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Angle-resolved photoemission study and neutron diffraction measurements on LaSb2

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ANGLE-RESOLVED PHOTOEMISSION STUDY AND NEUTRON DIFFRACTION MEASUREMENTS ON LaSb$_2$

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Department of Physics and Astronomy

by

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ABSTRACT

LaSb2 has recently been found to have unusual magnetoresistive properties despite the fact that neither La nor Sb are magnetic. The resistance is anisotropic, and at high magnetic fields presents an anomaly that might be a result of a charge density transition. The magnetoresistance is anisotropic and linear, and the resistivity presents high relative changes when a magnetic field is applied. Discovered in 1954, LaSb2, as the rest of the light rare-earth diantimonides, was poorly studied. The anisotropic magnetic properties reported in 1998 by Bud’ko, Canfield and their collaborators make the series very interesting. A description of the electronic structure and Fermi surface topology would be of great help in understanding the properties exhibited by LaSb2, and the rest of the diantimonides.

Single-crystals of LaSb2 were grown by metallic flux method using high-purity La and Sb. Single-crystal X-ray diffraction measurements confirmed the SmSb2 orthorhombic structure with a=6.38 b=6.23 and c=18.75Å. LaSb2 presents a micaceous structure, with layers of Sb separated by bi-layers of La-Sb chains. X-ray measurements revealed a mosaic spread of ~0.5-1° and it is likely that the material is highly twinned. After the material is cleaved in vacuo, STM measurements give flat terraces separated by half unit-cell step edges.

High-resolution angle-resolved photoemission spectroscopy has been performed on LaSb2 to study the electronic band structure near the Fermi level and provide information to the Fermi surface topology. Photoemission studies show that the electronic structure is highly two-dimensional, and the locations of the critical points $\Gamma$ and Z in band dispersion are identified.
Neutron diffraction reveals doublet structures as a result of the crystal twinning. At low temperature, new spots are identified, indicating two new substructures that are incommensurate with the main lattice.

The reduced dimensionality of the system, the nested Fermi surfaces, and the new periodicities that develop at low temperature can be reconciled in a model characterized by strong electron-phonon coupling that result in a charge-density wave due to an associated Peierls instability and a lattice distortion.
CHAPTER 1 INTRODUCTION

Rare earth elements are located in the periodic table between the atomic numbers 57 and 104. The group splits into two blocks: lanthanides (which start with lanthanum with atomic number 57) and actinides (which start with actinium with atomic number 89).

The lanthanides are placed in the 5d block of the periodic table, and lanthanum is the first 5d transition element. The rare earth elements are not actually that rare now, but 50-60 years ago it was difficult to obtain them, and long, tedious purification processes were required in order to obtain metals from oxides [1]. Today, pure, low-cost rare earth elements can be produced by ion-exchange and solvent extraction processes. Some of the lanthanide series of elements can form during the fission of uranium and plutonium. Lanthanides are well known for the “lanthanide contraction”: the radius of the $3^+$ lanthanide ion decreases steadily with increasing of the atomic number.

Lanthanides are very reactive; they oxidize quickly when exposed to air, altering their silvery-white appearance. They are soft materials, with high melting and boiling points. Lanthanides react with water and $\text{H}^+$ and liberate hydrogen; react exothermically with hydrogen, burn easily in air, and at high temperatures ignite and burn strongly, and are strong reducing agents. Lanthanide compounds are other ionic and the ions are of pale color due to the weak, narrow, forbidden $f\times f$ optical transitions. Many lanthanide compounds fluoresce strongly under UV light and are strongly paramagnetic. Lanthanides present high coordination numbers, 8, 9 or even 12. With non metals, lanthanides react and form binaries upon heating.
Rare earth diantimonides RSb$_2$ were first found for the light rare earths only. In 1954 Vogel [2] and Klose reported compounds for La and Sb, with LaSb$_2$ being the first compound discovered, and in 1966 Olcese [3] reported the formation of Ce and Sb compounds. In 1967 the first extended study on diantimonides was reported by Wang and Steinfink [4], and included LaSb$_2$, CeSb$_2$, and SmSb$_2$. In this study the diantimonide structure is reported to be orthorhombic, as determined by single-crystal X-ray diffraction, and defined as SmSb$_2$-type structure. Wang and Steinfink found the Sb-Sb bond to be very short in the orthorhombic structures. They postulated that the Sb-Sb repulsion from short bonds causes a decrease in bond strength, as the rare earth size decreases [4].

Thirty years later, in 1998, P.C. Canfield, S. L. Bud’ko and their collaborators studied the magnetic properties of light earth diantimonides including LaSb$_2$, CeSb$_2$, PrSb$_2$, NdSb$_2$ and SmSb$_2$ [5]. They performed susceptibility, resistivity, resistance and magnetoresistance as a function of temperature for a range of magnetic fields. The series of compounds shows an interesting and diverse range of physical properties. The magnetoresistance in the paramagnetic state was found to be anisotropic for all the members of the series. All compounds present a high relative change of resistivity in magnetic field. At low temperatures, the magnetoresistance was found to be very high, and the resistivity was found to be very low.

Except for LaSb$_2$, the rare earth diantimonides present ground states that are magnetically ordered. At zero magnetic field, CeSb$_2$ passes through several ordered phases, and in magnetic field and low temperatures it experiences metamagnetic transitions. Temperature dependent measurements of derivatives of both resistivity and
Figure 1.1. Inverse susceptibility of CeSb$_2$, inset: low-temperature susceptibility (after Bud’ko, Canfield and collaborators, [5]).

Figure 1.2. Zero-field resistivity of CeSb$_2$, I || (ab). Inset: temperature derivatives of resistivity and susceptibility [H || (ab)] (after Bud’ko, Canfield and collaborators, [5]).
Figure 1.3. Zero-field resistivity of PrSb$_2$, I $||(ab)$. Inset: enlarged low temperature part (after Bud’ko, Canfield and collaborators, [5]).

Figure 1.4. The 100K anomaly in resistivity of PrSb$_2$: effect of 55 kG magnetic field applied in different directions (after Bud’ko, Canfield and collaborators, [5]).
Figure 1.5. Zero-field resistivity of NdSb$_2$, I $\parallel$ (ab). Insets: enlarged low-temperature part; enlarged region around the anomaly at T=38K (after Bud’ko, Canfield and collaborators, [5]).

Figure 1.6. Inverse susceptibility of SmSb$_2$, inset: low temperature susceptibility (after Bud’ko, Canfield and collaborators, [5]).
Figure 1.7. Zero-field resistivity of SmSb$_2$, I $\parallel$ (ab) [open circles] and I $\parallel$ c [double crosses]. Note different Y scales on the graph. Inset: enlarged low-temperature part (after Bud’ko, Canfield and collaborators, [5]).

Figure 1.8. Temperature dependence of SmSb$_2$ at 55 kG, I $\parallel$ c, inset: low-temperature out-of-plane resistivity of SmSb$_2$ in zero and 55 kG applied field (after Bud’ko, Canfield and collaborators, [5]).
magnetization reveal three anomalies at 9.3K, 11.7K and 15.5K, as seen in Fig. 1.2. The derivative of magnetization presents an extra feature at 2.6K, and the origin of this anomaly remains unexplained as of today. The resistivity and magnetization measurements suggest that CeSb$_2$ experiences three magnetically ordered states at low temperature. By applying a magnetic field, changes in magnetization and magnetoresistance suggest transitions associated with spin-flip processes and rotation of spins, and these transitions take place at the same magnetic field values. It should be noted that these four magnetically ordered phases exist up to 2.5 kG; at magnetic fields greater than 2.5 kG only two phases occur.

Another member of the light rare-earth diantimonides series with interesting behavior is PrSb$_2$. Apart from the abrupt decrease in zero-magnetic-field resistivity for temperatures less than 5.1 K, the resistivity presents two anomalies at 100 K and just before the antiferromagnetic transition. The first anomaly is explained based on the loss of spin-scattering disorder in the AF transition, and might be similar to a phase transition associated with a charge- or spin-density wave. The idea is supported by the fact that an increase in the magnetic field does not create a shift in position for the anomaly. For the second anomaly the authors suggest a superzone gap formation at the Fermi surface due to AF ordering. Low temperature metamagnetic transitions are probed by magnetic field dependent magnetoresistance and magnetization data, for different field orientations.

NdSb$_2$ is another member of the diantimonides series that presents magnetic transitions at low temperatures. The anomaly present at 38K for temperature dependent zero-field resistivity measurements might be generated by a charge density wave. The behavior of NdSb$_2$ resembles a lot the PrSb$_2$ behavior.
SmSb$_2$ presents an anisotropic susceptibility that changes a few times with temperature, with an anomaly at 12.5K. In-plane and c-axis zero-field resistivity show an anomaly at the same 12.5K, due to the loss of spin-disorder scattering. The field-dependent magnetoresistance exhibits a very large increase at low temperatures (1.5K), which saturates for fields higher than 140 kG.

LaSb$_2$ is the only non magnetic compound of the series. Susceptibility measurements in magnetic fields up to 55 kG reveal a linear, almost isotropic susceptibility, and the compound appears to be an isotropic diamagnet, with a small temperature dependence. Zero-field resistivity measurements for temperatures larger than 50 K reveal a linear in-plane resistivity and a metallic behavior. Both in-plane and the c-axis magnetoresistivities are anisotropic in the field direction and this is more pronounced at low temperatures, but present up to 100-150K [5].

In figure 1.10., the curve plotted with open circles curve corresponds to a current applied in-plane, and the crosses correspond to a current applied parallel to the c-axis. The change in resistivity for a current parallel to the c-axis, $\rho_c$, is much larger (by a factor of 12.5) compared to the change of resistivity for a current applied in-plane, $\rho_{ab}$, for the same temperature interval. For a current applied parallel to the c-axis, the resistivity presents a pronounced anomaly at 260 K. For a current applied parallel to the (ab) plane, the anomaly is much less pronounced. Currently, the origin of this feature remains unexplained.

When a current is directed parallel to the c-axis, the magnetoresistance is large at low temperatures (0-50 K) for both magnetic field orientations: in plane or parallel to the c-axis. The magnetoresistance remains anisotropic up to temperatures of 100-150K.
Overall, the resistance decreases monotonically with decreasing temperature, typical of a metallic material. As shown in Fig 1.12, a magnetic field applied parallel to the c-axis creates a peak in the resistivity at low temperatures. The peak starts forming around 12 K and is evident at a magnetic field value of 25 kG. As the magnetic field increases, the peak position moves towards higher temperatures. At the highest field studied 180 kG, the peak is near 23K, where it also has a maximum height of unknown origin.

For LaSb$_2$ no indication regarding superconductivity was reported for temperatures as low as 1.8K.

The large linear magnetoresistance exhibited by LaSb$_2$ was further studied by Young, DiTusa and their collaborators, who described the field suppression of the density of states as a mechanism for large linear MR. LaSb$_2$ was preferred to other light rare earth diantimonides because it is non magnetic and transport properties at low temperature are not affected by magnetic phase transitions. They found that the magnetoresistance changes by a factor of 90 for a magnetic field ranging between 0 and 45T.

The absence of saturation in resistance indicates that at higher fields the system might suffer a field-induced metal-insulator transition. LaSb$_2$ is non magnetic, and no magnetic ordering has been reported, even for very low temperatures. Considering that the compound is a quasi two-dimensional material, the anomaly induced by the magnetic field, as well as could be a magnetic-field-induced density wave transition [6].

Overall, the light rare-earth diantimonides are characterized by a highly anisotropic temperature-dependent magnetization, a large magnetoresistance and low
Fig. 1.9. Anisotropic susceptibility of LaSb$_2$ with anisotropic magnetization at 2K as inset (after Bud’ko, Canfield and collaborators [5]).

Fig. 1.10. Zero-field temperature dependent resistivity of LaSb$_2$ (after Bud’ko, Canfield and collaborators [5]).
Fig. 1.11. Temperature dependent magnetoresistance of LaSb$_2$ for a magnetic field of 55 kG and an applied current parallel to the c-axis. The open circles correspond to a magnetic field parallel to the c-axis, the triangles to a magnetic field applied parallel to the (ab) plane (after Bud’ko, Canfield and collaborators [5]).

Fig. 1.12. High-field transverse magnetization measurements for LaSb$_2$ (after Bud’ko, Canfield and collaborators, [5]).
resistivity at low temperatures. The magnetic members of the series have magnetically 
ordered ground states, with CeSb$_2$, PrSb$_2$ and NdSb$_2$ experiencing metamagnetic 
transitions at low temperatures. For large magnetoresistance exhibited at low 
temperature, Canfield and Bud’ko suggested few theories that may be appropriate. One of 
the theories implies special orientations of the magnetic field with respect to the Fermi 
surface and features of the Fermi surface (or of the ground state) defined by a spin- or 
charge-density wave [8-10]. Another model explains a linear increase in the longitudinal 
and transverse magnetoresistance as a result of fluctuations into a spin- or charge-density 
wave state, due to electron-phonon and electron-electron interactions. However, electron-
phonon scattering is not dominant at very low temperatures, 2-10K.

The group of light rare-earth diantimonides is a good candidate for charge-density 
wave (CDW) transition. The low dimensionality of the RE-Sb$_2$ and the anomalies in 
magnetoresistance, susceptibility and resistance exhibited at low temperatures suggest a 
CDW like state at low temperature.

Charge density waves are periodic modulations of the conduction electron density 
triggered at low temperatures, a Peierls distorsion. The periodic modulations are usually 
“paired” with lattice distorsions, having the same period as the CDW. The Peierls 
distorsions are induced by strong electron-phonon interactions that develop due to nested 
Fermi surfaces.

So far, very little information exists on the electronic structure and Fermi surface 
topology of the light rare-earths diantimonides. Both descriptions would be very useful 
for a better understanding of the electronic properties. Existence of charge-density waves
would be identified as the mechanism for the anomalies and the large magnetoresistance exhibited at low temperatures.

Our goals were to determine the electronic structure of LaSb$_2$ using high-resolution angle-resolved photoelectron spectroscopy (ARPES) and to investigate the existence of CDW by neutron diffraction measurements. Aside from solving the electronic structure and the dimensionality of the compound, ARPES can probe the formation of CDW as well. ARPES can determine the distribution of energy and momentum of occupied electrons in a solid. The energy distribution curve measured at a fixed momentum will provide information on the electronic state of a system. The Fermi momentum $\mathbf{k}_F$ is measured as a point in momentum space corresponding to a band crossing the Fermi level, $E_F$. A Peierls instability will lower the energy of electrons with wavevectors near the Fermi surface, creating a superzone gap in the single-particle excitation spectrum. Neutron diffraction measurements can detect satellite peaks around or near main Bragg spots, which change with temperature. These satellites are attributed to lattice distortions that indicate a charge ordered state.

1.1. References


CHAPTER 2. EXPERIMENTAL TECHNIQUES

2.1 Photoelectron Spectroscopies

Based on the photoelectric effect, photoemission spectroscopy represents the most important experimental technique for extracting information about occupied electronic states in materials. It measures the kinetic energy and momentum of an electron ejected from the sample to the vacuum when the sample is irradiated with mono-energetic photons [1].

Fig. 2.1. Schematics of the angle-resolved photoemission spectroscopy

Depending on the energy range for the incident photons, the technique might be called UPS (UV Photoemission Spectroscopy – uses photons in the ultraviolet spectral range) or XPS (X-ray Photoelectron Spectroscopy – uses X-ray radiation). The radiation can come from laboratory sources, such as ultraviolet gas discharge lamps or Al and Mg anode X-ray sources, or from synchrotron radiation. From energy point of view, UPS uses photon energies below 200eV, and a valence or shallow core electron is detected. In XPS, a core electron is emitted. Synchrotron radiation covers a large spectral range, from near-UV to far X-ray region, allowing one to perform both types of measurements.
Compared to XPS, UPS offers higher energy resolution due to the small intrinsic width of the rare gas discharge lines. In the case of monochromatic synchrotron radiation a constant resolving power $R = \Delta E/E$ means that the line width $\Delta E$ is smaller for smaller incident energies, $E$. Today UPS represents the most powerful tool for studies of the electronic band structure. Also, UPS is useful in verifying the cleanliness of the samples due to its sensitivity to oxygen, and carbon surface contamination, and can be used to determine the work function of a solid.

![Schematic view of UPS and XPS](image)

**Fig. 2.2.** Schematic view of UPS and XPS
2.1.1 Theory of Photoemission

In the photoelectric effect, a photon of energy $h\nu$ penetrates the surface and creates the optical excitation of an electron from an initial state to a final state. The excited electron propagates to the surface, and is emitted from the solid into the vacuum, through the surface. The electron has a binding energy $E_B$ measured with respect to the Fermi level of the electron spectrometer and is emitted with a kinetic energy

$$E_{\text{kin}} = h\nu - E_B - (E_{\text{vac}} - E_{\text{Fermi}})$$  \hspace{1cm} (2.1a)

or

$$E_{\text{kin}} = h\nu - E_B - \Phi$$  \hspace{1cm} (2.1b)

With

$$E_B = E_i - E_f$$  \hspace{1cm} (2.1c)

**Figure 2.3.** Energy level diagram for a negative-bias on the sample. The spectrometer can measure the kinetic energy cut-off, and the work function of the sample can be determined.
The energy distribution of photoelectrons is related to the electron energy distribution, or density-of-states, in the solid surface. In a photoemission spectrum, the electron emission becomes zero at a kinetic energy exactly $h\nu$ above the Fermi level. Therefore, the photoelectron spectrum can be directly recorded as a function of binding energy. A negative bias on the sample increases the kinetic energy relative to the spectrometer. The distribution of binding energies is characteristic for each element. The transition probability for the optically excited electron is given by Fermi’s Golden Rule:

$$\Gamma_{fi} = \frac{2\pi}{h} |<f, k|H|i, k>|^2 \delta(E_f(k)-E_i(k)-\hbar\omega)$$

(2.2)

where $E_f(k)$ and $E_i(k)$ represent the electron final and initial states, $\hbar\omega$ represents the incident photon energy [2].

The Hamiltonian has the form:

$$H = \frac{1}{2m} \mathbf{P}\cdot\mathbf{P} + V(r) = T + V$$

(2.3)

where $\mathbf{P}$ is the momentum operator, $V$ is the potential energy of the ground state.

In the presence of a photon field, the momentum operator changes to

$$\mathbf{P}' = \mathbf{P} + \frac{e}{c} \mathbf{A}$$

(2.4)

where $\mathbf{A}$ is the vector potential of the incident light. The new Hamiltonian becomes

$$H = \frac{1}{2m} \mathbf{P}'\cdot\mathbf{P}' + V(r) - e\Phi$$

(2.5)

$$H = \frac{1}{2m} (\mathbf{P} + \frac{e}{c} \mathbf{A})\cdot(\mathbf{P} + \frac{e}{c} \mathbf{A}) + V(r) - e\Phi$$

(2.6)

$$H = \frac{1}{2m} \mathbf{P}\cdot\mathbf{P} + \frac{e}{2mc} (\mathbf{P}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{P}) + \frac{e^2}{2mc^2} \mathbf{A}\cdot\mathbf{A} + V(r) - e\Phi$$

(2.7)
Considering that $\mathbf{A}$ and $\mathbf{P}$ do not commute

$$[\mathbf{A}, \mathbf{P}] = \mathbf{A} \cdot \mathbf{P} - \mathbf{P} \cdot \mathbf{A} = i \hbar \nabla \cdot \mathbf{A}$$

(2.8)

and that

$$\mathbf{P} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{P} = -(\mathbf{A} \cdot \mathbf{P} - \mathbf{P} \cdot \mathbf{A}) + 2 \mathbf{A} \cdot \mathbf{P} = -i \hbar \nabla \cdot \mathbf{A} + 2 \mathbf{A} \cdot \mathbf{P}$$

(2.9)

By substitution, the Hamiltonian becomes

$$H = H_0 + \frac{e}{2mc} \left( -i \hbar \nabla \cdot \mathbf{A} + 2 \mathbf{A} \cdot \mathbf{P} \right) - e \Phi + \frac{e^2}{2mc^2} |\mathbf{A}|^2$$

(2.10)

$\mathbf{A}^2$ is small enough to be neglected, and we by choosing a gauge transformation such that

$$\Phi = 0 \text{ and } \nabla \cdot \mathbf{A} = 0$$

(2.11)
the Hamiltonian becomes

$$H = H_0 + \frac{e}{2mc} (2A \cdot P - \text{i} \hbar \nabla \cdot A) + V(r)$$

(2.12)

For a transverse wave

$$\nabla \cdot A = 0$$

(2.13)

therefore the Hamiltonian can be written as

$$H = H_0 + \frac{e}{mc} (A \cdot P)$$

(2.14)

For UV photon energies \(10<\hbar\omega<120\ eV\), the wavelength of the light is large compared to the atomic dimensions and the vector potential \(A\) can be considered constant, and only \(P\) is responsible for the perturbation. The transition probability becomes

$$\Gamma_n = \frac{2\pi}{\hbar} |A<f, k|P|i, k>|^2 \delta(E_f - E_i - \hbar\omega)$$

(2.15)

which represents the electric dipole approximation. The \(\delta\)-function describes the conservation of energy for an electron from an initial state \(E_i\) to a final state \(E_f\) of the electronic band structure. The corresponding wave functions represent the exact many-body eigenstates of the system before and after the photon absorption. The peaks in the photoemission spectrum represent single particle eigenstates which disperse with the photon energy.

2.1.2 Ultraviolet Photoelectron Spectroscopy (UPS)

UPS is the most powerful experimental tool used to determine the electronic band structure. UPS can be also used to determine the work function of a solid, and to verify the cleanliness of a sample (the technique is very sensitive to oxygen and carbon surface contamination).
2.1.3 Angle-Resolved Photoemission Spectroscopy

When a movable electron energy analyzer is used to record angle resolved spectra, the method is called Angle-Resolved UV Photoemission. It gives information that can be related to specific parts of the reciprocal space, mainly on densities of occupied electronic states.

Fig. 2.5. Transition between an initial and final state in the photoemission process.
Knowing the kinetic energy and the emission direction, one can determine the electron wave vector, and finally the dispersion of the electronic bands \( E(k) \) and \( E(k_{||}) \) for bulk and surface states.

In an angle-resolved photoemission experiment, a sample is illuminated with monochromatic light and the energy distribution of the emitted electrons is observed. The kinetic energies of the emitted electrons and their directions are measured, and the properties of the initial state can be defined if the properties of the excitation process are known. The analyzer should have a small aperture, accepting electrons in a small solid angle, and can move in the polar and azimuthal directions.

The electric field direction and the vector potential \( A \) for the photoexciting electromagnetic wave with respect to the crystal lattice depend on the angle of incidence \( \alpha \) and the polarization of the photons and the plane of incidence.

In the free-electron final-state approximation, the emitted electrons have a wave vector of magnitude

\[
k_f = \left(2m \frac{E_{\text{kin}}}{\hbar^2}\right)^{1/2}
\]  

(2.16)

and the emission direction is determined by the angles \( \theta \) and \( \varphi \). \( E_{\text{kin}} \) is the kinetic energy of the detected electrons.

In the photoemission process, the energy and momentum must be conserved. The reduced momentum is well defined, even if an electron in a valence band does not belong to a single atom only. The wave vector \( k \) can be written as

\[
k = k_{||} + k_{\perp}
\]  

(2.17)
where $k_\perp$ is the component of the wave vector perpendicular to the surface, and $k_\parallel$ is the component parallel to the surface. In order to be detected in vacuum, outside the solid, electrons need to have an energy larger than the vacuum energy $E_{\text{vac}}$ and the wave vector $k$ in the final state to be directed outside the surface ($k_\perp > 0$). During transmission of the electron through the surface, due to the 2D translational symmetry, the conservation laws require that

$$k_\parallel(\text{f}) = k_\parallel(\text{i}) + G_\parallel$$  \hspace{1cm} (2.18)

where $G_\parallel$ is the parallel component of the reciprocal lattice vector, $i$ and $f$ represent initial and final states, and $k_\parallel$ is the component of the wave vector parallel to the surface.

For the energy conservation

$$E_f - E_i = \hbar \omega$$  \hspace{1cm} (2.19)

The perpendicular component $k_\perp$ is not conserved during the transition through the surface, and the initial state perpendicular component of the wave vector $k_\perp(\text{i})$ remains unknown. In order to determine $k_\perp$ one should have information upon the final state energy $E_f(k)$.

$k_\parallel(f)$ can be determined using energy conservation:

$$E_{\text{kin}} = \frac{\hbar^2}{2m} k^2(f) = \frac{\hbar^2}{2m} [k_\parallel^2(f) + k_\perp^2(f)] = E_f - E_{\text{vac}}$$  \hspace{1cm} (2.20)

If we consider the work function $\Phi = E_{\text{vac}} - E_F$, and the binding energy $E_B$, then

$$\hbar \omega = E_f - E_i = E_{\text{kin}} + \Phi + E_B$$  \hspace{1cm} (2.21)

and the parallel component for the wave vector outside the crystal becomes
\[ k_{\parallel}(f) = \sqrt{\frac{2m}{h^2}} \left( \frac{h\omega - E_B - \Phi}{\sin \theta} \right) \]  \hspace{1cm} (2.22)

The perpendicular component of the wave vector is changed due to the surface potential \( V_0 \), and the outside component can be calculated using energy conservation.

\[ k_{\perp}(f) = \sqrt{\frac{2m}{h^2}} \left( \frac{E_{\text{kin}}}{\cos \theta} \right) = \sqrt{\frac{2m}{h^2}} E_{\text{kin}} \cos \theta \]  \hspace{1cm} (2.23)

Also, the kinetic energy for a free electron in a constant inner potential \( V_0 \) can be written as

\[ E_{\text{kin}} = \frac{\hbar^2}{2m} k^2 - V_0 \]  \hspace{1cm} (2.24)

The components for the wave vector in the initial state can be calculated as

\[ k_{\parallel}(i) = \sqrt{\frac{2m}{h^2}} \left( \frac{h\omega - E_B - \Phi}{\sin \theta} \right) \sin \theta = \sqrt{\frac{2m}{h^2}} E_{\text{kin}} \sin \theta \]  \hspace{1cm} (2.25)

and

\[ k_{\perp}(i) = \sqrt{\frac{2m}{h^2}} \left( E_{\text{kin}} \cos^2 \theta + V_0 \right) \]  \hspace{1cm} (2.26)

where the inner potential is given as

\[ V_0 = \Phi + E_F \]  \hspace{1cm} (2.27)

Only electrons with positive wave vector component \( k_{\perp}(f) > 0 \) are able to reach the vacuum side and be observed in the photoemission experiment; the rest will be internally reflected, because their kinetic energies are not large enough to surmount the surface barrier.

The total photocurrent measured in a photoemission experiment is proportional to the joint density of states for which the final energy \( E_f \) has the same value as the detection
energy. The external parallel component of the wave vector $k_{\parallel}(f)$ provides information on the internal parallel component $k_{\parallel}(i)$. The problem arises when it comes to the perpendicular component: as this is not conserved, it is difficult to get information on the internal $k_{\perp}(i)$ component based on the external component $k_{\perp}(f)$. $k_{\perp}(i)$ is important when 3D band structures of bulk electronic states are studied. One solution would be normal emission ($\theta = 0$) photoemission, in which the parallel components are vanishing, and energy conservation will provide information upon the perpendicular components.

For the final states the energy is approximated by

$$E_f(k_{\perp}) = \frac{\hbar^2}{2m} k_{\perp}^2(i)$$

(2.28)

and the electron kinetic energy in vacuum is given by

$$E_{\text{kin}} = \frac{\hbar^2}{2m} k_{\perp}^2(f) = \frac{\hbar^2}{2m} k_{\perp}^2(i) + V_0$$

(2.29)

In determining which peaks correspond to bulk emission bands and which to surface emission bands, there are few things that must be considered for the analysis:

a) at different photon energies, the dispersion for $E_f(k_{\parallel})$ must be the same.

b) surface treatments do not affect bulk states, only surface states. Therefore, if an emission band of the clean surface disappears after gas adsorption (oxidation/surface contamination), it might be from a surface state.

c) surface states emission band must fall into a bulk-band gap

d) for normal emission the parallel components of the wave vector vanish. The surface-state band contributes at the $\Gamma$ point, and will occur at the same energy in
the spectrum, for different photon energies. The bulk-emission band will vary in energetic position, as the photon energy is changed.

In practice, eq. 2.27 references $V_0$ to $E_F$. The value for $E_F$ depends on the location of the zero of potential in the crystal. This can be considered to be the location of the bottom of the energy bands, as well. Experimentally, $V_0$ is determined by several techniques including the determination of critical points in band dispersion or triangulation using different crystalline orientations.

2.1.4 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was developed by Kai Siegbahn and his collaborators at Uppsala, Sweden. The technique is a simple process: a photon of energy $\hbar \omega$ penetrates the surface of the sample and is absorbed by an electron of binding energy $E_1$ which is then emitted into the vacuum. The kinetic energy of the emitted electron is

$$E_{\text{kin}} = \hbar \omega - E_B - (E_{\text{vac}} - E_F)$$

(2.30)

Fig. 2.7. Schematic view of XPS
The energy distribution of the photoelectrons depends on the energy distribution of the electron states in the solid surface, but the process is complicated by other phenomena that may occur (plasmon excitations, electron excitations, electron correlation effects), and by the fact that the photon absorption probabilities are not the same for all electron states. The binding energies are measured with respect to the Fermi level.

The core-level positions depend on the chemical state of the atoms, and based on that, shifts in the core level binding energies are related to changes in the local charge and potential. The shifts are called chemical shifts, and their study offers information on the chemical binding of the atoms in a system. Chemical shifts are used to identify chemical states of the atoms and to determine the electronic structure of a system.

In photoelectron spectra, extra features appear frequently, and are usually denoted by satellite peaks, found mostly on the high binding energy side of the main peak, and are final state effects. These satellites can be shake-up satellites (bound state excitation), shake-off satellite (excitation into continuum), or shake-down satellites (low binding energy). The shake-down satellites appear in metallic systems based on rare-earths (La, Ce, Pr and Nd), on the low binding energy side of the main peak. They are related to the hybridization strength between conduction electrons and the 4f electrons, and are stronger for the elements in the beginning of the rare-earth group. An unfilled 4f level is pulled below the Fermi level in the presence of a core hole. The filling of the 4f level creates the satellites. The intensity of the shake-down satellites is related to the hybridization strength in the final state.

Based on quantum mechanics’ rules of addition for angular momentum, the s core level peaks orbital creates a single peak, and the p, d, f orbitals will determine two peaks,
due to spin-orbit splitting. The number of electrons that contribute to a peak is \( N = 2J + 1 \).

For a shell that is missing one electron, the quantum numbers \( S \) (spin) and \( L \) (angular momentum) equal the \( S \) and \( L \) numbers of that electron. Therefore \( S = \frac{1}{2} \) and \( J = L \pm \frac{1}{2} \).

**Fig. 2.8.** Energy level diagram for a Ce metal atom. The unoccupied \( 4f^2 \) level is pulled below Fermi level in the presence of a core hole, and is filled by hybridization to the conduction band.

For each orbital we can calculate the number of electrons that contributes to a peak:

- s- electron \( L = 0 \rightarrow J = \frac{1}{2} \) (2 electrons)
p- electron  $L = 1 \rightarrow J = \frac{3}{2}$ or $\frac{1}{2}$ (4 or 2 electrons)
d- electron  $L = 2 \rightarrow J = \frac{3}{2}$ or $\frac{5}{2}$ (4 or 6 electrons)
f- electrons $L = 3 \rightarrow J = \frac{7}{2}$ or $\frac{5}{2}$ (8 or 6 electrons)

For a given total angular momentum the intensity in each core level is proportional to the number of electrons in the energy levels, and the intensity ratios between the spin-orbit split components can be calculated for a core level spectrum.

The intensity of a core level peak can be estimated after the background of the inelastic scattered electrons has been subtracted.

2.2 Auger Electron Spectroscopy (AES)

In 1925 Pierre Auger discovered the Auger effect [5]. Either photons or energetic electrons can induce the ionization of a core level, producing a primary core hole. The primary electron and the core electron leave the atom in an excited state. In order to relax to the ground electronic state the initial hole in the core level is filled by an electron from a higher-energy shell. The transition may result in the emission of an X-ray photon or in an Auger transition, in which the electron that filled the hole transfers its excess energy to another electron, which will be emitted at a characteristic Auger energy. The emitted Auger electron has a well-defined kinetic energy which depends only on the differences in energy levels of the atom. By measuring the kinetic energy one can identify the atom that underwent the Auger transition.

Auger spectra are recorded using an electron energy analyzer with an electron gun, or using LEED optics as a retarding field analyzer. AES is used to determine surface cleanliness, surface structure and composition [1].
Fig. 2.9. Typical Auger spectra.

Fig. 2.10. The Auger process
Modulating the voltage on the analyzer and amplifying the signal, one can measure the derivative of the signal to suppress the background of the secondary electrons.

Standard Auger electron spectra have been published for all the elements of the periodic table. This way, the surface composition (quantitative Auger analysis) and cleanliness (presence of the oxygen and carbon peaks) can be determined. The composition of a sample as a function of depth into the surface can be determined, by removing layer by sputtering (Ar- or Ne-ion bombardment). The technique is called depth-profiling, and it depends of the sputtering rate, area of the sample and sample inhomogeneities.

Fig. 2.11. Schematic view of Auger spectroscopy.
2.3 Scanning Tunneling Microscopy (STM)

Scanning tunneling microscopy is a direct method for imaging atoms on surface and is probably the most powerful structure analysis tool available so far. It was developed by Binnig and Rohrer [6], and it provides direct real space images of surface topography on an atomic scale. A tiny metal tip (typically W or Pt/Ir) is scanned across the sample surface and the electron tunnel current between the tip and the sample is recorded as a function of position. The scanning provides a real-space image of the surface, and provides information on the roughness and general morphology of the surface, down to atomic resolution. The spatial resolution, vertically and parallel to the sample surface, is in the range of Ångstroms.

Tunneling is a quantum mechanical effect in which electrons from one material penetrate through a classically impenetrable potential barrier (the vacuum) into a second conductor [2]. The wave functions overlap within classically forbidden regions, the overlap being significant only over atomic-scale distances [2]. The tunnel current $I_T$ depends exponentially on the distance $d$ between the tip and the sample surface, and to a first approximation is given by the formula

$$I_T \sim \frac{U}{d} \exp\left(-Kd\sqrt{\Phi}\right)$$

where $U$ is the voltage between the tip and the sample, $\Phi$ is the work function ($\Phi >> eU$), and $K$ is a constant. $K = 1.025 \ \text{Å}^{-1} \ (\text{eV})^{1/2}$ for a vacuum gap. The exponential dependence of $I_T$ on $\sqrt{\Phi}$ and $d$ provides the high sensitivity of the instrument to the surface electron density corrugations.
The metallic tip is scanned over the sample surface with piezoelectric elements (x, y, z). In constructing an STM, it is crucially important to isolate the instrument from thermal drifts and mechanical vibrations. In the inchworm design, the piezoelements are long tubes with multiple metal electrodes. By applying appropriate voltage pulses to the 4 split electrodes, the tube can be tilted, inducing motion in xy plane. Experimentally, several problems arise, including mechanical vibrations of the equipment in the UHV chamber and tip preparation. Due to the small distance between the tip and the sample surface, the vibrational amplitude must be small, less than one Ångstrom. The problem is solved by suspending the central stage of the STM on very soft springs, and often by aided eddy current damping induced in copper counter plates by powerful magnets. The tip is usually prepared from Pt/Ir or W wire, and grounded at one end. Tips can be sharpened by chemical treatments.

Equation (2.31) establishes the dependence between the tunneling current on both the work function \( \Phi \), and \( d \), which is the distance between the tip and the surface. Based on that, a locally varying work function or the existence of corrugation on the surface might induce variations of the tunneling current. The two effects can be separated. A constant \( \Phi \) – constant \( I_T \) scan will provide the surface topography in terms of the corrugation function. At a constant \( I_T \), changes in the work function are compensated by changes in \( d \). Measurements of the derivative of the \( I_T \) versus the distance between the tip and the surface will provide a surface topography in terms of the changes in the work function. The dependence between the work function and the derivative of \( I_T \) versus \( d \) is given by

\[
\Phi = \left( \frac{\partial \ln I_T}{\partial d} \right)^2
\]  

(2.32)
and any change in the derivative or in the $U_z$ voltage will indicate a change in the work function.

The dependence of the STM signal on the sign and magnitude of the voltage between the tip and the sample offer information on the electronic structure of the surface. A positive bias (negative tip with respect to the sample surface) causes electrons to tunnel from occupied metal tip states to empty surface states. A negative bias (positive tip with respect to sample surface) causes a tunnel current from occupied states in the substrate. Therefore, information on state distribution can be derived from the dependence of the tunnel current $I_T$ on the bias direction.

For obtaining good images, both tip and sample play important roles. The tip requires a good preparation, since best images result from single atom tunneling. The sample should be flat, due to the piezoelectric mechanism which does not allow large movements of the tip; for large hills, the tip might crash into the sample, destroying both sample and tip. STM offers direct information on point defects, kinks, surface morphology, symmetry, atomic spacing, vertical distortions, being an extremely valuable tool for surface investigation.

2.4. Neutron Diffraction

Neutrons are uncharged nucleons that, together with the protons, form the nuclei of the atoms.

Identified in 1933, neutrons are highly penetrating neutral particles and nondestructive probes, particularly sensitive to light atoms where X-ray scattering cross sections are small [7]. They have a magnetic moment and thus can be used to study microscopic magnetic structure and magnetic fluctuations.
Neutron can be produced by fission or by spallation. Fission is a process involving a continuous flow, and one neutron/fission event is produced.

\[ n + ^{235}\text{U} = n + n + \text{fragments} \quad (2.33) \]

Spallation does not involve a chain reaction. When energetic protons interact with heavy nuclei, up to 30 neutrons/protons are produced.

\[ p + \text{heavy nucleus} = 20\ n + \text{fragments} \quad (2.33) \]

The proton has an energy of 1 GeV, the heavy nucleus can be W, Pb or U, and the neutrons have an energy of 23 MeV/n.

The neutrons have a continuous wavelength band with wavelength, separated from Maxwell spectrum by a chopper or a crystal monochromator.

\[ \lambda = \frac{\hbar}{p} = \frac{\hbar}{\sqrt{2mkT}} \quad (2.34) \]

In interaction with atoms, neutrons suffer a nuclear, isotropic scattering that depends on nuclear structure and is determined empirically by the experiment. Absorption is very small (exceptions include Gd, Cd, B). Neutrons interact with nuclei via nuclear force, and with unpaired electrons via magnetic coupling.

In order to better understand the theory of diffraction, we describe first the concepts of real space lattice and reciprocal lattice.

All crystals can be described in terms of a lattice, having a group of atoms attached to each lattice point. The group of atoms forms a basis, which by repetition in space forms the crystal structure. The lattice is defined by the three fundamental
translation vectors \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \), and consists of all the points with position vectors that can be written as

\[
\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3
\]

(2.35)

where \( n_1, n_2 \) and \( n_3 \) are integers. An infinite array of discrete points with an arrangement and an orientation that appears the same when viewed from any point forms a *Bravais* lattice. All points in a *Bravais* lattice should satisfy eq. (2.35). If \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) are primitive vectors for the direct lattice, the primitive vectors for the reciprocal lattice can be written as

\[
\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)}, \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}
\]

(2.36)

and

\[
\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3
\]

(2.37)

The reciprocal lattice represents the set of all \( \mathbf{K} \) vectors that yield plane waves with the periodicity of a given Bravais lattice. For all vectors \( \mathbf{R} \) in a Bravais lattice, the wave vectors \( \mathbf{K} \) must satisfy the equation

\[
e^{i\mathbf{K} \cdot \mathbf{R}} = 1
\]

(2.38)

Miller indices identify crystal planes, and are the reciprocal of the intercepts of the plane with the \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) axes of the unit cell. In order to determine the Miller indices for a plane, one has to identify the intercept of the plane with the unit cell’s axes, to calculate the reciprocal of the intercept, and multiply by the smallest number that would convert the reciprocal to integers. If the indices are negative, then the negative sign is
replaced by an overbar. If the plane is parallel to an axis, the intercept is infinity and the reciprocal is zero.

Incident X-ray or neutrons scatter from on crystal planes. The path difference between the scattered rays is given by:

\[ d \cos \theta + d \cos \theta' = d \cdot (n - n') \]  \hfill (2.39)

Fig. 2.12. Path difference in scattering

For constructive interference

\[ d \cdot (n - n') = m\lambda \] \hfill (2.40)

and

\[ d \cdot (k - k') = 2\pi m \] \hfill (2.41)

In case of an array of scatterers (e.g. sites of a Bravais lattice)

\[ R \cdot (k - k') = 2\pi m \] \hfill (2.42)

or

\[ e^{i(k-k') \cdot R} = 1 \] \hfill (2.43)

where \( R \) is a Bravais lattice vector and \( K = k - k' \) is the reciprocal lattice vector.
In 1913 W. H. Bragg and W. L. Bragg gave the celebrated Bragg condition for constructive interference [8, 9].

\[ n\lambda = 2d \sin \theta \]  

(2.44)

They found that crystalline materials gave characteristic patterns of reflected X-radiation, and for certain wavelength values and incident directions, sharp peaks of scattered radiation appeared. Considering the crystal structure formed by parallel planes of ions, intense peaks should form when the radiation is specularly reflected by ions and when for ray reflected from successive planes there is constructive interference. In eq. (2.44) \( \lambda \) is the wavelength of the incident radiation, \( \theta \) is the incident angle, \( d \) is the distance between two planes, and \( n \) is the reflection order. This means that for a given set of lattice planes, multiple Bragg spots are observed.

Equation (2.43) represents the von Laue condition for constructive interference: if \( \mathbf{K} = \mathbf{k} - \mathbf{k}' \) is a vector of the reciprocal lattice, constructive interference will occur [10]. The two formulations corresponding to Bragg and von Laue are equivalent: a Laue diffraction peak corresponding to a change in wave vector given by the reciprocal lattice vector \( \mathbf{K} \) corresponds to a Bragg reflection from the family of direct lattice planes perpendicular to \( \mathbf{K} \) [3]. The order of Bragg reflection is obtained dividing the length of the \( \mathbf{K} \) vector to the length of the shortest reciprocal lattice vector parallel to \( \mathbf{K} \).

If the tip of the wave vector lies on a k-space Bragg plane, a Bragg reflection occurs. This means that the wavelength of the incident beam or its direction must vary in order to obtain Bragg peaks. The diffraction pattern will determine the crystal structure.
In 1913 details of a geometrical construction for interpreting the diffraction pattern has been published by Peter Ewald, well known today as the *Ewald sphere* [11-13]. In 2D the sphere becomes a circle.

![Ewald construction](image)

**Figure 2.13.** The Ewald construction.

When the incident beam 1 hits the crystal, Ewald’s sphere shows the set of planes at the Bragg angles where diffraction occurs. There are three methods of obtaining Bragg peaks using Ewald construction:

- **The Laue Method**: the crystal and the incident beam direction are fixed, but the incident beam wavelength is varied. The Ewald sphere will expand in a space between two spheres of radius $k=2\pi n/\lambda$ and $k'=2\pi n'/\lambda'$, and any reciprocal lattice that exists in this region will give Bragg peaks.

- **The Rotating-Crystal Method**: the incident beam is monochromatic and the direction of incidence is varied. In reality, the incident beam is monochromatic and at fixed incident direction and the crystal is changing its orientation around
a fixed axis. The reciprocal lattice will rotate by the same amount around the same axis, drawing a circle around the axis. Whenever this circle intersects the Ewald sphere, a Bragg point appears.

- **The Powder (Debye-Scherrer) Method:** In case of a powder or polycrystalline sample, we can not define the crystal axis anymore. The random orientation of the axis will generate a pattern corresponding to all possible orientation of the crystal (Fig. 2.14).

![Figure 2.14. The Ewald construction for the powder method.](image)
For a fixed incident \( k \) vector, the reciprocal lattice will rotate through all possible angles about the origin, generating spheres of radius \( K \) about the origin. For \( K<2k \), each reciprocal lattice intersection with Ewald sphere will result in cones of scattered radiation at an angle \( \phi \) to the forward direction.

But not all points in the reciprocal lattice will have Bragg reflections associated with them. The intensity of a Bragg peak is related to condition of constructive interference. The geometrical structure factor gives the possibility of having a Bragg peak or not.

\[
S_K = \sum_{j=1}^{n} e^{ik \cdot d_j}
\]  

(2.45)

When the structure factor has zero value, no Bragg peak appears. However, the structure factor can not predict the intensity of a Bragg spot, though the intensity is proportional to the square of the structure factor. For a zero value of \( S_K \), the interference is destructive.

2.5. References


CHAPTER 3. INSTRUMENTATION

3.1 Synchrotron Light Sources

Synchrotron radiation was discovered accidentally in an electron synchrotron by General Electric Company in 1947 [1]. It consists of a continuous band of the electromagnetic spectrum and it ranges from infrared through visible and ultraviolet to X-rays. In early theoretical considerations, it was thought to be linked to other processes producing radiation emitted in particle accelerators. Today we know that it is the radiation emitted from the acceleration of charged particles traveling at relativistic speeds. Synchrotron radiation is a natural phenomenon that existed since the beginning of the worlds. We can see it at night, coming from charged particles of matter spiraling through cosmos. The mechanism for production of synchrotron radiation was postulated by theorists one century back, but it was almost 50 years ago when man made sources appeared [2]. Since that time there have been three generations of synchrotron radiation sources:

- first generation sources used photons created by electron accelerators operated for high-energy research. Synchrotron radiation experiments operated in a parasitic mode, but the results proved promising and towards 1980’s accelerators were built for synchrotron radiation only.

- second generation sources were built to optimize synchrotron radiation from bending magnets. Synchrotron radiation was generated using a number of curved sections (bending magnets) connected by straight sections, that formed a circular orbit. The spectral distribution of synchrotron light from a bending magnet is based on J. Schwinger’s work on the spectral and angular distribution of
The spectral distribution from an accelerating particle in a constant magnetic field was found to be dependent on the particle’s energy. The spectrum can be parameterized using the critical energy defined as

\[
E_c = \frac{3hc\gamma^3}{4\pi\rho}
\] (3.1)

where \(\gamma\) is the ratio of the particle’s kinetic energy to its rest mass energy, and \(\rho\) is the radius of the trajectory’s curvature.

The critical energy can be written as

\[
E_c = 0.6651 \text{B[kG]} \cdot E^2 \text{[GeV]} \] (3.2)

The angular distribution from a bending magnet has an average opening angle given by

\[
<\theta^2>^{1/2} = <\Psi^2>^{1/2} - \gamma^{-1}
\] (3.3)

The collimation is lost after deflection, and only the vertical opening angle is observed. The opening angle depends on the X-ray energy and can be written as

\[
\sigma_r \sim (0.57 \gamma^{-1})(\lambda/\lambda_c)^{0.425}
\] (3.4)

Radiation from bending magnets is linearly polarized and parallel to the orbital plane. Out of the plane, radiation that is emitted is elliptically polarized due to a perpendicular component which is phased out by \(\frac{\pi}{2}\).

- third generation sources were built to optimize synchrotron radiation using insertion devices [4]. Insertion devices consist of periodic arrays that produce a series of deflections of the charged particle beam. The devices are placed into the
straight sections of the storage ring, with arrays of magnets above around the charged particle beam path. This arrangement changes the electron trajectory and for multiple bends it can result in extremely intense synchrotron radiation. Wigglers produce intense energetic radiation over a wide range in energies while undulators produce radiation of selected energy and variable polarization at high brilliance. In United States there are two third generation synchrotron light sources specially designed to use insertion devices: the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, which provides radiation in the soft X-ray and ultraviolet region, and the Advanced Photon Source (APS) at Argonne National Laboratory, which provides radiation in the hard X-ray region.

Insertion devices can be characterized by the field index or the deflection parameter $K$, given by

$$K = \frac{eB_0\lambda_{1D}}{2\pi m_0 c} = 0.0934\lambda_{1D}[\text{cm}]B_0[\text{kG}]$$

where $\lambda_{1D}$ is the period of the insertion device and $B_0$ is the peak magnetic field. For $K >> 1$, insertion devices are called wigglers. Wigglers cause multiple direction changes in the electron beam at high radii of curvature resulting in intense radiation at short wavelengths. The spectral distribution of the emitted radiation varies with the photon energy, and can, be characterized by the critical energy. This radiation is an incoherent superposition of each pole’s radiation and can be characterized by a critical energy that depends on the horizontal opening angle.

$$E_c(\theta) = E_{c_{\text{max}}} \left[1 - \left(\frac{\theta}{\theta_{\text{max}}}\right)^2\right]^{1/2}$$

$$E_{c_{\text{max}}} = \frac{0.511MeV}{\lambda_{1D}}$$

where $\lambda_{1D}$ is the period of the insertion device and $B_0$ is the peak magnetic field.
The polarization in the plane of the orbit is linear, perpendicular to the magnetic field, but above and below the orbital plane the radiation is unpolarized. If the magnetic fields are in x and y direction, then on-axis radiation is elliptically polarized.

Undulators are insertion devices with $K \sim 1$ and typically have a horizontal deflection angle $(\gamma^{-1})$. Undulators cause periodic changes in the direction of the electron beam and are designed to generate ultra-brilliant, single-wavelength radiation. This radiation is the result of a coherent superposition of radiation coming from each pole of the undulator. The polarization as a function of angle can be varied. If the undulator has magnetic fields both horizontal and vertical, the on-axis radiation will be elliptically polarized. If the undulator is linear with magnetic fields in a single plane, the on-axis radiation is highly linearly polarized and perpendicular to the magnetic field of the undulator.

The properties of synchrotron radiation are determined by the following factors: flux, brightness (brilliance), pulse length, tenability, polarization and coherence [5-8].

- **Flux** measures the intensity integrated over the vertical opening angle of the photon beam and is measured in photons/(s · mrad · 0.1 bandwidth).
- **Brightness** measures the concentration of the radiation and is inversely proportional to the size and divergence of the electron beam. Brightness can be defined as the number of photons emitted per second per square millimeter of source size, per square milliradian of opening angle, within a given spectral bandwidth. High brightness places a large number of photons into a small spot size.
• **Pulse length.** The electron beam in a synchrotron is not continuous, it is bunched into a number of packets. The time that it takes for one of these bunches to pass a point is the pulse length of the emitted light.

• **Tunability** means that the wavelength of the radiation can be varied, typically from the infrared through the X-rays.

• **Polarization** is the alignment of the electric field vector of the emitted radiation. Linearly polarized light allows one to control selection rules in the electronic transitions in atoms, molecules, and solids. Circularly polarized light is very useful in surface magnetism studies since it allows one to vary the spin and orbital nature of the transitions that are excited.

• **Coherence** is the degree to which the waves are in phase within a light beam at any moment, and the degree to which they remain like this as the beam propagates.

### 3.2. CAMD Synchrotron Light Source

The J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices (CAMD) is a synchrotron radiation research center at Louisiana State University in Baton Rouge, LA. It is the only state-funded synchrotron facility in US, operated by LSU, and offers research possibilities in the area of basic and applied sciences, from physics, chemistry, biology, and engineering to environmental sciences and geosciences.

The heart of CAMD is a second generation electron storage ring that produces soft X-rays. The storage ring is injected at low-energy 200MeV, and ramped to its operational energy of 1.3 GeV. The ring has eight bending magnets with a radius of \( r = 2.928 \text{m} \). Synchrotron radiation is extracted through two ports of each of the dipole
magnet chambers with a maximum horizontal angle of 70 mrad. One insertion device is currently in place. It is a 3-pole superconducting wiggler with a maximum field of 7T at the central pole and 1.55T at the side poles. The critical energy of the radiation from a dipole magnet is 1.7 keV while that from the wigglers is 7.9 keV. The wiggler is essentially a wavelength shifter to enable higher energy X-ray experiments.

Electron Storage Ring Parameters

Beam Energy (GeV) 1.3
Beam Current (mA) 300 / 150
Bending radius (meters) 2.928
Critical wavelength 7.45 / 4.85
Critical Energy (keV) 1.66 / 2.56
Beam half-life (hours) 9.5 / 6
Harmonic number 92
Radiative power (watts/mrad/mA) 0.014 / 0.024
Injection energy (MeV) 200
Natural emittance (m-rad) ~2x10^{-7}
Electron-beam width (mm) ~0.6
Electron-beam height (mm) ~0.15

Fig. 3.1. Spectrum of radiation from CAMD
CAMD has thirteen beamlines which can be divided in three groups: Micromachining and X-ray Lithography for microfabrication, Vacuum UV and Soft X-ray, for UPS, XPS, X-ray absorption, and X-ray, for XANES and EXAFS spectroscopy, protein crystallography, and tomography.

The VUV beamlines are:

- PGM (Plane-Grating Monochromator, accepting 7 mrad) is a high-resolution, high-order rejection beamline, with energy range 25-1000 eV, and $E/\Delta E$ (resolving power) of 10,000. Currently it is being upgraded to include a variable-line-spacing grating.

- 3mTGM (3-meter Toroidal Grating Monochromator, accepting 24 mrad) is a moderate resolution, high flux beamline, with energy range 15-350 eV and resolving power greater than 1000.

- 6mTGM (6-meter Toroidal Grating Monochromator, accepting 28 mrad) is a moderate resolution, high flux beamline, with energy range 15-300 eV and resolving power greater than 2000.

- NIM (3-meter Normal Incidence Monochromator, 70 mrad) is a high-resolution, high-flux beamline, with energy range 2-50 eV and resolving power between 10,000 (high energy) and 50,000 (low energy).

Experimental equipment at the end stations of these beamlines include angle-resolved two-axis hemispherical analyzer, ellipsoidal mirror electron-energy analyzer, and a high-resolution SCIENTA 200 analyzer, as well as various smaller test and sample preparation chambers.
3.3. 3m-TGM Beamline at CAMD

There are four VUV beamlines at CAMD: 3m-TGM, 6m-TGM, PGM and NIM, their location being indicated in figure 3.3. The 3m-TGM beamline provides moderate resolution with a resolving power greater than 1000 and photons in the energy range of 15-350 eV. The primary use of this beamline is for photoemission studies of solids and thin films. It operates in ultra-high vacuum ($10^{-10}-10^{-11}$ Torr), and the specimen position can be modified. The use of a toroidal grating makes this beamline a simple design since it both disperses and focuses the radiation and provides a fixed focal spot. Two gratings
are used since only one grating can not cover the whole energy range: a low energy grating covers the 10-38 eV range, and a high energy grating covers the 38-155 eV range.

**Figure 3.3** CAMD experimental hall layout with the VUV beamlines.

Ellipsoidal pre- and post-mirrors are used and inclined at $7.5^\circ$ with respect to the horizontal plane to ensure that the light exiting the monochromator is in the horizontal plane. For the measurements reported here, the main chamber attached to the 3m-TGM beamline is equipped with a hemispherical analyzer HA50, which is the main tool in performing high-resolution angle-resolved spectroscopy.
Fig. 3.4. 3-meter TGM beamline at CAM
The chamber is also equipped with an ion sputtering gun for cleaning the samples and Low Energy Electron Diffraction (LEED) optics to determine the surface crystalline order. The samples are inserted into the main chamber from a separate side chamber using a magnetic transfer arm.

3.4 The Hemispherical Analyzer HA50A

3.4.1 General Theory

An electron analyzer is designed to allow only electrons within a certain range of energies to pass through it. In order to maintain a constant throughput independent of the electron energy, the electrons are retarded or are accelerated in the input lens to a constant pass energy. This pass energy determines the energy resolution of the spectrometer.

3.4.2 Principle of Operation

When radiation of energy $\hbar\omega$ strikes a sample, electrons of kinetic energy $E_{\text{kin}}$ are ejected, where

$$E_{\text{kin}} = \hbar\omega - E_B - \Phi$$  \hspace{1cm} (3.8)

where $E_B$ is the binding energy of the electrons before ejection, and $\Phi$ is the sample’s work function. At low kinetic energies there is a large peak in spectrum due to secondary electrons which have scattered inelastically. The cut off of the spectrum will be when the kinetic energy equals the vacuum level, i.e. the zero in kinetic energy just outside the sample.

$$E_{\text{kin}} = E_{\text{vac}}$$  \hspace{1cm} (3.9)
Electrons with kinetic energies lower than the work function will not be ejected from the sample. The highest kinetic energy electrons will come from the Fermi level when the binding energy tends is smallest

$$E_{\text{kin}} = \hbar \omega - \Phi$$  \hspace{1cm} (3.10)

In metals, this Fermi edge is readily apparent in the spectrum. At intermediate energies peaks corresponding to the discrete states from which electrons are ejected are found. The work function characteristic to each sample can be estimated from the difference between $\hbar \omega$ and the separation of the Fermi and vacuum level cut offs in the spectrum. Before entering the analyzer, the ejected electrons pass through the first lens element and are retarded by an amount $R$, which depends on the lens voltages. The analyzer will transmit only electrons at the pass energy, and they will be detected in an electron multiplier. The kinetic energy of the electrons can be written as

$$E_{\text{kin}} = R + E_{\text{pass}} + \Phi_a = \hbar \omega - E_B$$  \hspace{1cm} (3.11)

$\Phi_a$ represents the work function of the analyzer, and $R + E_{\text{pass}}$ is the kinetic energy for the electrons.

**Fig. 3.5.** Diagram of the concentric Hemispherical Analyzer
The hemispherical analyzer consists of two concentric hemispheres of mean radius $R_0$ and common center $O$. A potential $V$ is applied between the surfaces such that the outer surface becomes negative and the inner surface becomes positive. For an electron of kinetic energy $E_0$, traveling in an orbit of radius $R$, the relationship between the applied voltage and the kinetic energy can be written as

$$eV = E_0 \left( \frac{R_2}{R_1} - \frac{R_1}{R_2} \right)$$  \hspace{1cm} (3.12)

The inner and outer voltages of the hemispheres are given by the equations:

$$V_1 = E_0 \left( \frac{2R_0}{R_1} - 1 \right)$$  \hspace{1cm} (3.13)

$$V_2 = E_0 \left( \frac{2R_0}{R_2} - 1 \right)$$  \hspace{1cm} (3.14)

$E_0$ being the pass energy of the analyzer. The electrostatic field between the hemispheres is inverse proportional to $R^2$. 

**Fig. 3.6.** UPS experimental arrangement with the analyzer and HAC300
There are two modes of operation while scanning the kinetic energy: fixed retardation ratio and variable pass energy (Fixed Retardation Ratio or FRR) and fixed pass energy and variable retardation ratio (Fixed Analyzer Transmission or FAT). The FRR is used mainly for Auger spectroscopy. Electrons entering the analyzer are retarded by the lens stack by a constant value that is proportional to their kinetic energy. In this way, the ratio between the electron kinetic energy and the pass energy of the analyzer has a constant value during an experimental scan. The retardation ratio is calculated as

$$k = \frac{1}{E_o} (E_K - \Phi_a) = \frac{1}{E_o} (R + E_0) \quad (3.15)$$

Sensitivity and resolution are proportional to the kinetic energy, and at lower kinetic energies sensitivity is reduced. The area of the sample and the emission angle stay constant for the whole kinetic energy range.

The Fixed Analyzer Transmission (FAT) mode passes electrons through the hemispheres at a constant energy. This means that the lens uses a variable retarding voltage, and this mode of operation offers a constant energy resolution for the whole kinetic energy range. The analyzer sensitivity is inversely proportional to the kinetic energy, therefore at lower pass energies the resolution is better. The area of the sample that is imaged and the emission angle vary slightly with the kinetic energy.

The energy resolution is given by

$$\Delta E = E_{\text{pass}} (d/2R_0 + \alpha^2/4) \quad (3.16)$$
where \( d \) is the slit width, \( R_0 \) the mean radius of the hemisphere, and \( \alpha \) represents the entrance angle for the electrons. The energy resolution will depend on the pass energy, slit width and the acceptance angle of the lens system.

There is a compromise between resolution and throughput, since one cannot have both. Low pass energy results in high resolution, but the sensitivity is low.

The HAC300 Analyser Cotrol Unit is a high precision power supply that controls the hemispherical analyser over a voltage range of 0-300 V, and provides the necessary lens and voltages for both modes (FAT and FRR).

The detector for the analyzer is a single channel electron multiplier, a small, curved, glass tube, coated on the inside with a high secondary-electron material. An electron entering the tube will collide with the wall ejecting a small pulse of electrons. The secondary electrons are accelerated down the tube, further colliding with the wall, generating more electrons in an avalanche effect. One event at the entrance will result in an electronic cloud of about \( 10^6 \) electrons, proportional to the applied voltage.

### 3.5. The Aarhus STM

The Aarhus Scanning Tunneling Microscope (STM) was designed and constructed at the University of Aarhus in Denmark. It is a highly compact instrument, with high resonance frequencies and very fast scanning speeds [10].

A diagram of the Aarhus STM is shown in fig. 3.7. The STM head is housed in an aluminum block (mass \( \sim 1 \) kg) that has a large heat capacity and maintains a constant temperature with only a small drift. The design of the STM is based on a 4 mm long scanner tube, with inner diameter of 2.67 mm and outer diameter 3.18 mm. The piezo tube is made of a EBL#2 (Staveley), with a low Q (80), and a high Curie temperature (350\(^0\)C).
Two opposite pairs of electrodes on the tube are driven asymmetrically for the x and y deflections, and the z motion control is determined by the voltage applied to an inside electrode. An inchworm motor is responsible for the tip coarse approach. The inchworm consists of a SiC rod (3mm diameter) fitted in a piezotube by two bearings. The SiC rod is lubricated with MoS$_2$ powder.

The piezo electrodes are driven by high voltage op-amps with a voltage range of ±200 V. 16-bit Digital to Analog converters (DAC, ± 5 V range) drive the high voltages and set the tunnel voltage. The feed-back circuit for operation in a constant-current mode consists of a tunnel preamplifier with a 1 V/nA gain, and a main amplifier with an adjustable ± 110 gain with 12-bit resolution.
The STM is cooled by liquid nitrogen (LN$_2$) that is passed through a tube held in intimate contact with the Al block. This system reaches a temperature of 120 K within a few hours.

While the block is cooling, the STM scanner tube needs to be maintained at room temperature. This is accomplished by passing current through a 75 V Zener diode mounted on the bottom of the scanner tube. The STM is thermally isolated from the Al cradle by means of quartz balls, and the diode will require only 304 mA to keep a temperature of ~ 300 K for the STM. The cradle may be heated with an isolated power supply with two 500 $\Omega$, 5 W resistors coupled in series and plugged into two Zener diodes built into the cradle. Considering the maximum voltage 16 V and the Al-cradle heat capacity 1 kWs$/$°C, the maximum temperature rise is ~ 1°C/min.

![STM control electronics outline.](image)

**Fig. 3.8.** STM control electronics outline.
The STM is mounted in an UHV chamber that plays the dual role of a main experimental chamber and a sample preparation chamber. The chamber design permits it to be coupled to other endstations at CAMD, allowing both STM and synchrotron radiation characterization on the same sample.

The chamber is equipped with
- a sputtering ion gun for cleaning the sample (Ar⁺ or Ne⁺ ions)
- Low Energy Electron Diffraction (LEED) optics to determine the crystalline structure
- Cylindrical Mirror Analyzer (CMA) for Auger Electron Spectroscopy (AES) to test the cleanliness of the surface
- four viewports
- main pumping port
- two ports 180° apart corresponding to two metal evaporators
- flange-mounted quartz crystal oscillator microbalance thin film thickness monitor
- quadruple mass spectrometer
- XYZθ sample manipulator and holder

Samples are loaded onto the magnetic transfer load-lock system that can transfer the samples from atmospheric pressure to UHV within few hours. A wobble stick pinscher mechanism can remove the sample from the transfer arm and move it to the sample storage garage, the STM or the XYZθ sample manipulator.

3.6 Neutron Sources

Neutrons were discovered in 1932 by Chadwick [11]. The first Bragg scattering by crystal lattice planes was first demonstrated in 1936 by Mitchel and Powers, and
Halaban and Preiswerk. Fermi’s group measured nuclear cross-sections using Bragg scattering [12]. And after 1945 the use of neutron scattering as a probe developed with the availability of slow neutrons from reactors. A reactor moderates neutrons resulting from the fission chain reaction, giving a Maxwellian distribution peaking at 300K. Most of the neutron sources were built in the U.S. decades ago and include: reactors, pulsed reactors, and pulsed spallation sources. In the United States there are 5 neutron beam sources available for users: two research reactors, High Flux Isotope Reactor (HFIR) at Oakridge National Laboratory (ORNL) (1966) and Neutron Beam Split Core Reactor (NBSR) at National Institute of Standards and Technology (NIST) (MD, 1969), and three spallation sources, Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory (ANL) (1981), Manuel Lujan Neutron Scattering Center (MLNSC) at Los Alamos National Laboratory (LANL) (1985) and Spalation Neutron Source (SNS) at ORNL (2006).

Reactors are very good sources for cold neutrons. They provide a high time averaged flux and mature technology from source and instruments’ point of view. Pulsed spallation sources provide a higher peak neutron flux and a good time.

### 3.6.1 Intense Pulsed Neutron Source at Argonne National Laboratory

IPNS was commissioned in 1981, and was the first Department of Energy (DOE) facility dedicated to users: 75% of the time is available to outside users. The facility represents a national collaborative research center for universities, industry and government laboratories, and is operated by the University of Chicago for the U.S. Department of Energy. Most of the 1st generation neutron time-of-flight instrumentation was developed at IPNS [13].
The IPNS accelerator operates at an average beam current of 14-15 µA, and pulses of $3 \times 10^{12}$ protons at 450 MeV are delivered 30 times/s to the target. The accelerator consists of an H⁻ ion source, a Cockroft-Walton preaccelerator, a 50 MeV Alvarez Linac, a 450 MeV Rapid Cycling Synchrotron, transport lines and ancillary subsystems.

The H⁻ ion source is a magnetron type in which negative ions are extracted from the hydrogen plasma on the surface of the source cathode. The extractor electrode and the magnet poles are at terminal ground potential. The pulsed arc supply, pulsed H gas supply and Cesium supply are pulsed to -20 kV potential. Cesium increases the H⁻ generation. The extracted H⁻ beam is bent 90° by a magnetic dipole to remove electrons from the beam. Three quadrupole magnets ensure focusing, after which the beam is injected into the high-voltage column of the preaccelerator.

The water-cooled linac (0.2⁰ F, cavity tuned at 200.07 MHz±1kHz) is a copper-clad-steel structure (0.94 m diameter, 33.5 m length), constructed in 11 sections bolted together, with 124 drift tubes, each with a dc quadrupole magnet. The beam exiting the linac is 1 cm in diameter and has an energy of 50 MeV. The pulsed current is 10 mA, and the 70 microsecond pulses are delivered at a rate of repetition of 30 Hz.

The Rapid Cycling Synchrotron was initially developed as a booster for the Zero Gradient Synchrotron high-energy physics accelerator, used afterwards for the ZING experiment, and in 1981 started providing beam to the IPNS target. With a circumference of 42.95 m, it accelerates the beam from 50 MeV to 450 MeV. The beam orbital radius remains constant during the acceleration due to a variable 0.28-1 Tesla magnetic field produced by the ring magnets.
The \( \text{H}^\text{+} \) stripping injection occurs due to a carbon stripper foil, and the equilibrium orbit is deformed in the injection area by three pulsed magnets. The beam is injected through a singlet ring magnet, so the path matches the orbit that has been deformed. The proton beam is accelerated by 2 ferrite-loaded cavities, it circles the ring in less than 200 ns, and is extracted by two ferrite-loaded kicker magnets and two septum magnets. The extracted beam is transported to the neutron-generating target which is Uranium.

Fig. 3. 9. Intense Pulsed Neutron Source layout (ref. [13])
The high-energy neutron pulse is short, and a moderator is used to spread it out.

The moderator slows down the neutrons as the neutrons bounce off the atoms of the moderator and transfer their energy and speed during collisions. A good moderator should meet the following criteria:

- **high-scattering cross section**: the probability that a neutron will scatter from a nucleus; it has to be high so the neutrons undergo as many interactions as possible
- **low-absorption cross section**: the probability that a neutron is absorbed by a nucleus; it has to be low so the neutrons are not soaked by the moderator
- **high energy loss per collision**: every collision should have a high energy transfer, so the neutron undergoes fewer collisions during the slow down process

IPNS uses methane as a moderator. The methane presents the following advantages:

- high energy transfer per collision
- high neutron scattering cross section
- high density for a short time between collisions
- low neutron absorption cross section
- high thermal conductivity
- chemical stability under irradiation
- suitable for low energy modes in the medium to couple efficiently to long wavelength cold neutrons
- more efficient than hydrogen due to the free rotor modes of the tetrahedral molecules
The system reliability, calculated as the ratio of hours-available to hours-scheduled, is above 80% for the last 10 years, and yearly averages are about 95%. The target has to be replaced each five years. Since 1983 the current is limited by beam-loss, and the yearly average current has exceeded 14 µA, sometimes reaching 15 µA.

Operating hours at IPNS are rather funding-limited than machine-limited. It operates up to 30 weeks per year, 24/7 (over 4500 hours of beam-on-target).

Fig. 3.10. The Rapid Cycling Synchrotron at IPNS-ANL (ref. [13]).
3.6.2. General Purpose Powder Diffractometer (GPPD) at Intense Pulsed Neutron Source, Argonne National Laboratory

The GPPD endstation is a time-of-flight neutron powder diffraction instrument [14]. It is very versatile, allowing one to make measurements at high temperatures using furnaces for the 300-1700K range, as well as low temperatures using displex refrigerators for the 10-300K range. Experiments conducted there cover a large range of topics, from structural characterization of framework modified zeolites, radiation-induced amorphization of transuranic materials, to in situ chemistry and thermal behavior of advanced ceramic catalysts and residual stress measurements. In addition to powders, with appropriate settings, it can be used to perform single crystal measurements, as was the case in some of our studies.

The neutron wavelength ranges in a continuous spectrum between 0.2 to 5.7 Å, and the beam size is 1.27 cm wide and 5.08 cm high. The moderator (100K liquid methane) which produces these low energy neutrons from the initial spectrum, from the U target, is 19.96m away from the sample. The sample-to-detector distance is 1.5 m and there are multiple detectors banks centered at 2θ values of ±148° (0.26% resolution), ±90° (0.49% resolution), ±60° (0.76% resolution), +30° and -20° that can measure the anisotropy of various parameters (scattering intensity, lattice parameters, strain). In covering nearly 2π, there are 318 3He counters. The instrument has a resolution of Δd/d = 2.5x10⁻³ at 2θ = 148°. The extensive shielding around the instrument, the possibility of remote access and the inherent gamma radiation discrimination make possible experiments with high radioactive samples.
For powder experiments, vanadium cans are used since vanadium is a weak neutron scatterer. For air sensitive powders, vanadium cans with aluminum top and indium wire seal can be used to hold specimens.

3.11. General Purpose Powder Diffractometer at IPNS-ANL (ref. [13]).

The instrument uses dedicated micro-computers to focus time-of-flight events, and the data from different detectors is summed into one histogram. Due to the design that permits data to be collected over a large range of d spacing and scattering angles from $12^0$ to $157^0$, the resolution and count rates are maintained at high levels. The detectors are located in the scattering plane, at a constant radius of $1.5 \pm 0.0003$ m from the sample, and their dimensions are 1.27 cm in diameter and 38.1 cm active length.
The signal to noise ratio is increased due to the boron carbide baffles that reduce the off-angle scattering. The sample chamber is a tank made out of aluminum, with a diameter of 66 cm, height 130 cm, and 2.54 cm thickness, extending at the top and bottom of the instrument shielding. The neutron beam enters the chambers through a 0.5 mm thick aluminum window; the exit window is 0.8 mm thick and is located outside the instrument.

**Fig. 3.12.** Overhead view of the detector angles (ref. [13])
Fig. 3.13. Views of the instrument area
A chopper is mounted on neutron flight path as it comes out of the monolith. The T0 Chopper removes the fast neutrons, since only the slow neutrons are desired for the diffraction experiments.

**Fig. 3.14.** T0 Chopper: full assembly, exploding diagram of housing, exploded diagram of rotor (courtesy of the SNS and ref. [13]).

Neutrons are produced by the pulsed neutron source at low repetition rates of 10-100 Hz. This permits the design of the time-of-flight diffractometer with a long incident flight path, which results in higher resolution for the instrument.

State-of-the-art powder diffraction experiments require a wide range of scattering angles and large detector areas at any angle. Due to the extinction and absorption that long-wavelength neutrons may experience, and to the fact that the flux decreases with increasing wavelength, low scattering angle measurements are best for d-spacing peaks.
3.7. References


CHAPTER 4. HIGH-RESOLUTION ANGLE-RESOLVED PHOTOEMISSION

4.1. Outline

In this chapter we describe sample preparation and structure, the cleaning procedures, sample characterization using Auger spectroscopy and STM measurements, and the high-resolution angle-resolved photoemission experiment performed in order to determine the electronic structure of LaSb$_2$ and the Fermi surface topology.

4.2. Sample Preparation

Samples were provided by D. P. Young and M. Moldovan (LSU, Department of Physics and Astronomy). Single crystals of LaSb$_2$ were grown by the metallic flux method [1]. The advantage of the method is that it does not require special equipment and the growth temperatures are relatively low. The two constituents, La ingot (Ames Laboratory, 3N, purity 99.99%) and Sb shot (Alfa Aesar, 6N, purity 99.9%), were placed in an alumina (Al$_2$O$_3$) crucible inert to the melt that was sealed in an evacuated quartz ampoule, for environment protection and for easy crystal removal from the flux using centrifugal force (spinning). This is illustrated in Fig. 4.1. The material with the highest melting point was placed at the bottom. In order to avoid cracking the quartz tube due to the differential expansion between the tube and the crucible, the crucible was elevated from the bottom of the tube with quartz wool. A plug of quartz wool is also placed above the crucible. The wool has the role of a filter during crystal removal. The crucible along with the content were sealed into an evacuated quartz tube and heated to 1175$^\circ$C. After slowly cooling to 675$^\circ$C (90 hrs), the tube was inverted and centrifuged to remove the excess flux, and the LaSb$_2$ large single crystals were left in the crucible. The crystal size varied
from 5x5x5 to 10x10x10 mm$^3$. The crystals are sensitive to air, and become contaminated with adsorbed species very quickly.

![Diagram of metallic flux growth synthesis](image)

**Fig. 4.1.** Metallic flux growth synthesis

The crystal structure was determined by single-crystal X-ray diffraction by J. Y. Chan and F. Fronczek (LSU, Chemistry Department). A Nonius Kappa CCD diffractometer using K$_\alpha$ radiation from a Mo source ($\lambda = 0.71037\text{Å}$) was used. After refinement, the LaSb$_2$ was determined to have the orthorhombic SmSb$_2$ structure (cmca) and the lattice parameters were calculated to be $a = 6.319\text{ Å}$, $b = 6.1739\text{ Å}$, and $c = 18.57\text{ Å}$ [2]. The structure is micaceous, with layers that can be easily peeled off.

The first step in the experiment was to confirm the single crystal structure and to obtain a clean and stoichiometric sample surface. The first attempts to prepare the surface consisted of the standard method of sputtering and annealing. The samples were sputtered using cycles of Ar$^+$ or
Ne\(^+\) ions, at 500 eV for different time intervals, ranging from 15 to 45 minutes, followed by annealing at temperatures ranging from 150\(^0\)C to 850\(^0\)C, and for different time intervals, from 30 minutes to 15 minutes. None of the combinations time-temperature yielded the results we

Fig. 4.2. LaSb\(_2\) single crystal orthorhombic structure. This shows 2×2×1 unit cells with the 2 LaSb bilayers in the center of the unit cell c-edge. These bilayers are separated along the c-axis by rectangular sheets of Sb. La (light) and Sb (dark).
expected and all procedures resulted in non-stoichiometric surfaces with excess La.

![Auger spectra](image)

**Fig. 4.3.** Auger spectra taken after the sample was sputtered and annealed few consecutive times, and at different temperatures.

The next cleaning method we tried was scraping. The samples were placed in the magnetic transfer load-lock system, pumped down overnight and then introduced in the STM main chamber and placed on the XYZθ sample holder/manipulator. The transfer load-lock system was then replaced by the linear motion stage on which the diamond file was mounted. The scraping was performed in the STM main chamber, at a pressure of 1.5-2x10⁻¹⁰. After scraping, the samples were moved to the other side of the chamber where Auger spectroscopy was performed. The annealing temperature was varied from 300°C up to 850°C (Fig. 4.3). Sputtering resulted in larger intensities for the La peaks, and very small Sb peaks. The annealing that followed a sputtering always yielded in reduced intensities for the La peaks, but no significant difference in the Sb peaks was noticed. We were not able to completely remove the oxygen of the surface.

The next spectrum in fig. 4.4 shows the results for two consecutive scrapings followed by annealing. The first scraping resulted in significantly less La on the surface and a large increase
in the amount of Sb. This may be due to sample fracturing in a non-crystalline region with excess of Sb flux. After the second scraping, the La peak intensity increases almost three times, and the Sb intensity basically falls to half. Annealing the scraped surfaces again reduces the amount of La present on the surface, while the Sb intensity remains unchanged.

![Auger spectra for LaSb2 for two consecutive scrapings followed by annealing](image)

**Fig. 4.4.** Auger spectra for LaSb2 for two consecutive scrapings followed by annealing

In figure 4.5 we present the Auger results after scraping followed by two consecutive annealing treatments at high temperatures. The first spectrum, labeled “dirty”, is an Auger spectrum from the unscraped surface. The surface was being sputtered, scraped and annealed for few times the day before but it does not show evidence of C or O contamination. It shows a high Sb content, and little La on the surface. After the first scraping, the La content rises by a factor of 3 to 4, while the Sb decreases.
Fig. 4.5. Auger spectra for LaSb$_2$ for two annealings at 800°C and 850°C following scraping.

The first annealing, to 800°C, results in a decline in La content, but little difference for Sb. After second annealing, the La content increases, and Sb decreases significantly. The surface still presents traces of carbon and oxygen.

The next option for producing a clean stoichiometric surface was cleaving. Samples were glued on a sample plate using an epoxy (2:1), and baked for 2 hours at 140°C. A metal post was glued on top of the samples, and small insertions were made at the edges using low profile stainless steel microtome blades (Accu-Edge, Sakura), to help initiate a cleave. Electrical contact between the sample and the sample plate was obtained by using silver paint print (Leitsilber 200, Ted Pella Inc.). After baking, the sample was placed on the transfer arm of the STM chamber and pumped down overnight. After transferring to the STM main chamber (pressure 1.2x10^{-10} Torr), the sample was cleaved by knocking off the post with a wobble stick. A flat, clean, mirror-like surface resulted. The sample was further placed on the XYZθ sample holder and moved to the level A of the STM chamber, equipped for sample cleaning and preparation.
The Auger spectrum from the cleaved surface clearly exhibits the peaks corresponding to lanthanum La (at 59, 78 and 95 eV) and antimony Sb (at 388, 454 and 462 eV). There are no traces of carbon or oxygen (fig. 4.6).

![Auger spectra for LaSb2 after cleaving in UHV](image)

Fig. 4.6. Auger spectra for LaSb₂ after cleaving in UHV

The next issue to be addressed was the question on whether we had a crystalline order on the surface following cleaving. We were facing this problem especially due to the fact that we were unable to obtain LEED images, regardless of the cleaning method used. Also, Auger spectra taken after consecutive sputtering first, and then after consecutive sputtering followed by annealing, showed a variation in peak intensities for La and Sb that was inverse proportional. It looked as La and Sb kept sinking and rising, but not at the same time. The process appeared for both two cleaning methods that we first tried: sputtering followed by annealing, and scraping followed by annealing.

As shown in Figure 4.6, the Auger spectra from a cleaved surface shows no signs of O or C contamination, and only the Auger peaks of La and Sb are seen. Despite the fact that the
material cleaves nicely leaving mirror-like surfaces, we were not able to obtain a LEED diffraction pattern. LEED measurements only showed diffuse background with no evidence of even diffuse spots. Usually this indicates that the material must be amorphous or polycrystalline [3], or that the surface order is smaller than the LEED coherence length (~100Å). In this case, Auger shows both La and Sb at the surface so there is no clear preferential surface segregation of one component. Currently we do not know why LEED is not evident and this observation is even more curious in light of the x-ray diffraction and the photoemission results, below, which do show evidence of long-range order.

In Figure 4.7 we present a 150 nm x 150 nm STM image of LaSb₂ cleaved in uhv. The STM image shows a flat terrace through most of the image with a large step up to another flat terrace to the right. This height corresponds to a full 18.7 Å unit cell step. In the lower right of this image, one can see two steps edge of approximately 9.4 Å, which is in good agreement with a half unit-cell step. We were not able to obtain atomic resolution on this surface, although a quasi-periodic rumpling appeared in some images with a corrugation of ~0.2 Å.

These data present some clues into the cleavage plane for LaSb₂ (001). As shown in Figure 4.2, the crystal structure consists of bi-layers of LaSb separated by Sb layers. Normally, materials cleave in such a manner that they present non-polar surfaces, if possible, reducing the surface free energy of the newly exposed cleaved surfaces. This would be possible if the material were to cleave between the LaSb bilayers. In this cleave, two identical Sb terminated surfaces would result. The only other alternative for cleavage would be between a LaSb bilayer and the Sb sheet but this would leave two different surface terminations, and probably result in patches of Sb on both. As our STM shows flat terraces without additional material, we believe that cleavage occurs between the LaSb bilayers. This can be accomplished identically at both the
unit cell face as well as at half the unit cell height giving terrace separations as found in the STM measurement.

**Fig. 4.7.** STM image of LaSb$_2$ showing flat terraces with a step edge of ~9 Å, marked by the two dark arrows, and a total difference in height between the top most (light yellow) and bottom (dark red) surfaces of ~18 Å. These heights correspond to half and full unit cell dimensions, consistent with the double-layer crystal structure.
Figure 4.8 presents a 300 nm x 300nm STM image of LaSb$_2$ after cleaving \textit{in vacuo} that shows a layered compound with a long range ordering.

During our STM measurements performed for sample characterization, we obtained images that brought us to the idea of CDW existence in LaSb$_2$. Figure 4.9 shows a STM image taken at room temperature, in the (ab) plane, after the sample was cleaved in vacuo. The image shows strange formations in shape of rings that appear on all three layers (the difference in color corresponds to different layers). The dark (black) lines mark the step edges. The rings (or circles) do not appear to have an ordering. However, 300nm x 300nm STM images presented in Chapter 4 show a long range ordering for the LaSb$_2$.

A charge density wave implies a broken symmetry state and a periodic modulation of the valence charge. In a 2D system, STM can visualize these phase transitions and the interaction between lattice defects and the CDW oscillations. The defects may be seen as centers of
nucleation of the CDW. At lower temperatures, CDW can be pinned into domains by the defects. Due to the growth method used, we do not exclude the existence of defects in the LaSb$_2$ single crystals. In case of a defect, the material tends to minimize the perturbation created by the defect by rearranging its electron sea [4]. This will create a long-range oscillation in the charge density, with a wave vector equal to $2k_F$. [5]. The CDW will stabilize if the Fermi surface is nested. In case of LaSb$_2$, calculations of the Fermi surfaces provided by D. Brown and R. L.
Kurtz show highly nested Fermi surfaces [6]. The nesting of the Fermi surfaces can lead to a Kohn anomaly, and further on to a Peierls distortion [7, 8].

Experimentally, CDW’s can be associated with lattice distortions that generate changes in the electronic properties and these structural changes can be detected by X-ray, neutron or electron diffraction. Presently, scanning tunnel microscopy (STM) represents the best tool in detecting CDW in semiconducting and normal metallic materials, due to the fact that STM provides real-space pictures of the surfaces, and the tunneling conductance is proportional to the electronic density of states [9-13]. In comparison, the other structural probes only provide information on changes in the periodicities of a lattice and do not reveal the mechanism underlying them.

Figure 4.10. (a) Fermi surfaces of LaSb$_2$; (b) highly nested FS sheets that may be responsible for the charge-density waves in LaSb$_2$ (reference [6]).
Additional clues to the existence of a CDW can be provided by a number of other methods, and a correlation of observations from different methods provides the most compelling case. Other experimental techniques that can detect the existence of CDW are: ARPES, EXAFS, resistivity and its derivative, magnetoresistance, specific heat, Hall effect, magnetic susceptibility, tunneling spectroscopy, optical reflection spectroscopy, nuclear spin-lattice relaxation, and nuclear magnetic resonance measurements.

Further STM measurements on LaSb$_2$ at higher resolution are required in order to clarify the absence of order and the nature of the rings presented in Fig. 5.9. Low temperature measurements may be useful, though low temperature is not a necessary condition in CDW formation. Some materials develop CDW at room temperature, and there are compounds that present CDW state at two different temperatures.

4.3. Experiment

The angle-resolved photoemission spectroscopy experiment was performed at Center for Advanced Microstructures and Devices (CAMD, LSU) Synchrotron Light Source in Baton Rouge, Louisiana, on the 3 meter toroidal monochromator (TGM) beamline [14]. The 1.3 GeV electron storage ring generates soft X-rays, with critical wavelength of 7.45Å. Typical electron beam currents are 150 mA with a half-life of 6 hrs. The 3m-TGM operates for a photon energy range 15-350 eV, has a designed resolving power of 1,000, and energy resolution of 0.1-0.15 eV. Photoelectrons are analyzed by a hemispherical analyzer HA 50 mounted on the lower half of the main chamber. The analyzer resolution depends on the pass energy of the electrons that travel through the hemispheres. A pass energy of 25 eV was used in the experiments presented here. The sample manipulator mounted on the main chamber allows full 360º rotation around z-axis,
along with xyz translation motion. A preparation chamber is attached to the main chamber, and the sample transfer is performed with a magnetic transfer load-lock system.

Samples were cleaved in the (ab) plane in vacuo at room temperature in the preparation chamber and transferred with the magnetic load-lock system into the main chamber.

4.4. Theoretical Background

Total density of states (DOS) calculations were performed by Dana Browne and Richard L. Kurtz using WIEN2K software package [15]. A grid of 16x16x3 points was used for integration, with a total of 1000 points in the irreducible wedge of the Brillouin zone. The calculations include the spin-orbit interactions which have profound effects and local orbitals were used for both La and Sb empty states to improve the overall convergence [16]. The DOS was computed with a grid of 3000 points and the data was smoothed with a Gaussian of width 0.08 eV. WIEN2K software calculates using Density Functional Theory (DFT) [17] and employs the Generalized Gradient Approximation (GGA), which is an all electron calculation, and core electron states are computed as well.

Total DOS (red) is represented in fig. 4.11. and compared to a normal emission experimental spectrum (blue) taken at 300 K, for a photon energy of 65 eV, normal emission. The valence band region corresponds to energy interval from 0 to -15 eV. Partial contributions from La in green and Sb 1 (sheets) and Sb 2 (bilayers) in black to total DOS (red) are represented in figures 4.12 and 4.13

The shallow-core La 5p levels (peaks D and E) are seen spin-orbit split between 15 and 20 eV and the Sb 5s is found to give the peak C. Peak C includes La admixtures of varying character, although p character is predominant. These levels are in reasonable agreement with the experimental data, considering that LAPW calculations do not extract core-binding very
**Figure 4.11** Total density of states (red) compared to an experimental spectrum (blue) taken at room temperature, for a photon energy of 65 eV, normal emission. The A, B and C structures correspond to the valence band region, while D and E indicate the core level region.

**Figure 4.12** Partial contribution due to Sb1 and Sb2 to total DOS.

**Figure 4.13** Partial contribution due to La to total DOS.
precisely, but there are significant differences with the peaks A and B.

Peak B most closely matches the Sb $5p$ features in the calculated DOS but there is a nearly 1 eV shift between the centroids of their spectral weights. In this case the region of the spectrum labeled A would correspond to a portion of the band-structure where the Sb $5p$ states are heavily mixed with the La $5d$ states. The empty La $4f$ states are located about 2.4 eV above $E_F$. The last interval, 15-20 eV (peaks D and E) correspond to core levels and is dominated by La $5p$.

The differences between the calculated and the measured DOS are not yet clear. For the photon energies used here, ARPES probes a thin surface layer of about 5 Å. It may be possible that due to the material’s highly layered nature, the surface electronic structure differs from that of the bulk. This lack of agreement exists also for U-intermetallics [18] and transition metal oxides, with distinct peaks outside the theoretically-predicted bandwidth.

### 4.5. Results and Discussion

We performed angle-resolved photoemission spectroscopy in normal emission and in angle-dependent emission geometries at two temperatures: room temperature, 300K, and 140 K. The lower temperature was obtained by cooling the sample stage with liquid nitrogen. We are interested in this lower temperature data since the magnetoresistance is already significant at this temperature and the photoemission data may reflect underlying electronic structural changes. In these data, the photon energy was varied between 17 and 35 eV and normal-emission data were taken with 1 eV increments. Measurements were repeated on different samples from the same batch and on samples coming from different batches. All of the measurements yield similar spectra, and confirmed the reproducibility of the data.

Figures 4.14a and b show the valence band photoemission spectra for LaSb$_2$ in normal
Figure 4.14 Normal emission spectra taken at 300K (a) and 140 K (b) along the high symmetry line Γ-Z. Photon energy ranged between 17 and 35 eV, with 1 eV increments.
emission at 300 K and at 140 K. The experimental spectra reveal three distinct structures, present at both 300 K and 140 K, and labeled A at about 1 eV, B located at ~4.5 eV and C which is centered at about 9 eV. Bands A and B are each composed of two distinct features. Band A has two peaks located near 0.42 eV and 1.8 eV, and band B shows two features around 4.4 eV and 5 eV. In the case of structure C, the existence of two features, around 7.15 eV and 9.15 eV, is less obvious but is suggested in peak fitting calculations. All of the structures appear to be sharper at 140 K compared to measurements taken at 300 K. There is no evidence for an enhancement in the density of states near $E_F$ in these data as the temperature is lowered to 140 K, therefore we see no indication of charge density waves which have been proposed as one possible mechanism for the magnetoresistance behavior.

Figures 4.15 a and b present angle-dependent spectra measured for a photon energy of 30 eV at 300 and 140 K. The electron emission angle was varied from 0° to 25° with 1° or 2° increments. Both spectra present the three structures, A, B, and C, previously identified. Although the spectra look somewhat sharper at 300 K compared to 140 K, there are no regular changes in the binding energies of these peaks as a function of angle.

Additional information can be extracted by fitting these spectra as shown in Figure 4.14. Our procedure involved fitting with Gaussian peaks and this reveals that at least six features are required to model the valence band spectrum. In Fig. 4.16 an experimental spectrum, taken at room temperature in normal emission at a photon energy of 35 eV is given by the open circles. The solid line represents the curve obtained from the sum of six Gaussian peaks, also plotted, and the residuals to the fit are given above. We can see that our band labeled C consists of two peaks, 1 and 2, structure B is composed of peaks 3 and 4, and the valence band peak A is fit
Figure 4.15. High-resolution angle-resolved photoemission spectra taken at 300 K (a) and 14 K (b), for a photon energy of 35 eV, with 1° increments.
with peaks 5 and 6. The cross-section of these excitations changes with photon energy and peaks 2 and 4 are more intense at lower photon energies while peaks 1 and 3 are more intense as the photon energy increases. Peaks 5 and 6 maintain a fairly constant intensity for all photon energies.

![Graph with peaks labeled A, B, C, 1 through 6.](image)

**Figure 4.16.** Experimental spectrum (empty circles) taken at room temperature, for a photon energy of 35 eV, normal emission. The solid line represents the fitted curve obtained from the sum of six Gaussians (labeled 1 through 6).

Based on the theoretical DOS calculation presented earlier, we assigned peak A a La 5d/Sb 5p character, peak B a Sb 5p character and peak C a Sb 5s character. The Sb 5s states are totally filled and away from the Fermi level. The Sb 5p states are partially (more than half filled)
and show a dominant character in the valence band. Close to the Fermi level (peak A), the Sb 5p states are heavily mixed with the La 5d states. A similar structure was presented for the LaSb single crystal: the valence bands consist primarily of Sb 5p states that hybridize with La 5d states [19-21]. The 4f levels are located at 2 eV above the Fermi level and hybridize strongly with the valence band [22]. Most of the La 5d character manifests near the Fermi level, with some hybridization through the valence band. La Sb presents a low density of states at the Fermi level.

An additional feature of the band structure of LaSb$_2$ that is due to its highly layered nature, is the lack of dispersion in the direction of the “c” axis. The theory predicts nearly all bands to be flat as one moves along the Γ to the Z direction (by changing photon energy) but there are bands located near 2 eV that are predicted to show weak dispersion of ~0.5 eV versus $k_{\perp}$. We can probe this by conducting normal-emission photoemission measurements. This measures states at the $\Gamma$ symmetry point at the surface BZ center, and the energy dispersion is measured along the Γ to Z symmetry direction.

In Figure 4.17 we plot the binding energies of the six features fit with the Gaussian peaks for the 140K data of Fig 4.14 (b) after converting the data into $k_{\perp}$. These data are computed assuming an inner potential of 9 eV. As seen in Fig. 4.17(a) these data exhibit little dispersion versus $k_{\perp}$ consistent with the quasi-2D band structure. If we look closely at the bands nearest the Fermi surface, as plotted in Fig. 4.17(b) we see that there is some slight dispersion that is most clear for the band near 1.5 eV. For the LaSb$_2$ lattice parameters, the Brillouin zones are spaced by 0.3348 Å along Γ to Z, and this results in the critical point Γ located at the $k_{\perp}$ indicated in the figure. This corresponds to an excitation to the 8th through the 10th Brillouin zones for the data in Fig. 4.14.
Figure 4.17. (a) Experimental valence band structures along the Γ-Z symmetry line calculated for the 140 K measurements of Fig. 4.12 (b); (b) Experimental dispersion for $k_{\perp}$ corresponding to the La 5d/ Sb 5p (structure A) measured at 140 K.
4.6. Conclusion

We have performed a photoemission study of LaSb\(_2\) and have identified the salient features of the data. The valence band consists largely of strongly spin-orbit split Sb \(5p\) states, with a significant hybridization of the Sb \(5p\) and La \(5d\) states near the Fermi level. A prominent Sb \(5s\) peak is found just below the valence band. We measured dispersion for \(k_\perp\) from normal emission data and found that although most bands are relatively flat, dispersion can be seen for some Sb \(5p\) states, in agreement with theory. No significant dispersion for \(k_\parallel\) was found in angle-dependent measurements. Finally, no significant enhancements were observed at the Fermi level at low temperature, implying that charge density waves are not present in the region of the sample probed at the temperatures reached in this experiment. This does not imply that CDW do not exist in LaSb\(_2\). Again, higher resolution measurements might solve the problem.

4.7. References


[2] The lattice parameters were found to be \(a = 6.319 \, \text{Å}, \ b = 6.1739 \, \text{Å} \text{ and } c = 18.57 \, \text{Å}\). The interlayer distance was determined as 9.2 Å.


CHAPTER 5. SINGLE CRYSTAL NEUTRON DIFFRACTION

5.1. Outline

In order to correlate the observed electronic properties (and changes anticipated within it) with structural changes we conducted a series of neutron diffraction experiments. As mentioned previously, LEED studies gave us no evidence for long-range order on a cleaved surface. The neutron scattering study presented here shows clear evidence of significant structural changes with temperature in the bulk of LaSb₂.

5.2. Experiment

Neutron diffraction studies were performed on LaSb₂ as a function of temperature on the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory, Illinois. The neutrons emerge from the liquid methane moderator each 33.3 msec, and are sorted by velocity, which is inversely proportional to their wavelength \( \lambda = \frac{h}{mv} = \frac{h}{m \frac{t}{L}} \). Here, \( h \) is Planck’s constant, \( m \) is the neutron mass, \( v \) the velocity, and \( t \) is the time-of-flight corresponding to a pathlength \( L \).

The wavelength range is 0.2-5.7 Å, and the instrument resolution varies from 0.26% to 0.76%, depending on the detector angles. The beam size was 1.27 cm x 5.08 cm, and the moderator to sample distance 19.96m. The positions and intensities of the diffracted beams were measured with detectors placed in the scattering plane at a constant radius of 1.5 ± 0.0003 m from sample position. The detectors are 10 atm \(^3\)He proportional counters, with 1.27 cm diameter and 38.1 cm length, oriented perpendicular to the scattering plane. A proportional counter is based on the principle of gas multiplication to amplify ions resulted after an interaction of radiation within a gas. The gas multiplication may result in an ion cascade (Towsend avalanche). The gas amplification is a result of the
increase of the electric field. Neutrons have mass but no electrical charge, therefore they can not produce ionization in a detector. A neutron detector is based on a conversion process, in which an incident neutron interacts with a nucleus and produces a secondary charged particle. The charged particle is directly detected and based on it, the presence of neutrons is deduced.

A common reaction in neutron detection is:

\[ n + ^3\text{He} \rightarrow p + ^3\text{He} + 765 \text{ keV} \]

where the proton \( p \) and the \(^3\text{He} \) are detected by a gas filled proportional counter using \(^3\text{He} \) fill gas. These proportional detectors are efficient for thermal (low energy) neutrons only. High energy neutrons have small capture cross sections and are very unlikely to interact with the fill gas and cause a detection reaction. Usually those neutrons have to be slow down by means of a hydrogen-rich material (moderator) that surrounds the detector and the sample. \(^3\text{He} \) are very sensitive to neutrons due to their neutron cross section of 5330 barns.

As shown in figure 5.1, the scattering angles are limited to 12°-157° on sides, left and right, due to instrument shielding [1]. Sample to detector distance is 1.5m. The sample chamber, an aluminum tank of 66 cm diameter and 130 cm height, is aligned with respect to the beam. The sample lays 61 ± 0.03 cm below the center of the top cover.

GPPD was preferred over Single Crystal Diffractometer (SCD) due to a better angular resolution. GPPD is a time-of-flight diffractometer where data collected by different detectors is summed into a single histogram. High resolution and high count rates are combined over a wide range of d spacings for data collection. In the case of powder diffractometers, it is desirable to detect diffracted neutrons over a wide range of
scattering angles using a detector covering a large solid angle. Signals from the individual detectors are processed by on-line microcomputers, and data histograms are constructed.

**Figure 5.1.** Overhead view of the detectors. The center of the circle corresponds to the sample position.
Figure 5.2. 3D view of a diffraction event provided by ISAW.

The histograms are based on a pseudo-time (focused time) variable, instead of the actual time-of-flight. A relationship between the pseudo-time and the TOF can be derived using the de Broglie relation:

\[
\lambda = \frac{h}{mv} = \frac{ht}{mL} \tag{5.1}
\]

and

\[
d = \frac{\lambda}{2 \sin \theta} = \frac{ht}{2mL \sin \theta} \tag{5.2}
\]

where \( \lambda \) is the wavelength, \( h \) is Planck’s constant, \( m \) is the neutron mass, \( v \) is the neutron velocity, and \( t \) is the measured TOF. For an array of detectors placed at scattering angles \( 2\theta_i \) and path lengths \( l_i \), neutrons scattered by planes of \( d \) spacing will be detected by an \( i^{th} \) detector at a time

\[
t_i = \frac{(2md)}{h}l_i \sin \theta_i \tag{5.3}
\]
The pseudo-time registered by the detector at a reference position \((l_0, \theta_0)\) is
\[
t^* = t_i \frac{(l_0 \sin \theta_0)}{(l_i \sin \theta_i)}                             \tag{5.4}
\]
For each detector, the data histogram will record a pseudo-time \(t^*\), and neutrons scattered by the same plane spacing will be stored in the same channel of a data histogram. The d spacing is related to the time-of-flight by the relation:
\[
t = DIFC \times d + DIFA \times d^2 + ZP
\tag{5.5}
\]
where the coefficients DIFC, DIFA and ZP have different values for each detector bank. One detector bank contains up to 20 detectors.

The neutron-diffraction data collection was performed on a single-crystal of LaSb2 grown by the metallic flux method \([2]\). The sample \((15\text{mm} \times 15\text{mm} \times 2.5\text{mm})\) was enclosed tightly under vacuum in a silica glass tube to minimize atmospheric contamination. The GPPD was designed for powder diffraction in which the random crystalline order meant that there was no need for specimen alignment. In our studies, we needed to make fine adjustments so that the diffracted beams could be moved to strike a detector. For low temperature measurements, we designed an aluminum frame that held the silica tube in a horizontal position. The frame allowed a 360° rotation around its central vertical axis. A single crystal of LaSb2 was placed in the neutron beam with \((0\ 0\ 1)\) direction aligned vertically. This orientation fixes the “detected” diffraction spots to be of the \((h\ k\ 0)\) type.

Time-of-flight neutron single-crystal diffraction measurements were collected at four temperatures: \(295 \pm 5\text{K}, 200 \pm 5\text{K}, 100\pm5\text{K}\ and 10\pm5\text{K}.\ A goniometer was used for the room temperature scan; the silica tube containing the sample was glued to a
Figure 5.3. ISAW diffraction patterns in (a) $\Omega$ vs d-spacing representation and (b) $\Omega$ vs time-of-flight representation. The black horizontal lines mark the separation between successive banks of detectors.
Vanadium holder, and mounted in the goniometer. At low temperatures, a two-stage displex was used for the 200K, 100K and 10K diffraction pattern. The sample was
mounted on the aluminum frame and cooled using a helium flow cryostat. Data
collection times were 3 hours for RT, 6 hours for 200K and 100K, and 10 hours for 10K.
A longer time was set for the 10K run to obtain better statistics.

Figure 5.3. The GPPD goniometer sample orienter.
5.3. Results and Discussion

The sample was oriented with the $a$ and $b$ crystallographic axes in the horizontal plane to allow access to the $(h k 0)$ type reflections. The data was recorded and visualized using the IPNS Integrated Spectral Analysis Workbench (ISAW) software that allows multiple representations for analysis. The ISAW software is an ongoing development at IPNS with the goal of providing a flexible and powerful tool to perform neutron scattering data analysis and visualization [3]. ISAW provides a graphical user interface that allows loading and manipulation of multiple spectra from different “runs”. Operations like merging, summing, axes conversions, sorting etc. can be invoked on spectra from different runs and the results displayed as images or plots. Data can be saved on local disks in different file formats such as General Structure Analysis System (GSAS) for further analysis.

In Fig. 5.5 and 5.6 we present the diffraction patterns visualized with ISAW, at the four temperature values selected. The vertical axis corresponds to the $\Omega$ angle, and the horizontal axis to the d-spacing. The dark horizontal lines represent separations between the detector banks. For each spot, ISAW displays the corresponding detector ID number, the detector bank number, the time-of-flight value, the d-spacing, the intensity (counts) and the corresponding $\Omega$ angles. It also displays a time-of-flight or d-spacing vs counts graph in a window below the image (not shown), so the user gets a good idea of the profile of each diffraction spot.

The diffraction patterns for 295 K, 200 K and 100 K look very similar. The 10 K pattern differs, and contains all the spots observed in previous measurements, plus a lot of additional spots. In addition, many spots- but not all- show streaking in the vertical
direction corresponding to a range of $\Omega$'s.

We can identify the diffraction spots based on the $h$, $k$, $l$ values derived using the equations corresponding to the d-spacing and the angle between two scattering planes for an orthorhombic structure:

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{5.6}
\]

and

\[
\cos \rho = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\left(\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2}\right)^{1/2} \left(\frac{h_2^2}{a^2} + \frac{k_2^2}{b^2} + \frac{l_2^2}{c^2}\right)^{1/2}} \tag{5.7}
\]

In our case, for a $(h \ k \ 0)$ reflection, $l = 0$ and $\frac{l}{c} = 0$. Taking as reference the plane characterized by $(h_1 \ k_1 \ 0)$, we can calculate $d_1$ and $\rho$, and derive the values corresponding to $h_2$, $k_2$ and $d_2$. From (5.8) we obtain for $k_2$

\[
k_2^2 = b^2 \left(\frac{1}{d_2^2} - \frac{h_2^2}{a^2}\right) \tag{5.8}
\]

Then $h_2$ can be derived from (5.9), as follows:

\[
\cos^2 \rho \left(\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2}\right) \left(\frac{h_2^2}{a^2} + \frac{k_2^2}{b^2}\right) = \left(\frac{h_1 h_2}{a^2} + \frac{k_1 k_2}{b^2}\right)^2 \tag{5.9}
\]

or

\[
\cos \rho \frac{1}{d_1} \frac{1}{d_2} = \frac{h_1 h_2}{a^2} + \frac{k_1 k_2}{b^2} \tag{5.10}
\]
Figure 5.5. Diffraction patterns recorded at room temperature and 200 K. The horizontal axis corresponds to changes in d-spacing, the vertical axis corresponds to changes in $\Omega$. 
Figure 5.6. Diffraction patterns at recorded at 100K and 10K.
We isolate the term that includes $k_2$, substitute with (5.10) and square the relationship:

\[
\cos^2 \rho \frac{1}{d_1^2} \frac{1}{d_2^2} + \frac{h_1^2 h_2^2}{a^4} - 2 \cos \rho \frac{1}{d_1} \frac{1}{d_2} h_1 h_2 = \frac{k_1^2}{b^2} \left( \frac{1}{d_1^2} - \frac{h_2^2}{a^2} \right) \tag{5.11}
\]

\[
\cos^2 \rho \frac{1}{d_1^2} \frac{1}{d_2^2} + \frac{h_1^2}{a^2} \left( \frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} \right) - 2 \cos \rho \frac{1}{d_1} \frac{1}{d_2} h_1 h_2 - \frac{k_1^2}{b^2} \frac{1}{d_2^2} = 0 \tag{5.12}
\]

\[
\cos^2 \rho \frac{1}{d_1^2} \frac{1}{d_2^2} + \frac{h_2^2}{a^2} \frac{1}{d_1^2} - 2 \cos \rho \frac{1}{d_1} \frac{1}{d_2} h_1 h_2 - \frac{k_1^2}{b^2} \frac{1}{d_2^2} = 0 \tag{5.13}
\]

At the end we obtain a quadratic equation in $h_2$.

\[
\frac{1}{a^2 d_1^2} h_2^2 - 2 \cos \rho \frac{1}{a^2} \frac{1}{d_1} d_2 h_2 + \left( \cos^2 \rho \frac{1}{d_1^2} \frac{1}{d_2^2} - \frac{k_1^2}{b^2} \frac{1}{d_2^2} \right) = 0 \tag{5.14}
\]

Using $a = 6.319 \text{Å}$, $b = 6.174 \text{Å}$, $h_1 = 6$, $k_2 = 2$ and $d_1 = 0.997 \text{Å}$ (determined using 5.6.), we calculate the coefficients of $h_2$, solve (5.16) for $h_2$ and obtain the solutions:

\[
h_2 = d_1 h_1 \frac{\cos \rho}{d_2} \pm \sqrt{\left( d_1^2 h_1^2 - a^2 \right) \cos^2 \rho \frac{1}{d_1^2} \frac{1}{d_2^2} - a^2 d_1^2 k_1^2 \frac{1}{b^2 d_2^2}} \tag{5.15}
\]

Substituting in (5.8), $k_2$ becomes

\[
k_2 = b \sqrt{\frac{1}{d_2^2} - \frac{h_2^2}{a^2}} \tag{5.16}
\]

Based on experimental intuition and subsequent internal consistency we preliminarily identify the spot on the upper left in the 295, 200, 100 K data as a $(6 2 0)$ spot. The angle $\rho$ between the $(6 2 0)$ plane and any other plane can be calculated based on the $(h_2 k_2 0)$ indices and the experimental angle values of $\Omega$ corresponding to the observed angular spacing using:

\[
\rho = \Omega_{620} - \Omega_{h_2 k_2 0} \tag{5.17}
\]

$\Omega_{620}$ corresponds to the $(6 2 0)$ reflection and $\Omega_{h_2 k_2 0}$ corresponds to any $(h_2 k_2 0)$
reflection spot. Using (5.15) and (5.16) we calculate the \( h \) and \( k \) values for all spots that appear at 295K, 200K, and 100K, using \((6 \ 2 \ 0)\) as reference spot. Table 5.1 lists all the \((h \ k \ 0)\) values corresponding to a spot for which the d-spacing and the \( \Omega_{h00} \) have been determined experimentally during the 295-100K runs. The columns giving d and \( \Omega \) are the experimental data, \( \rho \) is given, followed by two sets of indices. Figure 5.6.a represents the diffraction pattern for the 200K run, with all the spots labeled according to the values listed in Table 5.1.

At 295K, 200K and 100K, the diffraction pattern consists of the following diffraction spots: \((2 \ 2 \ 0)\), \((0 \ 4 \ 0)\), \((4 \ 0 \ 0)\), \((2 \ 4 \ 0)\), \((4 \ 2 \ 0)\), \((4 \ 4 \ 0)\), \((2 \ 6 \ 0)\) and \((6 \ 2 \ 0)\). The 200K and 100K run present an additional spot labeled \((4 \ 1 \ 0)\).

In general, for an orthorhombic system, the reciprocal lattice vectors are given by:

\[
a_1 = \frac{\hat{x}}{a} ; \quad a_2 = \frac{\hat{y}}{b} ; \quad a_3 = \frac{\hat{z}}{c}
\]

The Bragg condition becomes in this case

\[
q_B = 2\pi G_{hkl} = 2\pi \left( \frac{h\hat{x}}{a} + \frac{k\hat{y}}{b} + \frac{l\hat{z}}{c} \right)
\]

The primitive lattice has only one atom at position \( r_1 = 0 \). The Cmca structure of LaSb_2 can be considered to be a base-centered lattice has two atoms at the positions:

\[
r_1 = 0 \text{ and } r_2 = \frac{a\hat{x} + b\hat{y}}{2}
\]

In this case the structure factor becomes

\[
S_G = \sum_j f_j \exp(-i\vec{G} \cdot \vec{r}_j) = f[1 + e^{i\pi(h+k+l)}]
\]

The structure factor \( S_G = 2 \) for \( h + k + l \) = even and \( S_G = 0 \) for \( h + k + l \) = odd. In our case \( l = 0 \), therefore we should see reflections only for the for \( h + k \) = even combinations.
Table 5.1. Calculated values for $h$ and $k$ based on the experimental values observed for $\Omega$ and d-spacing for 295 – 100K runs.

<table>
<thead>
<tr>
<th>d-spacing</th>
<th>Omega</th>
<th>Rho</th>
<th>h2</th>
<th>k2</th>
<th>l2</th>
<th></th>
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<tr>
<td>2.196</td>
<td>69.515</td>
<td>64.11</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>295-100K</td>
</tr>
<tr>
<td>1.106</td>
<td>70.03</td>
<td>64.62</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>295-100K</td>
</tr>
<tr>
<td>1.58</td>
<td>24.095</td>
<td>18.69</td>
<td>4</td>
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<td>0</td>
<td>295-100K</td>
</tr>
<tr>
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<td>24.868</td>
<td>19.46</td>
<td>0</td>
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</tr>
<tr>
<td>0.996</td>
<td>5.41</td>
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<td>6</td>
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<td>0</td>
<td>295-100K</td>
</tr>
<tr>
<td>1.373</td>
<td>-2.45</td>
<td>-7.86</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>295-100K</td>
</tr>
<tr>
<td>1.39</td>
<td>88.065</td>
<td>82.66</td>
<td>2</td>
<td>4</td>
<td>0</td>
<td>295-100K</td>
</tr>
</tbody>
</table>

Table 5.2. Allowed ($h$ $k$ $l$) reflections that are allowed by symmetry. The observed peaks are indicated in bold.

<table>
<thead>
<tr>
<th>$h$</th>
<th>$k$</th>
<th>$l$</th>
<th>$d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>3.158</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>0</td>
<td>3.094</td>
</tr>
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<td>2</td>
<td>0</td>
<td>2.210</td>
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<td>0</td>
<td>1.579</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>0</td>
<td>1.547</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0</td>
<td>1.406</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
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<td>1.389</td>
</tr>
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<td>4</td>
<td>0</td>
<td>1.105</td>
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<td>0</td>
<td>1.053</td>
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<td>6</td>
<td>0</td>
<td>0.863</td>
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<td>0</td>
<td>0.789</td>
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<td>0</td>
<td>8</td>
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<td>8</td>
<td>2</td>
<td>0</td>
<td>0.765</td>
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<tr>
<td>2</td>
<td>8</td>
<td>0</td>
<td>0.751</td>
</tr>
</tbody>
</table>
Figure 5.7. Diffraction patterns recorded at 200 K and at 10 K, with peaks labeled according to the $h$ and $k$ values listed in Table 5.1.
A set of the possible reflections for \((h \ k \ 0)\) and the corresponding d-spacing is given in Table 5.2. The table lists only the reflections that are observable in the instrument’s geometry.

The \((4 \ 0 \ 0)\) and \((0 \ 4 \ 0)\) reflections are clearly seen as a doublet in the 295 K - 100 K data. This is also the case with the \((2 \ 4 \ 0)\) and \((4 \ 2 \ 0)\) spots, and the \((6 \ 2 \ 0)\) and \((2 \ 6 \ 0)\) spots, though the \((2 \ 6 \ 0)\) spot is barely seen, located at the end of the detector. The doublet structure can be a result of twinning of the crystal. Twinning occurs during crystal growth when different parts of the crystal switch their \(a\) and \(b\) directions. This easily occurs in LaSb\(_2\) since the \(a\) and \(b\) directions differ only by 2%.

The \((2 \ 2 \ 0)\) and \((4 \ 4 \ 0)\) reflections do not show a doublet structure since they involve equal \(h\) and \(k\) indices and this results in a single spot, even in the case of twinned crystals.

Note that the \((4 \ 1 \ 0)\) reflection is forbidden. The fact that it is observed may suggest that the symmetry may be broken, perhaps due to subtle differences in the basis at the corners versus centered positions. Stacking faults parallel to the surface or twinning may also be a cause of this forbidden reflection [4].

The 10K run presents all the main spots that appear at previous temperatures, and new spots that develop in the vicinity of the main spots. Indexing the 10K diffraction pattern proved to be more difficult, since one reference spot did not yield good results for all the spots. Therefore we used two reference spots corresponding to two incommensurate lattices that allowed us to index both of the new paired spots. For a \((4 \ 2 \ 0)\) located at \(\Omega = 65.905\) with lattice parameters \(a = 11.3\text{Å}\) and \(b = 6.148\text{Å}\), with d-spacing = 2.080 we were able to fit one of the new periodicities. For \((6 \ 2 \ 0)\) indexing, the
lattice parameters are $a = 10.52\,\text{Å}$, $b = 6.148\,\text{Å}$, with d-spacing = 1.332 and $\Omega = 63.586$, which fit the other set of new spots. Note that these two new periodicities, 11.4 Å and 6.23 Å, are not quite twice the original 6.32 Å lattice constant. The results are presented in figure 5.7.b.

Another striking feature exhibited by all the additional peaks is the streaking that they show over a range in $\Omega$. Close inspection also reveals slight differences in d-spacing as well, consistent with the new lattice. An additional observation is that the original 295 K $(2 4 0), (4 2 0), (0 4 0), (4 0 0), (6 2 0)$ and $(2 6 0)$ reflections do not exhibit streaking over $\Omega$ at 10 K. The same holds for the $(4 1 0)$ reflection. The $(2 2 0)$ reflection differs, however, and it appears to be streaked at 10 K. We can not determine if the $(4 4 0)$ spot is streaked or not at 10 K since it is located very close to an area with no detectors (the black square to the left of the picture). This suggests that streaking occurs for points with $h = k$, and points with $h \neq k$ experience no streaking. So far, we have no explanation for the streaking that appears at 10 K. We can rule out the possibility of the crystal tilting due to contraction at low temperatures since this would result in streaking of (nearly) all observed spots.

Table 5.3 lists the d-spacing, $\Omega$ angle values, along with the $h$ and $k$ derived values for the additional spots present at low temperature.

Based on the $h$ and $k$ values calculated using equations (5.15) and (5.16), we can plot $k$ vs. $h$ for the diffraction spots, as shown in figure 5.8. The blue squares correspond to the main Bragg spots that are observed at 295, 200 and 100 K. The red circles correspond to the additional peaks that appear at 10 K. The green lines indicate the range of new indexing consistent with the streakings.
In table 5.4 we listed the \( h \) and \( k \) values for the Bragg spots that appear at 10K, along with the difference in d-spacing and \( \Omega \) calculated for each pair. The variation in d-spacing is less than 10% for most of the pairs.

Table 5.3. Calculated values for \( h \) and \( k \) based on the experimental values observed for \( \Omega \) and d-spacing at 10K.

<table>
<thead>
<tr>
<th>d-spacing</th>
<th>Omega</th>
<th>Rho</th>
<th>h2</th>
<th>k2</th>
<th>l2</th>
</tr>
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<tr>
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<td>65.905</td>
<td>60.5</td>
<td>3.99</td>
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<td>0</td>
</tr>
<tr>
<td>1.9</td>
<td>60.493</td>
<td>55.08</td>
<td>4.41</td>
<td>1.97</td>
<td>0</td>
</tr>
<tr>
<td>1.373</td>
<td>65.003</td>
<td>59.59</td>
<td>5.97</td>
<td>3.08</td>
<td>0</td>
</tr>
<tr>
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<td>63.586</td>
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<tr>
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<td>77.25</td>
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</table>
Table 5.4. Difference in $\Omega$ and d-spacing corresponding to the doublet structures observed at 10K. $\Delta$Omega and $\Delta$d-spacing represent the difference in width of $\Omega$, and the difference in d-spacing.

<table>
<thead>
<tr>
<th>Related 295K spot</th>
<th>h</th>
<th>k</th>
<th>l</th>
<th>$\Delta$ Omega</th>
<th>$\Delta$ d-spaci</th>
</tr>
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<td>0</td>
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<td>0.183</td>
</tr>
<tr>
<td></td>
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<td>0</td>
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</tr>
<tr>
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<td>4</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1.9</td>
<td>0</td>
<td>1.55</td>
<td>0.04</td>
</tr>
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<td>6.9</td>
<td>1.8</td>
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<td></td>
</tr>
<tr>
<td>4 4 0</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 2 0</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>4</td>
<td>0</td>
<td>0</td>
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<tr>
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<tr>
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<td>1</td>
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<td>0.024</td>
<td></td>
</tr>
<tr>
<td>5.9</td>
<td>0.9</td>
<td>0</td>
<td>1.29</td>
<td>0.024</td>
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</table>
Figure 5.8. Reciprocal space representations of the diffraction pattern at 10K.
Figure 5.8 reveals the diffraction pattern at 10K in the reciprocal space. The $k$ indices for the new periodicity (red) are close to integer values while the $h$ varies, suggesting a lattice distortion along the $a$ direction. To get the best indexing at 10K, different lattice parameters values were required for $a$, and this suggests that at low temperature two substructures are present, and are incommensurate with respect to the main lattice. This suggests that the incommensurate nature is along the $a$ direction. Calculations of the Fermi surfaces revealed that for LaSb$_2$ the surfaces are highly nested along [1 0 0] and [0 1 0] directions and this would be consistent with the development of a new lattice.

One interesting issue is the representation of streaking in reciprocal space. For most of the new points appearing at 10K, the streaking resembles an incomplete powder pattern. Overall, streakings follow similar inclinations, and seem to be along a circular path, centered around the $(0 0 0)$, $(2 0 0)$ or $(4 0 0)$ Bragg points.

By keeping $k$ fixed, we can plot the $\Omega$ profile converted to an “h” scale of a main Bragg spot and its additional spots showing the line shape of the streaking. The intensity of the satellites decreases as $h$ increases, otherwise, as we move away from the main spot. Figure 5. 9 reveals the Intensity vs. $h$ dependence for the $(4 0 0)$, $(2 2 0)$ and $(3 3 0)$ main spots, along with their satellites. In 5.9 (a) we plot along the $(h 0 0)$ with $h$ taking values from 4 to 8.2. At $(4 0 0)$ and $(0 4 0)$ we have the doublet that appears at all four temperatures. The additional peaks appear at 8 and 8.2.  In 5.9 (b) we plot the additional peaks that correspond to a $(6 1 0)$ reflection, as well as the extra peaks that appear close to the $(2 2 0)$ main spot. The $(4 2 0)$ formation (middle) presents a sharp increase in intensity, followed by a drop that includes a shoulder. This might correspond to two
Figure 5.9. Scans at 10 K along the (h 0 0), (h 3 0) and (h 2 0) lines in the reciprocal space.
peaks formed around the \((4 2 0)\) position in reciprocal space although it is not known why their intensities should differ. The total width of the formation is 6.443° in \(\Omega\) and 0.01 in d-spacing. The second formation shows a similar behavior, though the intensity is much less. We see a sharp increase followed by a shoulder. The width of these peaks is 4.896 in \(\Omega\) and 0.008 in d-spacing. Compared to the extremely small variation of \(h\) for a spot of \((h 0 0)\) type shown in figure 5.9 (a), the additional \((h k 0)\) type spots give a much broader distribution of \(h\)-indexing shown in 5.9 (b) and (c).

5.4. Conclusion

We have performed a single crystal neutron diffraction study on LaSb\(_2\) at four temperature values. The measurements at 295K, 200K and 100K reveal a very similar diffraction pattern. At 10 K the diffraction pattern contains all the spots present at previous temperatures plus additional spots. The indexing of the spots reveals the existence of two additional substructures at low temperature, which are incommensurate with the main lattice. This lattice deformation is consistent with highly-nested Fermi surfaces that can result in the development of CDWs. Neutron diffraction data on powder LaSb\(_2\) collected at room temperature and at 50K also supports the idea of CDWs existence in this compound [5]. The reciprocal lattices defined by the satellites appear to be incommensurate with the original one.

5.5. References


CHAPTER 6. SUMMARY AND DISCUSSION

In this chapter, we will consolidate the information that we have on the properties of LaSb$_2$, summarize the new measurements presented in this dissertation, and we will present a plausible explanation for these phenomena. The underlying physics for the behavior that we observe is consistent with the development of a charge-density wave instability that leads to a new incommensurate lattice in the [100] direction in LaSb$_2$.

Prior observations include:

- layered crystal structure from X-ray diffraction [1-2].
- anisotropic resistance: resistance for current parallel to c-axis is 12.5 times a-b orientation [3].
- linear magnetoresistance: extremely linear and changes by a factor of 90 to 45T [4].

Results of this work:

- electronic band structure is highly 2D.
- critical points in band dispersion are identified via photoemission
- STM shows cleaves occur at half-lattice intervals in c-direction.
- STM suggests periodic modulations on surface in 2 perpendicular directions
- neutron diffraction shows crystals are twinned.
- at low temperature, neutron diffraction shows new spots consistent with lattice distortions along [100].
The STM images taken after cleaving in vacuo show flat terraces with step edges equivalent to the half unit cell height. This suggests that cleavage occurs between the LaSb layers, and gives uniform and stoichiometric surfaces. These surfaces should be amenable to angle-resolved photoemission studies.

The angle-resolved photoemission results show no dispersion for $k_{//}$ from angle-dependent measurements. The normal emission measurements reveal some dispersion for $k_\perp$, mostly for the bands situated close to the Fermi surface. The lack of dispersion for $k_\perp$ is consistent with the quasi-2D band structure.

The neutron diffraction data collected at four temperature values reveals doublet structures for $(h k 0)$ reflections with $h \neq k$, which confirms the twinning of the crystal. The $(h h 0)$ type reflections result in a single spot. A forbidden $(4 1 0)$ reflection is observed at low temperatures.

At low temperature (10K) the diffraction pattern presents additional spots that form close to the diffraction spots observed at 295, 200 and 100 K. The new peaks can be attributed to two new substructures that develop (exist) at low temperatures, and are incommensurate with the main lattice.

Nearly all of the observed phenomena described above can be reconciled in a single model where strong electron-phonon coupling results in a charge-density wave (CDW) due to an associated Peierls instability and lattice distortion. We will briefly describe the characteristics of CDWs and their relationship to the underlying structural and electronic properties, and then we will summarize by indicating how our data, and previous observations support this model. We will finish by indicating specific future measurements that could provide valuable additional information.
About 60 years ago, a new crystalline form for electrons was suggested by E. Wigner [1]. At low electronic densities, the stationary ions that form the lattice may displace periodically, generating a periodic distortion of the lattice, also known as a Peierls distortion [2]. A potential well is created, trapping electrons inside and generating an electronic crystal. The periodic movement of the positive ions and the trapped electrons results in a periodic charge density variation, also known as a charge density wave (CDW). Low dimensional (quasi-one or two dimensional) crystals are more likely to experience a CDW. In three dimensional crystals, the Coulomb repulsion is large enough to prevent the electrons from forming a crystal.

Grunter et al. [3] proposed a classical particle model for describing a CDW description. A massive particle is located at the center of mass of the electron-hole pair. The motion of the CDW would be similar to the motion of the massive particle that travels along a ribbed surface in a gravitational field. The particle is connected to other particles via springs (Coulomb force). The CDW is considered commensurate if the equilibrium length of the spring is an integer multiple of the lattice parameter, and incommensurate if the spring equilibrium length is not an integer multiple of the lattice parameter. In the latter case, the CDW is free to float on top of the lattice until a defect will pin it down.

Charge density waves occur in low-dimensional materials with electronic instabilities that can lead to structural modulations [4]. In particular, Fermi surface nesting creates an instability that leads to a lower electronic energy via excitations involving $2k_F$ and an energy gap that opens at the Fermi surface [5]. The opening of a
gap suggests that the density of states should also change and strongly affect transport
properties.

CDW’s are most likely to appear in 1D materials, generated by a periodic
displacement in the ion chain, characterized by a wave vector $\mathbf{Q}$ of magnitude $2k_F$ ($k_F$
being the Fermi momentum). The periodic potential generates a dielectric gap, and all
filled electronic states are pushed down. One of the conditions for this occurrence is the
nesting of the Fermi surfaces. The response from the electron gas to the external static
charge is given by the polarization operator (response function):

$$\Pi_{1D}(q,0) = 2N_{1D}(0)\frac{k_F}{k_\perp} \ln \left| \frac{k_\perp + k_F}{k_\perp - k_\perp} \right|$$  \hspace{1cm} (5.6.)

where $q$ is the momentum transferred ($q^2 = k_{//}^2 + k_\perp^2$, with $k_{//}, k_\perp$ being the $q$-
components normal and parallel to the Fermi surfaces); $N_{1D}(0)$ is the background DOS
per spin direction for the 1D electron gas. $\Pi_{1D}(q,0)$ determines the spontaneous ion chain
distortion (Peierls transition) due to the logarithmic singularity.

In the 2D case, the nested Fermi planes are reduced to two lines, and the response
function becomes:

$$\Pi_{2D}(q,0) = N_{2D}(0) \text{Re} \left\{ 1 - \left[ 1 - \left( \frac{2k_F}{k_\perp} \right)^2 \right]^{1/2} \right\}$$  \hspace{1cm} (5.7)

where $N_{2D}(0)$ is the starting electronic DOS per spin direction.

In quasi-2D materials, as LaSb$_2$, a CDW can occur even if the FS nesting is
imperfect (e.g. SmTe$_3$ [6]). The nesting wave vector $\mathbf{Q}_{\text{nest}}$ does not coincide precisely to
the CDW vector $\mathbf{Q}$, but the energy can still be lowered. Quasi-2D materials present
partially nested Fermi surfaces, but under the right nesting conditions or saddle-point
singularities, CDW can develop due to the electronic susceptibility enhancement. The system can present metallic character in the CDW state since the Fermi surface is only partially gapped [7].

CDW formation in non-1 D systems is supported by the existence of hidden nesting [8]. In the case of AMo$_6$O$_{17}$ (A=K, Na), the lowest three filled $d$-bands form up to three 2D nonnested FSs, but overall the total FS can be partitioned into three sets of nested 1D FSs. The wave vector derived from the chain directions connects two chosen sets of nested FS sections.

Our results summarized in the list on page 117 help to set the scene for the development of charge density waves. First, the photoemission results provide the critical information that establishes that the underlying electronic structure is 2D. This reduced dimensionality is a strong necessary condition and supports the theoretical prediction for a highly nested Fermi surface, as well. By monitoring the dispersion of the features near $E_F$, we have established the location of the $\Gamma$ and Z critical points for LaSb$_2$. Although we would have liked to extract the Fermi surface from the photoemission results, we found that we did not see strongly dispersing features nor were we able to see structure at $E_F$ in off-normal emission. The subsequent neutron scattering measurements explained this: the crystals are twinned and this is probably the reason that LEED patterns were not seen. Without long-range coherence, periodic properties like the electronic band structure and surface-sensitive diffraction will be smeared out. Another feature expected in our photoemission experiment was a gap opening at the Fermi level, as a result of the system undergoing a Peierls instability. In our photoemission experiment, the spectra at both room temperature and 140K showed no difference at the Fermi level as a function of
temperature. Lowering the temperature to a value closer to the 10K from the neutron diffraction experiment may bring new behavior at lower temperature.

In addition to establishing the reduced dimension of the electronic structure, this work also demonstrated that new periodicities are established at lower temperatures: the lattice shows new features meaning that the periodicity modifies along the [100] directions of the twinned crystals. This is strong evidence for the development of a CDW: a new periodicity within a reduced-dimension system that has highly-nested Fermi surfaces. We currently do not have an interpretation for the streaking of the new peaks appearing within the diffraction pattern. There are some suggestions that the angular spread may be related to the variation in the directions of Fermi surface nesting wavevectors but this is currently a matter of debate.

At the same time, it is true that CDWs are incommensurate at higher temperatures, and become commensurate at low temperatures. As the terms “high” and “low” are specific for each material, it may be possible that the charge density waves may become commensurate at a temperature lower than 10K. There are materials that form charge-density waves at different temperatures, one at low temperature, and another at high temperatures [13].

Finally, the STM images provide tantalizing further evidence for the existence of a CDW. Periodic modulations of the surface charge density appear to be in perpendicular directions, which would be the case in a highly-twinned crystal.

If CDWs do exist in LaSb$_2$, the prior magnetic and transport phenomena can also be explained. First of all, the zero-field inflection point at 260 K may be related to the
critical temperature at which charge density waves set in. Magnetoresistance has also
been observed to result [14].

Future measurements that would help answer some of these questions include
additional studies of the Fermi surface and the expected gap to open there. The normal-
incidence monochromator at CAMD would be an appropriate place to perform this high-
resolution study, using lower photon energies and low temperature. In addition to the
potential for high energy resolution, the lower photon energy range would allow the
spectra to be more bulk sensitive as the electron mean-free path increases at low energy.

Additional low-temperature STM studies would also be very interesting and may
reveal convincing charge-density waves at the surface of LaSb2. Cleaving the sample at
low temperatures is expected to bring new insights.

6.1. References


1994.


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APPENDIX: LETTERS OF PERMISSION

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August 12, 2003

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202 Nicholson Hall, Tower Drive
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VITA

Alice Iulia Acatrinei was born in Iasi, Romania, on December 18, 1966. She attended the “Mihail Sadoveanu” High School (currently the National College), and graduated high school in 1986. Alice attended “Alexandru Ioan Cuza” University of Iasi from 1986 to 1990, at which time she earned a Bachelor of Science degree in physics. From 1990 to 1993 she taught physics at the Pedagogical College of Iasi, and in 1994 she joined the IDM Group as a foreign exchange trader. In August 1996 she was accepted in the doctoral program at Louisiana State University, Department of Physics and Astronomy. She earned the degree of Master of Science in 1998.