotope effect [47, 48] a major breakthrough in the understanding of SC occurred. In conjunction with an independent statement by Fröhlich [49], this strongly indicated that the electron-phonon interactions were primarily responsible for the SC. This suggestion was further supported in 1957, when Bardeen, Cooper and Schrieffer presented their BCS-theory [50]. Their theory hence gave a natural explanation to the fact that SC only occurred at very moderate temperatures (at least in 1957, see Fig. 4.6). However, in 1986 Bednorz and Müller [51] presented SC in the copper oxide compound LaBaCuO$_4$ at $T > 30$ K. This paper was the start of a very intense hunt for SC in similar compounds and within a couple of years the highest known $T_c$ climbed to almost twice the boiling temperature of nitrogen.

These so-called cuprate high-temperature superconductors (HTSC) all have a similar crystal structure. The common feature for these compounds is that they all consist of stacked CuO$_2$ layers intercalated with other oxide layers (see Fig. 4.7). There is
somewhat of a consensus today that the intermediate metal oxide layers merely function as charge reservoirs whilst both normal conduction and superconductivity occur in the CuO$_2$ layers. The latter are believed to be responsible for the HTSC since the Cu-O bands are the lowest-energy electronic states and therefore should determine the macroscopic electronic properties.

As can be clearly seen from Fig. 4.7 the cuprate HTSC have a very anisotropically crystal structure with a lattice constants normal to the CuO$_2$ layers (c) that is very much larger than the lattice constants within the planes (a & b) [52, 53]. This anisotropy is visible in many of the macroscopic properties e.g. the resistivity that is very different in the c vs. the a and b directions. When it comes to electronic structure and ARPES measurements these layered compounds are more or less considered to have a quasi-2D electronic structure with very weak dispersion along the z-axis (along c). Consequently no final state approximation is considered to be needed, not even at low photon energies. However, at these low energies the small $\lambda_{\text{mfp}}$ will result in an very bad $k_{\perp}$-resolution ($\Delta k_{\perp} \approx 1/\lambda_{\text{mfp}}$). Hence, it is very hard to draw any conclusions about a possible $k_{\perp}$-dispersion from low-energy data.

The aforementioned charge reservoir layers play a key role for the cuprate SC. The metal atom of these layers can in reality be doped by substitution for metal atoms with different valence. One of the first HTSC La$_{2-x}$Sr$_x$CuO$_4$ (LSCO), Fig. 4.7, is formed in this way. The parent compound La$_2$CuO$_4$ (LCO) is an antiferromagnetic
(AF) insulator. However, when substituting trivalent La atoms for divalent Sr the material is hole doped and turns into a metal already at very moderate doping. Most cuprate SC are hole-doped but one of the HTSC investigated in this thesis, Nd$_2$Ce$_x$CuO$_4$ (NCCO) is in fact electron doped. With increased doping level ($x$) these AF Mott-Hubbard insulators turn into metals at room-temperature due to the destruction of long range AF order. However, at low temperatures and moderate doping levels there exists a so-called “superconducting dome” in the phase diagram (see Fig. 4.8) that is bounded by the critical temperature $T_c$, under which these compounds display SC properties.

![Fig. 4.8: Schematic phase diagram for NCCO and LSCO showing how these compounds evolve from an AF insulator into metals and superconductors. $T_N$ is the Néel temperature and $T_c$ the critical temperature under which SC occurs.](image)

At present day there is no complete understanding regarding the mechanisms behind the superconductivity in cuprate HTSC. In fact not even the normal-state properties are fully understood or well described by calculations. Even though there is no shortage of proposed mechanisms, there is no consensus about which one (if any) is correct. This matter is heavily debated among the many research groups around the world that investigate HTSC. In order to understand the superconductivity in a specific compound on a microscopic level one needs to grasp the electronic structure. Here ARPES plays a major role because it is the most direct method of studying the electronic structure of solids. During the last five to ten years there has been a tremendous technical development in the field of ARPES, especially with the emergence of 2D electron analyzers with very high energy and momentum resolution. In addition, these analyzers make it possible to acquire a complete angle-resolved spectrum in a single measurement. In conjunction with the instrumental development, the quality of the samples has continuously improved. As a result, the number of publications regarding ARPES measurements on HTSC has literally exploded [54, 44] during the last five to ten years.
As mentioned, an important advantage of LSCO is that the hole concentration of the CuO$_2$ plane can be controlled by the Sr content ($x$). It is commonly believed that the understanding of the mechanism(s) behind high temperature superconductivity in the cuprates is intimately related to the understanding of the doping evolution of these systems i.e. how the Mott-Hubbard insulator evolves into a “normal” metal and SC. A detailed doping dependent ARPES study of the electronic structure and scattering processes in this compound is presented in Paper VIII-XI. The motivation for this study was initially the lack of high-quality ARPES data in the literature. Compared to e.g. Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) there were only very few papers presenting ARPES data from LSCO. The reason for the low quality of the previous ARPES data was most likely due to problems with sample homogeneity/quality in combination with surface degradation. The high quality of the samples used in this study [55, 56], had prior to the ARPES measurements been thoroughly verified by neutron scattering (NS) [57] and muon spin rotation ($\mu$SR) [58].

The present experiments were chosen to be performed at the SIS beamline of the SLS. There were many reasons for choosing this specific location:

- Extremely stable electron beam resulting in very stable photon energy$^*$
- Suitable photon energy range (VUV)
- High energy and momentum resolution
- Possibility to freely select the polarization of the light
- Low sample temperature (base-temperature of sample $\approx$ 11 K$^\dagger$)
- Motorized high-precision manipulator with five degrees of freedom ($x, y, z, \text{polar, azimuth}$) allowing versatile $\mathbf{k}$-space (FS) mapping
- Very good UHV conditions (crucial for measurements of these samples that tend to degrade very fast in bad vacuum)

In addition to the VUV measurements with very high resolution, one of the objectives was also to investigate differences between the surface and bulk electronic structure in these materials (Paper XII-XIII). PES experiments performed on other strongly correlated materials found in the literature [59], using less surface sensitive (higher) photon energies, have showed that the electronic structure and correlation effects could be very much different in the bulk than at the surface. By performing measurements at the ID08 beamline of the ESRF (NCCO) and the BL25SU beamline of SPring-8 (Nd-LSCO) using SX-ARPES it was possible to acquire more bulk sensitive information.

$^*$ Under optimal conditions no change in the photon energy (below a few meV) is visible even after measuring for several days

$^\dagger$ Currently being upgraded with a new manipulator having six uncoupled degrees of freedom and with a base-temperature of the sample $< 6$ K
Finally I will try to give my brief opinion on how the ARPES technique should and might evolve within a near future. As the quote at the top of this page enlightens us, predictions are always hard. Nevertheless, this might at least be an amusing chapter to read, especially in a couple of years.

5.1 Prospects for ARPES

- One thing that sometimes is forgotten is the size of the light-spot that probes the sample. In ARPES, and especially soft x-ray ARPES, it is crucial that the sample and surface is of very high quality in order to achieve good momentum resolution. Hence, the bigger light-spot is used the bigger volume of the sample needs to be single crystalline. The samples of interest have evolved from being pure elements to compounds with increasingly complex composition and crystal structure. This makes it more difficult to produce large single crystalline samples. The ideal development would be to aim for an **extremely small light-spot** e.g. sub 1 μm spot. This would allow APRES measurements to be performed even on a single domain of a polycrystalline sample*.

- The development of the **free-electron lasers** will allow time-resolved ARPES (pump-and-probe) similar to the laser measurements presented in this thesis, but at higher photon energies and with increased opportunity to tune the photon-energy.

- **Very low-temperature ARPES** experiments is something that have already begun to evolve [60]. Up till present day, experiments have been limited to base temperatures of approximately 10 K. To allow better comparison with low-temperature data from e.g. transport measurements and neutron scattering, it would be most interesting to aim for even lower temperatures also in ARPES. In addition, low temperatures also facilitate a smaller thermal broadening i.e. higher energy-resolution.

* Also interesting for single crystalline samples since a small spot will reduce the noise in the spectra.
- The improvement of analyzers and monochromators will allow both better momentum and energy resolution, hence making soft x-ray ARPES even more interesting. One of the possible (and according to me most interesting) developments would be to move away from the so successful hemispherical detectors (e.g. Scienta SES-2002 etc.). At present time both Scienta/Gammadata [61] and Specs [62] are developing two-dimensional (detection of both \( k_x \) and \( k_y \)) angle-resolved time-of-flight, \textbf{ARToF, electron analyzers}. Hence in a single measurement it is possible to acquire not only EDCs along a line (like the Scienta SES-2002 mentioned above) but for a complete \( k_x/k_y \) plane in momentum space via a single measurement. These types of detectors will allow extremely high energy resolution (a few hundred \( \mu \text{eV} \)) for ARPES measurements performed at low photon energies using e.g. a laser as the light source. In fact I also believe that \textbf{lasers will be increasingly important as a low-energy light source} used for very high resolution \((k & \omega)\) ARPES.

- The \textbf{combination of a soft x-ray light source and an ARToF} would be an even more powerful tool. The energy resolution will be improved and the large available momentum window will allow \( e.g. \) binding energy dependent “Fermi surface”-mapping in a single measurement, without having to move the sample at all (see Fig. 5.1). However, one of the drawbacks of a ToF analyzer is that the light source needs to be pulsed. Hence, in the case of a synchrotron, the bunches need to be separated enough in time. When ESRF is run in 16-bunch mode, the time between bunches is approximately 175 ns \( i.e. \) this could be a possible choice. However, the ideal source for the future will of course be a high repetition rate soft x-ray FEL.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{artof}
\caption{The combination of a 2D ARToF, bunched synchrotron radiation source (or XFEL), and a soft x-ray beamline will allow binding-energy dependent Fermi surface mapping [63] in a single measurement.}
\end{figure}
TARPES measurements on the clean Ge(111)c(2×8) surface reveal two normally unoccupied adatom states that can be followed throughout the whole surface Brillouin zone (SBZ). From a clear dispersion it is evident that the adatom states are not purely atom-like and in fact rather delocalized. The time-resolved data show that the two adatom states differ significantly in decay times and that the lifetime depends on localization in the SBZ. Finally by studying the time-resolved data from both valence band (VB) and the excited states (ExS) it is shown that the adatom to restatom charge transfer of this surface might possibly occur through the adatom backbonds and that one of the restatoms (R2) plays a major role in this process.

When evaporating 1/3 ML of tin onto this surface a (√3×√3)30° reconstruction of the partly empty Sn-adatoms is achieved. It is well known that the Ge(111):Sn(√3×√3)30° surface at room-temperature displays dynamic properties manifested by I. surface soft phonon assisted fluctuations of Sn adatoms in the z-direction and II. rearrangement of charge through a possible sliding charge density wave (CDW) or bond density wave. As a result, when performing time-integrated measurements (e.g. STM, PES, LEED) the surface displays (√3×√3)30° symmetry on average. This dynamic system is in a very sensitive state of equilibrium easily disturbed by adding (or removing) extra electrons into only a fraction of the Sn dangling bonds. Hence, when pumping electrons into the Sn dangling bonds the balance of the surface is disturbed. By scattering and recombination of the excited electrons the balance is restored. As a result an estimate for the time between each collective and coherent adatom flip (Δt) could be extracted from the lifetime of the excited state yielding Δt = 9 ps i.e. an adatom switching frequency vsW ≈ 0.1 THz. The results are found, contrary to scanning tunneling microscopy measurements [64], to agree well with values extracted from molecular dynamics simulations [65, 66] found in the literature.
Time-resolved photoelectron spectroscopy has been used to study the two polar InAs(111) surfaces. At the indium-terminated surface, InAs(111)A, a charge accumulation layer is formed in the surface and is seen in normal PES (no optical pumping) as a electronic structure just above the valence band maximum (VBM). Optical pumping merely resulted in a small expansion of this electronic structure. At the arsenic-terminated surface, InAs(111)B, no clear excited state was found, which finds its explanation in the charge removal from the surface into the bulk that occurs naturally in order to stabilize this surface. The very weak signal that is found is attributed to defect states of the surface. For both surfaces the lifetime of the excited state is found to be $\tau \approx 4-5$ ps. In line with previous measurements of the InAs(110) surface [38, 39] this fast decay is explained as a rapid diffusion of the excited carriers into the bulk. However, from calculations using the electron mobility of InAs and the depth from which electrons can be probed, the lifetime is expected to be even shorter. This discrepancy is most likely due to limitations in the experimental time-resolution.

Also the GaSb(001) surface has been studied both in time- and angle-resolved mode. A clear excited state is found approximately 250 meV above the VBM, which locates it in the middle of the fundamental bandgap. This state is found to be strongly confined to the centre of the surface Brillouin zone. In addition the lifetime of the excited state is found to be $\tau \approx 11$ ps, which again is explained as a rapid diffusion of excited carriers into the bulk.

**Contributions of the Candidate**

I had a large part in the preparations for the experiments and the data acquisition. I also played an important role in preparations and improvements of the experimental equipment used in Paper IV. Contribution was made to the data analysis and editing of manuscripts.

**Paper V – Charge density in solids**

In this paper a method for extracting the electron density from soft x-ray ARPES data is presented. Angle resolved photoelectron spectroscopy (ARPES) data is related to the spectral function of a system in a straight forward manner and can in principle be interpreted as the imaginary part of the Green function. By using high energy photons, it is possible to determine the evolution of the spectral function throughout the complete three-dimensional Brillouin zone of a material and thus to obtain information on the $k$ and $\omega$ dependence of the Green function. This study presents
ARPES data from a test system (Cu) collected using high photon energies (\(h\nu = 430-580\) eV). These data determine the spectral function \(\Lambda(\mathbf{k},\omega)\) at more than \(10^5\) k-points of the Brillouin zone of FCC Cu. By employing a Fourier-like transformation with approximate eigenfunctions it is demonstrated that the \(\mathbf{k}\)-dependent Green function can be transformed into the real-space equivalent. Further it is shown that this technique can extract the (real-space) electron density as a function of binding energy. The obtained charge density displays an interesting binding energy dependence with distinguished features directed towards (bonding) and away from (antibonding) nearest neighbor atoms. This picture agrees qualitatively with charge density extracted from LDA calculations and the principle is considered to be established.

**Contributions of the Candidate**

This paper is based on an original idea from Docent Oscar Tjernberg but has been a project where the candidate, Dr. Thomas Claesson and Docent Oscar Tjernberg all have made an extensive and major contribution to the work. I have contributed to experimental work, extensive data analysis, prepared all figures in the paper and the very first draft of the manuscript. The LDA calculations in the manuscript were performed by Dr. Thomas Claesson.

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**Paper VI – Soft x-ray ARPES on Cu\(_2\)O**

Cuprous oxide, Cu\(_2\)O has been probed by soft x-ray (hv=619 and 891 eV) ARPES. Novel data along the M-\(\Gamma\)-M direction of very high quality is presented. By the use of high photon energies and an effective background subtraction the present data give a much more apparent picture of the bulk band structure than previous studies [45]. As a consequence, it has been possible to make a direct comparison between experimental data and local density approximation (LDA) calculations, with and without the Hubbard potential \(U\). The clear band dispersion in the experimental data also made it possible to extract a refined \(U\) value, making the agreement even better than when using the values found in the literature. In addition the results confirm the existence of a hybridized Cu 3\(d\)–Cu 4\(s\) state located between the two main Cu 3\(d\) and O 2\(p\) band regions. This state has been predicted but, prior to this study, never experimentally proven.

**Contributions of the Candidate**

I was the project leader of the experiment, applied for beamtime and planned all experiments. I also took responsibility for the sample preparations, the data acquisition and performed the initial data analysis. In addition, I prepared most figures in the paper and had a large part in the editing of the final manuscript. The LDA calculations in the manuscript were performed by Dr. Thomas Claesson.
Paper VII – The on-board sample cleaver

In this instrumental paper a novel method for cleaving single crystal samples is presented. To acquire good cleaves from rigid samples, such as oxides, the alignment of the cleaving blade with respect to the internal crystallographic planes of these usually very small samples is crucial. This is extremely hard to realize as soon as the sample is introduced into vacuum. The system presented here is based on the idea to have the crystal cleaver incorporated into the sample holder. It is then possible to mount and align the sample ex situ before introducing it into the UHV chamber, which has many advantages:

- The blade can ex situ be aligned to a crystallographic plane using Laue x-ray diffraction. As a result the blade will always apply its force along the desired cleavage plane.
- Overall better sample cleaves/surfaces
- Even very rigid samples can easily be cleaved if aligned properly
- Very small samples can be cleaved since the sample and blade can be aligned using a stereo microscope.
- The cleaver and sample will have the same temperature.

The on-board sample cleaver was primarily designed for the specific purpose of cleaving LSCO samples at the SIS beamline of the SLS synchrotron radiation facility. These samples are known to be very hard to cleave but using this method it is now possible to more or less routinely achieve very nice cleaves from LSCO and similar rigid samples. Deducing from the nice results obtained at these experiments, (Paper VIII-XIII) this cleaving system has at present time also been exported to the ID08 beamline [25] of the ESRF.

Contributions of the Candidate
This is my original idea and I have produced all blueprints, developed the first prototype in collaboration with the workshop, and further developed the concept. Further, I prepared all figures and wrote the entire paper.
**Paper VIII-XI – Doping dependent ARPES study of LSCO**

These papers are founded on extensive experimental work performed during in total 7 weeks of beamtime at the SIS-beamline of the Swiss Light Source (SLS). To summarize, a doping dependent ARPES study of the high-temperature superconductor (HTSC) La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) have been performed, ranging from underdoped ($x = 0.10$) to overdoped ($x = 0.22$) samples. By careful mapping of the underlying Fermi surface for samples with different doping it has been possible to extract a number of novel results that can be summarized:

- The high-energy anomaly ($E_1$) is identified and it is disclosed how it disperses towards lower binding energies when moving from the nodal to antinodal point.

- The dispersion of $E_1$ displays a shape related to that of the $d$-wave superconducting gap, which is the first indication that the high- and low-energy responses might in some way be interconnected.

- It is also found that the inelastic scattering rate at both high and low binding energy is highly anisotropic. For optimally and close to optimally doped samples the scattering rate is elevated when moving towards the antinodal point.

- In Paper X intriguing results reveal how the anisotropy of the scattering rate between the low energy kink $E_0$ and $E_1$ is reversed when passing the $x = 1/8$ doping level. Supported by theoretical predictions these novel results can be connected to a quantum phase transition between two different superconducting states.

- In addition, the superconducting gap for the optimally doped samples is acquired. Contrary to results found in the literature, a simple $d$-wave gap is found and no evidence of the alleged “double-gap” structure can be distinguished.

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**Contributions of the Candidate**

These papers are a result of an extensive collaboration with the people of PSI/SLS. I had the key role in the sample surface preparation through the work presented in paper VII. In addition, a contribution was made through writing of applications for beamtime, extensive experimental work, initial and further development of computer scripts for data analysis of the FS mappings. In paper X, I have performed the data analysis, prepared all figures and written the paper. To paper VIII & IX the contribution is (in addition to the above mentioned) in the form of editing of figures and final manuscripts.
Paper XII-XIII – Photon-energy dependent Fermi surface investigation of Nd-LSCO and NCCO

In principle all ARPES studies performed on cuprate HTSC have been performed at photon energies in the 10-100 eV range. At these energies PES is a very surface sensitive technique and the acquired data only contain information about the topmost atomic layer(s). In these two papers, the ARPES data have been collected in bulk sensitive mode ($h\nu = 400/500$ eV) as well as surface sensitive mode ($h\nu = 55$ eV) for the case of $\text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4$ (Nd-LSCO).

In Paper XII, soft x-ray ($h\nu = 400$ eV) ARPES is performed on $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ (NCCO, $x = 0.15$). The near Fermi level electronic structure was investigated by acquiring a set of momentum cuts crossing the FS. When compared to low-energy results found in the literature [67, 68] the FS was still found to be centered on the $\Gamma$-point but the shape was considerably different. For the high-energy data the shape was found to be more “diamond-like”. From the FS volume the doping-level was found to be approximately the same as for the low-energy data. Hence, the change in FS shape was not attributed to doping-effects.

In Paper XIII, Nd-LSCO has been investigated by both high- and low-energy ARPES. The low-energy data ($h\nu = 55$ eV) show substantial differences compared to the only other data set found in the literature [69]. The data presented here show a distribution of near Fermi level spectral weight that is almost uniform along the entire Fermi surface (FS) outline. In addition, the FS contour is almost circular and with a radius of curvature centered on the $(\pi,\pi)$ point, i.e. very different from the small linear patches presented in Ref. 69. Consequently, our data show no signs of strong charge modulations. When shifting to $h\nu = 500$ eV, both shape and intensity distribution changes. The FS contour is still almost circular but now with the radius of curvature centered at the $\Gamma$-point rather than $(\pi,\pi)$. In addition possible small pocket segments appear near the $(\pi,0)$ points.

The results presented in these two papers clearly highlight the photon energy dependence of the FS in cuprate HTSC. The most probable cause of these differences is found in the increased probing depth of the soft x-ray light. Consequently, for these samples the electronic structure of the atomic planes closer to the surface are found to be very different from the planes located deeper into the bulk. These results raise imperative questions regarding the relevance of low energy ARPES data for the understanding of HTSC.

Contributions of the Candidate

For both papers, I have made a contribution to the experimental work, editing of figures and final manuscripts. For paper XIII, I was the project leader and planned the experiment. I also had a major part in the data acquisition and performed the initial data analysis.