Quantitative Convergent Beam Electron Diffraction and Charge Density Studies

by

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Source: The CBED art works gallery at Tanaka’s group,
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Summary

Very accurate low-order structure factors have been measured in copper, magnesium and strontium titanate using quantitative convergent beam electron diffraction (QCBED). The charge density distribution in these materials has been studied using the measured structure factors. The results have also been compared to ab initio density functional theory (DFT) calculations.

In the case of copper, we combined our low-order structure factors with higher order $\gamma$-ray structure factors, in order to obtain a larger experimental data set for maximum entropy and multipole analysis. The results show that bond formation induces a large change in the 3$d$ orbital radial function. As expected for metallic bonding, no asphericity of the orbitals has been observed. These results are in perfect agreement with DFT calculations.

For magnesium it was shown that the anisotropic displacement parameters could be determined accurately from the low order QCBED data, if structure factors from DFT calculations were used as a static lattice reference. This data set was combined with X-ray structure factor measurements and used to test some commonly used DFT functionals and self interaction correction (SIC) schemes. It was found that the local density approximation combined with the SIC of Lundin and Eriksson (2001) gave the best agreement with experiments. Using this functional no non-nuclear maximum was found in beryllium, but not in magnesium.
Preface

This thesis is the result of more than three and a half years studies at Department of Physics at the Norwegian University Science and Technology (NTNU). It can be seen as a continuation of the long tradition in Trondheim, established by Prof. Ragnvald Høier (Department of Physics, NTNU) and continued by Prof. Knut Marthinsen (now Department of Materials Technology, NTNU) and Prof. Randi Holmestad (Department of Physics, NTNU), to use convergent beam electron diffraction for accurate structure factor determination and charge density studies.

During this thesis I have visited Arizona State University (ASU) twice, first six months in spring 2001 and later one month in April 2002. Together with Dr. Bin Jiang’s (Department of Physics and Astronomy, ASU) visits here in Trondheim (October 2001 and November 2002), these have been the most productive periods of the thesis.

This work is divided into four parts:

The first part is an introduction to quantitative convergent beam electron diffraction and methods for studying the charge density using experimentally derived structure factors. These methods include direct Fourier synthesis, multipolar modeling and maximum entropy. A brief description of density functional theory is also included in chapter 3.

The second and main part contains the papers:

**Paper 1:** *Quantitative Convergent Beam Electron Diffraction Measurements of Low Order Structure Factors in Copper*

**Paper 2:** *On the Consistency of QCBED structure factor measurements for TiO$_2$ (Rutile)*

**Paper 3:** *Retrieval of anisotropic displacement parameters in Mg from convergent beam electron diffraction*
J. Friis, K. Marthinsen and R. Holmestad.
In press.

**Paper 4:** *Magnesium: Comparison of Density Functional Theory Calculations with Electron and X-ray Diffraction Experiments*
J. Friis, G. K. H. Madsen, F. K. Larsen, B. Jiang, K. Marthinsen and
R. Holmestad.

Paper 5: A Study of Charge Density in Copper
J. Friis, B. Jiang, K. Marthinsen and R. Holmestad.
Aimed for Acta Cryst. A.

Paper 6: Electron Density and Implication for Bonding in Cu and Ag
Submitted to Phys. Rev. B.

Paper 1, 5, and 6 are based on experiments on copper performed during my visit at ASU the spring 2001. My contribution to paper 2 is limited to the generation of figure 6. Paper 3 and 4 are based on experiments on magnesium during my second visit to ASU, April 2002.

After the papers follows a short chapter on the unpublished and unfinished results on strontium titanate.

Finally two appendices are included, one containing a derivation of the Mott formula and another containing derivation of formulas for error analysis of the experimental structure factors.

Acknowledgements

First of all I want to thank my supervisors Randi Holmestad and Knut Marthinsen for assistance, many clarifying discussions and their always good mood. Their overview, especially in dynamical diffraction theory, has been of great help. Randi was the driving force for my visits to ASU, on which all the published results are based. I also want to thank John Spence, who welcomed me in his group during my visits at ASU.

I also really want to thank Bin Jiang, who learned me everything I know about operating a transmission electron microscope, and has been an invaluable collaborator, teacher, and friend. The discussions with Jian Min Zuo (Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign) have also been of great help.

The collaboration with Georg Madsen and Finn Krebs Larsen at Århus University resulted in my probably most important article, Paper 4. Many thanks to both for giving me the chance to work with them, and for their generosity. I am also grateful to Morten and Maria Fredriksen for welcoming me home whenever I visited Aarhus University and to Frode Mo, who suggested the contact.

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Thanks to the TEM group for their friendship and to Nils Sandberg and Rasmus Jansson for reading through this manuscript.

Above all I want to thank my always patient wife, Kris. Thanks also for reading through the manuscript and for your very inspiring illustrations.

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Jesper Friis
Trondheim, November 11, 2003
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#### 1 Quantitative Convergent Beam Electron Diffraction Measurements of Low Order Structure Factors in Copper

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Part I
Introduction and background to quantitative convergent beam electron diffraction and charge density studies
TEM  ZOLZ

dispersion surface diffraction mode
Chapter 1

Introduction

The aim of this work has been to investigate theoretically and experimentally, different methods and aspects of the determination of charge density and bonding by convergent beam electron diffraction (CBED). This work is motivated by the fact that an increased knowledge of the microscopic properties, such as bonding and charge distribution, is required to design and use new and advanced materials.

Traditionally electron microscopy has been a qualitative science both for imaging and diffraction. A lot of information about crystal symmetry and crystal structure can be derived from the position of the diffraction spots. The first convergent beam electron diffraction pattern was produced already in 1937 by Kossel & Möllenstedt (1939) in order to further investigate the newly discovered Kossel and Kikuchi patterns seen in X-ray diffraction experiments. With the development of the dynamical theory in the 1950s and 1960s, it became clear that dynamical effects have to be taken into account in order to explain effects such as the occurrence of forbidden reflections (Gjønnes & Moodie, 1965) and small shifts in the Kikuchi-line positions (Uyeda, 1968; Høier, 1969; Gjønnes & Høier, 1971). Quantitative measurements of structure factors started in the early 1980s (Voss et al., 1980), taking not only the position of the features in the diffraction pattern into account, but also the exact intensities. Shortly after, phase measurements of the structure factors for non-centrosymmetric crystals were also performed (Taftø & Spence, 1982; Taftø, 1983; Marthinsen & Høier, 1986, 1988). The use of energy filters, CCD cameras/image plates and the increase of computer power during the 1990s have greatly increased the accuracy and made convergent beam electron diffraction an accurate tool for measuring the low order structure factors in small unit-cell crystals (e.g. Zuo, 1993; Saunders et al., 1993; Holmestad et al., 1995; Høier et al., 1993; Tsuda & Tanaka, 1995; Deininger et al., 1995; Saunders et al., 1996; Zuo et al., 1997; Birkeland et al., 1997;
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Nüchter et al., 1998; Saunders et al., 1999; Holmestad et al., 1999; Zuo, 1999; Jiang et al., 2003).

The new challenge is to combine the low order structure factors from quantitative CBED with higher order structure factors from X-ray diffraction, in order to obtain a better description of the charge density (Zuo et al., 1999; Streltsov et al., 2001) and to test band theory (Zuo et al., 1997; Friis et al., 2003).

References


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CHAPTER 1. INTRODUCTION


Chapter 2

Quantitative electron diffraction

This chapter is intended to introduce the reader to the quantitative electron diffraction (QED) theory needed for the papers following in Part II. A simple and general introduction to electron microscopy is given by Williams & Carter (1996). For an overview of the electron diffraction theory, the excellent review by Humphreys (1979) is recommended. A complete and very good introduction to quantitative convergent beam electron diffraction (QCBED) is given in Spence & Zuo (1992).

2.1 Electron diffraction

In transmission electron microscopy, a beam of (high-energy) electrons is sent through the specimen, with which the electrons interact, and is recorded on the other side. All modern transmission electron microscopes (TEMs) have two main modes, an imaging (or microscopy) mode, and a diffraction mode. In the image mode, the recorded pattern shows the projection of the spatial distribution of the scattering, while in the diffraction mode, the recorded pattern shows the angular distribution of the scattering. One of the great advantages of TEM, e.g. compared to X-ray diffraction, is the possibility to easily switch between these modes.

In “ordinary” parallel beam electron diffraction, the diffraction patterns consist of bright spots (see Fig. 2.2a), corresponding to beam directions that satisfy the well known Bragg’s law

$$2d’ \sin \theta_B = n \lambda \quad (2.1)$$

where $d’$ is the spacing between lattice planes, $\theta_B$ is the Bragg angle, $n$ is
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an integer and $\lambda$ is the electron wave length. However, it is convenient to introduce $d = d'/n$ which simplifies Bragg’s law to

$$2d \sin \theta_B = \lambda$$  \hspace{1cm} (2.2)

and to regard this as first order reflections from planes with spacing $d = d'/n$. The quantity $s = \sin \theta / \lambda$ is often referred to as the Bragg angle, where $s = |\mathbf{g}| / 2$ at the Bragg angle, where $\mathbf{g}$ is a reciprocal lattice vector corresponding to the planes $d$, with $|\mathbf{g}| = 1/d$.

Another condition for diffraction maximum, which is more suitable for quantitative work, is the Laue condition

$$\mathbf{K}' - \mathbf{K} = \mathbf{g},$$  \hspace{1cm} (2.3)

where $\mathbf{K}$ and $\mathbf{K}'$ are the incident and diffracted beams respectively. By assuming elastic scattering $|\mathbf{K}'| = |\mathbf{K}|$, Bragg’s law (2.2) follows immediately, with the Bragg angle $\theta_B$ defined in Fig. 2.1.

2.2 Convergent beam electron diffraction

The principles of CBED are the same as for ordinary selected area diffraction (SAD), but instead of using a parallel beam, the electron probe is focused onto the specimen. As seen in Fig. 2.2, this causes the spots to broaden out into disks. Each incident beam direction (e.g. $a$ in Fig. 2.3) gives rise to a complete diffraction pattern, with one diffraction spot $a'$ contributing to each CBED disk. Thus, if an incoherent electron source is used, such as a LaB$_6$ filament, the CBED pattern can be seen as a superposition of independent diffraction patterns with different incident directions. For coherent sources, such as a field electron gun (FEG), one has to account for interference phenomena in the regions where the disks overlap (Zuo & Spence, 1993).

Figure 2.4 shows a CBED pattern tilted away from the major zone axis, to a position where the (101) and (101) reflections satisfy the Bragg condition along the lines pointed out in the figure. This is called a systematic row orientation. Three reflections, $(0\bar{3}1)$, $(130)$ and $(231)$, in the first order Laue zone (FOLZ), are also visible. At incident beam angles satisfying the Bragg conditions for these three reflections, intensity is scattered away from the
2.2. CONVERGENT BEAM ELECTRON DIFFRACTION

Figure 2.2: Parallel (a) versus convergent beam (b) electron diffraction patterns of the [101] zone in Mg. In the SAD pattern (a) the direct beam is blocked in order to protect the CCD camera. April 5, 2002.

Figure 2.3: Schematic drawing of CBED. The CBED pattern is a superposition of diffraction patterns with slightly different incident beam directions. A CBED pattern is hence an image of the intensity variation as a function (called rocking curve) of incident beam direction.
center disk to corresponding reflections. The dark FOLZ-line, corresponding to the (130) reflection, is marked in figure 2.4a. From kinematic theory, one would expect this to be a straight line, like all the other thin dark lines visible in the center disk, but because of strong dynamical coupling between the (130) and (231) reflections, the line seems to split up and bend where it crosses the (231) FOLZ-line. The position of the high order Laue zone (HOLZ)-lines, which are not strongly coupled to other lines, is easily determined from the incident beams $\mathbf{K}$ satisfying the Laue condition for reflection $g$. For elastically scattered electrons\(^1\), the absolute value of the scattered beam $|\mathbf{K}'| = |\mathbf{K} + \mathbf{g}|$ equals the absolute value of the incident beam $|\mathbf{K}|$, i.e.

$$K^2 = |K'|^2 = |K + g|^2$$

(2.4)

from which it follows that

$$\mathbf{K} \cdot \mathbf{g} = -g^2/2.$$  

(2.5)

Since the amplitude $|\mathbf{K}| = 1/\lambda$ is fixed, this equation defines a circle of incident beams $\mathbf{K}$ making an angle of $90^\circ - \theta_B$ with the lattice vector $\mathbf{g}$, as illustrated in Fig. 2.5. The position of the HOLZ-lines corresponds to the projection of this ring onto the zero order Laue zone (ZOLZ)-plane (plane

---

\(^1\)Thermal diffuse scattering (TDS) can also be regarded as nearly elastic, since the loss in energy (up to 0.1 eV) is much smaller than the beam energy. This is the reason why Kikuchi-lines just continue the HOLZ-lines outside the disk.

April 9, 2002.
perpendicular to the zone axis). For high-energy electrons, the HOLZ-lines appear straight since the radius of the cone is very large (\(\lambda\) is very small).

From Fig. 2.4b one sees that the HOLZ-lines continue out of the CBED disks. These lines, called Kikuchi-lines, are due to elastic scattering of inelastic scattered electrons. They are very useful for an initial determination of the crystal orientation.

The last important feature seen in Fig. 2.4a is the thickness fringes. These too have a dynamical origin and the distance between them is closely related to the crystal thickness (see Eq. 2.15). The thicker the crystal, the closer are the fringes.

Together with the huge amount of information, the most important advantage of CBED is the small probe size, typically 10 nm in a conventional TEM, and down to a few Ångström in a microscope with a FEG source. The small probe, combined with the image mode, makes it easy to find a perfect crystalline region of the specimen for the CBED experiment.

Because of the strong interaction between the incoming electrons and the crystal, multiple scattering occurs, despite the small sample thickness (500–2000 Å). Hence, dynamical theory is required when calculating the intensities in the CBED pattern. Since the scattering comes from a single-crystalline region, it is possible to use the Bloch-wave method (described in more detail in Section 2.3) resulting in very accurate simulations. This is the same
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technique as is used in the X-ray Pendellösung method. However, the X-ray Pendellösung method is limited to very few materials, such as Si and diamond, for which large single crystals can be produced.

Since normal X-ray diffraction (not Pendellösung) utilizes kinematic theory, there will be problems with extinction (dynamical effects) for the strong low order reflections. However, these are exactly the reflections that can be measured with QCBED. Hence X-ray and QCBED can be seen as complementary techniques and their combination has proven very successful (Zuo et al., 1999; Friis et al., 2003b).

2.3 Dynamical intensities

There are two common methods for simulation of electron diffraction intensities, the Bloch-wave and the multi-slice method. For perfect crystals with relatively small unit cells, the Bloch-wave method is preferable because of its accuracy.

Since the exchange and correlation between the beam and crystal electrons can be neglected for high energy electrons (Rez, 1978), the propagation of an incident electron is described by the time-independent Schrödinger equation

\[
\left( -\frac{\hbar^2}{8\pi^2m} \nabla^2 - |e|V(r) \right) \Psi = |e|E\Psi
\]  

(2.6)

where \(V(r)\) is the crystal potential (in units of Volts) and \(-E\) is the acceleration voltage. For a periodic potential

\[
V(r) = \sum_g V_g e^{2\pi i g \cdot r}
\]

(2.7)

equation (2.6) has the Bloch-wave solution

\[
\Psi(r) = \sum_j c^{(j)} e^{2\pi i k^{(j)} \cdot r} \sum_g C^{(j)}_g e^{2\pi i g \cdot r}
\]

(2.8)

where \(k^{(j)}\) is the wave-vector of the \(j\)th Bloch-wave and \(g\) is a reciprocal lattice vector. Substitution of Eq. (2.7) and (2.8) back into Eq. (2.6) yields the standard dispersion equation for high-energy electron diffraction

\[
[K^2 - (k^{(j)} + g)^2] C^{(j)}_g + \sum_{h \neq g} U_{h-g} C^{(j)}_h = 0
\]

(2.9)

where we have introduced the electron structure factor

\[
U_g = \frac{2m|e|}{\hbar^2} V_g.
\]

(2.10)
The amplitude of the incident beam wave-vector is related to the acceleration voltage by $K^2 = 2m|e|(E + V_0)/h^2$ where $V_0$ is the mean inner potential. Even though $V_0$ is a very small quantity (around 5-25 V depending on material) compared to $E$ (120 kV in the microscope used for the experiments in this thesis) it is not negligible (Friis et al., 2003a).

![Figure 2.6](image)

**Figure 2.6:** Two-beam dispersion surface construction, showing the quantities $\gamma^{(j)}$, $k^{(j)}$, etc... The dispersion surface shows the allowed $k$ vectors inside the crystal for a given electron beam energy.

It follows from continuity of $\Psi(r)$ at the entrance surface of the crystal, that the tangential components of $k^{(j)}$ must equal the tangential components of $K$, which can be expressed as $k^{(j)} = K + \gamma^{(j)}n$, where $n$ is the normal vector of the surface and the coefficient $\gamma^{(j)}$ is known as the Anpassung. Some of these quantities are shown for the two beam case in Fig. 2.6. Since backward scattering can be neglected for high energy electrons (Hirsch et al., 1977), Eq. (2.9) can, after renormalization (Metherell, 1975) and assuming that the beam is nearly antiparallel to the entrance surface, be simplified to

$$2KS_g C_g^{(j)} + \sum_{h} U_{g-h} C_h^{(j)} = 2K_n \gamma^{(j)} C_g^{(j)},$$

(2.11)

where $S_g$ is the deviation from the Bragg condition and $K_n = K \cdot n$ (Spence & Zuo, 1992). This is an eigenvalue problem, with eigenvalues $2K_n \gamma^{(j)}$ and eigenvector matrix $C$. Because of continuity, no reflected beams can be excited at the entrance surface, leading to a condition $\sum_{j} c^{(j)} C_0^{(j)} = 1$ for the excitation coefficient $c^{(j)}$ of the $j$th Bloch-wave.

The diffraction intensities are given by the wave function at the exit surface. The intensity in a point specified by the incident beam $K$ in disk $g$
is given by

$$I_g(K) = |\Psi|^2 = \left| \sum_j C_0^{(j)} C_g^{(j)*} e^{2\pi i r^{(j)} t} \right|^2$$

(2.12)

where \( t \) is the thickness of the crystal.

Absorption can be included in a phenomenological way, by introducing a complex component to the crystal potential

$$V(r) \rightarrow V(r) + iV'(r)$$

(2.13)

leading to a damping

$$k^{(j)} \rightarrow k^{(j)} + iq^{(j)}$$ and $$c^{(j)} \rightarrow c^{(j)} e^{-2\pi i q^{(j)} t}$$

(2.14)

of the intensity. From the Fourier transform of \( V(r) \) and \( V'(r) \) one obtains the, in general complex, electron structure factor \( U_g \), and absorption \( U'_g \), respectively.

If there is only one strongly exited beam \( (g) \) beside the direct beam \( (0) \) (the so called \textit{two beam condition}), it is easy to solve Eq. (2.11) analytically, resulting in the intensities

$$I_g(K) = 1 - I_0(K) = \frac{|U_g|^2 \sin^2 \left( \frac{\pi t}{K \sqrt{K^2 S_g^2 + |U'_g|^2}} \right)}{K^2 S_g^2 + |U'_g|^2}.$$  

(2.15)

This equation explains the oscillating “thickness fringes”, seen in Fig. 2.4, when we move away from the Bragg condition. It also tells us that the intensity will oscillate with thickness variations. These simple observations are still valid, though more complicated, in the general \( n \)-beam condition.

### 2.4 Structure factor refinement

There exist several approaches for structure factor determination by QED (see Holmestad 1994, page 22 for an overview). For QCBED there are two main approaches, one using zone-axis patterns (Bird & Saunders, 1992a,b) and one using the systematic row orientation (Zuo & Spence, 1991). Both techniques can provide low order structure factors accurate enough for bonding studies. The zone-axis approach has the advantage that the diffraction patterns are easy to index and a lot of structure factors can be refined from a single experimental pattern. However, the computation might be more difficult since more parameters have to be refined and the patterns contain...
a lot of HOLZ-lines, that are affected by the temperature factor\(^2\) and lattice parameters. In the systematic row orientation, on the other hand, the specimen is tilted to a position with only a few strongly excited reflections. This makes the intensity around the Bragg position very sensitive to the corresponding structure factor. In addition it is possible to find regions with only few HOLZ-lines, reducing the problems with the temperature factor. In this work the systematic row approach has been used. The experimental setup and the importance of energy filtering and deconvolution of the point spread function are covered in Paper 1 and 4. More details are found in Zuo (1999).

### 2.4.1 The least square procedure

The EXTAL program by Zuo (1998) has been used for all structure factor refinements presented in this thesis. It follows the ideas of Goodman & Lehmpfuhl (1967), Voss \textit{et al.} (1980) and Gjønnes \textit{et al.} (1988), but has developed into an advanced algorithm for refining high voltage, lattice parameter, and structure factors. In short one chooses pixels along lines for which the intensity is extra sensitive to the parameters one wants to determine (see Fig. 2.7 and Friis \textit{et al.} 2003b). A set of refined parameters (structure factors, absorption, thickness, beam direction, etc...) are varied until a best fit is obtained between the calculated and the experimental intensities. The SIM-

![Figure 2.7](image)

\textbf{Figure 2.7}: (a) A CBED pattern of the (220) systematic row in copper. The line scans, along which pixels are compared with theory are marked. (b) Plot of pixel intensities for the best fit between calculation and experiment. \textit{By B. Jiang, Sep. 2001.}

\(^2\)This can, on the other hand, be used for measuring the temperature factor (Saunders \textit{et al.}, 1999).
PLEX algorithm of Nelder & Mead (1965) is used for the minimization in EXTAL. This seems to give a good balance between robustness and efficiency.

If one removes outlier pixels arising from X-rays striking the CCD-camera, the errors can be assumed to be normal-distributed (see Zuo 1999 for a discussion). Hence a \( \chi^2 \) test may be used as a goodness-of-fit criterion

\[
\chi^2 = \frac{1}{n - p - 1} \sum_{i=1}^{n} \frac{|I_{i}^{\text{obs}} - cI_{i}^{\text{calc}} - I_{i}^{\text{bgr}}|^2}{\sigma_i^2}.
\]

Here \( I_{i}^{\text{calc}} \) and \( I_{i}^{\text{obs}} \) are the calculated and observed intensities for pixel \( i \) while \( I_{i}^{\text{bgr}} \) is a refined background intensity, which is assumed constant for each disk (Saunders & Bird, 1995). \( n \) is the number of pixels, \( p \) the number of refined parameters and \( c \) a refined factor, which scales the calculated intensity to counts. Ideally \( \chi^2 \) should be very close to one, provided normal-distributed errors and that correct values are used for the standard deviation of the intensities \( \sigma_i \).

In order to ensure convergence of the refinement procedure, good starting values for the refined parameters must be chosen. First the thickness, which is a trivial but important parameter, and the incident beam direction have to be estimated. The beam direction is usually estimated by visually comparing the experimental Kikuchi- and HOLZ-line pattern with kinematic calculations (Zhu & Zuo, 1994). The absorption is estimated using the ATOM subroutine of Bird & King (1990), even though better routines are available nowadays (Weickenmeier & Kohl, 1991, 1998).

The initial structure factors can either be taken from density functional theory (DFT) calculations, or be calculated from the electron scattering factor as

\[
U_g = \frac{2m|e|}{h^2} \frac{1}{\Omega} \sum_j f_j^e(s)T_j(s) e^{-2\pi i g \cdot r_j},
\]

where \( f_j^e \) is related to the X-ray scattering factor (via Eq. A.7), for which good extrapolations to Hartree-Fock calculations exist (Doyle & Turner, 1968; Su & Coppens, 1997). In either case, the atomic temperature factor \( T_j(s) \) at the experimental temperature also has to be estimated. It is important to get a good estimation of the displacement parameters\(^3\) (DPs), since all the non-refined structure factors depend on them.

\(^3\)\(T_j(s)\) is in the harmonic approximation given by \( T_j(s) = \exp(-2\pi\langle u' u^k \rangle_j g_i g_k) \), where the elements of the atomic displacement tensor \( \langle u' u^k \rangle_j \) are the anisotropic DPs. Summation over repeated indices is assumed. In the isotropic case this equation reduces into \( T_j(s) = \exp(-B_j s^2) \), where \( B_j = 8\pi^2\langle u^2 \rangle_j \) is known as the Debye-Waller factor in the electron microscopy literature. However, this name is not recommended according to a commission on nomenclature sat down by IUCr (Trueblood et al., 1996).
Good isotropic estimates for the DPs can in many cases be obtained from analytical fits to phonon density-of-state calculations (Sears & Shelley, 1991). A problem with this approach, as well as using X-ray or neutron diffraction results, is that the exact temperature of the specimen is unknown. A better method is therefore to determine the DPs directly from the CBED data (Holmestad et al., 1993; Nüchter et al., 1998; Saunders et al., 1999; Friis et al., 2003c).

2.4.2 Beam selection and Bethe perturbation

Since Eq. (2.11) has to be solved for each pixel along the chosen line scans, one has to limit the number of beams included in the diagonalization. This is solved by only including the strongest beams in the diagonalization (∼50), and treating the rest of the non-negligible beams by perturbation (∼300). See Zuo & Weickenmeier (1995) and Birkeland et al. (1997) for a discussion of beam selection criteria. Using the effective Bethe potential, the following perturbations of the eigenvalue system (2.11) can be derived (Spence & Zuo, 1992)

\[
U_{g}^{\text{eff}} = U_{g} \left( 1 - \sum_{h} \frac{U_{g-h}U_{h}}{2KS_{h}U_{g}} \right)
\]

\[
2KS_{g}^{\text{eff}} = 2KS_{g} - \sum_{h} \frac{U_{g-h}U_{h-g}}{2KS_{h}}
\]

(2.18)

that are caused by dynamical interaction between the strong beam \(g\) and the weak beams \(h\). Eq. 2.18 is used in EXTAL with the beam selection criterias of Zuo & Weickenmeier (1995).

References


CHAPTER 2. QUANTITATIVE ELECTRON DIFFRACTION


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CHAPTER 2. QUANTITATIVE ELECTRON DIFFRACTION


Chapter 3

Charge density

3.1 The independent atom model

Since only a minor part of the electrons of an atom belongs to the valence shell, the atomic electron density is well described by a spherically averaged density (except for the lightest elements H, He...). If one furthermore assumes that the radial dependence is equal to that of the theoretical ground state atom, one ends up with the independent atom model (IAM), in which the atoms are assumed independent of each other. It describes a procrystal where independent atoms are brought from infinity to the lattice positions of the crystal. From calculations of the spherical atomic charge density \( \rho_{\text{atom}}(r) \) the atomic IAM X-ray scattering factors are given by

\[
f^X(s) = \mathcal{F}\{\rho\} = 4\pi \int_0^\infty r^2 \rho_{\text{atom}}(r) \frac{\sin(4\pi sr)}{4\pi sr} \, dr, \quad (3.1)
\]

where \( \mathcal{F} \) is the Fourier transform and \( s = \sin \theta / \lambda \) is the scattering angle.

In International Tables for Crystallography (1992, page 500) interpolated coefficients for the scattering factors are listed for many common elements and ions based on the relativistic Hartree-Fock calculations of Doyle & Turner (1968). More recent similar tables have been published by Su & Coppens (1997) based on multiconfiguration Dirac-Hartree-Fock calculations.

The IAM model gives very good values of \( f^X \) for large scattering angles and is a good approximation for small scattering angles too. However, by construction, it contains no information about the fine charge redistribution due to bonding. For this, one needs a model which takes the interaction between atoms into account.
CHAPTER 3. CHARGE DENSITY

3.2 Deformation density

The shape of the deformation of the electron charge distribution, when bonding features are added to the IAM model, gives a good qualitative measure of chemical bonding. This deformation is given by the deformation density, defined as

\[ \Delta \rho = \rho(r) - \rho_{IAM}(r) \]  

(3.2)

where \( \rho \) is the true charge density and \( \rho_{IAM} \) is the procrystal density.

The deformation density includes information about atomic orientation, hybridization, charge transfer, and covalent bond formation. A peak between atoms indicates covalent bonding. However, the opposite statement, that the absence of a peak implies no covalent bonding, is not necessarily true, since for elements with more than half-filled shells, the neutral spherical atoms that are subtracted have more than one electron per orbital (Coppens, 1997). Metallic bonding is typically recognized as a spherically charge depletion at the atomic sites (Friis et al., 2003a).

The deformation density is normally obtained by Fourier synthesis of experimentally measured structure factors \( F_{obs} \) as

\[ \Delta \rho = \rho_{obs}(r) - \rho_{IAM}(r) = \frac{1}{\Omega} \sum_{g} (F_{obs}^g - F_{IAM}^g) e^{-2\pi i g \cdot r}. \]  

(3.3)

An example of a deformation density map of the (110) plane in Cu is shown in Fig. 3.1a.

The deformation density calculated in this way contains uncertainties, arising both from the errors in measured structure factors and from the fact that the number of measured structure factors is limited, which may result in non-negligible truncation errors. An approximate expression for the variance of the deformation density was derived by Rees (1976) where it is assumed that all beams up to \( g_{\text{max}} \) are measured. Rees puts all uncertainties of the measured values into a factor \( \sigma^2(\rho_{obs}^G) \) corresponding to the variance at a general position

\[ \sigma^2(\Delta \rho_G) \approx \frac{1}{\Omega} \sum_{g \leq g_{\text{max}}} \sigma^2(F_{obs}^g). \]  

(3.4)

The variance of \( \Delta \rho \) at position \( r \) is then given by

\[ \sigma^2(\Delta \rho)(r) = \sigma^2(\Delta \rho_G) \left[ 1 + \sum_{i=2}^{n} C(2\pi|r - T_i r - R_i||g_{\text{max}}|) \right] \]  

(3.5)

where the sum runs over the \( n \) symmetry equivalent positions, \( T_i \) is the \( i \)th symmetry operator and \( R_i \) is the crystal sub-lattice translation vector which
3.2. DEFORMATION DENSITY

Figure 3.1: (a) The deformation density of the (110) plane in Cu calculated from the 6 lowest order structure factors ($|g_{\text{max}}| = 1.58$ Å$^{-1}$). The zero level is marked with a thick black contour line. Positive (black) and negative (white) contour intervals are 0.05 eÅ$^{-3}$ and 0.1 eÅ$^{-3}$, respectively. (b) A corresponding map of the standard deviations. Contour intervals are 0.05 eÅ$^{-3}$. Source: Friis et al. (2003a).

minimizes $|r - T_i r - R_i|$. The identity operator $T_1 = I$ is moved out of the summation in order to simplify the discussion below, about the limit when $|g_{\text{max}}| \to \infty$. The function $C$ is given by

Figure 3.2: The function $C(u)$ in expression 3.6.

$$C(u) = 3(\sin(u) - u \cos(u))/u^3$$  \hspace{1cm} (3.6)

and is plotted in Fig. 3.2.

From Fig. 3.1b it is clear that the standard deviation of the deformation density $\sigma(\Delta \rho)$ shows large peaks close to high-symmetric positions. This is
because, when $r$ is close to a high-symmetric position, $u = |r - T_i r - R_i| g_{\text{max}}$ will be small and hence $C(u)$ will be large for all terms $i$ in (3.5) for which $T_i r \approx r$. From (Eq. 3.5) it follows that this is an effect caused by truncation errors. If $|g_{\text{max}}| \to \infty$ then $C(u) \to 0$ and the variance $\sigma^2(\Delta \rho)(r)$ will be flat and reduced to the variance of a general position $\sigma^2(\Delta \rho_G)$.

These truncation errors can be avoided in deformation densities derived from a multipole model or a maximum entropy simulation. In the former case, one fits a set of multipolar parameters to create a model reproducing the observed structure factors $F_g^{\text{obs}}$. From this model it is possible to directly find $\rho^{\text{obs}}$, without any Fourier summation. In the latter case the Fourier summation is also avoided, since one is already working in real space.

### 3.3 Density functional theory

Density functional theory (DFT) has shown to be an efficient and accurate approach for solving the many-electron system of a crystal. It is based on the statement that there exists a one-to-one correspondence between the ground state density $\rho(r)$ of a many-electron system and the external potential $V$ (Hohenberg & Kohn, 1964). From this statement it follows that the energy can be written as a functional of the electron density. In the formalism of Kohn & Sham (1965) the total energy is given by

$$E[\rho] = E^{\text{KS}}_{\text{kin}}[\rho] + E_{eN}[\rho] + E_{\text{xc}}[\rho] + E_{\text{NN}}$$

(3.7)

where the terms are, respectively, the kinetic energy$^1$, the attractive Coulomb electron-nucleus interaction, the repulsive Coulomb electron-electron interaction, the exchange-correlation energy and finally the nucleus-nucleus Coulomb repulsion, which does not depend on the electron density. The exchange-correlation term does not have a simple classical interpretation. It incorporates the effect of the Pauli principle, i.e. that the wave-function is anti-symmetric under the exchange of two electrons, and the Coulomb correlation between electrons, thus the name.

The energy of a system of electrons in an external field is given by minimizing the density functional$^2$ in Eq. (3.7). This is equivalent to solving a

---

$^1E^{\text{KS}}_{\text{kin}}$ is the energy of a fictitious non-interaction system. A correction ($E_{\text{kin}} - E^{\text{KS}}_{\text{kin}}$) is built into the exchange correlation $E_{\text{xc}}[\rho]$ (Friedrich, 1999).

$^2$This follows from the variational principle, which states that given a normalized wave function $\Phi$, which satisfies appropriate boundary conditions, the expectation value of the Hamiltonian is an upper limit to the exact ground state energy $\langle \Phi | H | \Phi \rangle \geq E_0$. 

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set of Kohn-Sham equations, comprising a one-particle Schrödinger equation

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}[\mathbf{r}, \rho(\mathbf{r})] \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \tag{3.8}
\]

with

\[
V_{KS}[\mathbf{r}, \rho(\mathbf{r})] = V_{\text{ext}}(\mathbf{r}) + V_{\text{ee}}(\mathbf{r}) + \frac{\partial}{\partial \rho(\mathbf{r})} E_{\text{xc}}[\rho(\mathbf{r})], \tag{3.9}
\]

where the Kohn-Sham orbitals \( \phi_i(\mathbf{r}) \) are related to the electron density by

\[
\rho(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2 \tag{3.10}
\]

with orbital occupation numbers \( f_i \). The terms in the Kohn-Sham potential (3.9) are, respectively, the external potential\(^3\), the Coulomb potential corresponding to \( \rho(\mathbf{r}) \) (also known as the Hartree potential) and the functional derivative of the exchange-correlation with respect to the density, representing the many-body effects of the system. The Kohn-Sham equations (3.8) and (3.9) may be solved iteratively. Beginning with an initial potential, Eq. (3.8) is solved and the electron density is obtained from the orbitals via Eq. (3.10). Then this density is used to form a new potential for Eq. (3.8). This self-consistency cycle is continued until the potential and density satisfy some convergence criteria, which often involve many iterations, since the self-consistency procedure is inherently unstable. Sophisticated ‘feedback’ or ‘mixing’ techniques are necessary to prevent oscillations.

In order to solve the Kohn-Sham equations, one needs an approximation for the exchange-correlation term, which in general depends on \( \rho(\mathbf{r}) \) in every point \( \mathbf{r} \). The traditional approximation, proposed by Kohn & Sham (1965), is referred to as the local density approximation (LDA) and takes the form

\[
E_{\text{xc}} = \int \varepsilon_{\text{xc}}[\rho(\mathbf{r})] \rho(\mathbf{r}) \, d\mathbf{r} \tag{3.11}
\]

where \( \varepsilon_{\text{xc}} \) is the exchange correlation energy of a homogeneous electron gas with the density \( \rho(\mathbf{r}) = \rho \). Although this form of the exchange correlation energy appears to be valid only when the electron density is slowly varying, it is a good approximation for a wide range of systems. A common extension of the LDA approximation is to include a dependence of \( \nabla \rho(\mathbf{r}) \). This is the generalized gradient approximation (GGA), which in general performs slightly better than LDA in estimating non-local properties, such as lattice parameters and bulk modulus. A popular variant of GGA is the parametrization of Perdew et al. (1996).

\(^3\)The nucleus potential is normally called \( V_{\text{ext}} \), since the electrons “see” the nucleus potential just like any other external potential.
When solving the Kohn-Sham equations, another important issue is to choose an appropriate basis set to represent the single particle wave-functions $\phi_i(\mathbf{r})$. All calculations in this thesis have been carried out with WIEN2k (Blaha et al., 2001), which uses the linearized augmented plane wave (LAPW) or augmented plane wave plus local orbital (AWP+lo) basis sets, that are among the most accurate methods for performing electronic structure calculations for crystals. Here the unit cell is divided into non-overlapping atomic centered, so called “Muffin-Tin” spheres and an interstitial region (Fig. 3.3). Inside the spheres, the wave-function is represented by spherical harmonics and radial functions. Outside it is represented by plane waves, with the requirement that the wave-function and its first derivative have to be continuous on the sphere boundaries.

Although DFT is a very successful tool for studying properties of materials, and normally reproducing experimental results with errors less than a few percent, notable problems still exist. One of them is the unphysical self-interaction of an electron with itself, addressed in Friis et al. (2003b). The $E_{ee}$ term of Eq. 3.7 contains the mean-field interaction energy of an electron with itself. This contribution would exactly have been canceled if the exchange-correlation functional is exact. However, for systems where the electrons are localized, or close to localized, the approximations in the exchange-correlation functional result in a non-negligible self interaction. Several corrections for this have been proposed (Perdew & Zunger, 1981; Lundin & Eriksson, 2001), but they are not yet a standard option in the WIEN2k program. Some modifications of the code was therefore necessary for Paper 4.

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Chapter 4

Multipole formalism

When studying chemical bonding, it is necessary to account for the perturbation of the spherically IAM electron density caused by interaction with other atoms. In the multipole formalism by Hansen & Coppens (1978) the aspherical corrections to IAM density are described by a set of atom-centered multipolar functions, obeying the symmetry of the atomic site. The multipolar functions are strongly related to the well known spherical harmonics forming the solution of the hydrogen atom. It is possible to show, for an isolated atom, that the multipole formalism is equivalent to a single-Slater determinant atomic wave function description composed of orthogonal spin-orbitals (Koritsanszky et al., 2003, sec. 1.8). In a multipole model, based on a set of measured structure factors, the population and expansion parameters for each included multipolar function are fitted in order to reproduce the observed structure factors.

In this chapter we will only give a brief resume of the multipole method and focus on the multipole refinement of electron diffraction data. The details and further development of the model are well described in Coppens (1997) and Coppens (2001).

4.1 The multipole model

In the multipole formalism of Hansen & Coppens (1978), the atomic electron density

\[ \rho_{\text{atom}}(r) = \rho_{\text{core}}(r) + \rho_{\text{valence}}(kr) + \sum_{l=0}^{l_{\text{max}}} \kappa_l^3 R_l(kr) \sum_{m=0}^{l} \sum_{p=\pm} P_{\text{imp}} d_{\text{imp}}(\theta, \phi). \]  (4.1)
CHAPTER 4. MULTIPOLE FORMALISM

is described by three parts; a spherically core part populated with \( P_c \) electrons, a spherical valence part which is allowed to expand \((\kappa < 1)\) or contract \((\kappa > 1)\) with population \( P_v \), and a series of multipolar functions accounting for an aspherically redistribution of the electron density, each populated with \( P_{lm} \) electrons.

The multipolar functions are characterized by a radial function \( R_l(\kappa r) \) (which also may be expanded or contracted with the \( \kappa \)-parameter) and the density functions \( d_{lm\pm} \), that are real spherical harmonics, normalized such that

\[
\int |d_{lm\pm}| \sin \theta \, d\theta \, d\phi = \begin{cases} 1 & \text{for } l = 0 \\ 2 & \text{for } l > 0 \end{cases}.
\]

This normalization implies that a multipole population \( P_{lm\pm} = 1 \) corresponds to one electron for the spherically symmetric \( d_{00} \), and that both the positive and negative lobes of \( d_{lm\pm} \) for \( l > 0 \) integrate to one electron each. The shape of the density functions for \( l \leq 3 \) are illustrated in Fig. 4.1.

![Multipolar functions](http://odin.math.nau.edu/~jws/dpgraph/Yellm.html)

**Figure 4.1:** Multipolar functions. The difference between the \( d_{l m+} \) and \( d_{l m-} \) functions is that they are rotated 90° around the \( z \)-axis compared to each other. *Source: [http://odin.math.nau.edu/~jws/dpgraph/Yellm.html](http://odin.math.nau.edu/~jws/dpgraph/Yellm.html)*

Since the multipolar functions form the solution of the hydrogen atom, and approximate heavier atoms very well, the series in Eq. 4.1 converges very quickly. For second and third row elements, it is usually sufficient to include up to quadropoles \((l=2)\), but for 3d transition metals hexadecapoles \((l=4)\)
also have to be included (Stewart et al., 2000). Occasionally, higher order multipoles might be necessary to include, which e.g. was the case in the old study of beryllium (Stewart, 1977), and might, for the same reasons, also be necessary in a future study of magnesium. The number of independent multipole functions is strongly reduced by the site symmetry of the atom. These symmetry-constrains are easily obtained by the index picking rules of Kurki-Suonio (1977). For instance, for the cubic site symmetry of the Cu atoms in pure fcc copper, all terms in the multipole expansion up to \( l = 4 \) vanish, except for the monopole and a linear combination of hexadecapoles (known as cubic harmonics, von der Lage & Bethe, 1947). In other words, the multipole model is a very flexible model for the electron distribution which incorporates the required symmetry, but at the same time only requires a limited set of parameters to be fitted to the experimental data.

The choice of the radial functions \( R_l(r) \) is the most difficult part in multipole modeling. Even for the spherical parts, it is not obvious which electrons should be included in the core, valence, or monopole terms. Often the core and valence densities are calculated from Roothaan-Hartree-Fock atomic wave functions and expanded in terms of Slater-type basis functions

\[
O_l(r) = \sqrt{\frac{(2\zeta_l)^{2n_l+1}}{2n_l!}} r^{n_l-1} e^{-\zeta_l r},
\]

for which the expansion coefficients and the parameters \( n_l \) and \( \zeta_l \) are tabulated by Clementi & Roetti (1974).

The radial dependence of the multipolar functions \( R_l(r) \) is given by products of atomic orbitals of the form \( O_{l'}O_{l''} \). Table 4.1 shows which multipoles can be constructed from the different orbital products. In the case of e.g. copper, which for \( l \leq 4 \) only has a hexadecapole, we see that the radial function must be constructed by the \( 3d \times 3d \) orbital product. It is often sufficient to describe the multipolar radial function by only one term \( O_{l'}O_{l''} \), so called single zeta-functions.

**Table 4.1:** \( l \) values for the allowed multipoles formed by the orbital product \( O_{l'}O_{l''} \), where \( l', l'' = 0, 1, 2 \) for \( s \) \( p \) and \( d \) orbitals, respectively (Koritsanszky et al., 2003).

<table>
<thead>
<tr>
<th>( l' \backslash l'' )</th>
<th>s</th>
<th>p</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>p</td>
<td>0</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>d</td>
<td>0</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>
4.2 Aspherical contribution to atomic scattering

From the Fourier transform of Eq. (4.1) aspherically atomic scattering factors are obtained as

\[ f(s) = P_c f_{\text{core}}(s) + P_v f_{\text{valence}}(s/\kappa) + \sum_{l=0}^{l_{\text{max}}} \sum_{m=0}^{l} \sum_{p} P_{lmp} f_{lmp}(s/\kappa'), \] (4.4)

where the deformation scattering factors \( f_{lmp}(s) \) are given by

\[ f_{lmp}(s) = 4\pi i^l \langle j_l \rangle d_{lmp}(\beta, \gamma). \] (4.5)

The relation between the reciprocal angular coordinates \( \beta \) and \( \gamma \) and the real space angular coordinates \( \theta \) and \( \phi \) is shown in Fig. 4.2. \( \langle j_l \rangle \) is the Fourier-Bessel transform of the radial function \( R_l(r) \), defined as

\[ \langle j_l \rangle = \int j_l(2\pi sr) R_l(r) r^2 dr \] (4.6)

with \( j_l \) being the \( l \)th order Bessel function.

![Figure 4.2: The angles \( \theta \), \( \phi \), \( \beta \) and \( \gamma \).](image)

4.3 Multipole refinement of electron diffraction data

In multipole refinement, the population and \( \kappa \)-parameters are determined from least square fitting between structure factors calculated from the multipole model \( F_{g}^{\text{calc}} \) and the observed structure factors \( F_{g}^{\text{obs}} \). The model structure factors are obtained from Eq. (4.4) as

\[ F_{g}^{\text{calc}} = \sum_{j} f_j(s) T_j(s) e^{-2\pi g \cdot r_j}. \] (4.7)
where $T_j(s)$ is the temperature factor of atom $j$. For electron diffraction, one normally converts the observed structure factors to their corresponding static lattice values, at which the temperature factors $T_j(s)$ are set to one. The reason is that the temperature factors have to be determined anyway, in order to convert the measured electron structure factors $U_{ij}^{\text{obs}}$ into X-ray structure factors $F_g^{\text{obs}}$ (see appendix A), since all well-tested multipole refinement programs (such as XD, VALRAY, MOLLY, etc...) are made for X-ray data and do not accept $U_{ij}^{\text{obs}}$ as input. Another reason is that one wants to refine as few parameters as possible. In the X-ray community a rule of thumb is a redundancy of about ten observed structure factors for each refined parameter. Such an over-determination is not necessary with electron diffraction data, since the low order structure factors, containing almost all bonding information, are measured very accurately. In addition, the low order data is not very sensitive to the isotropic or anisotropic temperature parameters. However, in order to obtain reliable results, the electron diffraction data set is usually not large enough. As mentioned, the solution is to combine with X-ray (or $\gamma$-ray) measurements. In these cases one may as well convert the electron diffraction data to the temperature of the X-ray measurements.

The multipole refinement programs mentioned above offer a lot of corrections specific to X-ray or neutron diffraction data (such as scaling, extinction and absorption correction, etc...) that safely can be turned off, but that may be useful in the case electron diffraction data are combined with some high order X-ray structure factors. VALRAY was used for the multipole refinements in Paper 6.

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computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data.


Chapter 5

Maximum entropy

You should call it ‘entropy’ and for two reasons: first, the function is already in use in thermodynamics under that name; second, and more importantly, most people don’t know what entropy is, and if you use the word ‘entropy’ you will win every time!

von Neumann

5.1 A short introduction to the maximum entropy method

The maximum entropy method (MEM) is based on information theory and was first developed for radioastronomy to enhance the information from incomplete and noisy data (Frieden, 1972; Gull & Daniell, 1978). MEM was first introduced into crystallography by Collins (1982) and has been very successful in order to optimize the information that can be extracted from an incomplete and noisy experimental data set and to produce the least possible biased density. An excellent review of modern applications of MEM in crystallography is given by Gilmore (1996).

The formalism is very similar to that of statistical thermodynamics. Both the statistical entropy and the information entropy deal with the most probable distribution. In thermodynamics, this is the distribution of particles, while in information theory it is the distribution of numerical quantities over the ensemble of pixels. Statistical arguments, taken from thermodynamics, can therefore be used to derive an expression for the entropy function to be maximized.

The probability for a distribution of \( N \) particles over \( m \) boxes, each with
the prior probability $q_i$ to contain $n_i$ particles, is given by

$$P = \frac{N!}{n_1! n_2! \ldots n_m!} q_1^{n_1} q_2^{n_2} \ldots q_m^{n_m}. \quad (5.1)$$

The entropy $S$ is defined as $\ln P$. So, by using Stirling’s formula ($\ln n \approx n \ln n - n$) the entropy, apart from a constant (only depending on $N = \sum_i n_i$), becomes

$$S = -\sum_{i=1}^m n_i \ln \frac{n_i}{q_i}. \quad (5.2)$$

If we digitize the unit cell (or an appropriate subunit) of volume $V$ into $M$ pixels, each with volume $V/M$ and density $\rho(r_j)$, the entropy of the electron distribution can, in accordance with Eq. (5.2), be written as

$$S[\rho(r)] = -\sum_{j=1}^M p_j \ln \frac{p_j}{m_j}, \quad (5.3)$$

where $S$ now becomes a functional of the sought charge density $\rho(r)$. The quantities $p_j = p(r_j)$, the probability of the density associated with pixel $j$, and $m_j = m(r_j)$, the corresponding probability for the prior (model) density $\rho_0(r)$ at pixel $j$, are defined as

$$p_j = p(r_j) = \frac{\rho(r_j)}{\sum_{i=1}^M \rho(r_i)} \quad (5.4)$$

$$m_j = m(r_j) = \frac{\rho_0(r_j)}{\sum_{i=1}^M \rho_0(r_i)}. \quad (5.5)$$

We want to maximize the entropy functional $S[\rho(r)]$, given our knowledge of the prior density, the values $F_{h}^{\text{obs}}$ and the standard deviation $\sigma_h$ of the $N$ measured structure factors. The observed structure factors are taken into account by introducing the constraint

$$C[\rho(r)] = \chi^2 = \frac{1}{N} \sum_h \left| F_{h}^{\text{obs}} - F_{h}^{\text{calc}} \right|^2 / \sigma_h^2 \lesssim 1, \quad (5.6)$$

where

$$F_{h}^{\text{calc}} = \frac{V}{M} \sum_{j=1}^M \rho(r_j) e^{-2\pi i h \cdot r_j} \quad (5.7)$$

are structure factors calculated from the sought charge density. Note that Eq. (5.7) remains valid even when only a subunit of the unit cell is digitized into
5.1. A SHORT INTRODUCTION TO THE MAXIMUM ENTROPY METHOD

$M$ pixels, provided that this subunit remains a multiple of the asymmetric unit.

If the constraint (5.6) were not introduced, maximizing the entropy would result in a uniform distribution. To enforce the constraint, the maximization of $S = S[\rho(\mathbf{r})]$ is performed by introducing the Lagrangian function $L = S - \lambda \chi^2$, where $\lambda$ is the Lagrange multiplier (Skilling & Bryan, 1984). At convergence $\nabla_\rho L = 0$ or, equivalently, $\nabla_\rho S = \lambda \nabla_\rho \chi^2$. For each pixel $j$, this corresponds to

$$\frac{\partial S}{\partial \rho_j} = \lambda \frac{\partial \chi^2}{\partial \rho_j}, \quad (5.8)$$

where $\rho_j = \rho(\mathbf{r}_j)$. Note that we here use the same Lagrangian multiplier $\lambda$ for all observed structure factors, as is common in crystallographic applications (Collins, 1982; Gull & Skilling, 1991; Kumazawa, 1993; Burger, 1998; Tanaka et al., 2002).

Equation (5.8) is non-linear, and has to be solved iteratively for both $\lambda(n + 1)$ and $\rho_j(n + 1)$ coming from $\lambda(n)$ and $\rho_j(n)$. The starting values are $\lambda(0) \geq 0$ and the prior density $\rho_j(0) = \rho_0(\mathbf{r}_j)$. To achieve convergence, the $\chi^2 \leq 1$ constraint must first be satisfied, and thereafter the entropy $S$ is maximized while keeping $\chi^2 \leq 1$.

Using Eq. (5.3), the left-hand side of Eq. (5.8) can be written as

$$\frac{\partial S}{\partial \rho_j} = - \sum_{j=1}^{M} \frac{\partial \rho_j}{\partial \rho_j} \left( \ln \frac{\rho_j}{m_j} + 1 \right)$$

$$= - \sum_{j=1}^{M} \frac{\delta_{jk} - \rho_j}{\rho} \left( \ln \frac{\rho_j}{m_j} + 1 \right)$$

$$= - \frac{1}{\rho} \left( \ln \frac{p_k}{m_k} - \sum_{j=1}^{M} p_j \ln \frac{p_j}{m_j} \right)$$

$$= - \frac{1}{\rho} \ln \frac{\rho_k / \rho_{0k}}{B}, \quad (5.9)$$

where $\rho = \sum_j \rho_j$ is the total number of electrons in the unit cell and $B = \exp(\sum_j p_j \ln \rho_j / \rho_0)$. Note that $B$ is very close to unity when the prior density is very close to the true density. In the case of an uniform prior density, $\rho_0(\mathbf{r}_j) = \rho_0 = \rho / M$, $B$ is reduced to $B = AM / \rho$, where $A = \exp(\sum_j p_j \ln \rho_j)$ is the weighted logarithmic average of the converged entropic density $\rho(\mathbf{r})$ over the unit cell. $A$ corresponds to the expected density far away from any atom. Reconstructed density values smaller than $A$ are considered unreliable.
Substitution of Eq. (5.9) into (5.8) leads to

$$\rho_j / \rho_0 = Be^{-\lambda_0 (\partial \chi / \partial \rho_j)}.$$

(5.10)

From this we can set up the iteration formulas

$$\lambda(n+1) = \left( \ln \rho_k(n)/\rho_0 - \sum_{j=1}^{M} \rho_j(n)/\rho_0 \right)$$

$$\times \left( F_0 \sum_{h} 2 |F_{hb}^{obs} - F_{hb}^{calc(n)}| / \sigma_h^2 \cdot e^{-2\pi i h \cdot r_j} \right)^{-1}$$

(5.11)

and

$$\rho_j(n+1) = \rho_0 \exp \left( \sum_{j=1}^{M} \rho_j(n) \ln \rho_k(n)/\rho_0 \right)$$

$$+ \lambda(n+1) F_0 \sum_{h} 2 |F_{hb}^{obs} - F_{hb}^{calc(n)}| / \sigma_h^2 \cdot e^{-2\pi i h \cdot r_j} \),$$

(5.12)

where $F_h^{calc(n)} = V/M \sum_h \rho_j(n) \exp(-2\pi i h \cdot r_j)$ and $F_0 = V/M \rho$.

### 5.2 Weaknesses of MEM

For the old, but accurate, Pendellösung data of silicon by Saka & Kato (1968), it was found that the distribution of the discrepancies between $F_{hb}^{obs}$ and $F_{hb}^{calc}$ after the MEM analysis (Sakata & Sato, 1990) deviates from the ideal Gaussian distribution (Jauch & Palmer, 1993; Jauch, 1994). This points to a weakness in the constraint (5.6): It constrains the variance of the distribution, but not its shape. An improvement has been reported (De Vries et al., 1994) by assigning a weighting factor proportional to $|h|^{-4}$ to the summation of Eq. (5.7).

Another related weakness is that MEM tends to sharpen strong features but flatten weak features, when the dynamic range is large. This may be a problem when the aim is to recover the fine details of the density (which is often the case in bonding studies) (Papoular et al., 1996; Iversen et al., 1997). In the next section we will describe how the dynamic range can be greatly reduced by applying MEM to the deformation density instead of the full density.
5.3 Two-channel MEM

Since the probabilities \( p(\mathbf{r}) \) and \( m(\mathbf{r}) \) have to be positive, a positive charge density \( \rho(\mathbf{r}) \) is required over the whole unit cell. This is not the case for the deformation density \( \Delta \rho(\mathbf{r}) = \rho^{\text{obs}}(\mathbf{r}) - \rho^{\text{IAM}}(\mathbf{r}) \), which takes both positive and negative values. The average of \( \Delta \rho(\mathbf{r}) \) over the unit cell must be zero, since bonding effects only redistribute the electron density. In the two-channel method, the deformation density is written as \( \Delta \rho(\mathbf{r}) = \rho^+(\mathbf{r}) - \rho^-(\mathbf{r}) \), where the two functions \( \rho^+(\mathbf{r}) \) and \( \rho^-(\mathbf{r}) \) are positive and represent the densities of excess and lack of electrons, respectively. This method was first developed for magnetization densities (Papoular & Gillon, 1990) and for neutron scattering (Sakata et al., 1993) for which both positive and negative scattering densities occur.

In each pixel \( j \), the functions \( \rho_j^+ = \rho_j^+(\mathbf{r}_j) \) and \( \rho_j^- = \rho_j^-(\mathbf{r}_j) \) are mutually exclusive, and have the corresponding probabilities \( p_j^+ = \rho_j^+ / Q \) and \( p_j^- = \rho_j^- / Q \), where \( Q = \sum_j (\rho_j^+ + \rho_j^-) \). The prior deformation density \( \Delta \rho_{0j} \), at pixel \( j \), is in a similar way divided into two positive functions \( \rho_{0j}^+ \) and \( \rho_{0j}^- \) with the corresponding probabilities \( m_j^+ \) and \( m_j^- \). In analogy to Eq. (5.3), the two-channel entropy is defined as

\[
S[\Delta \rho] = - \sum_{j=1}^{M} \left( p_j^+ \ln \frac{p_j^+}{m_j^+} + p_j^- \ln \frac{p_j^-}{m_j^-} \right). \tag{5.13}
\]

Since \( \partial \chi^2 / \partial \rho_j^+ = - \partial \chi^2 / \partial \rho_j^- \), the positive and negative scattering densities are related by

\[
\rho_j^+ \rho_j^- = B^2 \rho_j^+ \rho_j^- \tag{5.14}.
\]

Inserting the entropy (5.13) into Eq. (5.8) leads, with the help of Eq. (5.14), to the following iteration formulas

\[
\lambda(n+1) = - \frac{1}{Q} \frac{\ln \rho_{0j}^+ + \ln \rho_{0j}^-}{C_{j}^{\rho_j^+}(n) + C_{j}^{\rho_j^-}(n)} \tag{5.15}
\]

\[
\rho_j^+(n+1) = \rho_{0j}^+ B(n) e^{-\lambda(n+1)Q C^{\rho_j}(n)}, \tag{5.16}
\]

where

\[
B(n) = \exp \left[ \sum_{j=1}^{M} \left( p_j^+(n) \ln \frac{\rho_j^+(n)}{\rho_{0j}^+} + p_j^-(n) \ln \frac{\rho_j^-(n)}{\rho_{0j}^-} \right) \right] \tag{5.17}
\]

and

\[
C_j^{\rho_j}(n) = \frac{\partial \chi^2}{\partial \rho_j^2}(n) = \frac{V}{M} \sum_{\mathbf{h}} 2 \frac{\Delta F_{\mathbf{h}}^{\text{obs}}(n) - \Delta F_{\mathbf{h}}^{\text{calc}}(n)}{\sigma_{\mathbf{h}}^2} e^{-2\pi\mathbf{i}\mathbf{h} \cdot \mathbf{r}_j}. \tag{5.18}
\]
CHAPTER 5. MAXIMUM ENTROPY

A problem with applying the two-channel MEM to the deformation density $\Delta \rho(r)$, is that the quantity $Q$, the sum of positive and negative densities over the unit cell, is unknown (Nishibori, 2003). However, by introducing a rescaled Lagrangian multiplier $\mu = \lambda Q$, Eqs. (5.15) and (5.16) become

$$\mu(n + 1) = -\frac{\ln \rho_{0j}^+ + \ln \rho_{0j}^-}{C_j^+(n) + C_j^-(n)}$$
$$\rho_j^+(n + 1) = \rho_{0j}^+ B(n) e^{-\mu(n+1)C_j^+(n)}$$

which are independent of $Q$. One can therefore use an ordinary two-channel MEM algorithm designed for neutron diffraction (e.g. the MEND algorithm by Burger (1998)) on deformation densities (Friis et al., 2003).

5.4 Applications of MEM to QCBED

MEM is the method of choice when one wants to extract useful information from poor or limited experimental data. Since the data from QCBED is of outstanding quality, one would normally prefer to use other methods, e.g. multipole analysis, for charge studies. However, the QCBED data set often needs to be extended with structure factors of less quality. This may result in an inconsistent data set, especially if rescaling or other corrections are applied to the foreign data set (Friis et al., 2003).

In these cases, MEM may be an alternative method to obtain a least biased charge density from all the observed data. As pointed out in section 5.2 it seems however to be important to use the two-channel method in order to reduce the dynamical range and avoid sharpening of strong and flattening of weak features.

References


REFERENCES


CHAPTER 5. MAXIMUM ENTROPY


Part II
Papers
The Teddy Bear Cactus, Arizona 2001
Paper 1

Quantitative Convergent Beam Electron Diffraction Measurements of Low Order Structure Factors in Copper

TEM image of the thin area of the Cu sample used for experiments. Magnification: 4000 times.
Quantitative Convergent Beam Electron Diffraction Measurements of Low-Order Structure Factors in Copper

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Abstract: Accurate low-order structure factors for copper metal have been measured by quantitative convergent beam electron diffraction (QCBED). The standard deviation of the measured structure factors is equal to or smaller than the most accurate measurement by any other method, including X-ray single crystal Pendellösung, Bragg γ-ray diffraction, and high-energy electron diffraction. The electron structure factor for the (440) reflection was used to determine the Debye-Waller (DW) factor. The local heating of the specimen by the electron beam is determined to be 5 K under the current illumination conditions. The low-order structure factors for copper measured by different methods are compared and discussed. The new data set is used to test band theory and to obtain a charge density map. The charge deformation map shows a charge surplus between the atoms and agrees fairly well with the simple model of copper 2+/H11001 ions at the atomic sites in a sea of free uniformly distributed electrons.

Key words: quantitative convergent beam electron diffraction, QCBED, structure factor, copper, bonding, free electron model

INTRODUCTION

The aim of the present work is to get a better understanding of the role of the free electrons in the bonding of copper. The structure factors for copper have been studied by many researchers using different methods over the last 30 years. A new data set is added here using the quantitative convergent beam electron diffraction (QCBED) method (see Zuo, 1998; Holmestad et al., 1999, and references therein). The electron diffraction method measures Fourier coefficients of the ground state electrostatic Coulomb potential, including the nuclear contribution (electron structure factors). These may then be converted to X-ray structure factors (Fourier coefficients of the electron charge density) using the reciprocal space form of Poisson's equation if the temperature factors and nuclear coordinates are known. The operation of this equation provides the enhanced sensitivity of electron diffraction to bonding effects by comparison with X-ray diffraction, as does the elimination of extinction errors discussed further below. There has recently been considerable discussion of low-order structure factor measurement methods (Zuo et al., 2000; Jiang et al., 2002, 2003a, 2003b). The study of copper provides a good opportunity to compare the accuracy and credibility of different methods.

Low-order structure factors are crucial when studying bonding in crystals. The accuracy of the measurements should normally be below 1% in order to see the deformation of the charge density due to bonding effects.
Various methods have been used for low-order structure factor measurements. They are: (1) Bragg X-ray or γ-ray diffraction, (2) critical voltage (CV), (3) X-ray single crystal Pendellösung, and (4) quantitative convergent beam electron diffraction. These methods all have their advantages and disadvantages, which will be discussed briefly here.

Bragg X-ray or γ-ray diffraction normally suffers from large extinction errors in the strong low-order reflections of inorganic crystals. The advantage is that these methods can very accurately measure high-order reflections, which are sensitive to atomic coordinates and Debye-Waller (DW) factors, and can be used for crystal structure determination.

The CV method is capable of measuring the ratio of two low-order structure factors. Errors may be as small as 0.1% (Spence & Zuo, 1992). The disadvantage of this method is that one structure factor must be accurately known to calculate the other.

The X-ray single crystal Pendellösung and the QCBED methods are similar techniques in terms of the underlying theory. Both use perfect crystals and are based on dynamical theory. Both give highly accurate low-order structure factor data. A disadvantage of the X-ray Pendellösung method is that it requires large perfect crystals, which limits its application to a few semiconductor crystals such as silicon, diamond, and so forth. The QCBED method, on the other hand, takes advantage of the small probe of a transmission electron microscope (TEM), which allows one to use a perfectly crystalline region of near nanometer size. This is smaller than the size of one mosaic block. The disadvantage of QCBED is that it cannot be used to measure high-order reflections accurately. Because of their high accuracy and credibility, structure factors measured by these two methods are often used to test band theory. In this way, random errors can be made very small—systematic errors can only be minimized by comparing the results of different techniques.

**Experiment**

**Sample Preparation and Experimental Setup**

The specimen was prepared by electrolytic polishing. The electrolyte was 33% phosphoric acid and 67% water (Hirsch et al., 1977). A pure copper foil (99.999%) of a 25-μm thickness was polished at 10 V and 4 A/cm² at room temperature.

We found that copper was easily oxidized when exposed to air, which may cause extra diffraction spots and introduce a large standard deviation in the refined data. Therefore, newly prepared samples were mounted on a Gatan liquid nitrogen holder and put into the microscope vacuum immediately after thinning.

A LEO 912B transmission electron microscope, operating at 120 keV, with in-column Ω-filter and a Gatan MSC CCD (14-bit dynamical range) camera, was used. The CCD camera was properly characterized to compensate for the point spread function (Jiang et al., 2003a, 2003b). The energy window used in the experiments was 10 eV. The experiments were done at liquid nitrogen temperature, using a Gatan double tilt cooling holder. This avoids contamination and reduces the phonon scattering background, which is otherwise difficult to fit. The temperature readout from the holder varied between the experiments from 107 K to 112 K. The CBED patterns were acquired using a probe size of less than 100 Å, using a systematic row orientation far away from major zone axes. This small probe eliminates any effects due to local bending of the ductile copper foil.

**High-Voltage Calibration**

The high voltage must be calibrated for accurate electron structure factor measurements (Spence & Zuo, 1992). An accurate value is also needed when converting the electron structure factors to X-ray structure factors. This was done using high-order Laue zone (HOLZ) lines. It is well known that the position of HOLZ lines is very sensitive to both electron beam energy and lattice parameters (Spence & Zuo, 1992). Because high voltage and lattice parameters have similar effects on the position of HOLZ lines, it is not possible to measure both these quantities simultaneously. The lattice parameter of silicon, however, is well known and so may be used to calibrate the high voltage. Figure 1 shows the central disk of a silicon [133] zone axis CBED pattern. The two triangles formed by HOLZ lines, shown enlarged in Figure 1b,c, were used for the calibration. The size of these triangles is very sensitive to the high voltage, because the HOLZ lines originate far out on the Ewald sphere. Furthermore, the HOLZ lines are arranged so that they all will move toward each other in Figure 1b and away from each other in Figure 1c, as the high voltage increases. The high voltage is therefore obtained by comparing the ratio between the areas of triangle (b) and (c) with dynamical Bloch wave simulations (Zuo, 1998) done at different voltages (Fig. 2). This gives a high voltage of 119.60 kV.
The filament of the microscope was changed in March 2001. In Figure 1d,e, we compare the same pattern taken with the same microscope before the filament change in May, 1997. The high voltage was then found to be 119.52 V, which also was confirmed in May 2000 (Jiang et al., 2003a, 2003b). It can be seen that a change of 80 V in the electron beam energy is easily detected, corresponding to a change in wavelength from 0.0033553 nm to 0.0033563 nm.

### Lattice Parameter

Highly accurate lattice parameters are needed for structure factor refinement. In particular, the lattice parameters are important to determine the HOLZ line positions, which define the beam direction ($\mathbf{k}_t$) in the patterns used for refinement.

The crystal structure of copper and its thermal expansion have been studied for many years. Accurate crystal data and the thermal expansion coefficient are available. The measured lattice parameter at room temperature is $a = 3.61496(2)\ \text{Å}$ (Schneider et al., 1981). From this, lattice parameters at other temperatures can be calculated by using the expansion coefficient of Hahn (1970). At 115 K we obtain $a = 3.60540(3)\ \text{Å}$.

### Experimental DW Factor and Temperature Determination

A knowledge of DW or temperature factors is essential for accurate QCBED refinement. Saunders et al. (1999) have shown that good $\chi^2$ values (see equation (1) below) can only be obtained if the correct value of the DW factor is used. Even though the refined electron structure factors are not sensitive to the DW factor, the converted X-ray structure factors will depend on the DW factor. If an incorrect DW factor is used, it will introduce systematic errors in the converted X-ray structure factors, particularly at higher scattering angles. For example, a 5-K change in temperature (around 110 K) will introduce a 3% change in the DW factor and change the converted X-ray structure factor by $\pm 0.02$ electrons/cell (0.025%) for the (200) reflection and by $\pm 0.4$ electrons/cell (1.1%) for the (440) reflection. In addition, accurate temperature factors are needed for all the

Figure 1. a: The (000) disk of Si [133] zone axis taken with the LEO 912B microscope at Arizona State University, June 2001. The high voltage was measured on this image to be 119.60 kV. b,c: Magnifications of the regions around the sensitive triangles made by HOLZ lines. d,e: Images are from the same sensitive regions, but taken May 1997 with the same microscope. At that time the high voltage was measured to be 119.52 kV.
other reflections in the simulation not being refined that affect the refined value through multiple scattering.

The effective isotropic DW factor $B$ for copper has been measured accurately by Schneider et al. (1981) to 0.167(8) $\text{Å}^2$ at 50 K and 0.544(7) $\text{Å}^2$ at room temperature. These values fit well with the expansion of $B$, given by Sears and Shelley (1991) using the phonon model. This gives us an opportunity to measure the sample temperature, by measuring the DW factor.

A well-known problem in electron diffraction experiments is that the local heating of the specimen by the illuminating electrons is unknown. The local heating depends on the thermal conductivity of the specimen and the illumination conditions. The sensitivity to the DW factor of the converted X-ray structure factor for the (440) reflection suggests that we can measure the DW factor and specimen temperature accurately.

Therefore, the systematic row of (220) and (440) was carefully measured to calibrate the temperature. A region with few HOLZ lines (which makes the refinement easier and more accurate) could be found by tilting about 16.6° from the (001)-zone axis. These data were collected with a temperature readout of 107 K. The $U_{440}$ refined from different diffraction patterns and different rocking curves of the same diffraction pattern was then converted into X-ray structure factors using the Mott formula (Spence & Zuo, 1992). Because the (440) structure factor is not affected much by bonding, the value should be very close to the neutral atom value. Choosing the DW factor to be $B = 0.2478 \pm 0.0013$ $\text{Å}^2$ gave good agreement with the neutral atom X-ray structure factor (Doyle & Turner, 1968), considering the standard deviation in the measurement of $U_{440}$. This DW factor corresponds to 112.3 ± 0.7 K (Sears & Shelley, 1991). Thus, we conclude that the local specimen heating is about 5.3 K under the current TEM settings.

Because the TEM settings were kept constant, we assume the same local heating for all our experiments, even though the readout temperature of the GATAN holder varied between 107 K and 112 K, due to small leaks in the vacuum surrounding the nitrogen reservoir in the holder.

Figure 2. High voltage calibration curve. The $y$-axis shows the ratio between the area of the two sensitive triangles shown in Figure 1b,c. The circles show the ratio obtained from simulations at different voltages, and the horizontal line is the ratio measured on the experimental image. The high voltage is determined from the crossover to be 119.60 kV.
Low-Order Structure Factor Refinement

The idea behind the QCBED method is to refine the input parameters in a Bloch wave simulation until a best fit with experiment is obtained. Only pixel intensities along some carefully chosen rocking curves are calculated. In Figure 3, a CBED pattern from the (220) systematic row is shown, with some rocking curves drawn onto it together with the fit along these curves.

As a goodness-of-fit measure, we use $\chi^2$, defined as

$$\chi^2 = \frac{1}{N - f - 1} \sum_{i=1}^{N} \frac{(I_i^{(\text{exp})} - c I_i^{(\text{theo})} - I_i^{(bgr)})^2}{\sigma_i^2},$$

where $N$ is the number of data points, $f$ is the number of refined parameters, $c$ a scaling factor, $\sigma$ the standard deviation of the experimental intensities, and $I_i^{(\text{exp})}$, $I_i^{(\text{theo})}$, and $I_i^{(bgr)}$ are the experimental, theoretical, and background intensities, respectively. The sum goes over all pixels in the line scans shown in Figure 3. The refinement parameters are

Figure 3. The top image shows the systematic row for (220) and (440) together with the rocking curves chosen for refinement. The graph below shows the pixel values along the above chosen linescans (circles) compared with calculated values (solid line). The $\chi^2$ for this fit is 1.46.
Table 1. Experimental Results for the (200) Structure Factor of Copper

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Orientation</th>
<th>Rocking curve</th>
<th>( \chi^2 )</th>
<th>( U_{200} ) (Å(^2))</th>
<th>( U_{200}^{\text{lab}} ) (Å(^2))</th>
<th>( F_{200} ) (e/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryst 1</td>
<td>5.68°, 0.60°</td>
<td>1</td>
<td>1.26</td>
<td>0.08626</td>
<td>0.00346</td>
<td>20.090</td>
</tr>
<tr>
<td>Cryst 1</td>
<td>5.68°, 0.60°</td>
<td>2</td>
<td>1.12</td>
<td>0.08664</td>
<td>0.00343</td>
<td>20.068</td>
</tr>
<tr>
<td>Cryst 1</td>
<td>5.18°, 0.58°</td>
<td>1</td>
<td>1.40</td>
<td>0.08585</td>
<td>0.00382</td>
<td>20.114</td>
</tr>
<tr>
<td>Cryst 1</td>
<td>5.18°, 0.58°</td>
<td>2</td>
<td>1.25</td>
<td>0.08671</td>
<td>0.00383</td>
<td>20.064</td>
</tr>
<tr>
<td>Cryst 2</td>
<td>(-35.3°, 0.73°)</td>
<td>1</td>
<td>1.79</td>
<td>0.08673</td>
<td>0.00370</td>
<td>20.063</td>
</tr>
<tr>
<td>Cryst 2</td>
<td>(-35.3°, 0.73°)</td>
<td>2</td>
<td>2.00</td>
<td>0.08603</td>
<td>0.00390</td>
<td>20.103</td>
</tr>
<tr>
<td>Cryst 2</td>
<td>(-11.1°, -0.76°)</td>
<td>1</td>
<td>3.13</td>
<td>0.08760</td>
<td>0.00370</td>
<td>20.013</td>
</tr>
<tr>
<td>Cryst 2</td>
<td>(-11.1°, -0.76°)</td>
<td>2</td>
<td>3.14</td>
<td>0.08755</td>
<td>0.00385</td>
<td>20.016</td>
</tr>
<tr>
<td>Cryst 2</td>
<td>(-11.1°, -0.76°)</td>
<td>3</td>
<td>2.90</td>
<td>0.08760</td>
<td>0.00375</td>
<td>20.013</td>
</tr>
<tr>
<td>Cryst 2</td>
<td>5.25°, -0.65°</td>
<td>1</td>
<td>2.96</td>
<td>0.08784</td>
<td>0.00382</td>
<td>19.998</td>
</tr>
</tbody>
</table>

Average (\( \mu \)) | 0.08698 | 0.00373 | 20.054 |
Standard deviation (\( \sigma \)) | 0.00072 | 0.00016 | 0.041 |
Relative standard deviation, (\( \sigma/\mu \), in %) | 0.83 | 4.3 | 0.21 |
Standard error (\( \sigma/\sqrt{n} \)) | 0.0002 | 0.00005 | 0.013 |

*Orientation is given as a tilt from the (001) zone around the x- and y-axes, respectively, where the x-axis is chosen to be in the (100) direction. The temperature was, in all cases, 114 K, except for the last case, where it was 115 K, corresponding to a DW factor of 0.251 Å\(^2\) and 0.252 Å\(^2\), respectively. A lattice constant of 3.60542 Å was used to calculate the X-ray structure factors in the last column. To show the consistency of the QCBED method and to improve the statistics, all together 10 refinements were done on two different crystals with different orientations and different rocking curves drawn on each pattern.

certain low-order complex structure factors (including absorption), beam direction \( k_i \), scaling factor \( c \), background intensity \( I^{\text{bg}} \) (which is assumed constant for each disk), and sample thickness.

The Bethe potential approximation is used in the multiple-scattering calculations. Here, strong beams are treated exactly, whereas weak ones are calculated using perturbation theory. The beams were selected for diagonalization or perturbation according to three criteria (Zuo & Weickenmeier, 1995; Birkeland et al., 1996): (1) \( 2K_S \) (proximity to the Ewald sphere), (2) length of \( g_{\text{max}} \), (3) \(|U_{g}/2K_S|_{\text{min}} \) (perturbation strength). \( 2K_S \) is used to select the beams included in the diagonal matrix, \(|U_{g}/2K_S|_{\text{min}} \) to select the weak beams for perturbation, and \( g_{\text{max}} \) as a cut-off parameter for high-order reflections. Normally, good convergence can be obtained by choosing values of 3.5 Å\(^2\), 4.0 Å, and 35, respectively, for the three criteria. For more details on QCBED refinement we refer to Zuo (1998).

Consistency Test

To ensure that our results are consistent, refinements have been done on different crystals, at different orientations and with different rocking curves. We then take the average of the results. The relative standard deviation is less than 1% in all cases. In Table 1, all refinements of the (200) reflection are listed with their \( \chi^2 \) and the corresponding X-ray structure factor. The data set is consistent for measurements from different crystals and different tilts.

Mean Inner Potential and Its Effects on the Refinements

The mean inner potential, \( V_0 \), is also considered in the current refinements. We use \( V_0 = 23.5 \text{ V} \) for copper (Williams & Carter, 1996). Although this term produces only an unobservable phase factor on zero order Laue zone (ZOLZ) diffraction patterns, it may affect the intensity in three-dimensional multiple scattering. Our refinements show that including the mean inner potential has a small effect on the refined electron structure factors, but it improves the \( \chi^2 \) values significantly. The reason may be that changes in the mean inner potential introduce significant HOLZ line shifts, which are critical in the determination of \( k_i \) for the experimental patterns. To avoid systematic errors, the mean inner potential was also considered in the high voltage calibration and in the conversion of electron structure factors to X-ray structure factors.
Table 2. List of Measured Static Lattice X-ray Structure Factors for Cu$^\text{a}$

<table>
<thead>
<tr>
<th>$hkl$</th>
<th>Neutral atom</th>
<th>Bragg $\gamma$-ray diffraction</th>
<th>White X-ray Pendellösung</th>
<th>Electron diffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>22.05</td>
<td>21.51(5)</td>
<td>21.68(14)</td>
<td>21.80(6)</td>
</tr>
<tr>
<td>200</td>
<td>20.69</td>
<td>20.22(4)</td>
<td>20.38(13)</td>
<td>20.28(11)</td>
</tr>
<tr>
<td>220</td>
<td>16.74</td>
<td>16.45(5)</td>
<td>16.76(12)</td>
<td>16.75(8)</td>
</tr>
<tr>
<td>311</td>
<td>14.74</td>
<td>14.54(4)</td>
<td>14.68(11)</td>
<td>14.74(4)</td>
</tr>
<tr>
<td>400</td>
<td>12.42</td>
<td>12.29(6)</td>
<td>12.42(10)</td>
<td>12.46(6)</td>
</tr>
<tr>
<td>440</td>
<td>8.82</td>
<td>8.92(11)</td>
<td>8.92(11)</td>
<td>8.82(4)</td>
</tr>
</tbody>
</table>

$^a$Calculated values for a neutral atom model are shown for comparison. Units are in electrons per atom.

$^b$The results of Fox and Fisher (1988) were published in Tabbernor et al. (1990).

**RESULTS**

**Refinement Result**

Because the temperature varies with each experiment, the refined structure factors were converted into static X-ray structure factors (for which $B = 0.0 \text{ Å}^2$) by dividing with the temperature factor $\exp(-B \sin^2 \theta/\lambda^2)$ before averaging. Approximately 10 refinements were completed for each reflection. The results are listed in Table 2 and compared with other measured X-ray structure factors for copper. In Figure 4, the difference between our experimentally measured X-ray structure factors and neutral atom calculations is shown as a function of scattering angle, $\sin \theta/\lambda$. A significant difference between the measurements and the neutral atom values is observed for the three lowest order structure factors.

**Deformation Density**

The deformation charge density, defined as

$$\Delta \rho(r) = \frac{1}{\Omega} \sum_{\mathbf{g}} [F_{\mathbf{g}}^X(\text{crystal}) - F_{\mathbf{g}}^X(\text{free atom})] e^{2\pi i \mathbf{g} \cdot \mathbf{r}},$$  \hspace{1cm} (2)

where $\Omega$ is the unit cell volume, measures the redistribution of charge due to bonding. As reference density $F_{\mathbf{g}}^X(\text{free atom})$, the interpolated relativistic Hartree-Fock structure factors of Doyle and Turner (1968) have been chosen. Because the difference between $F_{\mathbf{g}}^X(\text{crystal})$ and $F_{\mathbf{g}}^X(\text{free atom})$ is so small (around 1%), this requires careful consideration of the experimental errors. An electron deformation density map consisting of a section of the (110) plane passing through the nuclei is shown in Figure 5a. Only the six lowest structure factors, up to the (400) reflection ($\sin \theta/\lambda = 0.56 \text{ Å}^{-1}$), were included. All others were assumed equal to their neutral atom values and will therefore not to contribute to the deformation density map. One has to be very careful when interpreting such a map because...

![Figure 4](image-url)
of truncation errors and because the errors in the measured structure factors tend to accumulate at the high symmetry points. Anyway, the map shows a spherical charge depletion at the atomic sites and an evenly distributed charge surplus of about 0.1 e/Å³ between the atoms.

In Figure 5b,c, we have made similar maps based on two very simple models, assuming (b) Cu⁺ ions and (c) Cu⁺² ions at the atomic sites in a sea of one and two fully delocalized electrons, respectively. The maps are created by setting $F_g^X$ (crystal) to the structure factors calculated from Doyle and Turner’s interpolated Cu⁺¹ and Cu⁺² scattering factors, respectively. The $g = 0$ term of equation (2) is, in this case, omitted in order to keep the total charge difference zero. The models with one free electron do not agree at all with our experimental map, whereas good agreement is achieved in the interstitial region with the model using two free electrons per atom.

**DISCUSSION**

Various sets of experimental and theoretical structure factors have been published for copper (see, e.g., Mackenzie and Mathieson (1992) and Tabbernør et al. (1990)). We list here some of them for comparison with the current QCBED results. To compare the different sets, they have all been converted to static lattice values.
Comparison with Other Experimental Data

In Table 2, we list some of the earlier diffraction results on copper derived from electron diffraction (CV), Bragg γ-ray diffraction, and white X-ray single crystal Pendellösung. The values obtained by electron diffraction measurement are in good agreement, with no significant differences from the current QCBED measurement. This demonstrates the consistency of the electron diffraction method. The reason is that all these electron diffraction results use perfect crystals as diffraction objects and the full dynamical theory in the calculations.

The difference is quite obvious for the Bragg γ-ray diffraction measurements of Schneider et al. (1981), which are systematically lower than all the other experimental values. This has been pointed out in several previous papers (Mackenzie & Mathieson, 1979, 1984, 1992; MacDonald et al., 1982). The γ-ray diffraction measurements may have scaling problems (Tabbernor et al., 1990). Mackenzie and Mathieson (1984) have also pointed out that the extinction correction used by γ-ray diffraction is not sufficient. They proposed a new correction method and obtained $F_{220}^\gamma = 16.76 \text{ e/Å}^2$ for the (220) reflection, which is close to the electron diffraction result $F_{220}^\text{e} = 16.68(3) \text{ e/Å}^2$, but still outside the standard deviation. Petrillo et al. (1998) reanalyzed the values of Schneider et al. (1981). They subtracted the kinematic correction $\Delta$ and scaled the original data to fit the neutral atom values for scattering angles greater than 0.5 Å$^{-1}$. These new values are close to the electron diffraction values but have large error bars.

As mentioned in the Introduction, the X-ray Pendellösung method can measure low-order structure factors very accurately because of its fully dynamical nature, but requires a large perfect wedge-shaped single crystal for accurate measurements. Takama and Sato (1982) have modified this method by doing experiments on relatively small single crystals using white X-ray radiation. This method has the advantage of easy specimen preparation and only requires a tiny single crystal. The accuracy, however, is lower than the conventional X-ray Pendellösung method and electron diffraction. Their original published data set (Takama & Sato, 1982) is, in general, close to the electron diffraction values, but it has large standard deviations for the low-order reflections.

Comparison with Solid-State Calculations

Because of the accuracy of QCBED, it can be used to test band theory, as has been done for silicon by Zuo et al. (1997). Over the past 40 years, many theoretical calculations have been completed for the X-ray structure factors of copper. In Table 3 we list the calculated structure factors of copper. In Table 3 we list the calculated structure factors of copper. 

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Cu$^{+1}$</td>
<td>Cu$^{+2}$</td>
<td>Cu$^{-1}$</td>
<td>Cu$^{+1}$</td>
<td>Cu$^{-1}$</td>
<td>Cu$^{-1}$</td>
</tr>
<tr>
<td>111</td>
<td>22.05</td>
<td>22.12</td>
<td>21.89</td>
<td>21.72</td>
<td>21.76</td>
<td>21.73</td>
</tr>
<tr>
<td>400</td>
<td>12.42</td>
<td>12.42</td>
<td>12.42</td>
<td>12.34</td>
<td>12.48</td>
<td>12.62</td>
</tr>
<tr>
<td>440</td>
<td>8.82</td>
<td>8.82</td>
<td>8.78</td>
<td>8.51</td>
<td>8.15</td>
<td>0.17</td>
</tr>
<tr>
<td>$R(%)$</td>
<td>0.55</td>
<td>0.68</td>
<td>0.48</td>
<td>0.51</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>$a (\text{Å})$</td>
<td>3.6032</td>
<td>3.6032</td>
<td>3.6032</td>
<td>3.6032</td>
<td>3.6145</td>
<td>3.615</td>
</tr>
</tbody>
</table>

*As a measure of agreement between calculation and our experiment, we use the residual, $R$, listed at the bottom of the table. Because different lattice parameters, $a$, were used in the calculations, they are also listed at the bottom of the table. Units are in electrons per atom. 
how well these calculations fit our experiments, we give the residual $R$, defined as $R = 1/n \sum_i |F_i^N(\text{theory}) - F_i^N(\text{exp})|/F_i^N(\text{exp})$, at the bottom of the table. Because the calculations were done using different lattice parameters, they are also listed in Table 3. All calculations are self-consistent.

The band-structure calculation of Bagayoko et al. (1980), using Gaussian orbitals and a local exchange-correlation potential, gives a good fit to photo-emission spectra as well to the current QCBED experiment. Also, the relativistic field calculations by MacDonald et al. (1982) agree very well with the current experiment. Eckardt et al. (1984) show higher values than the previous studies and this experiment, even though they agree very well with experimental photo-emission spectra.

**CONCLUSION**

Accurate low-order structure factors for copper have been measured by electron diffraction. The local heating of the electron beam has been measured to be 5 K under our experimental conditions. Charge density deformation maps, generated from the six inequivalent lowest order reflections, indicate that copper has two delocalized electrons per atom. This result may help to understand how cohesive energy relates to the number of bonding electrons (Brewer, 1981).

**ACKNOWLEDGMENTS**

We thank Prof. Marthinsen (NTNU) and Prof. Zuo (University of Illinois at Urbana-Champaign) for useful discussions. J. Friis acknowledges the funding of the Research Council of Norway (NFR), project 135270/410. B. Jiang is funded by DOG DE-FG03-02ER45596. The experiments were done at the CHREM center at Arizona State University.

**REFERENCES**


Paper 2

On the Consistency of QCBED structure factor measurements for TiO$_2$ (Rutile)
On the Consistency of QCBED Structure Factor Measurements for TiO$_2$ ( Rutile)

Bin Jiang, Jian-Min Zuo, Jesper Friis, and John C.H. Spence

Abstract: The same Bragg reflection in TiO$_2$ from 12 different (CBED) patterns (from different crystals, orientations, and thicknesses) are analyzed quantitatively to evaluate the consistency of the quantitative CBED method for bond-charge mapping. The standard deviation in the resulting distribution of derived X-ray structure factors is found to be an order of magnitude smaller than that in conventional X-ray work, and the standard error (0.026%) for $F_{X}(110)$ is slightly better than obtained by the X-ray Pendellösung method applied to silicon. This is sufficiently accurate to distinguish between atomic, covalent, and ionic models of bonding. We describe the importance of extracting experimental parameters from CCD camera characterization, and of surface oxidation and crystal shape. The current experiments show that the QCBED method is now a robust and powerful tool for low-order structure factor measurement, which does not suffer from the large extinction (multiple scattering) errors that occur in inorganic X-ray crystallography, and may be applied to nanocrystals. Our results will be used to understand the role of $d$-electrons in the chemical bonding of TiO$_2$.

Key words: electron diffraction, CBED, structure factor, rutile

INTRODUCTION

The ultimate aim of this work is to understand the role of $d$ electrons in the chemical bonding of TiO$_2$ (rutile) and the charge state of Ti(IV) ions common to many important electronic ceramics. Here we analyze the consistency of the convergent-beam electron diffraction (CBED) method used to measure the bond-charge density, by comparing measurements of the same structure factors in different crystals and orientations. The excellent agreement increases confidence that possible systematic errors, ranging from sample inhomogeneity to convergence of calculations, have been minimized. Some final structure factor measurements, and details of the experimental methods, are provided. By comparison with our earlier work on silicon, GaAs, Cuprite, and MgO (Zuo et al., 1998), a number of new problems arose, indicating the sensitivity of the method to TEM sample quality and shape (boundary conditions) resulting from the sensitivity of TiO$_2$ to ion beam thinning and the use of crushed samples. A new detector system, with improved dynamic range over our previous camera, had to be characterized, for which we give details. We compare a total of 12 different data sets (CBED patterns). For an earlier comparison of the same reflection refined at different thicknesses (and structure-factor phase measurement with an accuracy of about 0.1$^\circ$), see Zuo and Spence (1993). Random errors as small as 0.026% are obtained here for rutile crystal, quite sufficient.
to see bonding effects and test theoretical approximations, and the smallest random error yet obtained. In a subsequent paper, we will report details of the multipole analysis of the final charge density, and discuss its implications for the molecular orbitals that take part in bonding.

Several methods have been used to measure low-order structure factors: (1) the X-ray single crystal Pendellösung method, (2) Bragg diffraction by X rays and γ rays, (3) the critical voltage (CV) of electron diffraction, and (4) quantitative convergent beam electron diffraction (QCBED).

The X-ray Pendellösung method can measure structure factors very accurately (standard error 0.07% at best for silicon; Aldred & Hart, 1973). We use the term standard error to refer to the standard deviation of the mean value, and distinguish this from the standard deviation, which we also evaluate. (The X-ray community uses mostly standard error, especially for Pendellösung work.) The Pendellösung accuracy is about the same as the best accuracy obtained by CV and QCBED. The sensitivity to structure factors is about the same for CV and QCBED; however, accurate measurement of structure factors by CV requires known high-order structure factors (see below). The disadvantage of the Pendellösung method is that it requires large defect-free crystals, which severely limits its application to crystals such as silicon, diamond, GaAs, and germanium single crystals that have low defect density.

Conventional Bragg X-ray diffraction from inorganic materials normally suffers from large extinction errors (due to multiple scattering) for the strong low-order reflections that are crucial for charge density maps of bonding. Bragg γ-ray diffraction using high-energy radiation may reduce absorption and extinction effects, but does not eliminate them, and the flatter Ewald sphere may increase multiple scattering (Lippmann & Schneider, 2000).

The CV method of electron diffraction is capable of highly accurate measurements of the ratio of the two lowest order structure factors (Spence & Zuo, 1992). Errors may be as small as 0.1%. The disadvantage is that this method can only give the ratio of the two structure factors. One must be known accurately to calculate the other one.

Recent progress in energy-filtered QCBED has made extinction-free measurements of low-order structure factors possible on an absolute scale (Zuo et al., 1999). This method takes advantage of the small electron probe (of nanometer dimension, smaller than one “mosaic block”) and of the sensitivity of QCBED to low-order bonding reflections that results from the $\Theta^{-4}$ dependence of electron scattered intensity on scattering angle $\Theta$ for low angles (Spence & Zuo, 1992). When combined with TEM, the crystal can be imaged at the atomic level, and it is easy to find a defect-free crystal region for electron diffraction, to which the dynamic diffraction theory can be applied. Using this method, combined with X-ray diffraction to measure the high-order structure factors, Zuo et al. (1999) recently directly observed the $d$ orbital holes and Cu-Cu bonding in Cu$_2$O crystal (for discussion of this work, see Zuo et al., 2000). Readers are referred to our earlier paper (Jiang et al., 2002) and book (Spence & Zuo, 1992) for more details and background.

**Experiment**

**TEM and Ω-Filter**

CBED patterns were obtained on a Leo-921B Ω electron microscope operating at 120 keV, with in-column imaging Ω-filter and a Gatan MSC CCD camera. Two types of commercial energy filters are available—the in-column Ω energy filter and the postcolumn Gatan Imaging Filter (GIF). For electron diffraction, the geometric distortion, isochromaticity, and angular acceptance are the most important characteristics of the energy filters (Rose & Krahl, 1995). Theoretically the in-column Ω-filter has smaller distortion due to its midplane symmetry, and is particularly simple to use, with a large acceptance angle, acceptable variation of energy-window center energy with angle, and little or no alignment needed. The energy window used for diffraction recording is normally 10 eV.

**CCD Characterization**

A new $1,024 \times 1,024 \times 14$ bit GATAN MSC CCD camera was installed in the Leo-912B microscope in March 2000. Detector characterization is a crucial aspect of QCBED work, and, for CCD cameras especially, the goodness-of-fit (GOF) indexes obtained depend sensitively on how the detector response is measured and deconvoluted. For a detailed comparison of CCD, image-plate, and film systems (with comparisons of measured modulation transfer function (MTF), detective quantum efficiency (DQE), and gain for each) see Zuo (2000). The CCD characteristics were measured by the noise method (Zuo, 1996), in which the shot noise from the electron beam is used to derive an equally weighted spectrum of spatial frequencies. The important characteristics of the CCD to be used in deconvolution of CBED data are MTF function, gain, and DQE.
Gain is defined as the ratio of the average number of CCD output counts \( \bar{I} \) to the electron dose per pixel \( N_e \):

\[
g = \frac{\bar{I}}{N_e}.
\]  

(1)

The gain was obtained by making absolute intensity measurements of the electron beam (using the calibrated Fuji image plate system) and comparing these with the numbers per pixel output by the Digital Micrograph program.

The resolution of the slow-scan (SSC) CCD camera is described by its point spread function. The best achievable resolution in the SSC camera is one pixel. For our CCD, additional spreading occurs, mainly in the scintillator and fiber-optics coupling (crosstalk). In both cases, the spreading has approximate rotational symmetry. The MTF function is defined as the modulus of the Fourier transform of the point spread function (PSF). If the PSF function is \( \delta \)-function, the MTF will be unity for all spatial frequencies. The MTF function can be modeled for Gatan CCD cameras by the simple function (Zuo, 1996):

\[
M(\omega) = \frac{a}{1 + \alpha \omega^2} + \frac{b}{1 + \beta \omega^2} + c.
\]  

(2)

Here \( \omega \) is spatial frequency in units of 1/pixel. The MTF is given, in all essentials, by the noise spectrum in the Fourier transform of an image of a uniformly illuminated field, averaged over many exposures.

The DQE is defined as the square of the ratio of output signal-to-noise ratio to input signal-to-noise ratio. A figure of unity is only possible if every beam electron is detected, with no noise added and the ideal PSF. DQE can be shown (Zuo, 1996) to be given by

\[
DQE(I) = \frac{mg\bar{I}}{\text{var}(I)}.
\]  

(3)

where \( m \) is a mixing factor measuring crosstalk between pixels (obtainable from the area under the MTF), \( g \) is the gain, \( \bar{I} \) is the average number of CCD counts per pixel, and \( \text{var}(I) \) is the variance in that number. These quantities are obtained by recording a uniformly illuminated field at different average intensity. The dependence of DQE on intensity has been modeled by an expression involving the parameters of the CCD (Zuo, 1996):

<table>
<thead>
<tr>
<th>HV (kV)</th>
<th>( a )</th>
<th>( \alpha )</th>
<th>( b )</th>
<th>( \beta )</th>
<th>( c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>119.52</td>
<td>0.113</td>
<td>3.396</td>
<td>0.858</td>
<td>6.67</td>
<td>0.0228</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HV (kV)</th>
<th>( m )</th>
<th>( g )</th>
<th>( \Delta )</th>
<th>( 1 + F + 1/mG )</th>
</tr>
</thead>
<tbody>
<tr>
<td>119.52</td>
<td>0.25767</td>
<td>1.55</td>
<td>2.40</td>
<td>4.57e-6</td>
</tr>
</tbody>
</table>

\( DQE = \frac{\text{SNR}_{out}^2}{\text{SNR}_{in}^2} = \left[ 1 + F + \frac{1}{mG} + \frac{\Delta N_e}{m} + \frac{\text{var}(B)}{m g^2 N_e} \right]^{-1} \)  

where \( F, G, \Delta, \text{var}(B) \) are constants. Readers are referred to Zuo (1996) for practical details of DQE measurement.

The measured gain, MTF, and DQE characteristics are shown in Table 1, and in Figures 1 and 2. Compared with our earlier 12-bit Gatan SSC CCD (Zuo, 1996), this new CCD has larger gain, and better MTF and DQE, which all contribute to the better quality and accuracy of the CBED data, resulting in smaller \( \chi^2 \) values.

### TEM Alignment

TEM alignment is very important for accurate QCBED measurement, particularly diffraction astigmatism correction. The TEM was aligned to its best condition to ensure the quality of the measured data. The diffraction astigmatism was corrected using a standard aluminum specimen, resulting in no observable astigmatism in the diffraction pattern. Figure 3 shows one of the ring patterns of an aluminum fine powder. Direct measurement of the circle shows that the deformation from circularity is negligible.

### Beam Energy Calibration

It is well known that HOLZ lines shifts due to accelerating voltage and lattice constant changes are not independent; thus it is not possible to measure both high voltage and crystal constants from a single diffraction pattern. A crystal with known lattice constant was therefore used to calibrate the high voltage. The silicon (133) zone pattern shown in Figure 4 was used for this purpose. The “Extal” software...
was used to refine the high voltage, by matching of calculated patterns (including multiple scattering) to experimental CBED patterns. The high voltage was thus measured to be 119.52 keV.

Specimen Preparation for Rutile

Because rutile is rather sensitive to ion beam radiation, samples prepared by the standard ion milling specimen preparation method left a thin oxygen-deficient layer, giving extra diffraction spots. This introduces large random and systematic error in the refined data. This subtle effect on the refinement took some time to identify and resulted for a long time in reasonably good $\chi^2$ figures, but obviously incorrect structure factors. We attribute the good $\chi^2$ figures

Figure 1. Experimental measured MTF of Gatan MSC 14-bit CCD camera.

Figure 2. Experimental measured DQE curve of the Gatan MSC 14-bit CCD camera.

Figure 3. TEM diffraction astigmatism was corrected by a standard aluminum powder. The ring pattern is quite circular with no observable astigmatism.
to the parallel-sided nature of the ion-beam samples (the EXTAL program does take into account a tilted, but parallel-sided sample). High accuracy in structure-factor measurement requires the thickness estimate to be accurate to within a few Ångstroms (Zuo et al., 1997). Crushed samples were finally used to ensure cleanliness of the sample surfaces, and these produced both excellent $\chi^2$ values at a deep minimum (see Fig. 6) and correct structure factors. Fortunately, large thin areas can be found on the edge of the crushed crystals for CBED experiments. The samples were crushed in a mortar and pestle under alcohol, and collected on holey carbon grids. This produced wedge-shaped cleavage surfaces, which introduced other problems due to the inclined boundaries. It was found that the best GOF factors were obtained from systematic rows running parallel to the wedge edge, which greatly limited the number of useful crystals. This problem is similar to the much earlier finding (Goodman, 1974) that CBED patterns from wedge-shaped crystals do not display the correct point group for a crystal, because the patterns show the symmetry of the sample (including its boundaries, which may destroy symmetry elements) rather than that of an infinite lattice. We use an LaB$_6$ source with a probe size of 10 nm (measured), smaller than in earlier work. The even smaller probe possible with a field-emission gun would reduce these artifacts.

**Refinement**

**Specimen Thickness**

The experimental conditions have to be chosen carefully. The thickness should be between 600 and 1,500 Å, depending on individual reflections for a 120-kV electron beam, and is returned by EXTAL at an early stage of the refinement. A reasonable thickness was chosen to ensure that the CBED fringes within the CBED disk could give accurate thickness information; normally three or more thickness fringes were required and the inclusion of 2g and $g$ reflections in the refinement improves the reliability of the technique. Higher accelerating voltage would produce more fringes.

**Experimental Intensity Measurement**

Due to the point-spread function H of the CCD camera, the raw data collected is the convolution between the PSF and the incident beam intensity, plus the noise introduced in the detection process. The raw image recorded can be written as

$$\chi = H \otimes I + n.$$  \hspace{1cm} (5)

Here $\chi$ represents the image recorded by the CCD and I is the incident CBED pattern and $\otimes$ denotes convolution. The PSF has been experimentally measured, and its Fourier transformation is the modulation transfer function.

The effects of the PSF can be removed partially by deconvolution. But direct deconvolution in reciprocal space, using the measured MTF function, produces excessive amplification of noise, due to the amplification of high spatial frequencies, which reflects mostly pixel-to-pixel variations from noise. Therefore we use the Richardson–Lucy image restoration algorithm, which is optimized for images with Poisson noise (Snyder et al., 1993; Zuo, 2000). The image restoration works by repeat iteration using

$$Q(u,v) = \frac{H^*(u,v)}{H^*(u,v)H(u,v) + \alpha P(u,v)}.$$  \hspace{1cm} (6)

The iteration is stopped when

$$\| \chi - H \otimes \hat{I} \| = \| n \|. \hspace{1cm} (7)$$

Here the $\chi$ and $\hat{I}$ are the recorded and deconvoluted CBED patterns, $n$ is the estimated additional noise introduced during the recording process, and $\alpha$ (typically smaller than one) is a parameter.
Figure 5 shows an example of a deconvoluted image. It is clear that the edge of the pattern is much sharper than the recorded one.

Refinement Convergence Tests

Our dynamical calculations typically include about 500 beams, both in the zero and higher order Laue zones. Beams selected for inclusion in the multiple scattering calculations were selected according to three criteria (Zuo & Weickenmeier, 1995): (1) proximity to the Ewald sphere; this is measured by $2KS_g$; (2) length of $g_{\text{max}}$ vector; and (3) perturbation strength $\omega_{\text{max}}^{-1} = |U_g/2KS_{\text{min}}|$.

The criteria $2KS_g$ is used as the weak-beam criterion. It selects the beams included in the diagonal matrix, whereas others are treated by Bethe’s perturbation method. Here $g_{\text{max}}$ is used as a cutoff parameter for high-order reflections. Because the width of the HOLZ lines falls off as $g^{-3}$, the intensity decreases by a factor of $g^{-4}$. As a result, the high-order reflections with $g > g_{\text{max}}$ become localized, and their effects can be ignored. The third criteria $|U_g/2KS_{\text{min}}|$ is called perturbation strength, and selects weak beams for...
perturbation treatment. The beams within the $g_{\text{max}}$, but with larger excitation error, will contribute to the beams and excitation error by perturbation. These criteria will be used to discard those beams with large excitation error. The beams selected in the refinement were tested for convergence by changing the above three criteria until the refined value converges. Normally the use of $3.0$ (for $2K_{S_g}$), $3.5$ (for $g_{\text{max}}$), and $35$ (for $\omega_{\text{max}}$) were found to give a good refinement convergence for rutile crystals.

$\chi^2$ Map

A preliminary refinement is used to obtain approximate values of thickness and orientation (assignment of $K$, values to each pixel in the CBED pattern). The program then adjusts the following parameters for lowest $\chi^2$: thickness, orientation, thermal background, the two structure-factor values being refined, and the two corresponding absorption coefficients. Absorption coefficients are taken from Bird and King (1990). The following parameters are not adjusted, and treated as known: all structure factors other than those under refinement, anisotropic, harmonic Debye–Waller factors (taken from Restori et al., 1987, who worked at the temperature of 100 K, were interpolated to our experimental temperature at 113 K), absorption coefficients other than the two being refined, accelerating voltage, cell parameters, and atom positions (obtained from Restori et al., 1987). The background beneath each disk (mainly phonon inelastic scattering, as plasmon-scattered electrons are removed by our energy filter) is assumed to be constant, and this constant, different for each CBED disk, is treated as a refinement parameter. Absorption parameters were found to need little adjustment, and to have a small effect. Experience shows that the simplex method is a very robust method to find the global minima (Zuo et al., 1998). To show that a global minima had been found in our refinement procedure, we did a $\chi^2$ map versus the structure factors of the $(110)$ and $(220)$ reflections, for the case of $(110)$ systematic refinement. This is shown in Figure 6. It clearly shows that near the global minima there is no other local minimum. This property ensures that the refinement program can find the real global minima. It is interesting to note that, for the $(110)$ reflection, the minimum point is almost independent of the $(220)$ reflection. This ensures the reliability of the

![Figure 6. $\chi^2$ versus structure factor (110) and (220) reflections of rutile crystal. It shows a deep global minimum. No other local minimum is found nearby.](image-url)
measured (110) reflection, and is one of factors that allows such high accuracy to be obtained by QCBED.

**Error Analysis**

The errors quoted in the tables were obtained using the following statistical formulas:

\[
\text{Standard deviation: } \sigma = \sqrt{\frac{\sum_{j=1}^{N} (x_j - \bar{x})^2}{N-1}} \tag{8}
\]

\[
\text{Standard error: } \varepsilon = \frac{\sigma}{\sqrt{N}} \tag{9}
\]

where \(N\) is the number of measurements. We note that \(\sigma\) is independent of the number of measurements; however, the error in the mean (the standard error) decreases with increasing number of measurements, as required.

**QCBED Results for TiO\(_2\) (110) Systematics**

Table 2 shows the 12 data sets used for the consistency tests. These consist of CBED patterns from two different crystals, from which the same reflection was found in various different orientations and thicknesses. Each row in the table refers to a different thickness. The orientations were: (i) from (111) zone axis, tilted about 8° along the (110) systematics; (ii) from the (001) zone for (110) systematics (tilted 7°), and (iii) (1–10) systematics (tilted 8°). The results listed in Table 2 give the measured \(U(110), Ua(110), U(220), \) and \(Ua(220)\)
structure factors (in units of Å⁻²), where Ua indicates an absorption parameter. Each measurement was done on a different diffraction pattern. The measurement was done by comparing the intensity of theoretical calculations and experimental intensities across the CBED disks (rocking curve), using the goodness of fit (χ²) as the fitting criterion. Figure 7a,b gives an example of this fitting for the (110) and (220) reflections. About 500 beams are included in the calculations, not confined to the systematics row.

The different data sets are entirely consistent with each other. The overall standard deviation of the 12 values is 0.0002 and standard error (standard deviation of the mean) is 0.00006 = (0.0002/√12). This is an error of about 0.09% in the measured U(110) and 0.16% in the measured U(220) electron structure factors.

Transforming these values into X-ray structure factors using the Mott formula (Spence & Zuo, 1992), using temperature factors for 110 K (Restori et al., 1987), the resulting

Figure 7. Example of the electron structure factor refinement for rutile crystal (110) and (220). a: Experimental recorded and deconvoluted CBED pattern. b: Best fit along the line indicated in a. The x-axis is pixel displayed sequentially and the y-axis in counts.
X-ray structure becomes \( F_\text{x}^{110} = 37.30 \pm 0.01 \) (in units of electrons per unit cell), and \( F_\text{x}^{220} = 25.50 \pm 0.04 \). The standard error (std. dev. of the mean) is 0.026% for \( F_\text{x}^{110} \) and 0.14% for \( F_\text{x}^{220} \). The accuracy is improved after transforming into X-ray structure factors owing to the Mott formula, as electron diffraction is more sensitive at smaller scattering angles.

### DISCUSSION

We have shown that the QCBED measurement method can give highly accurate and consistent data by comparing different measurements of equivalent reflections from different crystals in different orientations. This experiment on TiO\(_2\) shows that the QCBED method is now a robust technique for low-order structure factor measurement if sufficiently sophisticated software is used and the detector is well characterized.

The accuracy obtained here on TiO\(_2\) by QCBED is slightly better than the previously most accurate structure factor measurements, which were based on the X-ray single-crystal Pendellösung method, applied to silicon (Aldred & Hart, 1973). These two methods use a similar perfect-crystal Bloch-wave theory, and both require perfect crystals. That is the reason why they can give such accurate results. Compared with QCBED, however, the X-ray single crystal Pendellösung method requires large perfect crystals, and this has limited its application to the few semiconductor crystals that are available free of defects. The QCBED method, when combined with TEM imaging and the nanometer probe, can be applied to almost any kind of crystal. However, the QCBED method becomes less accurate than the X-ray method for large scattering angles, which are more sensitive to atomic positions and thermal effects than the bond-charge distribution.

A comparison with Bragg X-ray results is given in Table 3. The X-ray data sets are inconsistent with the same reflection from a different crystal, or equivalent reflections on the same crystal; thus the measurement depends on the crystal used. The difference between their measurements is much larger than their standard deviations, which indicates large systematic errors. These large systematic errors stem from the statistical description of the crystal used in the extinction correction. This may also be the main reason for the large difference between different groups. An accurate nonstatistical model is needed for improved extinction (multiple X-ray scattering) correction.

When combined with X-ray results for the higher order reflections, it should be possible to map out the charge density of TiO\(_2\) accurately. According to band theory calculations, the oxygen 2\( s^2 \)p orbital hybridizes with titanium 4\( s^4p^3d \) orbitals to form bonding orbitals (Sorantin & Schwartz, 1991). The current measurements will make it

| Table 3. Comparison of the X-Ray Structure Factors of (110) and (220) Reflections Measured by QCBED and Bragg X-Ray Diffraction* |
|---|---|---|---|---|---|---|
| | \( F_\text{x}^{110} \) | \( F_\text{x}^{1-10} \) | \( y_{ext}^{110} \) | \( F_\text{x}^{220} \) | \( F_\text{x}^{2-20} \) | \( y_{ext}^{220} \) |
| QCBED | Crystal 1 (111) zone | 37.295 | NA | NA | 34.077 | NA | NA |
| | Crystal 2 (001) zone | 37.306 | 37.275 | NA | 34.240 | 34.266 | NA |
| | Average | 37.29 | 37.29 | NA | 34.17 | NA | NA |
| | Standard deviation: | | | | (±0.032 or ±0.086%) | | |
| | Standard error: | | | | (±0.01 or ±0.026%) | | |
| | Gonschorek et al., 1982 | 38.89 | 36.69 | NA | 34.53 | 34.36 | NA |
| | (±0.17) | (±0.17) | | (±0.2) | (±0.2) | | |
| | Restori et al., 1987 | 37.78 | NA | 0.864 | 34.48 | NA | 0.945 |
| | (±0.18) | | | (±0.26) | | |

*All the data here are assumed to be at the temperature of 100 K or converted to their 100 K values. (The X-ray structure factors are in units of electrons per cell.)
possible to test these band theory predictions, and to give accurate and reliable information on the role of $d$ electrons in bonding in rutile.

Our experiments on rutile showed that QCBED is extremely sensitive to the quality of the TEM specimen. Rutile offers a good example of specimen problems with QCBED. We recommend that experimentalists carefully study the specimen before undertaking a QCBED analysis. First, crystals should be checked for point defects, strain, surface/interface relaxation, twin boundaries, and chemical inhomogeneity. All these inhomogeneous defects reduce the accuracy of the measured structure factors and increase the $\chi^2$ factor. Second, check the crystal for nonstoichiometry. A deviation of chemical composition from the exact chemical formula would introduce large systematic errors in the structure factors that are fixed in the refinement procedures. Nonstoichiometry will produce diffuse scattering in point diffraction patterns, and may also be checked by X-ray microanalysis and by very accurate X-ray measurement of lattice constants. Nonstoichiometry will change the lattice constants. Thus it is possible that crystal constants could also be refined in order to calculate the exact chemical formula, and QCBED refinement could then be based on measured chemical ratios and crystals constants. Finally, crystals should be checked for any bulk or surface damage caused by the TEM specimen preparation procedures. The damage can be observed by high-resolution TEM imaging or from conventional electron diffraction patterns. We strongly recommend that experimentalists search for the best method for TEM specimen preparation for each material before undertaking a QCBED analysis. As this case showed, methods that produce a rough surface lead to a much poorer fit and less accurate values of the structure factors, as revealed by the error analysis.

Acknowledgments

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References


Paper 3

Retrieval of anisotropic displacement parameters in Mg from convergent beam electron diffraction
Retrieval of anisotropic displacement parameters in Mg from convergent beam electron diffraction experiments

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Abstract. We present an accurate Wilson plot-like method, based on convergent beam electron diffraction, for measuring the anisotropic displacement parameters in magnesium, and compare it with the method proposed by Saunders et al. A generalization of this method to isotropic crystals with more than one type of atoms is also discussed.

1. Introduction

With quantitative convergent beam electron diffraction (QCBED) [1, 2] it is possible to very accurately measure the low order structure factors in small-unit cell crystals. This technique is based on a pixel to pixel comparison between an experimental CBED pattern and a Bloch-wave simulation. The input parameters (such as structure factors, beam direction, etc.) in the Bloch-wave simulation are refined until the best fit is obtained.

In structure factors measured by QCBED, the largest source of errors comes from uncertainty in the thermal displacement parameters (DPs). Even though the DPs might be known as a function of temperature, either from phonon calculations, or from X-ray or neutron measurements, the exact sample temperature is unknown. Several methods have therefore been proposed for measuring the DPs directly by electron diffraction [3-7]. Most of these methods, except [7], require separate experiments for the determination of DPs and structure factors. The same experimental conditions, e.g. sample temperature, can therefore not be guaranteed. We will here investigate a Wilson plot-like method based on the values of the refined electron structure factors, and compare it with the method proposed by [7].

2. CBED experiment and refinement

The experiments were performed using a 120 kV LEO 912B TEM with an in-column Ω-filter and a Gatan CCD camera. The systematic row orientation was used and the sample was cooled to liquid nitrogen temperature. Eleven low order structure factors, listed in Table 1, were measured and refined with the EXTAL program [2]. For Mg the DPs have been measured at different temperatures by neutron diffraction [8]. Hence, good initial estimates of the anisotropic DPs of \( \langle u_1^2 \rangle = 0.0076 \, \text{Å}^2 \) (a-direction, parallel to 2-fold axis) and \( \langle u_3^2 \rangle = 0.0085 \, \text{Å}^2 \) (c-direction, parallel to 6-fold axis) at the experimental temperature (around 110 K) have been used in the refinements.
Table 1. Refinement results. The scattering angles $s$ are in units of $\AA^{-1}$ and the electron structure factors $U_g$ are in units of $10^{-4} \AA^{-2}$.

<table>
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<th>$hkl$</th>
<th>1 0 0</th>
<th>0 0 2</th>
<th>1 0 1</th>
<th>1 0 2</th>
<th>1 1 0</th>
<th>1 0 3</th>
<th>2 0 0</th>
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<td>0.193</td>
<td>0.205</td>
<td>0.264</td>
<td>0.313</td>
<td>0.341</td>
<td>0.361</td>
<td>0.385</td>
<td>0.478</td>
<td>0.528</td>
<td>0.626</td>
</tr>
<tr>
<td>$U_g$</td>
<td>184.5</td>
<td>346.9</td>
<td>279.6</td>
<td>115.3</td>
<td>185.8</td>
<td>143.8</td>
<td>77.21</td>
<td>141.0</td>
<td>52.42</td>
<td>44.71</td>
<td>67.0</td>
</tr>
<tr>
<td>±0.7</td>
<td>±0.4</td>
<td>±0.9</td>
<td>±0.5</td>
<td>±0.2</td>
<td>±0.3</td>
<td>±0.15</td>
<td>±0.3</td>
<td>±0.15</td>
<td>±0.16</td>
<td>±0.5</td>
<td></td>
</tr>
</tbody>
</table>

The measured electron structure factors $U_g$ (Fourier coefficients of the crystal potential) are converted to X-ray structure factors $F_g$ (Fourier coefficients of the electron density) with the Mott-Bethe formula [1]

$$F_g = \sum_i Z_i T_{i,g} e^{-2\pi i g \cdot r_i} - \frac{8\pi^2 e_0 h^2 \Omega s^2}{\gamma m e c^2} U_g.$$  \hspace{1cm} (1)

The sum goes over all atoms, where $Z_i$ and $T_{i,g}$ are the atomic number and temperature factor of atom $i$, respectively. $\Omega$ is the unit cell volume, $s = \sin \theta / \lambda$ the scattering angle and $\gamma = 1 + E_0 / (m_e c^2)$ a relativistic correction, with $E_0$ being the acceleration voltage of the microscope.

3. Determination of DPs using the method proposed by Saunders et al.

A strategy for determination of DPs by comparing the refined structure factors with calculations was proposed by [7]. In short, each refinement is performed for a range of fixed DP values, where the same DPs are used for conversion to X-ray structure factors. If the order of the structure factor is sufficiently high, so that bonding effects can be neglected, the X-ray structure factor obtained with the correct DPs should equal the calculated value from an independent atom model (IAM) [9].

In Fig. 1a this method is applied to the (204) structure factor ($\sin \theta / \lambda = 0.528 \AA^{-1}$) of Mg. The neutron diffraction measurement [8] is used to relate the two anisotropic DPs for Mg to each other and to assign them to a temperature. The refined structure factors, converted to X-ray values intersect the IAM values at 102 K, corresponding to $\langle u_1^2 \rangle = 0.0074 \AA^2$ and $\langle u_3^2 \rangle = 0.0082 \AA^2$.

![Figure 1](image)

Figure 1. (a) The refined and converted (204) structure factor as a function of the temperature used in the refinement. The dashed line represent the IAM value. (b) The difference between electron structure factors and their mean value as a function of the temperature used in the refinement.
4. Wilson-like method for determination of DPs

The refinement procedure for low order structure factors itself is not very sensitive to the DPs, since they mainly affect the non-refined high order structure factors responsible for HOLZ-lines. This is demonstrated in Fig. 1b, where four structure factors are refined for a range of (fixed) temperatures. No dependence between $U_{tg}$ and the temperature is observed. However, one should keep in mind that this result is obtained in a systematic row orientation when strong HOLZ-lines are avoided. The case might be different in the zone-axis orientation used in [7]. The conversion to X-ray structure factors is, on the other hand, sensitive to the DPs because of the atomic temperature factors $T_i$. The method for determination of DPs presented here is purely based on this fact.

In the harmonic approximation the atomic temperature factor for Mg is

$$T_{tg} = \exp[-(h^2 + hk + k^2)P - l^2 Q]$$  \hspace{1cm} (2)

where

$$P = 2\pi^2 \frac{4}{3a^2} \langle u_1^2 \rangle \quad \text{and} \quad Q = 2\pi^2 \frac{1}{c^2} \langle u_3^2 \rangle.$$  \hspace{1cm} (3)

Since Mg only has one atom species, the X-ray structure factors can be written as $F_{tg} = f_{tg} C_{tg}$, where $f_{tg}$ are static lattice scattering factors and $C_{tg} = \Sigma_i \exp(2\pi i g \cdot r_i)$. This, together with Eq. (1) and (2), gives

$$-\ln T_{tg} = -\ln \left[ \frac{8\pi^2 \varepsilon_0 h^2 \Omega^2 U_{tg}}{\gamma m_e e^2 C_{tg}(Z - f_{tg})} \right] = (h^2 + hk + k^2) P + l^2 Q.$$  \hspace{1cm} (4)

Given $f_{tg}$, the left hand side of Eq. (4) can be calculated. Hence $P$ and $Q$ can easily be obtained by least square fitting. In Fig. 2 we have plotted the left hand side of Eq. (4) against the right hand side for the fitted values of $P$ and $Q$. We do therefore expect the points to follow a straight line with a slope of 1. We have used $f_{tg}$ from both Dirac-Fock [10] and density functional theory (DFT) [11] calculations. The latter includes bonding effects and brings even the low order points nicely onto the line (Fig. 2b). Using the DFT values this gives $\langle u_1^2 \rangle = 0.00777(4) \text{ Å}^2$ and $\langle u_3^2 \rangle = 0.0082(1) \text{ Å}^2$. These values are so close to the initial values used that new refinements were not performed. However, if the initial DPs were less accurate, one would have to redo the structure factor refinement with the new DPs until convergence is achieved.

This method benefits from the large number (eleven) of measured structure factors. Usually one does not measure that many structure factors with the CBED technique. In

![Figure 2. Wilson-like plot for low order data. The static lattice reference scattering factors are taken from both DFT (×) and Dirac-Fock (○) calculations. The slope of the line is 1. (b) shows an enlargement around the three first structure factors in (a), where the disagreement between the two models is pronounced. In (c) the same fit is performed using only the five lowest order structure factors.](image-url)
Fig. 2c we have therefore redone the fit by only considering the five lowest order structure factors. The fitted DPs now become $\langle u_1^2 \rangle = 0.0079(3)$ Å$^2$ and $\langle u_2^2 \rangle = 0.0082(7)$ Å$^2$. In this case it is really essential to consider bonding effects in the static lattice reference scattering factors $f_g$. If even fewer structure factors are measured, it is probably sensible to constrain $\langle u_2^2 \rangle$ to $\langle u_1^2 \rangle$ or use an isotropic model.

This method can be generalized to crystals with more than one type of atoms, in the case where only one independent DP needs to be determined per atom type. This is the case for isotropic DPs, which we will consider here. We can then write $T_i = \exp(-B_i s^2)$, where the $B_i$ are known as Debye-Waller factors. Eq. (1) can now be rewritten as

$$U_g = \frac{m e^2}{8 \pi^2 \varepsilon_0 \hbar^2 \Omega s^2} \sum_i \left( Z_i - f_{g,i} \right) e^{-2 \pi i \mathbf{g} \cdot \mathbf{r}_i} e^{-B_i s^2} \tag{5}$$

resulting in a set of equations (one for each $g$) each containing a sum of exponentials in $-B_i s^2$. These exponents can be determined with non-linear fitting, giving the Debye-Waller factors.

5. Discussion and conclusion

The very good fit in Fig. 2 shows that there is enough information in the CBED data to accurately determine DPs.

We have here compared two different methods for determining the DPs in Mg. The method proposed here differs from the one in [7] in that all structure factor refinements are initially carried out only once with assumed DPs. As seen from Fig. 1b, errors in the DPs will not affect the refined structure factors very much when a HOLZ-line free region is used in the refinement. The determination of DPs in the method proposed here is purely based on the Mott-Bethe formula, and involves all measured structure factors via least square fitting. Another improvement, is that DFT, instead an IAM, is used in the calculations of static lattice reference scattering factors. A minor drawback of this is that a systematic error in the DFT model will bias the experimental structure factors towards the DFT-values, making them less appropriate for testing the DFT model [12]. Nevertheless, we believe that the DPs obtained by this method are the most accurate as long as the number of refined structure factors exceeds the number of fitted DPs with a factor of at least two or three.

Acknowledgments

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References

Paper 4

Magnesium: Comparison of Density Functional Theory Calculations with Electron and X-ray Diffraction Experiments
Magnesium: Comparison of density functional theory calculations with electron and x-ray diffraction experiments

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Accurate experimental structure factors for Mg have been measured and compared with density functional theory (DFT) to test some commonly used functionals and self-interaction correction (SIC) schemes. Low order structure factors, free of extinction and on absolute scale, were measured accurately by quantitative convergent beam electron diffraction. In addition, a complete set of structure factors up to $\sin \theta \lambda = 1.6 \text{ Å}^{-1}$ was measured by x-ray diffraction at 10 K. The DFT calculations were performed using the full potential linearized augmented plane wave method. It was found that the agreement with experiment increases when going from the local density approximation (LDA) to the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof and further to the GGA of Engel and Vosko. Applying the SIC of Perdew and Zunger to the core states for LDA does not improve the agreement with theory, while applying the SIC of Lundin and Eriksson results in a significantly improved agreement. This implies that the main source of error in the LDA functional comes from the description of the core densities. Using the functional which agrees best with experiment, a non-nuclear maximum is established in the calculated electron density of beryllium but not of magnesium. © 2003 American Institute of Physics. [DOI: 10.1063/1.1622656]

I. INTRODUCTION

In density functional theory (DFT) new functionals are mainly tested against energies\(^1\) or energy-derived properties such as structure or bulk moduli.\(^2,3\) Although the electron density is the key quantity in DFT, direct testing against experimentally measured structure factors is relatively rare. One of the reasons for this is that a very high precision and accuracy of the experimental structure factors are needed to discriminate between the small discrepancies in the results of modern computational methods. Figure 1(b) shows furthermore that for a small unit cell system such as magnesium, the scattering of the valence electron density has dropped to a very low value already at the lowest symmetry allowed reflection ($\sin \theta \lambda = 0.181 \text{ Å}^{-1}$) of magnesium. Exactly these reflections are difficult to measure with x-ray diffraction due to extinction. The extinction effects can be taken into account by using the Pendellö sung method and interpretation by dynamical theory, but this requires a perfect crystalline sample which has limited the method to a few crystals, such as Si (Ref. 4) and diamond.\(^5\) Another problem is if the computational method is compromised by the use of limited basis sets or the pseudopotential approximation. In the present work, we overcome these two problems by the use of convergent beam electron diffraction (CBED) to measure the low order reflections and the full potential linearized augmented plane wave (LAPW) method\(^6,7\) in the DFT calculations.

In a transmission electron microscope (TEM) it is possible for many crystals to focus the incident electron beam onto a region much smaller than one mosaic block. This technique produces a set of rocking curves for every diffracted beam simultaneously. The small probe and large amount of information, combined with the strong interaction between the fast incident electrons and the crystal potential, make electron diffraction sensitive to the strong, low order structure factors. It is therefore well suited for quantitative work.\(^8\) The LAPW method has the clear advantage that the basis set quality is essentially controlled by only one parameter, namely the plane wave cutoff.\(^6,7\) When basis set convergence is achieved, any deviation from experiment must be purely due to inadequacies of the applied exchange-correlation potential within the DFT.

Some tests of density functionals with systematic comparisons between accurate calculations and measured struc-
ture factors have been carried out for silicon,\textsuperscript{10} germanium,\textsuperscript{11} and beryllium.\textsuperscript{12} Other tests against electron density derived properties, such as hyper fine fields\textsuperscript{13} or electric field gradients,\textsuperscript{14} have also appeared. Both these studies\textsuperscript{13,14} highlight a well-known inadequacy of most density functionals, namely that the ground-state energy is not self-interaction-free. This is expected to be mainly a problem for core electrons or for highly contracted $d$- or $f$ shells. The self-interaction correction (SIC) of Perdew and Zunger (PZ)\textsuperscript{15} has been very successful in overcoming some of the shortcomings of DFT in the treatment of strongly correlated materials,\textsuperscript{16} but the tests of the PZ-SIC have mainly been based on total energy derived properties.\textsuperscript{16} Lundin and Eriks\r\nson (LE)\textsuperscript{17} pointed out that the PZ-SIC is not fully self-interaction-free and constructed the LE-SIC so that it is fully self-interaction-free by construction.\textsuperscript{17} The results of Novak et al.\textsuperscript{13} showed that the LE-SIC is superior to pure local density approximation (LDA) and the PZ-SIC in predicting the hyperfine fields for the 3$d$ ferromagnets. This could indicate that the LE-SIC provides a better electron density than the more common functionals. In this work we have therefore tested the effect of applying a SIC to the core electrons of Mg.

Simple hcp metals show a wide range of the $c/a$ ratios. For Be this value is abnormally low, $c/a = 1.5684$, in contrast to the almost ideal value of $c/a = 1.6224$ for Mg. This lead to an interest in determining the charge density distribution of these metallic structures\textsuperscript{18,19} and subsequently a controversy over the possible existence of a non-nuclear maximum (NNM) in the total charge density, in particular for beryllium.\textsuperscript{12,20–24} Recently, the electron density in Be, Mg, Na, and Li was studied with the LAPW method,\textsuperscript{12} and it was found that at ambient pressure the electron density in hcp Be and bcc Li exhibits NNM. While F centers have been found to manifest themselves as quite large and well defined NNM,\textsuperscript{25–27} the NNM in simple metals are extremely small and we will further investigate their existence by establishing the functional that gives the best agreement with the experimental structure factors.

II. EXPERIMENTAL STRUCTURE FACTORS

A. Sample preparation

Both a single crystal magnesium block grown by zone refinement at the University of Aarhus and a 0.15 mm thick 99.8% assay Mg ribbon from Alfa Aesar were used for the TEM sample preparation. The former was cut to 3 mm disks with normal in the [110] direction and the latter to disks with normal in the [001] direction. As a first try, the samples were prepared with a precision ion polishing system, which however left a too uneven surface, even for incident ion beam angles as low as 4°. The rest of the samples were therefore prepared by dimpling to around 100 $\mu$m thickness and then electropolishing in a solution of 5% HNO$_3$, and 93.5% methanol at 10 V and 0.5 A at room temperature. As soon as a hole was created, the samples were cleaned with methanol and directly brought into the vacuum in the TEM to avoid oxidation.

In the zone-refinement preparation of a magnesium single crystal, a bar of the metal (more than 99.5 wt % Mg) of 15 mm diameter and 60 mm length filled the borehole in a BN crucible and was induction heated by a single loop coil in a high-temperature furnace. In order to prevent magnesium from reacting with oxygen or nitrogen, the furnace chamber was carefully fluxed with helium before heating the magnesium bar, and during the crystal synthesis, the helium pressure was maintained at 0.3 MPa in the oven. The pass velocity through the coil was 5 mm h$^{-1}$. The five-pass zone-refined bar developed into a few single crystals. The above-mentioned magnesium block used for the TEM sample preparation was cut from a single-crystal grain. During the zone refinement a little magnesium sublimed and condensed at the top of the BN container in the form of almost spherical single crystals.

One crystal with diameter of 0.25 mm and with well-developed {001} and {111} facets was selected for x-ray diffraction data collection.
structure factors. The other rocking curves are included for exchange and correlation effects can be neglected. 30 The energy beam electrons passing through the sample, for which the Schrödinger equation is solved in reciprocal space for the high order Laue zone lines, since they depend on high order structure factors that are sensitive to the unknown sample temperature. An example of this geometry is shown in Fig. 2 for the (002) systematic row. The intensities along the rocking curves 3 to 7 are very sensitive to the (002) and (004) structure factors. The other rocking curves are included for increased sensitivity to sample thickness (curves 1, 3, 8), orientation (curves 2, 5), and absorption (curve 1).

The CCD camera was well characterized, 28 allowing to compensate for nonlinearity and point spreading by postprocessing the recorded CBED patterns.

2. Structure factor refinement

The pixel intensities along the rocking curves are calculated with the Bloch wave method. 9, 29 In short, the Schrödinger equation is solved in reciprocal space for the high energy beam electrons passing through the sample, for which exchange and correlation effects can be neglected. 30 The crystal potential is conveniently expanded into electron structure factors $U_g = (2me/\hbar^2)V_g$, where $V_g$ are the Fourier coefficients of the potential and $m$ and $e$ are the electron mass and charge, respectively. The electron structure factors are determined by a refinement procedure, minimizing

$$
\chi^2 = \frac{1}{n-p-1} \sum_i \frac{1}{\sigma_i^2} (I_i^{\exp} - cI_i^{\text{theo}} - I_i^{\text{bgr}})^2,
$$

where the sum runs over the number of pixels $n$, and $p$ denotes the number of refined parameters, $I_i^{\exp}$, $I_i^{\text{theo}}$, and $I_i^{\text{bgr}}$ are the experimental, theoretical, and background intensities of pixel $i$, respectively, $\sigma_i$ is the standard deviation of $I_i^{\exp}$ and $c$ is a scaling of the calculated intensities. Only structure factors corresponding to the normally one or two strongly excited Bragg reflections are refined. The structure factors have a refined complex component $U_g$ accounting for absorption, which mainly comes from the thermal diffuse scattered electrons that cannot be removed by the energy filter. In addition to the structure factors, the sample thickness, the electron beam orientation, the scaling $c$, and the background $I_i^{\text{bgr}}$ (assumed constant for each diffraction disk) are also refined.

Lattice and anisotropic displacement parameters (ADPs) were not refined, but obtained by interpolation from earlier neutron diffraction experiments. 31 This was done by assuming that the actual temperature of the sample under the beam was 5 K higher than the readout temperature from the sample holder, 32 which varied between 107 and 112 K. Figure 3 shows the best fit after refinement of the rocking curves in Fig. 2.

In total, 36 refinements of 7 systematic rows were performed. The resulting structure factors are averaged and listed in Table I. The average and variance of the structure factors are calculated by

$$
U_g = \sum_i w_i U_{g_i},
$$

$$
\sigma^2(U_g) = \sum_i w_i^2 \sigma_{g_i}^2 + \sum_i w_i^2 (U_g - U_{g_i})^2,
$$

where $\sigma_{g_i}$ is the standard deviation of refinement $i$ and the weights $w_{g_i}$ are $(1/\sigma_{g_i})/(\sum g_i/\sigma_{g_i})$.

The x-ray structure factors $F_g$ are related to the electron structure factors through the reciprocal version of Poisson’s equation, known as the Mott–Bethe formula. 9 For Mg,

FIG. 2. CBED pattern of the (002) systematic row in magnesium. Eight rocking curves sensitive to the refined parameters are marked on the pattern.

FIG. 3. Best fit between experimental (points) and theoretically calculated (lines) intensities after structure factor refinement of the (002) systematic row CBED pattern shown in Fig. 2. Seven hundred and twelve pixels along the rocking curves drawn on Fig. 2 were included in the refinement. Pixels belonging to different rocking curves are separated by vertical lines. The $\chi^2$ for this particular refinement is 1.47.
which has a hexagonal structure (space group $P6_3/mmc$, no. 194) and two atoms per unit cell at special positions $c$ with $6m2$ site symmetry, we have

$$F_g = ZC_gT_g \frac{8 \pi^2 e_0 h^2 \Omega s^2}{\gamma me^2} U_g.$$  \hspace{1cm} (4)

Here $Z$, $T_g$, $e_0$, $\Omega$, and $s$ are the atomic number, the temperature factor, the vacuum permittivity, the unit cell volume, and the scattering angle, respectively. The trigonometric factor $C_g$ is defined as the sum $\sum_i \exp (2 \pi i g \cdot r_i)$, where $r_i$ is the position of atom $j$, and equals $2 \cos (2 \pi [(h+k)/3]+1/l/4)$ for $Mg$. The three symmetry-allowed sets of reflections have $C_g = 2\sqrt{3}$ or 1, corresponding to $h=k, l=2n$; $h \neq k, l=2n+1$, and $h \neq k, l=2n$, respectively. Finally, $\gamma = 1 + E_0/(mc^2)$ is a relativistic correction, where $E_0$ is the accelerating voltage of the microscope.

The intensity distribution in the diffraction patterns depends on the temperature through the nonrefined structure factors, but the sensitivity is not strong enough to refine ADPs. However, the conversion from the electron structure factors to x-ray structure factors is sensitive to the temperature. The choice of ADPs was therefore tested with Wilson-type fitting. The temperature factor can be written as

$$T_g = \exp[-(h^2+k^2+l^2)P - l^2Q],$$  \hspace{1cm} (5)

where

$$P = 2 \pi^2 \frac{4}{3a^2} \langle u_1^2 \rangle, \quad Q = 2 \pi^2 \frac{1}{c^2} \langle u_3^2 \rangle,$$  \hspace{1cm} (6)

and where $\langle u_1^2 \rangle$ and $\langle u_3^2 \rangle$ are the ADPs in the $a$ and $c$ lattice directions, respectively.

Given the temperature factors, x-ray structure factors can finally be calculated from Eq. (4). The so-obtained x-ray structure factors, converted into static lattice values $F_0^\alpha = F_g/T_g$ are shown in Table I. Taking the uncertainty in the temperature factors into account, the variance of $F_0^\alpha$ has been calculated as

$$\sigma^2(F_0^\alpha) = (f_0^2 + Z^2) \sigma^2(T_g) \sum_i \exp(-4 \pi i g \cdot r_i) + \left(\frac{K \Omega s^2}{\gamma}\right)^2 \sigma^2(U_g).$$  \hspace{1cm} (7)

By rewriting Eq. (4), using Eq. (5) and the fact that the x-ray structure factors for Mg are given by $F_g = f_g T_g C_g$, we obtain

$$-\ln T_g = -\ln \left[ \frac{8 \pi^2 e_0 h^2 \Omega s^2 U_g}{\gamma me^2 C_g(Z-f_g^2)} \right] = (h^2+k^2+l^2)P + l^2Q,$$  \hspace{1cm} (8)

Given $f_g$, the left-hand side of Eq. (8) can be calculated. Hence, $P$ and $Q$ can easily be obtained by least-square fitting. In the present study we have used $f_g$ obtained from both Dirac–Fock and DFT calculations. The latter includes bonding effects, which, as illustrated in Fig. 4, brings the (002) and (101) structure factors up to a straight line and reduces the standard deviations in the ADPs. Using the DFT results.
values, we obtain $\langle u^2_1 \rangle = 7.77(4) \times 10^{-3}$ Å$^2$ and $\langle u^2_2 \rangle = 8.20(10) \times 10^{-3}$ Å$^2$. Considering that the refinements only depend weakly on the ADPs, these values were so close to the initial values used in the CBED refinements that new refinements were not performed.

C. X-ray diffraction

1. X-ray experiment

X-ray diffraction data were collected with the crystal cooled to 10.2 K on a type 512 HUBER four-circle diffractometer equipped with a type CS202 DISPLEX closed-cycle He cryostat at the Department of Chemistry, University of Aarhus.38

Graphite monochromated Ag K$_\alpha$ ($\lambda = 0.5608$ Å) was used to collect a complete set of data from the single crystal bar up to $\sin \theta \lambda = 1.50$ Å$^{-1}$. A total of 4282 reflections was measured, giving 294 unique data of 12.3 overall average measurement multiplicity. The internal agreement was $R_f(F^2) = 0.025$. The unit cell parameters were obtained by least-square fit to the setting angles of 60 reflections with $41.0^\circ < 2\theta < 43.8^\circ$, yielding $a = b = 3.1925(4)$ Å$^{-1}$, $c = 5.1795(9)$ Å$^{-1}$, $d_s = 1.768$ g cm$^{-3}$, and $\mu = 3.694$ g cm$^{-3}$.

Data were reduced using the local KRYS TAL program package.36 Integration was performed with the $\sigma(f)/f$ method 37 and equivalent reflections were averaged using the program SORTAV.38

2. X-ray refinement

The structure factor in monoatomic crystals takes the form

$$ F_g = f_g C_g T_g. \tag{9} $$

Comparing with Eq. (5), it is seen that $\ln T_g$, as a function of $(\sin \theta \lambda)^2 = (h^2 + k^2 + l^2)/(3a^2) + F/(4c^2)$, should give a straight line for the each of the three symmetry-allowed sets of reflections. Figure 5 illustrates this and shows that the ADPs are reasonably isotropic, as expected for low temperature. Figure 5 also shows how the lowest order x-ray data deviate strongly from a straight line, showing that they are strongly affected by extinction. The high-order data nicely follow a straight line and thereby fix the scaling and ADPs. Figure 1(b) shows how the 2$p$ semicore shell gives a contribution out to $\sin \theta \lambda > 1.2$ Å$^{-1}$. A possible core relaxation would influence the refined ADPs and we have therefore refined them only against data with a higher $\sin \theta \lambda$ using the relativistic Dirac–Fock scattering factors of Su and Coppens,39 yielding $\langle u^2_1 \rangle = 4.86(7) \times 10^{-3}$ Å$^2$ and $\langle u^2_2 \rangle = 5.10(7) \times 10^{-3}$ Å$^2$. Keeping these parameters fixed, we also tried to refine an isotropic extinction model.40 The resulting x-ray structure factors corrected for extinction are shown in the small graph of Fig. 5. It is seen that the extinction correction brings the x-ray data onto a reasonably straight line. However, the deviations are still significant, considering that the scale is exponential and the expected deviations from a spherical atom model should be very small. No sign of anisotropic extinction was found in the data, and a model was therefore not attempted.

The small graph of Fig. 5 also shows the CBED data that have been multiplied with a $T_g$, corresponding to the ADPs found from the high-order x-ray data. It is seen that the deviation is very small, as expected.

III. THEORETICAL MODELING

In the present study, we have employed the LAPW method as implemented in the WIEN2K package.34 The 1$s$ and 2$s$ electrons were treated fully relativistically as core
TABLE II. Agreement factors $R_{\text{w}}(F) = \frac{\sum |F_{\text{calc}} - F_{\text{obs}}|}{\sum F_{\text{obs}}}$ and $R_{\text{r}}(F) = \frac{\sum w|F_{\text{calc}} - F_{\text{obs}}|}{\sum w F_{\text{obs}}}$ for various density functionals with the ED data. The symbols refer to Fig. 6.

<table>
<thead>
<tr>
<th>Method</th>
<th>$R_{\text{w}}(F)$</th>
<th>$R_{\text{r}}(F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>0.4870.146</td>
<td>0.1670.041</td>
</tr>
<tr>
<td>PBE</td>
<td>0.3670.132</td>
<td>0.2580.023</td>
</tr>
<tr>
<td>EV</td>
<td>0.2770.026</td>
<td>0.3770.033</td>
</tr>
<tr>
<td>LE-SIC</td>
<td>0.8980.414</td>
<td>4.8170.056</td>
</tr>
<tr>
<td>EV</td>
<td>0.8980.414</td>
<td>4.8470.058</td>
</tr>
</tbody>
</table>

A. Valence densities

Figure 6 shows the differences between the calculated structure factors and the ones measured by ED. The estimated standard deviations of the experimental values are also shown in the plot. Table II gives the overall agreement factors, which shows that there is a small improvement when going from LDA to PBE to EV, in agreement with the findings of Zuo.10

The results of applying a SIC to the core states are also shown in Fig. 6 and Table II. When applying the PZ-SIC15 only a small improvement is achieved over the LDA results. On the other side a large improvement is gained by applying the LE-SIC, which indicates that it provides a better density. This conclusion agrees perfectly with that of Novák et al.13 with the added advantage that structure factors sample the whole electron density, not just the spin density in the small Thompson sphere around the nucleus as the hyperfine fields. Considering the conceptual attractiveness of the LE-SIC scheme17 the agreement is quite satisfying. It is somewhat surprising that the application of SIC to the core states gives a smaller improvement when using GGA. This is probably because the GGA functionals are parametrized to confirm to certain exact relationships1 or by optimizing the virial relationship.43 When an SIC is applied to the core orbitals, these parameters can no longer be expected to hold.

Calculations where the SIC was only applied to the 1s core state were also performed. Only small differences were found for the low-order structure factors. This could be expected because the 1s contribution to the Mg scattering factor is very flat in this region, Fig. 1.

B. Core densities

The improvement of the $R$ factor by applying the SIC to the core states suggests that the main discrepancies between the densities calculated with the standard DFT functionals and experiment are due to poor descriptions of the core densities. This is not surprising, since an inadequate treatment of self-interaction is mainly expected to be important for the core orbitals. It is noted that the LDA is exact for a free-electron gas which should be a good approximation of the valence electrons in Mg.

The low-order reflections analyzed in the previous section contain information about both the core, the semicore, and the valence density. The x-ray structure factors form a complete set out to 1.6 Å−1, and as the high-order reflections are not influenced by extinction they give an excellent possibility for comparisons based only on contributions from the core density. By comparing the calculated electron density from the 2sp shell of a free-atom calculation with the calculated density in the crystal, we find a small relaxation of this semicore state which extends out to approximately 1.2 Å−1 in reciprocal space. As we also wish to compare with the Dirac–Fock atomic calculations of Su and Coppens39 where this could be masked as thermal motion, we will only use reflections with $|\theta\beta|>1.2$ Å−1.

Table III shows that when the ADPs are refined, the $R$ factor is the same for all core densities, while the ADPs vary. The EV and LDA LE-SIC functionals give thermal parameters that agree best with the ones obtained from the Dirac–Fock scattering factors.39 Based on the fact that a Fock solution is explicitly self-interaction-free, we can assume that the Dirac–Fock method gives a good core density. Therefore, these results show that the LE-SIC and EV potentials give the best core densities. The poor agreement between EV and

TABLE III. Agreement factors for various density functionals with the high-order, $|\theta\beta|>1.2$ Å−1, x-ray data.

<table>
<thead>
<tr>
<th>Method</th>
<th>$R_{\text{w}}(F)$ (%)</th>
<th>$\langle u^2_1 \rangle$ (10−3 Å−2)</th>
<th>$\langle u^2_2 \rangle$ (10−3 Å−2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirac–Fock (Ref. 39</td>
<td>0.89</td>
<td>4.85(7)</td>
<td>5.07(7)</td>
</tr>
<tr>
<td>LDA</td>
<td>0.89</td>
<td>4.78(7)</td>
<td>5.03(7)</td>
</tr>
<tr>
<td>PBE</td>
<td>0.89</td>
<td>4.81(6)</td>
<td>5.06(6)</td>
</tr>
<tr>
<td>EV</td>
<td>0.89</td>
<td>4.85(6)</td>
<td>5.09(6)</td>
</tr>
<tr>
<td>LDA LE-SIC</td>
<td>0.89</td>
<td>4.84(6)</td>
<td>5.08(7)</td>
</tr>
</tbody>
</table>
IV. THE ELECTRON DENSITY IN HCP METALS

Figure 7 shows the deformation density calculated with the LE-LDA functional in the (001) plane of Be and Mg. The Be plot shows a good agreement both in features and magnitude with the experimental deformation maps derived from high accuracy x-ray structure factors. A main difference between the Be and the Mg maps is that Mg shows no depletion of charge in the octahedral holes. The Mg map is conspicuously more flat, in agreement with the expectation that Mg is closer to a free-electron metal.

The present results have shown that the measured CBED structure factors can be used to quantitatively discriminate between different DFT functionals which can be used for the discussion of the presence of NNM in these simple metals. Using the same kind of argumentation, it was earlier found that the application of the PBE favored the existence of NNM and, compared to the LDA, improved the agreement between calculated and experimental structure factors for Be. It was therefore argued that it was very likely that an NNM would also be found if the unknown exact functional could be applied. In the present study (Table II) we have shown that the calculated charge density can be further improved by applying the LDA LE-SIC functional. If we apply the LDA LE-SIC functional to Be and Mg, an NNM ((3,−3) critical point) is found for Be (Table IV) but not for Mg (Table V), in agreement with the earlier findings. The NNM for Be is extremely small (Table IV) and of the same magnitude as the uncertainty of the electron density derived from experimental structure factors. The procedure applied in the present study can be viewed as applying a model that is very flexible, but at the same time constrained to the physical constraint of self-consistency within a systematically constructed functional. We therefore argue that the present study is the closest yet to experimental evidence for the existence of NNM in Be.

Figure 8 illustrates the variation of the total density between atomic positions in the Be and Mg hcp structures. It shows how the core density of Mg is more extended than the very contracted (unscreened) core density of Be, which means the existence of NNM is most probable for the elements belonging to the second period.

V. CONCLUSION

It has been shown that sufficient accurate low-order structure factors can be measured by CBED to experimentally test DFT functionals. The core densities can be tested against high-order x-ray data that are not affected by extinction. It was found that the agreement with experiment increases when going from the LDA to the PBE to the EV. The improvement of the EV comes mainly from a better description of the core states. Applying the PZ-SIC to the core states for LDA did not improve the agreement with theory, while applying the LE-SIC of Lundin and Eriksson resulted in a significantly improved agreement. The LDA LE-SIC functional also agreed well with the x-ray data at scattering angles larger than 1.2 Å⁻¹. Using this functional an NNM in the electron density was found for Be but not for Mg.

ACKNOWLEDGMENTS

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References

Paper 5

A Study of Charge Density in Copper
A Study of Charge Density in Copper

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Quantitative convergent beam electron diffraction (QCBED) experiments allow absolute scale measurements of low order structure factors with very high accuracy. In this paper, eight low order structure factors for copper measured by QCBED have been combined with the higher order γ-ray structure factors in order to obtain a larger high-accurate experimental data set. The γ-ray values were relativistically corrected and rescaled. The new data set was then used for studying the charge distribution in copper. Charge deformation maps have been produced and both a maximum entropy and a multipole analysis have been applied to the data. The result is compared to density functional theory calculations. We find an almost spherical charge depletion around the atomic sites showing typical metal bonding in copper.

1. Introduction

Recently, very accurate measurements of low order structure factors in copper have been performed (Friis et al., 2003). In this work we have enhanced the accuracy of the measurements somewhat further. The new data set is then combined with the corrected (Petrillo et al., 1998) γ-ray measurements of Schneider et al. (1981), and used for a more detailed study of the charge distribution in copper.

The deformation density, defined as the difference between the observed density and the procrystal density, where independent atoms are placed at the atomic sites, describes the redistribution of electronic charge due to bonding. Since this charge redistribution mainly occurs in the valence region where the charge density varies slowly, the bonding effect is mainly seen in the differences between the lowest order observed and independent atom model (IAM) structure factors. Since these differences are very small (around or less than 1%), very accurate measurements are required. Such an accuracy is difficult to obtain for the strong low order reflections using ordinary X-ray diffraction, due to extinction and the contribution of anomalous scattering. A way to overcome this problem is to combine different techniques.

Copper has for a long time been used as a test case for theoretical models of elements containing the complicated d electron bands. It is non-magnetic, and is relatively uncomplicated by relativistic effects because of its small mass. It is therefore not surprising that there has been many experimental measurements of the structure factors.

By using γ-ray diffractometry, Schneider et al. (1981) could reduce the anomalous scattering and extinction effects in copper, compared to earlier powder and single crystal X-ray experiments (Batterman et al., 1961; Jennings et al., 1964; Hosoya & Yamagishi, 1966; Temkin et al., 1972; Freud, 1973). However, the available scattering angles were at the same time reduced.

Since it is difficult to obtain large perfect crystals of copper, required for traditional X-ray Pendellösung experiments, Takama & Sato (1982) measured a few low order structure factors using a white beam X-ray Pendellösung method. Although not as accurate as the ordinary Pendellösung method, this technique does not require so large single crystals. More recently, accurate structure factors have been measured by electron diffraction techniques. A big advantage of these methods is that they are performed in a transmission electron microscope (TEM), making it possible to select a perfect single crystalline region for the experiment. However, the accuracy of these techniques is reduced for higher order structure factors. Smart & Humphreys (1980) and Fox & Fisher (1988, in Tabbernor et al., 1990) used the critical-voltage method, which is capable of measuring the ratio between structure factors as accurate as 0.1%. A limitation is that this method relies upon the accuracy of the reference used. The intersecting Kikuchi-line method, proposed by Gjønnes & Höier (1971), uses the sensitivity of the separation between high order Kikuchi-lines to certain structure factors. This method was combined with convergent beam electron diffraction (CBED) by Matsuhata et al. (1984) for measuring the (111) and (020) reflections of copper. However, the most accurate experiments on copper so far are probably the quantitative CBED (QCBED) measurements by Saunders et al. (1999) and Friis et al. (2003). The strong multiple scattering of the electrons is here fully taken into account by using dynamical theory, which at the same time eliminates extinction and scaling problems. More detailed overviews of the above experiments on copper can be found in Tabbernor et al. (1990), Mackenzie & Mathieson (1992) and Friis et al. (2003).

The γ-ray experiment by Schneider et al. (1981) is probably the most referred structure factor measurement for copper. The reasons for this is probably the good internal consistency of the data and that the data set is comparably large; 19
structure factors were measured up to $\sin \theta/\lambda = 1.6 \, \text{Å}^{-1}$ at 50 K and room temperature (Schneider, 1976). However, compared to other experiments these structure factors are somewhat low. The absolute scale and even the extinction correction of the $\gamma$-ray data has therefore been questioned and several different corrections have been proposed. By applying an improved extinction correction scheme to the (220) structure factor, Mackenzie & Mathieson (1984) obtained a value closer to that of other experiments. On the other hand Tabbernor et al. (1990) pointed out that good agreement also can be achieved by rescaling the data set to fit the (111) reflection of Fox & Fisher (1988). The idea that the discrepancy is due to problems with absolute scale, and not to the extinction correction, is also approved by Schneider (Tabbernor et al., 1990). In a new analysis of Schneider et al.’s (1981) data, Petrillo et al. (1998) chose a slightly smaller Debye-Waller factor for Cu at 50 K. More important, Petrillo et al. (1998) applied a kinematic correction (in the order of the experimental errors), which importance first was realized by Dewey et al. (1994). This correction is due to the relativistic energies of the $\gamma$-rays and can be interpreted as a relativistic change of the electron mass. Finally a correction (in the order of the experimental errors), which impor-

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3. Combination with $\gamma$-ray data

In order to reduce truncation errors due to the limited set of measured structure factors in the study of charge density, the QCBED data have been combined with the $\gamma$-ray measurements of Schneider et al. (1981). However, three corrections have been applied to the $\gamma$-ray data (in the given order) before combining them with the QCBED data:

(i) Subtraction of the relativistic correction $\Delta$, calculated by Petrillo et al. (1998), from the $\gamma$-ray values.
(ii) As suggested by Petrillo et al. (1998), we use the value $B = 0.153 \, \text{Å}^2$ from Svensson et al. (1969) as the 50 K Debye-Waller factor for copper, which is almost identical to the value obtained from a Wilson plot of the relativistically corrected data ($B = 0.152 \, \text{Å}^2$, Fig. 2). This should be compared to the Debye-Waller factor of $B = 0.167 \, \text{Å}^2$ obtained from a Wilson-plot of the original data (Schneider et al., 1981).
(iii) Rescaling of the data with a scaling factor $k = 1.0084$, defined from

$$
\left| F^0_\text{obs} \right| = \left| F^0_\text{exp} \right| \exp(-B s^2) \left| F^0 \right|
$$

in order to obtain a best fit to the QCBED data. Here $s = \sin \theta/\lambda$ is the scattering angle and $F^0$ are static lattice structure factors obtained from DFT calculations (using the WIEN2k program, Blaha et al., 2001).

These corrections are all of the order of the standard deviations and are largest for the low order reflections. We have applied the same small increase of the standard deviations, due to the uncertainties introduced by the corrections, as used by Petrillo et al. (1998). The corrected and combined data sets are shown in Table 1, respectively labeled as “corrected” and “combined”.

The new data set is plotted with error bars in Fig. 3 relative to values obtained from the IAM. Except for a few outliers, (600), (800) and (10,0,0), we see no significant difference between the combined and the IAM data sets for scattering angles $\theta/\lambda > 0.5 \, \text{Å}^{-1}$.

4. Charge deformation density of copper

The kinematic non-forbidden structure factors for Cu take the form

$$
F(s) = 4f(s) \exp(-Bs^2)
$$
where $f$ is the atomic scattering factor (or form factor). For the IAM, several good parameterizations of the scattering factors exist (Macchi & Coppens, 2001; Peng, 1998; Su & Coppens, 1997). The most famous and widely used is probably the relativistic Hartree-Fock scattering factors of Doyle & Turner (1968), which are used for the IAM in this paper. A commonly used quantity for recognition of bonding features is the deformation density

$$
\Delta \rho(r) = \frac{1}{V} \sum_h \left( F_h^{\text{obs}} - F_h^{\text{IAM}} \right) \exp(-2\pi i \cdot r \cdot h)
$$

(3)
defined as the difference between the crystal and the IAM densities. $V$ is the unit cell volume. The deformation density shows charge accumulation in bonding regions, but quantitative applications cannot be drawn too long, since the deformation density depends on the definition of the reference density and is thermally averaged. Another practical limitation of deformation densities calculated from a set of measured structure factors is the errors due to series truncation. As shown in Fig. 5, these errors are mainly concentrated to high-symmetric regions. For copper it is common to plot the charge density in the (110)-plane since this plane contains both nearest, second nearest and third nearest neighbors. Fig. 4 shows the deformation density calculated from the 12 lowest order structure factors (sin $\theta$/$\lambda$ $\leq$ 0.79 $\text{Å}^{-1}$) in the combined data set. The standard deviations of the deformation density, shown in Fig. 5, were calculated according to the formalism of Rees (1976) and Rees & Mitschler (1976). The strong dependency of the number of surrounding symmetry equivalent points, with maximum at high-symmetric regions, is an effect of truncation errors.

The deformation density in Fig. 4 shows, as expected from metallic bonded crystals, charge depletion at the atomic sites and a build up of charge in the interstitial regions. A maximum of 0.19 e$\text{Å}^{-3}$ is seen at the interstitial octahedral sites. However, this maximum is not significant due to the large standard deviations, $\sigma(\Delta \rho) = 0.26$ e$\text{Å}^{-3}$ at the octahedral sites.

In the following two sections more sophisticated methods are used in order to deal with the truncation and other errors due to the incompleteness of the data.

5. Maximum entropy fitting of direct-space charge density

The maximum-entropy method (MEM) is a method based on information theory to enhance information from limited or poor data. Applications in crystallography have been reviewed by Gilmore (1996). It has often been used to calculate the charge density distribution from a limited set of structure factors (Collins, 1982; Sakata & Sato, 1990; Papoular et al., 1996). The basic idea is to find the charge distribution which maximizes the entropy, under the constraint that structure factors calculated from this distribution must match the measured structure factors.

But, as pointed out by Jauch & Palmer (1993) and Jauch (1994), the traditional maximum entropy algorithm is limited when fine details, such as bonding deformation, are to be studied, and the charge density to be reconstructed has a large dynamic range. However, if one uses the deformation density $\Delta \rho(r)$ as the key quantity when maximizing the entropy, the dynamic range is substantially reduced and the small bonding features become more pronounced. Since MEM relates the charge density directly to probabilities, the use of the deformation density, which takes both positive and negative values, requires a two channel method. This method has successfully been used for magnetization densities (Papoular & Gillon, 1990), in neutron diffraction involving scattering lengths of opposite signs (Sakata et al., 1993) and deformation densities (Papoular et al., 1996).

In the two channel method the deformation density is split into two quantities, a positive $\rho^+(r)$ and a negative $\rho^-(r)$ part, such that $\Delta \rho(r) = \rho(r) - \rho^{\text{IAM}}(r) = \rho^+(r) - \rho^-(r)$. The unit cell is divided into $M$ pixels, each of size $V/M$ centered at $r_j$ and with densities $\rho_j^+ = \rho^+(r_j)$ and $\rho_j^- = \rho^-(r_j)$. The entropy functional, to be maximized, is given by

$$
S[\Delta \rho] = - \sum_{j=1}^{M} \left( \rho_j^+ \ln \rho_j^+ + \rho_j^- \ln \rho_j^- \right),
$$

(4)

where $p_j^+ = \rho_j^+ / Q^+$, with $Q^+ = \sum \rho_j^+$, are the corresponding probabilities for the positive and negative parts of the deformation density associated with pixel $j$. The maximization of $S[\Delta \rho]$ is performed under the constraint that the difference between the structure factors calculated from the MEM charge density and the IAM structure factors

$$
\Delta F_h^{\text{calc}} = \frac{V}{M} \sum_{j=1}^{M} \left( Q^+ \rho_j^+ - Q^- \rho_j^- \right) \exp(2\pi i h \cdot r).
$$

(5)

agrees with the difference between the observed structure factors and IAM structure factors $\Delta F_h^{\text{obs}}$ within the standard deviation $\sigma_h$. This condition is expressed as

$$
\chi^2 = \frac{1}{N} \sum_h \left( |\Delta F_h^{\text{obs}} - \Delta F_h^{\text{calc}}| \right)^2 / \sigma_h \lesssim 1.
$$

(6)

The problem is solved by maximizing the Lagrange functional $L[\rho] = S[\Delta \rho] - \lambda \chi^2$, where $\lambda$ is the a Lagrange multiplier. At convergence $\nabla \rho L = 0$, resulting in the normalized densities

$$
p_j^\pm = m_j^\pm \exp \left( \pm \lambda \frac{\partial \chi^2}{\partial p_j^\pm} \right),
$$

(7)

where $m_j^\pm$ are prior density distributions. The deformation density is obtained by solving Eq. (5), (6) and (7) iteratively for both $p_j^\pm$ and $\lambda$, starting from a flat deformation density and $\lambda \gtrsim 0$.

It has been argued that a problem with two-channel MEM applied to the deformation density, is that $Q^+$ and $Q^-$ are unknown. However, since the total amount of charge is conserved in the formation of the deformation density, we must have $Q^+ = Q^- = Q$. It is then easy to show that, by introducing a scaled Lagrange multiplier $\Lambda = \lambda Q$, one can move all dependence of $Q$ into this Lagrange multiplier. Hence, the value one choose for $Q$ doesn’t matter, since the Lagrange multiplier


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6. Multipole analysis

In multipole analysis the atomic charge density is expanded in terms of a series of multipolar functions centered at the nucleus. The multipole populations and radial expansion parameters, are determined from least square fitting to the measured structure factors. This method has the advantage that it provides an analytical expression for the charge density, allowing for easy calculation of physical properties based on the charge distribution. Another interesting feature is that the multipole populations can be related to orbital occupancies.

In the valence-density formalism of Hansen & Coppens (1978) the atomic electron density

\[
\rho_{\text{atom}}(r) = P_c \rho_{\text{core}}(r) + P_v \rho_{\text{valence}}(kr) + \sum_{l=0}^{\infty} \kappa^l R_l(kr) \sum_{m=-l}^{l} P_{lm} d_{lm}(\theta, \phi). \tag{8}
\]

described by three parts; a spherically core part populated with \( P_c \) electrons, a spherically valence part which is allowed to expand (\( \kappa < 1 \)) or contract (\( \kappa > 1 \)) with population \( P_v \) and a series of multipolar functions accounting for an aspherical redistribution of the electron density, each populated with \( P_{lm} \) multiplets. The multipolar functions are characterized by the radial functions \( R_l(kr) \) and the density functions \( d_{lm}(\theta, \phi) \), that are density-normalized real spherical harmonics (Coppens, 1997, Chap. 3). Because of the strong symmetry imposed by the cubic atom site symmetry of copper, all terms in the multipole expansion up to \( l_{\text{max}} = 3 \), except for the monopole will vanish (Kurki-Suonio, 1977). For the hexadecapoles (\( l = 4 \)) only one independent cubic population parameter \( P_{4\text{hex}} \) will remain.

In Jiang et al. (2003) a multipole analysis for the combined data set was performed. Assuming that the 3d radial wave function has a tail that does not contribute significantly to the measured reflections; a model that reproduces very well the observed structure factors could be obtained. This deformation of the 3d orbital was simulated by writing the 3d orbital as

\[
3d_{\text{deformed}} = 3d^{10-4s^n} \text{ with } n = 1.27, \text{ where } 3d \text{ and } 4s \text{ here refers to Clementi & Roetti’s (1974) Slater-type radial functions.}
\]

This model results in a negligible aspherical contribution to the charge density in copper (\( P_{\text{hex}} = -0.0001 \)), which is also seen from the spherical charge depletion around the atomic sites in the deformation density (Fig. 7). The fact that spherical model seems to give a very good description of copper, also validates our special construction of the \( 3d_{\text{deformed}} \) radial function. More details are given in Jiang et al. (2003).

7. Discussion and conclusions

For comparison, several sets of low order scattering factors for copper are listed in Table 1. The theoretically calculated values are the IAM scattering factors by Doyle & Turner (1968), the self-consistent band structure calculation by Bagayoko et al. (1980) and a full-potential DFT calculation using the generalized gradient approximation (GGA) performed with the WIEN2k program package (Blaha et al., 2001). Experimental values are the \( \gamma \)-ray diffractometry measurements by Schneid et al. (1981), the QCBED experiment by Saunders et al. (1999) and the QCBED experiment presented here. The two last rows show the scattering factors obtained by applying MEM and multipolar analysis to the combined data set. The difference between the scattering factors and the IAM values are plotted in Fig. 3. The difference between the DFT, MEM, observed and multipole scattering factors and the IAM values are also plotted in Fig. 3.

First of all, the R-factors show that the agreement between \( \gamma \)-ray measurements and our experiments increases a lot by the corrections. Compared to the old calculation by Bagayoko et al. (1980) the DFT calculation shows a significant improvement in the R-factor for our experiment. However, the agreement for the DFT calculation is worse, when the higher order corrected \( \gamma \)-ray data is also taken into account. Since the GGA method is usually more accurate for higher orders, this might imply that there are still some problems with the \( \gamma \)-ray data, despite the corrections.

In Jiang et al. (2003) it is seen from the DFT calculations that the scattering from the valence 3d and 4s orbitals is very small at \( \sin \theta/\lambda = 0.8 \text{ Å}^{-1} \) and almost vanish for scattering angles larger than 1 Å\(^{-1}\). One would therefore expect the true scattering factors to be very close to the IAM values for \( \sin \theta/\lambda > 1.0 \text{ Å}^{-1} \). This is the case for the DFT calculations and the multipole model, but not for the (600), (800) and (10,0,0) corrected \( \gamma \)-ray scattering factors.

It is clear from Fig. 3 that our multipole model fits the observed scattering factors very well. The only exceptions are the (600), (800) and (10,0,0) reflections, for which it gives the scattering factors expected from DFT. In fact, the agreement between DFT and the multipole model is excellent, and justifies our construction of the 3d multipolar orbital. The charge deformation density from the DFT calculation is shown in Fig. 8. It is very close to the multipolar deformation density in Fig. 7. Both these maps show a spherical charge depletion at the atomic
sites, typical for metallic bonding, but also a small charge surplus between the nearest neighbors.

The maximum entropy method tends to move the structure factors toward the IAM-values (Fig. 3), that are the structure factors maximizing the entropy for the two-channel method used in this work. This does not seems to provide much physical insight. However, MEM can be seen as a statistical method to reduce the problems with incomplete data sets and truncation errors in deformation density maps obtained by Fourier synthesis. And indeed, the MEM deformation density map (Fig. 6) shows similar features to those from DFT (Fig. 8), but the radius of the spherical charge depletion around the nucleus is too small.

In summary DFT and the multipole model seem to provide a very good description of copper, which shows typical metallic bonding.

We thank prof. J.C.H. Spence (Arizona State University) and prof. J.M. Zuo (University of Illinois) for helpful discussions. Funding from the Research Council of Norway (NFR), project 135270/410 is gratefully acknowledged. B. Jiang is funded by DOE DE-FG03-02ER45596.

References
### Table 1

Theoretical and experimental static lattice scattering factors for Cu. The row labeled “combined” is the same as this experiment, but with the missing values replaced by the corrected $\gamma$-ray data. The agreement factors $R_{\text{this exp.}}$ and $R_{\text{combined}}$ are given by $R = \left( \sum |F - F^{\text{ref}}| \right) / \sum F^{\text{ref}}$ and shows the agreement with the this experiment and the combined data, respectively.

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**R**this exp. (%) = 0.69 0.31 0.15 1.09 0.24 — 0.27 0.10 0.64 0.30 0.30 0.96 0.14 0.24 — 0.38 0.27

**R**combined (%) = 0.69 0.31 0.15 1.09 0.24 — 0.27 0.10

---

**Figure 1**

(a) CBED pattern of the (220) systematic row in copper. The selected rocking curves are shown with white lines. (b) Best fit from Bloch-wave refinement of the selected rocking curves. The points are measured intensities while the solid line is calculated intensities. The discrepancy for each pixel between theory and experiment is also shown with dots.

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$^a$ Calculated from Doyle & Turner (1968).

$^b$ Calculated with the WIEN2k program of Blaha et al. (2001).

$^c$ Kinematic correction of the $\gamma$-ray structure factors from Petrillo et al. (1998).

$^d$ Estimated standard deviations are from Petrillo et al. (1998).

$^e$ Estimated by interpolation.
Figure 2
Wilson plot of the $\Delta$-corrected $\gamma$-ray data at 50 K. The theoretical structure factors are taken from DFT calculations. The Debye-Waller factor $B$, scaling factor $k$ and correlation coefficient $R$ are shown for the best fit (dashed line), the used values (solid line) and Schneider et al. (1981) original values (dotted line), respectively. When only considering the nine highest orders $B$ becomes 0.154 Å$^2$ for the best fit.

Figure 3
The difference between static lattice scattering factors and Doyle & Turner (1968) independent atom values versus scattering angle. Units in e/atom. The solid line is for the multipole analysis.

Figure 4
Electron deformation density calculated from the combined data set for $\sin \theta/\lambda \leq 0.79$ Å$^{-1}$. Zero is marked with a thick black contour line. Negative contours (white) are drawn with intervals of 0.1 eÅ$^{-3}$ and positive contours (thin black) are drawn with intervals of 0.05 eÅ$^{-3}$.

Figure 5
Standard deviation in the deformation density calculated from the combined data set, $\sin \theta/\lambda \leq 0.79$ Å$^{-1}$. Contour intervals are 0.05 eÅ$^{-3}$.

Figure 6
The deformation density from a two-channel MEM simulation. Zero level is marked with a thick black contour. Negative contours are at intervals of 0.05 eÅ$^{-3}$ and positive at intervals of 0.02 eÅ$^{-3}$. 
Figure 7
The deformation density of the (110) plane from multipole analysis. Note the small contour intervals of 0.002 e\(\text{Å}^{-3}\). The difference density is 0.081 e\(\text{Å}^{-3}\) at the small local minimum in the octahedral sites, while it is close to 0.090 e\(\text{Å}^{-3}\) in the rest of the interstitial region.

Figure 8
The deformation density of the (110) plane calculated from density functional theory. Negative contours (white) are at intervals of 0.1 e\(\text{Å}^{-3}\) and positive contours (fine black) are at intervals 0.01 e\(\text{Å}^{-3}\).

Synopsis

A study of charge density in copper from combination of QCBED and \(\gamma\)-ray diffractometry structure factors.
Paper 6

Electron Density and
Implication for Bonding in Cu
and Ag
Electron Density and Implication for Bonding in Cu and Ag

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ABSTRACT

We report highly accurate measurements for the low-order Fourier components of the electron density in copper. These were obtained by transmission electron diffraction using a small probe and multiple scattering analysis. They were used to refine the Cu 3d radial wave function. An accurate charge-deformation map and a 3d orbital radial wave function were obtained by using a multipole refinement of the structure factors obtained from combined quantitative electron diffraction and x-ray diffraction measurements. The results show a large change in the 3d orbital radial function from d-band formation and d-s band crossing (d-s hybridization). Band theory calculations are in excellent agreement with the measurements and show that the charge deformation in Ag is very similar to that in Cu. Our findings are in general agreement with the monovalent description of these metals.
I Introduction

The measurement of valence electron radial wave functions and charge densities has long been recognized as a challenging problem. It requires highly accurate Fourier components of charge density and a sound multipole refinement model. The Fourier components of charge density are equal to the X-ray structure factors, whose amplitude, in principle, can be obtained experimentally by measuring the diffraction intensities. In simple inorganic materials like copper, it is difficult to obtain the crucial low-order structure factors by kinematic photon (X-ray or γ-ray) diffraction with sufficient accuracy for charge density analysis due to uncertainties in extinction corrections and other factors. Electron diffraction, on the other hand, is inherently more sensitive for small scattering vectors and is free from extinction effects, so that low order structure factors can be obtained with much higher accuracy. Using a combination of electron (for low order) and X-ray (for higher order) diffraction data, detailed information about the valence electron distributions has recently been obtained in simple inorganic crystals such as Cu, Mg, MgO, TiO₂, Cu₂O.

First-principles electronic structure calculations provide an excellent account of properties such as cohesive energy, interatomic distances and elastic properties for metals like copper, but there is no unambiguous (and hence meaningful) direct way to project out orbital occupancies and wave function from plane-wave calculations. In contrast the analysis of experimental electron densities in crystals is very often made using a pseudoatom (multipole) fitting which approximates crystal charge density based on single-electron orbital radial wave functions and occupancies. This simple model has
been found experimentally sufficient flexible to describe charge density in a variety of crystals.

Here we present our recent results on Cu and Ag, using experimental electron diffraction, band theory calculations, and multipole analysis. We find that a large change in the $d$-orbital radial wave function is required in the multipole model to account for the differences in X-ray structure factors of crystals and that obtained by superimposing spherical atoms. Brewer’s hypothesis $^9$, that the binding energy per electron is approximately constant for metals, is also discussed.

II Method

In the multipole model, the atomic charge density in a crystal is expanded into three parts; the spherical inner-shell electrons (core electrons), spherical valence shells (monopoles), and a series of nucleus-centered local symmetry-adapted spherical harmonic functions which reflect the small but important non-spherical valence charge distribution (higher order multipoles). The X-ray structure factors are fitted by adjusting the refinement parameters (monopoles and multipoles). Following Hansen and Coppens $^{10}$, the charge of a pseudoatom is described as:

$$r_{\text{pseudoatom}}(r) = r_{\text{core}}(r) + P_{v} * k^{2} * r_{\text{valence}}(k^{r}) + \sum_{l} a_{l}^{s} R_{l}(a_{l}, r) \sum_{m=0}^{l} P_{lm} d_{lm}^{s} (q, f)$$ (1)

The first and second terms represent the spherical atomic core, which is well-described by atomic modelling and is fixed in our multipole refinement, and the spherical (monopole) valence charge density, respectively. The third term is a summation over the
multipoles. It should be noted that first two terms are real charge densities, while the third term only redistributes valence density non-spherically in real space. The volume integration of this term is zero. Slater type orbitals (STO) calculated by Su et al.\textsuperscript{11} were used for the density functions of the core, $r_{\text{core}}(r)$, and valence electron monopole, $r_{\text{valence}}(kr)$. The valence shell can be further divided into two monopoles to simulate the charge transfer between different orbitals on the same atom site (orbital hybridization effect) or orbital deformation effect. The multipole radial functions, $R_l(\alpha r)$, are calculated using single exponential functions, or an atomic orbital product. The refined parameters are the valence electron population, $P_v$, and its radial function scaling factor, $k$, and the multipole populations, $P_{lm\alpha}$, and their radial function scaling factors, $a_l$. In the copper refinement, the radial function of the hexadecapole is constructed from a $3d^*3d$ orbital wave function. In this case, the radial scaling factor $k$ will be refined. This simple model can produce meaningful information on bonding, as demonstrated in several cases, such as TiO\textsubscript{2}, MgO, Cu\textsubscript{2}O and Si\textsuperscript{4-6,12}.

Accurate measurements of the low-order structure factors were made using the quantitative convergent-beam electron diffraction technique (QCBED) that we have developed recently.\textsuperscript{13} The experiment was performed using a LEO-912 in-column energy-filtering transmission electron microscope (TEM) with a Gatan liquid nitrogen cooled sample holder. The TEM specimen used is a Cu foil sample prepared by electrolytic polishing and cooled down to 105 K to reduce phonon scattering. The electron illumination heating effect is considered and refined to be about 5 K.\textsuperscript{2} A 10 eV energy-filtering slit was placed around the zero-loss peak to remove the contribution from inelastically scattered electrons, which form a background due to plasmon and other loss

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processes. Off-zone-axis systematic diffraction patterns were collected for seven low
order reflections and recorded on a Gatan CCD camera. The “Extal” software package \(^{13}\)
was used for CBED refinement – this takes full account of multiple scattering and
“absorption” in Bloch-wave formalism. The small electron probe size (about 10nm
diameter) ensures that the data are collected within a single mosaic block.

Band theory calculations were performed using the augmented plane wave plus
local orbital method (APW+lo) \(^{14}\), as implemented in the program Wien2K \(^{15}\). Exchange
and correlation effects are treated within density functional theory, using the generalized
gradient approximation (GGA) \(^{16}\). A muffin tin radius of 2.3 au is used for Cu and Ag.

III Results and Discussion.

We have measured seven low order structure factors for copper using QCBED.
These are reported in table 1. Also reported in the table are the results of band theory
calculation and multipole models. It is seen that theory and experiment are in excellent
agreement. This is an important observation as the experimental results come with (small)
error bars and they thus serve to provide limits to the possible error of the theory.

The QCBED data were merged with X-ray diffraction results \(^{17}\) for higher orders
(where the electron diffraction is less accurate) and subject to multipole refinement using
the program VALRAY \(^{18}\). The refinement parameters are the electron populations in the
valence shell orbitals (monopoles), one cubic hexadecapole, with corresponding radial
scaling parameters \(^{11,19}\). It is seen from table 1 that there are significant differences
between the multipole fits and QCBED/theory for low orders. To understand the origin of
these differences, the scattering factors of Cu orbitals are plotted in figure 1. We see that
the 4s orbital affects reflections below \( s = 0.2 \) Å\(^{-1}\) \((s=sin\theta/\lambda\) is the scattering vector\), and
contributes to small negative values between \( s=0.2 \) and \( s=0.4 \), while the 3d orbital
contributes at higher scattering angles up to \( s=0.8 \). This analysis suggests that the
differences in the X-ray structure factors for (111) \((s=0.24 \) Å\(^{-1}\)\), (200), (220) and (310)
cannot be attributed to changes in the 4s orbital. A large deformation in the 3d orbital
radial wave function must be responsible for these differences. To find a suitable model
for multipole refinement, we see that for the low order reflections, the measured X-ray
structure factors are systematically lower than those for neutral atoms, indicating partial
delocalization of the 3d orbital. We suggest that the 3d orbital radial wave-function has a
tail that does not contribute significantly to the measured reflections, and we use
additional occupancy of the Cu 4s orbital to simulate this effect. Thus the 3d radial wave
function in copper is written as \( 3d_{\text{deformed}}=3d^{10}n4s^{n} \) \((n\) is a refinement parameter\) with
small changes in the radial scaling factors to simulate 3d radial wave-function
deformation effects.

This proved to be a good approximation, as shown by the multipole refinement
results given in table 1. The results are given for a \( 3d^{10}4s \) model \(\)only radial scale
parameters are refined\); for a \( 3d_{\text{deformed}}104s \) model \(\)refinement considering 3d orbital
deformation\), and an agreement index \( R\)-factor \(\)residual\), calculated from the seven
QCBED measurements alone. It is found that \( 3d_{\text{deformed}} \) constructed from the \( d \) orbital of
the \( d^{9} \) electron configuration \(\)3d orbital in Cu\(^{+2}\) ion\) produces a better fit in multipole
refinement, indicating that the localized 3d orbitals are more like 3d orbitals in Cu\(^{+2}\) ions,
due to the reduced screening effect of delocalized 3d electrons. For the \( 3d^{10}4s \) model, \( R = \)
0.64 % and the fit is outside the range of experimental error (note especially (111) and (200)). For the $3d_{\text{deform}}^{10}4s$ model, $R = 0.08$ % (ten times less) and all calculated values agree with experiment within experimental errors. The refined value of $n$ is 1.27(6) (in table 2).

The resulting valence charge density difference map shown in figure 2 shows a spherical charge deficiency region (0.9Å in radius) around the copper atom and a charge surplus region between atoms. The charge surplus in the interstitial region is about 0.05 e/Å$^3$, or a 25% increase in valence electron density. Note the small hexadecapole population, which indicates a very small nonspherical charge deformation (see Table 2). Charge redistribution due to this is less than $10^{-6}$ e/Å$^3$ between nearest-neighbor atoms, much smaller than the valence electron density, which is about 0.2 e/Å$^3$. Thus, the covalent contribution to bonding can be neglected. This finding agrees with the theoretical result of Ogata et al.\textsuperscript{7}, who concluded that Cu has a homogeneous charge distribution with little bond directionality.

There are two possible interpretations of the refined number $n$. Brewer\textsuperscript{9} has proposed that the electronic configuration in copper is $3d^{10-n}4s^14p^n$, with $n=1.5$. This hypothesis, with 3$d$ electrons being promoted into 4$p$ free-electron-like orbitals, is used to explain the strong cohesion in noble metals, such as Cu, Ag, Au, but has been questioned by several researchers\textsuperscript{20}. This first possible explanation of our refinement would assume $dsp$ hybridization, with 1.27 electrons ‘promoted’ from the 3$d$ to the 4$s$ orbital. However, owing to the $e_g$ and $t_{2g}$ energy splitting (about 1 eV), in that case the charge deformation density would be non-spherical, there would be high-intensity white lines in L$_3$-edge electron energy-loss spectra (EELS) and X-ray absorption spectra (XAS); and the 3$d$
orbital holes would be expected to give rise to magnetic properties similar to those of the earlier 3d metals. However experimental results show that EELS and XAS spectra have no white lines, copper is a weakly diamagnetic metal and our charge density refinement shows a spherical deformation density. The ratio of the $e_g$ and $t_{2g}$ orbital electron populations is $\frac{1,99994(14)}{3}$ calculated from multipole population, equal to $\frac{4}{6}$ within error, thus, none-spherical charge deformation is negligible, in strong contrast to the very non-spherical distribution found for the formal $d^{10}$ shell of Cu in $\text{Cu}_2\text{O}$. Further evidence in support of a monovalent model in copper comes from the free electron plasma oscillations. The number of free electrons per atom contributing to the plasmon is $1.04(4)$, where $m^*$ is the electron effective mass and $E_p$ is the plasmon energy, as calculated using the free electron model from the first plasmon energy using ($E_p = 9.3$ eV from measured optical properties and the free electron mass). This is in agreement with a monovalent description of Cu. An additional plasmon peak, however, also occurs at $E_p = 19.3$ eV, (not due to double scattering), and if we use the free-electron plasmon model we then obtain 3.4 electrons per atom contributing to the bulk plasmon from this second peak. These 3.4 electrons may however stem from the relatively delocalized 3d electrons. The two volume plasmon energies in copper thus reflect the different properties of free electrons, and those of delocalized 3d electrons.

The second interpretation possible is that the Cu 3d orbital has large deformation, and so becomes much more diffuse compared with the neutral-atom ground state 3d orbital. Multipole refinement quantitatively measures the 3d-band orbital radial wave function in Cu, which is shown in figure 3. It is constructed from the $3d^{10-n}4s^n$ electron.
configuration (with $k_{3d}=1.006$, $k_{4s}=1.1$, see table 2). We see that the 3$d$ orbital in Cu has a long tail, and electrons are delocalized. Experimental Slater orbital parameters were fitted and are given in table 3. This kind of deformation cannot be simulated by refining radial scaling factors alone in the multipole model. That is the reason for the failure of the ground state neutral-atom model. It has been proposed that 3$d$ band electrons contribute substantially to the cohesive energy of Cu by $d$-$s$ orbital hybridization\textsuperscript{24}. Thus of the total cohesive energy of 0.26 Ry, the calculated contribution from the 4$s$ band is 0.11 Ry and thus $d$-$s$ orbital hybridization contributes significantly to the cohesive energy of Cu (Note that renormalization energy is -0.4 Ry for Cu, therefore, $d$-$s$ orbital hybridization contributes 0.19 Ry )\textsuperscript{24}.

We have also completed a multipole refinement for silver, to measure the 4$d$ orbital deformation. Calculated X-ray structure factors were used and refined using similar refinement procedures. The results are listed in table 2. We conclude that charge deformation is again spherical (from the small multipole population) and the 4$d$ orbital in silver has a similar amount of deformation to the 3$d$ orbital in copper. The ratio of the $e_g$ and $t_{2g}$ orbital electron populations is, and again the charge deformation is very close to spherical. The Ag 4$d$ orbital radial wave function is shown in figure 3 and the Slater orbital parameters are given in table 3. The number of free electrons, from the plasmon energy ($E_p = 9.2$ eV) is 1.0\textsuperscript{23}. We conclude that Ag is a monovalent metal.

It is important to point out that the orbital radial wave functions are deduced from the charge density refinement based on an atomic model. It is well known however, that electrons form bands in crystals and so loose their individuality. Our refinement thus provides an example of how a one-electron model can nevertheless retains useful validity.
in the transition metals. We expect that this method can also be used in the transition metal compounds, where valence $d$ orbitals form $d$-bands.

IV Summary

Accurate low order X-ray structure factors have been measured for copper by quantitative convergent beam electron diffraction. Charge density deformation maps refined using a multipole model show a spherical charge deformation in copper and silver. Valence $d$ orbital radial wave functions obtained from multipole refinement, show a large deformation when compared with neutral atoms. Results support the monovalent metal model in Cu and Ag.

Funded by DOE DE-FG03-02ER45596 (JCHS P.I.). J. Friis funded by Research Council of Norway (NFR), project 135270/410. Thanks to Dr. P. Rez (ASU) and Dr. P. Blaha (Vienna Tech.) for helpful discussions.
Table 1. Measured (QCBED) and calculated structure factors for Cu. The column headed $3d^{10}4s$ is a multipole refinement with fixed orbital occupation; the column headed $3d_{\text{deformed}}^{10}4s$ ($3d_{\text{deformed}} = 3d^{10-n}4s^n$ with 3d orbital wave function from Cu$^{2+}$ and 4s from neutral atom, and gives the best refined value of $n=1.27$). The residual $R$ calculated for the seven structure factors listed shows the agreement of theory with QCBED experiment. The experimental structure factors are converted to their 0K static value.

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<td>222</td>
<td>0.481</td>
<td>56.96 (32)</td>
<td>56.89</td>
<td>56.80</td>
<td>56.58</td>
<td>56.84</td>
</tr>
<tr>
<td>400</td>
<td>0.555</td>
<td>49.80 (40)</td>
<td>49.93</td>
<td>49.68</td>
<td>49.49</td>
<td>49.82</td>
</tr>
<tr>
<td>440</td>
<td>0.785</td>
<td>35.41 (16)</td>
<td>35.44</td>
<td>35.27</td>
<td>35.17</td>
<td>35.40</td>
</tr>
<tr>
<td>$R$ (%)</td>
<td></td>
<td>0.15</td>
<td>0.71</td>
<td>0.64</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Multipole refinement results for Cu and Ag. Refinements use the ion core plus $d$ orbital from a $d^9$ configuration ($d$-orbital in Cu$^{+2}$ or Ag$^{+2}$ ion) and 4s or 5s orbitals from neutral atoms. Multipoles up to forth-order are chosen for refinement. The allowed multipoles are selected according to the index-picking rules of Kurki-Suonio. The $d$-orbital deformation is included in the refinement (by refining $n$). The 4s or 5s electron population ($P_s$) is fixed at one. The corresponding kappa for monopoles or multipole is refined. (Note, Dawson normalization is used for multipole populations, see VALRAY manual for details.)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cu</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_d = (10-n)$</td>
<td>8.73(6)</td>
<td>8.65(1)</td>
</tr>
<tr>
<td>$k_d = k_d$</td>
<td>1.006(5)</td>
<td>1.0083(7)</td>
</tr>
<tr>
<td>$k_d$</td>
<td>1.1(1)</td>
<td>1.15(1)</td>
</tr>
<tr>
<td>$P_{hex}$</td>
<td>-0.0001(2)</td>
<td>0.024(6)</td>
</tr>
<tr>
<td>$R$</td>
<td>0.06%</td>
<td>0.02%</td>
</tr>
</tbody>
</table>
Table 3  Slater orbital parameters of Cu 3d and Ag 4d radial wave functions.

Radial wave function $R_{nl}(r)$ is defined by

$$R_{nl}(r) = \tilde{\alpha} c_i \cdot c_i(r)$$

where,

$$c_i(r) = (2n_i!)^{-1/2} (2z_i)^{n_i + 1/2} r^{n_i - 1} e^{-z_i r}$$

See Clementi *et al*\textsuperscript{25} for details.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$n$</td>
<td>3 3 3 3 3 3</td>
</tr>
<tr>
<td></td>
<td>$c$</td>
<td>0.02947 0.15822 0.52916 0.33576 0.23600</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
<td>1.80063 9.01160 4.81777 2.37701 0.91309</td>
</tr>
<tr>
<td>Ag</td>
<td>$n$</td>
<td>3 3 3 3 3 3</td>
</tr>
<tr>
<td></td>
<td>$c$</td>
<td>0.00632 0.09693 0.30863 -0.45737 0.07110 -0.55814 -0.30714 -0.10501</td>
</tr>
<tr>
<td></td>
<td>$z$</td>
<td>34.01846 15.42014 7.71913 5.10149 13.67176 3.49371 1.70772 0.80052</td>
</tr>
</tbody>
</table>
Figure 1. Scattering factors of Cu $3d$ and $4s$ orbitals. The scattering angles of lowest order reflections are shown. Note the contribution to these reflections from $4s$ orbital is small.
Figure 2. Valence charge density deformation map on the (110) plane of copper. The map shows the difference between an experimental charge density and a neutral atom model as reference. The dashed lines are for contours with $\mathbf{D}_{\mathbf{r}} < 0$, the solid lines are for contours with $\mathbf{D}_{\mathbf{r}} > 0$, the increment between contours is $0.01\text{e}/\text{Å}^3$. 
Figure 3  Cu 3d and Ag 4d orbital radial wave functions. It is seen that valence d orbitals in the crystal spread outward, owing to d-band formation and d-s band hybridization. This kind of deformation can not be simulated by refining scaling parameters in the multipole model. (Note, the charge density peak of 4s or 5s orbitals at nuclear center is omitted to construct 3d or 4d orbitals to conform to the requirement that d orbital approach zero at nuclear center. It has negligible effect on scattering factor.)
References

Part III

Unpublished results
Chapter 1

QCBED measurements of SrTiO₃

1.1 Introduction

Strontium titanate (SrTiO₃) is a typical perovskite structure, with phase transitions from a cubic to a tetragonal structure at 110 K and from a tetragonal to an orthorhombic structure at 65 K (Table 1.1). A phase transition to a rhombohedral phase may also exist at 10 K. SrTiO₃ was intensively studied during the 1960s and 1970s because of the interesting phase-transitions (see e.g. Lytle, 1964; Devanarayanan & Narayanan, 1968; Shirane & Yamada, 1969; Golding, 1970; Blazey, 1971; Willemsen et al., 1976).

Neutron diffraction experiments of SrTiO₃ were performed by Hutton et al. (1981). The intention of their work was to test the extinction model of Becker & Coppens (1974), but they also provide very accurate anisotropic displacement parameters (ADPs). More recent, quantitative convergent beam electron diffraction (QCBED) experiments have been performed for accu-

Table 1.1: Phases in SrTiO₃ when the temperature is lowered from room temperature to 35 K (Lytle, 1964). α is the linear thermal expansion coefficient in the cubic phase.

<table>
<thead>
<tr>
<th>Temperature range (K)</th>
<th>Structure</th>
<th>Space group</th>
<th>Physical constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>300-110</td>
<td>Cubic</td>
<td>Pm3m</td>
<td>α = 9.4 × 10⁻⁶ K⁻¹</td>
</tr>
<tr>
<td>110-65</td>
<td>Tetragonal</td>
<td>I4/mcm</td>
<td>c/a = 1.00056</td>
</tr>
<tr>
<td>65-35</td>
<td>Orthorhombic</td>
<td></td>
<td>a : b : c = 0.9998 : 1 : 1.0002</td>
</tr>
</tbody>
</table>

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rate determination of lattice parameters and ADPs of the tetragonal low-temperature phase (Tsuda & Tanaka, 1995).

Since the material has got an important application as substrate for thin film high temperature superconductors, is simple with a small unit cell (around 4 Å), and is well characterized, SrTiO$_3$ seems to be a promising candidate for charge density studies by QCBED. Careful experiments of the cubic phase were performed by Bin Jiang at Arizona State University (ASU) and the experimental data were brought to Trondheim for structure factor refinements and further analysis. During our refinements, Zhurova & Tsirelson (2002) published their charge density studies, based on multipole analysis of X-ray measurements performed by Abramov et al. (1995). However, it seems possible to improve these X-ray results, by combining them with the present high-accurate low-order QCBED measurements.

### 1.2 Experiments

The experiments were performed with the Zeiss 912 electron microscope (operating at 120 kV) at ASU, equipped with an in-column Ω-filter and a 14 bit dynamic range 1k×1k CCD camera. With a liquid nitrogen sample holder, the temperature was kept just above the phase transition at 110 K. Read-out temperatures from the holder varied from 108 K to 113 K, but we know by experience (Friis et al., 2003a,b) that the true sample temperature is some degrees higher. There were no evidence that the tetragonal phase was reached in the diffraction patterns. After removing X-ray spots, the CBED patterns were deconvoluted with the LUCY algorithm (Zuo, 1999) in order to compensate for point spreading in the CCD.

### 1.3 Refinements

For structure factor refinements the high voltage, lattice parameters and ADPs need to be known in advance to high accuracy. The high voltage calibration of the microscope is described in Friis et al. (2003a).

#### 1.3.1 Anisotropic displacement parameters

A schematic drawing of the SrTiO$_3$ structure is shown in Fig. 1.1. The Sr and Ti atoms are at cubic site symmetry positions $m\bar{3}m$ while the O atoms have the site symmetry $4/mmm$. Neglecting anharmonicity, the isotropic vibrations of Sr and Ti are therefore described by only one parameter, $2\pi^2 U_{\text{Sr}} = \beta_{\text{Sr}}^{11} = \beta_{\text{Sr}}^{22} = \beta_{\text{Sr}}^{33}$ and $2\pi^2 U_{\text{Ti}} = \beta_{\text{Ti}}^{11} = \beta_{\text{Ti}}^{22} = \beta_{\text{Ti}}^{33}$, respectively, where $\beta$ denotes
1.3. REFINEMENTS

Figure 1.1: Schematic drawing of the SrTiO$_3$ structure.

the anisotropic displacement tensor (see Appendix B.3). The oxygen atoms can vibrate both in the plane spanned by the four closest Sr atoms, $U^1_{O}$, and along the line between the closest two Ti atoms, $U^2_{O}$. In the refinements we have used the ADPs found in the neutron diffraction experiment at 112(1) K by Hutton et al. (1981). The values of the ADPs derived from this experiment are $U_{Sr} = 0.00252(5)$ Å$^2$, $U_{Ti} = 0.00196(6)$ Å$^2$, $U^1_{O} = 0.00552(5)$ Å$^2$ and $U^2_{O} = 0.00228(5)$ Å$^2$.

1.3.2 Lattice constant

The lattice constant was determined from refinements of the high order Laue zone (HOLZ) line positions in the center disk, close to the [014]-zone axis. Dynamical calculations of the exact HOLZ-line positions (Zuo et al., 1998), were performed for three areas in the central disk (Fig 1.2). The areas were chosen in order to avoid overlap with neighboring disks and to reduce the influence of low order structure factors, which might be affected by bonding and hence differ from their IAM values. Since only the HOLZ-line positions are of interest, the CBED pattern in Fig 1.2a was made binary using a threshold of 25% of the full image intensity (Fig 1.2b). The refinement was performed in a two step procedure. First, a full-intensity refinement of the experimental parameters (incident beam angle, sample thickness and pattern geometry) was performed. These values were then used as a starting point in the lattice parameter refinement of the binary pattern. The lattice parameter at the goodness-of-fit minimum was $a = 3.89975$ Å. Using this lattice parameter, it might be possible to derive the true experimental temperature, by e.g. comparing with the thermal expansion experiments (Devanarayanan & Narayanan, 1968; Golding, 1970; Willemsen et al., 1976).
CHAPTER 1. QCBED MEASUREMENTS OF SrTiO$_3$

Figure 1.2: Determination of the lattice constant. (a) CBED pattern of the central disk, close to the [014]-zone axis in SrTiO$_3$. The three areas chosen for lattice parameter refinement are shown. (b) A binary version of the CBED pattern in (a). The calculated HOLZ-line positions are shown in red.

Figure 1.3: A CBED pattern of the (100) systematic row in SrTiO$_3$. Since the (100) disk is too weak to show up in the full dynamical (color) range (a), the same pattern is also shown in a reduced color range (b). The four line scans used in the refinements are shown in red.
1.3. REFINEMENTS

Figure 1.4: Best fit between theoretically calculated intensities (lines) and experiment (circles) after structure factor refinement of the (100) systematic row shown in Fig. 1.3. The differences between theory and experiment are shown with small dots. For this refinement of the (100) and (200) structure factors, 324 pixels were included along four line scans.

1.3.3 Preliminary structure factor refinements

Twelve structure factors have so far been refined. It was even possible to refine the very weak (100) reflection. For this very low order structure factor we had to choose a small condenser aperture in order to avoid overlapping disks. A CBED pattern of the (100) systematic row is shown in Fig. 1.3 with the corresponding best fit between theoretically and experimentally intensities in Fig. 1.4. For the refinement shown Fig. 1.4 we see that the $\chi^2$ is even less than one. This is a much lower value than what is normally obtained with larger condenser aperture (around 1.5). Probably this low value is due to an overestimation of the standard deviation in the pixel intensities, since the characterization of the CCD was performed for an average count at about 3000.

The refined structure factors, converted to their corresponding X-ray values, are listed in Table 1.2 together with structure factors obtained from the independent atom model (IAM), density functional theory (DFT) calculations and the X-ray diffraction experiment used by Zhurova & Tsirelson (2002). Even though these are preliminary results, it is clear that the QCBED and X-ray results differ quite a lot. However, it is interesting to notice that for the weak (100) reflection, for which extinction effects should be small, the agreement between X-ray and QCBED is within one standard deviation. The general agreement of the DFT calculations is also better compared to the QCBED values than to the X-ray values.

Further work on SrTiO$_3$ includes some more independent refinements of
CHAPTER 1. QCBED MEASUREMENTS OF SrTiO$_3$

Table 1.2: Preliminary experimental and theoretical static lattice structure factors for the cubic phase of SrTiO$_3$. The IAM values are those of Doyle & Turner (1968) and the DFT values are calculated with WIEN2k (Blaha et al., 2001) using the generalized gradient approximation (GGA) of Perdew et al. (1996). The X-ray data are from Zhurova & Tsirelson (2002) and QCBED is the present experiments. $n$ is the number of independent QCBED refinements performed so far for each reflection.

<table>
<thead>
<tr>
<th>hkl</th>
<th>sin $\theta$/(\lambda)</th>
<th>IAM</th>
<th>DFT</th>
<th>X-ray</th>
<th>QCBED</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.128</td>
<td>7.891</td>
<td>7.801</td>
<td>7.86(5)</td>
<td>7.89(3)</td>
<td>5</td>
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<tr>
<td>110</td>
<td>0.181</td>
<td>42.48</td>
<td>41.06</td>
<td>40.63(10)</td>
<td>40.96(2)</td>
<td>1</td>
</tr>
<tr>
<td>111</td>
<td>0.222</td>
<td>29.43</td>
<td>30.38</td>
<td>30.65(10)</td>
<td>30.38(4)</td>
<td>3</td>
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<tr>
<td>200</td>
<td>0.256</td>
<td>56.13</td>
<td>56.51</td>
<td>56.91(14)</td>
<td>56.52(6)</td>
<td>9</td>
</tr>
<tr>
<td>211</td>
<td>0.314</td>
<td>34.27</td>
<td>34.14</td>
<td>33.95(8)</td>
<td>34.25(7)</td>
<td>5</td>
</tr>
<tr>
<td>220</td>
<td>0.363</td>
<td>45.39</td>
<td>45.41</td>
<td>45.06(11)</td>
<td>45.62(10)</td>
<td>1</td>
</tr>
<tr>
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<td>0.405</td>
<td>30.13</td>
<td>30.30</td>
<td>30.23(7)</td>
<td>29.98(16)</td>
<td>3</td>
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<tr>
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<td>0.425</td>
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<td>19.77</td>
<td>19.77(5)</td>
<td>19.85(17)</td>
<td>4</td>
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<td>0.444</td>
<td>39.31</td>
<td>39.31</td>
<td>38.89(10)</td>
<td>39.27(7)</td>
<td>3</td>
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<td>321</td>
<td>0.480</td>
<td>27.34</td>
<td>27.42</td>
<td>27.34(6)</td>
<td>27.34(20)</td>
<td>4</td>
</tr>
<tr>
<td>400</td>
<td>0.513</td>
<td>35.39</td>
<td>35.52</td>
<td>35.07(10)</td>
<td>35.33(11)</td>
<td>4</td>
</tr>
<tr>
<td>422</td>
<td>0.628</td>
<td>30.49</td>
<td>30.54</td>
<td>30.43(7)</td>
<td>30.40(24)</td>
<td>4</td>
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</tbody>
</table>

The (110)-(220) systematic row and some fine adjustments of the refinements, which seem to have been trapped in local minima. A Wilson plot, based on DFT as a static lattice reference (Friis et al., 2003b), should also be performed in order to check the consistency of ADPs taken from Hutton et al. (1981). The QCBED data set could then be combined with the 131 structure factors from Zhurova & Tsirelson (2002) for a multipole refinement. Including our very accurate low order structure factors and by comparing with DFT, it may be possible to describe the bonding in strontium titanate in detail.

References


URN:NBN:no-7231
REFERENCES


Part IV

Appendix
Appendix A

Mott formula

A.1 A short derivation of Mott formula taking the thermal motion into account

This derivation of the Mott formula follows the derivation in Spence & Zuo (1992) but treats the thermal motion more rigorous.

The electron atomic scattering factor is defined by

\[ f^e(s) = \mathcal{F}\{V\} = \int V e^{-4\pi is\cdot r} dr \]  

where \( \mathcal{F} \) denotes the Fourier transform, \( V = V(r) \) is the atomic potential and \( s \) is the scattering vector. The thermal average of Eq. (A.1) is given by

\[
\langle f^e(s) \rangle = \int \langle V \rangle e^{-4\pi is\cdot r} dr \n\]

\[
= -\frac{1}{16\pi^2s^2} \int \langle V \rangle \nabla^2 e^{-4\pi is\cdot r} dr 
\]

\[
= -\frac{1}{16\pi^2s^2} \int \left( \nabla^2 \langle V \rangle \right) e^{-4\pi is\cdot r} dr 
\]

\[
= -\frac{1}{16\pi^2s^2} \int \langle \nabla^2 V \rangle e^{-4\pi is\cdot r} dr 
\]  

(A.2)

where we in the third step have used integration by parts and assumed that \( V(r) \to 0 \) when \( r \to \infty \). From Poisson’s equation we have

\[
\langle \nabla^2 V \rangle = \left\langle -\frac{|e|}{\epsilon} (\rho_n - \rho) \right\rangle = -\frac{|e|}{\epsilon} \left( \langle \rho_n \rangle - \langle \rho \rangle \right) 
\]  

(A.3)
where $\rho_n$ and $\rho$ are the nucleus and electron charge densities, respectively. By inserting Eq. (A.3) into (A.2) we obtain

$$\langle f^e(s) \rangle = \frac{|e|}{16\pi^2\epsilon s^2} \int (\langle \rho_n \rangle - \langle \rho \rangle) e^{-4\pi i s \cdot r} dr$$

$$= \frac{|e|}{16\pi^2\epsilon s^2} [\mathcal{F}\langle \rho_n \rangle - \mathcal{F}\langle \rho \rangle] \quad (A.4)$$

If $\mathbf{u}$ is the thermal displacement of an atom, the time-averaged nucleus density for that atom is

$$\langle \rho_n(r) \rangle = \int Z\delta(\mathbf{r} - \mathbf{u})P(\mathbf{u}) d\mathbf{u} = ZP(r) \quad (A.5)$$

where $P(\mathbf{u})$ is the displacement probability distribution of the nuclei and $Z$ is the atomic number. The Fourier transform of $\langle \rho_n(r) \rangle$ is then given by

$$\mathcal{F}\langle \rho_n \rangle = ZT(s) \quad (A.6)$$

where $T(s) = \mathcal{F}\{P(\mathbf{u})\}$ is the temperature factor. Inserting Eq. (A.6) into (A.4) yields

$$\langle f^e(s) \rangle = \frac{|e|}{16\pi^2\epsilon s^2} \left[ ZT(s) - \langle f^X(s) \rangle \right] \quad (A.7)$$

where $f^X(s) = \mathcal{F}\{\rho\}$ is the X-ray scattering factor. By rearranging Eq. (A.7) we obtain

$$\langle f^X(s) \rangle = ZT(s) - \frac{16\pi^2\epsilon s^2}{|e|} \langle f^e(s) \rangle \quad (A.8)$$

We introduce the structure factors

$$F_g = \sum_j \langle f^X(s) \rangle e^{-2\pi g \cdot r_j}$$

$$V_g = \frac{1}{\Omega} \sum_j \langle f^e(s) \rangle e^{-2\pi g \cdot r_j} = \frac{h^2}{2m|e|} U_g = \frac{h^2}{2m_0\gamma|e|} U_g \quad (A.9)$$

where $F_g$ and $U_g$ are known as the X-ray structure factor and the electron structure factor, respectively. By multiplying Eq. (A.8) with a phase factor $e^{-2\pi g \cdot r_j}$ and sum over all atoms in the unit cell, we obtain

$$F_g = \sum_j Z_j T_j(s) e^{-2\pi g \cdot r} - \frac{16\pi^2\epsilon \Omega s^2}{|e|} V_g$$

$$= \sum_j Z_j T_j(s) e^{-2\pi g \cdot r} - \frac{8\pi^2 e h^2 \Omega s^2}{m_0\gamma|e|^2} U_g \quad (A.10)$$

\[1\] An interesting discussion with Tsirelson & Olaussen (2003) about the the validity of Eq. (A.5) motivated this appendix.
This equation gives a relation between the X-ray and electron structure factors and is usually referred to as Mott\textsuperscript{2} formula.

**References**


\footnote{In the literature this formula is also known as the Mott-Bethe formula. Some authors refer instead to the relation between electron and X-ray scattering factors, Eq. (A.8). The name has probably its origin in a relation similar to Eq. (A.8) derived by Mott (1930).}
Appendix B

Structure factor error analysis

Here follows a short description of the error analysis applied to the structure factor measurements of Mg (Friis et al., 2003b) and SrTiO$_3$ (Part III).

B.1 Motivation

Doing QCBED experiments, it is common to take several diffraction patterns under different experimental conditions (e.g. different geometry and sample thickness) in order to get better statistics and to be able to check the consistency of the data. From each refinement one gets a value for the standard deviation based on the depth of the $\chi^2$ minimum. However, these standard deviations are usually underestimated, since uncertainties in the non-refined parameters are neglected. Therefore it is common to obtain the standard deviation as a simple spot check standard deviation of the measured structure factor values (Jiang et al., 2003; Friis et al., 2003a).

However, a more rigorous analysis, as shown in the two next sections, should also use the information in the standard deviation of the individual refinements and, more importantly, take the uncertainties in the temperature factors into account.

B.2 The expectation value and variance

Let’s assume that we have performed $n$ refinements of a certain reflection resulting in the structure factors $U_i$ and standard deviations $s_i$, with $i = 1..n$. If we assign a weight $w_i$, with $\sum_i w_i = 1$, the weighted average of the structure factors is

$$\bar{U} = \sum_i w_i U_i. \quad (B.1)$$
APPENDIX B. STRUCTURE FACTOR ERROR ANALYSIS

It is possible to show that the expectation value and variance of the true structure factor are given by $\bar{U}$ and

$$s^2 = \sum_i w_i^2 s_i^2 + \sum_i w_i(U_i - \bar{U})^2,$$  \hfill (B.2)

respectively. In the analysis of Mg and SrTiO$_3$ the weighting were, as normally, simply chosen proportional to $1/s_i$, i.e.

$$w_i = \frac{1/s_i}{\sum_j 1/s_j}.$$  \hfill (B.3)

The expectation value of $\bar{U}$ equals the expectation value of the refinements $\mu = E(U_i)$ as seen from

$$E(\bar{U}) = E\left(\sum_i w_i U_i\right) = \sum_i w_i E(U_i) = \sum_i w_i \mu = \mu,$$  \hfill (B.4)

where we have assumed that the measurements $U_i$ are independent.

Similarly, we want to show that $E(s^2)$ equals the distribution variance of the measurements $V(U_i)$. Since, the variance of $\bar{U}$ is

$$V(\bar{U}) = V\left(\sum_i w_i U_i\right) = \sum_i w_i^2 V(U_i) = \sum_i w_i^2 E(s_i^2)$$  \hfill (B.5)

we have

$$E(s^2) = E\left(\sum_i w_i^2 s_i^2\right) + E\left(\sum_i w_i(U_i - \bar{U})^2\right)$$

$$= \sum_i w_i^2 E(s_i^2) + E\left(\sum_i w_i(U_i - \mu)^2 - (\bar{U} - \mu)^2\right)$$

$$= V(\bar{U}) + E\left(\sum_i w_i(U_i - \mu)^2\right) - E\left((\bar{U} - \mu)^2\right)$$

$$= V(U)$$  \hfill (B.6)

Q.E.D.
B.3 Error in the final X-ray structure factors

We are often interested in X-ray structure factors at a certain temperature (e.g. at static lattice temperature where \( T_j(s) = 1, \forall j \)). The Mott formula (A.10) gives the X-ray structure factor \( F_{\text{initial}} \) at the experimental temperature. In the case of only one kind of atoms (at equal site symmetry) in the unit cell, the structure factor at the wanted temperature is simply

\[
F_{\text{final}} = \frac{T_{\text{final}}}{T_{\text{initial}}} F_{\text{initial}}. \tag{B.7}
\]

For more than one atom in the unit cell \( F_{\text{final}} \) can be approximated by

\[
F_{\text{final}} \approx \sum_j f_j T_{\text{final}} e^{-2\pi i \mathbf{g} \cdot \mathbf{r}_j} \frac{1}{\sum_j f_j T_{\text{initial}} e^{-2\pi i \mathbf{g} \cdot \mathbf{r}_j} F_{\text{initial}}}, \tag{B.8}
\]

where \( f_j \) is the scattering factor of the \( j \)th atom. Note that if only one kind of atoms is present, Eq. (B.8) reduces to Eq. (B.7).

From the Mott formula (A.10) the variance of \( F_{\text{initial}} \) is given by

\[
V(F_{\text{initial}}) = \sum_j \left( Z_j e^{-2\pi i \mathbf{g} \cdot \mathbf{r}_j} \right)^2 V(T_j) + \left( \frac{C \Omega s^2}{\gamma} \right)^2 V(U) \tag{B.9}
\]

where

\[
C = \frac{8\pi^2 \hbar^2}{m_0 |e|^2} = 131.2625 \text{ Å} \tag{B.10}
\]

if \( U \) and \( T_{\text{initial}}^i, i = 1..n \) are independent.

The temperature factor is, in the harmonic approximation, given by

\[
T_j = T_j(s) = e^{-\beta_j \cdot \mathbf{g}_j \cdot \mathbf{g}_k} \tag{B.11}
\]

where \( \beta_j \cdot \mathbf{g}_j \cdot \mathbf{g}_k \) and where \( \langle u^i u^k \rangle_j \) is the anisotropic displacement tensor for atom \( j \). Summation over repeated indices is implicitly assumed according to Einsteins summation convention. The variance of \( T_j \) can now, using the Gauss approximation formula for the variance of a function of a stochastic variable \( X \)

\[
V(g(X)) \approx V(X)[g'(E(X))]^2, \tag{B.12}
\]

be written as

\[
V(T_j) = e^{-2\beta_j \cdot \mathbf{g}_j \cdot \mathbf{g}_k} V(\beta_j \cdot \mathbf{g}_j \cdot \mathbf{g}_k) = T_j^2 \sum_{ik} (g_i g_k)^2 V(\beta_j \cdot \mathbf{g}_j \cdot \mathbf{g}_k) \approx \sum_{ik} (g_i g_k)^2 V(\beta_j \cdot \mathbf{g}_j \cdot \mathbf{g}_k) \tag{B.13}
\]
where we in the last step have used that $T_j$ is close to unity at low temperatures and small scattering angles (which is the case for QCBED).

By taking the variance of Eq. (B.8) and use (B.9) and (B.12) it follows that the variance of $F_{\text{final}}$ is given by

\[
V(F_{\text{final}}) \approx \sum_j (Z_j e^{-2\pi i g \cdot r_j})^2 V(T_j) + \left(\frac{C\Omega s^2}{\gamma} \right)^2 V(U) + 2 \sum_j (f_j e^{-2\pi i g \cdot r_j})^2 V(T_j).
\]  

(B.14)

### B.4 Correction due to lattice expansion

Since the structure factors depend on the lattice parameters, via the scattering factor, a small correction is needed in order to account for the change in lattice parameters, when converting structure factors between temperatures. When converting from a higher to a lower temperature, this effect tends to counteract the reduction of the structure factor, caused by the smearing accounted for by the temperature factor $T_j$. However, this is a very small effect of the size of the uncertainties (around 0.2% when converting from liquid nitrogen temperature to static lattice, see e.g. the rescaled values in Table 1. in Tabbernor et al. (1990)).

This effect can easily be accounted for by also considering the change of scattering angle in Eq. (B.8)

\[
F_{\text{final}} \approx \frac{\sum_j f_j (s_{\text{final}}^j T_{\text{final}}^j e^{-2\pi i g \cdot r_j})}{\sum_j f_j (s_{\text{initial}}^j T_{\text{initial}}^j e^{-2\pi i g \cdot r_j})} F_{\text{initial}}.
\]  

(B.15)

### References

