

DESY SR 90-01
January 1990

Accurate Structure Analysis with Synchrotron
Radiation.

The Electron Density in Al_2O_3 and Cu_2O

A. Kirfel

Universität des Saarlandes, Saarbrücken

K. Eichhorn

Hamburger Synchrotronstrahlungslabor HASYLAB at DESY, Hamburg

Eigentum der	DESY	Bibliothek
Property of		library
Zugriff :		
Accession :	26. FEB. 1990	
Leihfrist :	7	days

ISSN 0723-7979

NOTKESTRASSE 85 · 2 HAMBURG 52

DESY behält sich alle Rechte für den Fall der Schutzrechtserteilung und für die wirtschaftliche Verwertung der in diesem Bericht enthaltenen Informationen vor.

DESY reserves all rights for commercial use of information included in this report, especially in case of filing application for or grant of patents.

To be sure that your preprints are promptly included in the
HIGH ENERGY PHYSICS INDEX ,
send them to the following address (if possible by air mail) :

DESY
Bibliothek
Notkestrasse 85
2 Hamburg 52
Germany

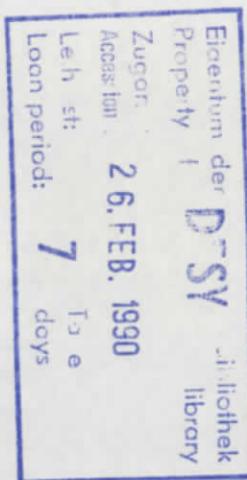
**Accurate Structure Analysis
with Synchrotron Radiation.
The Electron Density in
 Al_2O_3 and Cu_2O .**

by

A. Kirfel
Universitaet des Saarlandes, FR Kristallographie,
D-6600 Saarbruecken 11, FRG

and

K. Eichhorn
Hamburger Synchrotronstrahlungslabor HASYLAB
am Deutschen Elektronen-Synchrotron DESY
Notkestr. 85, D-2000 Hamburg 52, FRG



Accurate room temperature structure analyses have been carried out on the two well known structures of Cuprite, Cu_2O , and Corundum, $\alpha\text{-Al}_2\text{O}_3$, using synchrotron radiation, in order to assess the accuracy of single crystal X-ray diffraction data that can be obtained at such a source. The two compounds were chosen, since results can be rigorously cross-checked against deposited data from careful X-ray tube measurements which have been analyzed in terms of electron density distributions. The synchrotron radiation data were collected on the 5-circle-diffractometer at HASYLAB during dedicated mode of DORIS II (3.7 GeV) within normal beam time allowance at the same wavelengths as the tube experiments. The final Cu_2O data set included 21 "forbidden" reflections whose intensities cannot be measured using tube radiation. The intensities of these latter reflections turned out to be predominantly determined by the anisotropic vibration of Cu. Refinements using multipole expansion models yielded agreement indices $R = 0.0173$ and 0.0078 for Cu_2O and Al_2O_3 , respectively. Structure factors as well as static model deformation properties including electric field gradients are compared with the corresponding literature results. Most findings are in satisfactory agreement implying that high quality diffraction data can be obtained at a synchrotron radiation source within reasonable time, provided proper attention is given to the experiment and the data reduction procedure. In particular, use of synchrotron radiation allows recording of weak and very weak reflection intensities with an accuracy that could never be achieved in conventional tube experiments. An additional data collection on Cu_2O during parasitic mode (5.3 GeV) shows that also under less favorable conditions data can be collected at a synchrotron radiation source with an accuracy sufficient for standard structure analyses.

Introduction

During the last decade synchrotron radiation has increasingly attracted the attention of crystallographers to make use of its unique properties for a large variety of experiments. Most of these are novel while "conventional" structure analyses, especially on the level of an analysis of fine structure features, like electron density distributions and thermal vibrations, are still rare.

In principle, synchrotron radiation offers important advantages for accurate work. Its tunability in energy and in particular its high intensity and small divergence allow the collection of virtually extinction and absorption free data on micro-crystals (Bachmann, Kohler, Schulz & Weber, 1985). With normal sized crystals it offers the opportunity of improving the accuracy of weak reflection intensities beyond what can be achieved with sealed X-ray tubes. Considering the limited access to synchrotron radiation sources, accuracy and resolution of conventionally collected data sets could be considerably enhanced by combining them with synchrotron measurements of selected reflections.

This principle advantage may, however, be easily offset by the instability of the synchrotron source, both in space and time, and by related experimental and data processing problems.

Thus, not only scarcity of beam time but also lack of experience with the data quality that can be obtained from the available instruments seem to have discouraged accurate structure studies. Encouragement can come from feasibility studies. Nielsen, Lee & Coppens (1986) have carried out such a study at CHESS (Cornell University) collecting data on an organometallic compound of hexagonal symmetry at the short wavelength of 0.302 Å. Their results are a demonstration that high quality data can be obtained with synchrotron radiation, provided proper precautions are taken.

In order to assess the accuracy that can be obtained on the 5-Circle-diffractometer at HASYLAB/DESY (Kupcik, Wendschuh-Josties, Wolf & Wulf, 1986), we have performed another feasibility study, with a somewhat different approach from that of the above authors. While their results can be judged from their unquestionable internal consistency and the features of the resulting deformation density maps, they have not been compared with tube data. We choose to collect data on the two well known compounds cuprite, Cu_2O , and corundum,

$\alpha\text{-Al}_2\text{O}_3$, for direct comparison with earlier investigations. Restori & Schwarzenbach (1986) and Lewis, Schwarzenbach & Flack (1982) have thoroughly studied both compounds by means of conventional single crystal diffractometry. Hereafter these studies are referred to as RS and LSF, respectively. In both cases the data were refined with multipole expansion models to agreement indices close to or even below 0.01 and are therefore generally considered very accurate. Additional reasons for selecting Cu_2O and Al_2O_3 are given below.

The aim of our work was therefore primarily the assessment of an appropriate data collection and reduction strategy, and of the data accuracy. The study was conducted in the following steps:

- measurement of data sets (as complete as possible within the allocated beam time) at the wavelengths of the tube experiments by RS and LSF,
- data reduction according to the special conditions of synchrotron radiation,
- comparison of the derived structure factors with the literature data,
- structure refinements with independent atom (IAM) and multipole expansion models: for both compounds synchrotron data and literature data separately, for Cu_2O also combined tube and synchrotron data (see below).

Structures and Samples

Crystallographic data of both compounds are summarized in Table 1. The structure of corundum has been described in detail by LSF. Here it suffices to mention that it is composed of AlO_6 octahedra while O is tetrahedrally coordinated by Al atoms. Though bonding is usually described as essentially ionic, LSF derived significant deformation density features, with the oxygen charge distribution being polarized towards the adjacent Al atoms.

Corundum is well suited as standard material since the high symmetry allows collection of sufficient numbers of equivalent reflections for the determination of internal consistency and the detection of multiple scattering effects. It is chemically stable, and the hardness ($H = 9$) of the material and its elastic constants (Hellwege, 1966) imply little TDS. The light elements preclude problems caused by absorption of $AgK\alpha$ -radiation. Finally, as kindly suggested by D. Schwarzenbach, perfectly spherical Verneuil-grown crystals with negligible Cr contamination and diameters between 0.10 - 0.25 mm could be obtained from the firm Jean Sandoz et fils, SA (CH-1482 Cugy, Switzerland). The crystal selected for the measurements had a diameter of 0.200 mm.

The structure of semi- and photoconducting Cuprite has attracted much interest by both experimental crystallographers and theoreticians. The outstanding feature is a perfectly linear and symmetric O-Cu-O arrangement (Cu-O 1.848 Å) as result of the two interpenetrating lattice complexes of Cu and O which are F and I, respectively. This Cu coordination requires bonding that is not purely ionic. Theoretical calculations by Nagel (1985) and Marksteiner, Blaha & Schwarz (1986) indicated a $Cu d^8$ plus doubly occupied $3d_{2,2}-4s$ hybrid state which allows removal of charge from the bond axis resulting in a Cu-O distance significantly shorter than permitted by the ionic radii.

Considering symmetry, hardness ($H = 4$), and stability at ambient temperatures, Cuprite seems also well suited as standard material though absorption and TDS ($\Theta_D = 184$ K) are less favorable than in corundum. As an interesting consequence of the special positions of the atoms the structure factors can be divided into four parity groups with different mean intensities. The contributions of

each class characterized by even (e) and odd (o) Miller indices are:

M(Cu), M(O),	H_1 (Cu), H(O)	eee - strong
M(Cu)	Oct(O), H_1 (Cu)	ooo - strong
M(O), Q(Cu),	H_2 (Cu), H(O)	ooe - weak
Q(Cu), Oct(O), H_2 (Cu)		eeo - very weak

M, Q, Oct, $H_{1,2}$ denote atom centered multipolar density distributions up to hexadecapoles (Kurki-Suonio, 1977), including the U_{12} (Cu) harmonic temperature factor element into Q(Cu) and the free atom scattering factors into M.

This reflection scheme shows that the bulk density distribution is determined by the first three parity groups alone. For spherically symmetric p.d.f.'s all reflections (eoo) have zero intensities due to general or special absence rules. Since M(Cu) dominates all other contributions, the density fine structure is mainly accessible in the (ooo) and (eoo) reflections. A thorough structure and electron density analysis requires therefore accurate measurements of the so-called "oxygen" (ooe)-reflections and the "forbidden" (eoo)-reflections. Especially the latter are expected to be decisive for a separation of anisotropic thermal smearing and chemical bonding effects. They are also important for the calculation of difference density maps, since their omission produces pseudo-symmetric patterns. With tube radiation RS failed to observe more than two "forbidden" reflections (221, 421), and the reported $I/o(I)$ are hardly significant.

Thus, for Cuprite the synchrotron measurements were intended as both an accuracy test and an enhancement of the 100 K data of RS in order to contribute to the understanding of the electron density distribution.

From a natural sample of imprecisely specified origin (Canada) crystal spheres were prepared in a grinder. The crystal finally selected for the measurements was a sphere of 0.173 mm diameter (maximum asphericity 5 μ m).

Experimental

All measurements were carried out on the 5-Circle diffractometer at HASYLAB beamline D3. In principle, this instrument is a commercial STOE 4-circle diffractometer with modified software (Wulf & Wendschuh-Josties, 1989) and angular resolution of 0.001° . A fifth circle permits rotation of the goniostat about the primary beam axis. For conventional diffraction experiments the scattering plane is always vertical in order to minimize beam divergence and to maximize the intensity yield. A combined intensity/polarization monitor (Smend, Schaupp, Czerwinski & Schenk-Strauss, 1984) allows real-time monitorization of both intensity and polarization of the primary beam. Monochromatic radiation was obtained from a Ge(111) double-crystal monochromator with 0.3 - 2.2 Å wavelength range, $\Delta E/E = 4 \cdot 10^{-4}$ energy resolution at 1 Å, and a harmonic suppression of $I_0(\lambda/3) / I_0(\lambda) < 10^{-3}$.

The majority of the measurements was carried out during dedicated shifts (3.7 GeV) of the DORIS II storage ring. Average runs lasted up to 6 h with the ring current decreasing from 90 to 30 mA. Beam steering used the position monitors in beam port D where the diffractometer is located. An additional data set on Cu_2O was collected during parasitic mode (high energy operation at 5.3 GeV). Then, fills last only about 60 min under considerably less stable conditions (no beam steering). A high parasitic background from > 80 KeV photons is present, and the intensity is reduced on average by about 60 % (ring current 40 - 20 mA). The latter measurements served to check the data reduction procedure and to assess the accuracy of data taken under less favorable working conditions.

For all cases the wavelength was set close to 0.56 Å, and the beam was collimated to 1 mm diameter. For strong reflections ($> 20,000$ cps) the intensity was reduced by insertion of appropriate filter combinations.

a) Preliminary Work

After optical centering of the crystal and refinement of the orientation matrix careful checks were made for:

- stability of crystal alignment and beam homogeneity by comparison of equivalent reflection intensities,
- beam contamination by third and fourth order harmonics. Scanning of extinct reflections or of reflections with broken indices yields the remaining contribution of higher order harmonics alone. The effect was then reduced to negligible importance by both slightly detuning the monochromator and adjusting the single channel analyzer (SCA).
- optimal detector aperture. Intensity profiles of equivalent reflections at medium scattering angle were measured at various aperture settings in order to obtain the full intensity record at lowest possible background.
- optimal scan range. Though the small beam divergence yields sharp intensity profiles which are mainly determined by the mosaic spread of the crystal (typical FWHM 0.03° for Cu_2O and 0.02° for Al_2O_3), scans of increasing widths show long ranging intensity tails which must be taken into account for valid background subtraction. Fig. 1 shows as an example reflection (220) of Cu_2O recorded with both synchrotron and $\text{AgK}\alpha$ -radiation. For correct numerical integration of the intensity profiles sufficiently small setting increments around the peak maximum are required. As already described by Nielsen et al. (1986), such profiles can be recorded most efficiently by using spread scans. Unfortunately, no such option was available for our experiment, so that considerable time was "wasted" on background measurements due to the equidistant step scans. This point deserves attention in forthcoming work. Even a pessimistic estimate shows that the data collection rate could be easily improved by a factor of 2 by reasonable tailoring of the step sizes.

b) Beam monitorization, filters, and dead time correction

The preliminary work was completed by determination of the filter correction factors and the effective dead time of the counting chain (amplifier-discriminator, typically 4-8 μs). Using the method by Chipman (1969), these parameters can be derived simultaneously from repeated measurements of reflections that require different filtering at the begin and end of a fill. In the high energy

shifts the intensity drop of the primary beam is usually not large enough to make the method work satisfactorily. In this case additional filters have to be inserted to ensure a sufficiently wide variation of the primary intensity I_0 .

Contrary to the considerations of Nielsen et al. (1986) the time structure of the non-continuous source caused no problems in our case. With $4 \cdot 10^6$ bunches/s (DORIS II, 4 bunch mode) the average bunch separation of 0.25 μ s is much smaller than the dead time of the counting chains. With a limitation to a maximum count rate of 20,000 cps only negligible corrections are obtained using the above authors equations (see also Arndt, 1978).

Beam monitorization and intensity normalization were then checked by measuring a strong reflection continuously during one or two complete fills. This measure provides a good test for the validity of the time-dependent corrections. Significant increase of the intensity with time indicates overload of the detector, e.g. due to insufficient filtering. In this case the monitor count rate was observed to decrease with decreasing ring current while the maximum peak count rate remained almost unaffected.

An apparent change of the reflection intensity with time can be attributed to a systematic error in the dead time correction and the on-line normalization of the detector counts according to:

$$N_{\text{corr}} = N_c \{ 1 - t_m N_m \} / N_m \{ 1 - t_c N_c \} \quad (1)$$

$$= N_c / N_m \cdot [1 - t (N_c + N_m) + t^2 (N_c N_m + N_m^2)]$$

N_c and N_m are the detector and monitor count rates recorded for the window settings of their respective single channel analyzers (SCA's), and $t_m \approx t_c \approx t$ are the associated dead times. However, N_c and N_m may not represent the true load of the detectors if they receive significant amounts of stray radiation of predominantly higher energy. This occurs only rarely during dedicated ring operation, but decrease of the normalized reflection intensity by a few % has been observed repeatedly during parasitic runs when DORIS II is operated at 5.3 GeV. Then, correct assessment of the reflection intensity would require in principal additional records of the SCA's integral mode outputs (for every scan step or at least before and after a scan) and/or beam shielding within the monochromator and around the detectors that guarantees complete absorption of all synchrotron light of undesired energy. This deserves consideration in future designs of diffraction stations.

According to equ. (1) a simple empirical correction can be made by deriving an effective monitor dead time $t'_m > t_m$ from the check reflection's intensity decrease and by applying t'_m in the course of data reduction. Fig. 2 shows, as an example, that using 16 μ s effective dead time removes the intensity decrease completely, thus indicating a valid treatment of the problem.

c) Data collection

Details of data collection are summarized in Table 2. A prescan was used to adjust the scan speed to the actual reflection intensity. The time per step was such that the counts at the peak maximum did not exceed 5,000 per step (after insertion of filters). The allowed time range was 0.5 - 2 s for Cu_2O and 0.3 - 2 s for Al_2O_3 , respectively.

Cu_2O

The orientation matrix was refined from the optimized angular settings of 16 reflections ((511) and symmetry equivalents, $2\theta = 39.85^\circ$) yielding $a_0 = 4.2685(5)$ Å. (511) was also used as check reflection remeasured every 30 min and at the beginning of each fill. The data collection comprised ($s = \sin\theta/\lambda$):

- i) 125 reflections of all parities with $0 < s \leq 1.087 \text{ \AA}^{-1}$, $h \geq k \geq l \geq 0$, 120 unique,
- ii) 37 (ooe) "oxygen" reflections with $1.08 < s \leq 1.40 \text{ \AA}^{-1}$, $h \geq k \geq l > 0$, 34 unique,
- iii) 127 (eoo) "forbidden" reflections with $0 < s \leq 1.055 \text{ \AA}^{-1}$, 23 unique. Including 53 check reflections, a data set of 342 reflections (hereafter referred to as CUL) was recorded within 64 h of which 35 h were effectively spent on the intensity scans. The scattering distribution of the check reflection is given by the relative e.s.d. $\sigma_{\text{scatter}}/I = 0.019$ equalling the mean relative e.s.d. $\sigma(I(511))/I(511) = 0.019$.

A second data set (CUH) was collected during high energy operation (no beam steering, polarization 65 - 90 %). Using scan parameters identical to those of the previous measurements 324 reflections were recorded: $h \neq k \neq l$, $0 < s \leq 0.82 \text{ \AA}^{-1}$; $h \geq k \geq l \geq 0$, $0.82 < s \leq 1.25 \text{ \AA}^{-1}$.

Al₂O₃

The orientation matrix was refined from 16 reflections with $41^\circ < 2\theta < 64^\circ$ yielding $a_0 = 4.7570(5)$, $c_0 = 12.9877(35)$ Å. Two check reflections (3,3,±18) were used similar to Cu₂O. Including 205 standard measurements, a total of 1758 reflections $\pm h, \pm k, l$ with $0 < s < 1.024 \text{ \AA}^{-1}$ were recorded in 68 h effective beam time. Since inspection of the integral intensities indicated insufficient filtering for the strong reflections (even with the maximum available filter combination), 176 of these with maximum peak count rate exceeding 20,000 cps were removed and remeasured in 6 h using an additional Al filter placed in front of the filter box.

No significant differences or scatter was observed for the two check reflections. Their internal agreement was $R(I) = 0.026$ which compares well with the mean relative e.s.d. $\sigma(I) / I_{\text{check}} = 0.027$.

Data Reduction

Data reduction was carried out using the program REDUCE (Eichhorn, 1987), including some of the ideas of Blessing, Coppens & Becker (1972), adapted to synchrotron data.

a) Integral Intensities

Normalization to monitor counts and allowance for beam polarization may introduce both random and systematic errors into the profile data. For each profile count C_i there are two additional counts from the beam monitors for the horizontally and vertically polarized components, C_H and C_V , respectively. Assuming proper dead time correction, beam intensity I_i and polarization ratio Q_i can be defined as

$$I_i = C_{H,i} + C_{V,i} \quad \text{and} \quad Q_i = (C_{H,i} - C_{V,i}) / I_i \quad (2)$$

The simplest approach would be to scale each profile point individually to its associated I_i and Q_i . However, this method has a serious disadvantage. Since C_V is usually less than 10% of C_H , and the counting time per step is determined (within preset limits) by the reflection intensity, the small C_V would introduce an unacceptably large counting error. The total error would then be dominated by the monitors rather than by the reflection profile.

A better approach uses $\langle C_H \rangle$ and $\langle C_V \rangle$ averaged over the N profile steps, provided that drift and fluctuations in the beam can be properly accounted for. This improves statistics by a factor of \sqrt{N} , and since N is typically about 100, the error will be reduced to 10% of that obtained by the "naive" method.

Thus, the following calculations are performed in REDUCE:

- without significant drift in C_H and C_V averages are taken and

$$I_o = \langle C_H \rangle + \langle C_V \rangle, \quad Q = (\langle C_H \rangle - \langle C_V \rangle) / I_o$$

- otherwise a least squares line fitted to $C_{H,i} + C_{V,i}$ is used to correct both monitor and profile counts.

- if there are significant fluctuations in the monitor counts ("bumps") the "naive" method, i.e. a point per point normalization is applied.

Since the contributions from both counting statistics and error propagation are taken into account, a profile with fluctuating monitor counts is automatically given a larger e.s.d. than data collected under stable conditions.

b) LP-correction

Integral intensities were determined using the Lehman-Larsen algorithm (Lehman & Larsen, 1974), and the LP correction was applied in the usual way. For synchrotron radiation and vertical scattering geometry the polarization factor is given by:

$$P = 0.5 \cdot [(1 + Q) + (1 - Q) \cdot (1 + \cos^2 2\theta)] \quad (3)$$

The LP-correction is not a critical point in data reduction. Fig. 3 shows that for a medium scattering angle (35°) and complete neglect of the polarization correction even a change in polarization from 90 to 100% would affect the derived intensity by only 1.7%. Thus, errors in the assessment of the degree of polarization are less dramatic than might be expected. In agreement with Nielsen et al. (1986), Fig. 3 shows also that choice of a short wavelength reduces the sensitivity of the measurements to the polarization.

c) Absorption- and TDS-correction

Absorption corrections were computed using the factors A^* tabulated by Dwiggins (1975). For Cu_2O absorption factors A^* ranged from 4.07 to 5.34 (CUL) and 4.27 to 5.34 (CUH); for Al_2O_3 they do not vary over the data range.

The correction $(1 + \alpha)$ for thermal diffuse scattering was evaluated with a modified version of the program SXTDS1 by Merisalo & Kurittu (1978). The elastic constants for the Cu_2O TDS correction were taken from Hallberg & Hanson (1970). The correction is nearly isotropic as pointed out by RS. The maximum corrections were 1.318 at 1.4 \AA^{-1} (CUL) and 1.204 at 1.25 \AA^{-1} (CUH). For Al_2O_3 elastic constants of Hellwege (1966) were used; the correction is almost negligible with a maximum value of 1.0053.

d) Data averaging

Weighted averages of symmetry equivalent and multiply measured reflections were calculated in the usual way with e.s.d.'s being determined by both counting statistics and scatter.

Cu_2O

Averaging of the reduced CUH data yielded 134 unique reflections with internal consistency $R_{int}(F) = 0.017$. 20 (ooe) and (eoo) reflections were considered unobserved ($\langle I \rangle < 3\sigma$).

The complete reduced and averaged data set CUL consisted of 133 unique reflections (22 (eee), 17 (ooo), 71 (ooe), and 23 (eoo)) of which 5 (ooe) and 4 (eoo) were considered unobserved ($\langle I \rangle < 2\sigma$). A conventional refinement showed that the intensities of the three strongest reflections, (111), (200), and (220), were calculated too large, probably due to insufficient filtering. Therefore, these reflections and seven other dubious reflections (5 (ooe), 2 (eoo)), possibly affected by Umweganregung, were excluded from all ensuing calculations, and the residual index dropped to $R(F) = 0.022$. Considering the relatively large amount of weak and very weak reflections, this result signalled already a data quality comparable to careful tube measurements.

A comparable data set (RS, $s_{max} = 1.5 \text{ \AA}^{-1}$) was prepared from the 100 K literature data deposited by RS.

In order to estimate the agreement between the RS and CUL data (though taken from different crystals at largely differing temperatures) and to test a merged data set, the following procedure was carried out: (Adjusting the data to ambient temperature was necessary because there was no way to correctly predicting low temperature structure amplitudes of the measured (eoo)-reflections. Thus, the vice versa procedure had to be discarded.)

i) the RS-data were conventionally refined, including isotropic extinction (as described below) to $R(F) = 0.0103$ in agreement with RS.

ii) using the linear temperature dependencies of the Cu and oxygen U_{ij} as obtained from neutron diffraction experiments by Mullen & Fischer (1981), the atoms were allocated room temperature values, and corresponding $F_c(RT)$ and $F_c(100\text{ K})$ were calculated.

iii) the observed RS-data were individually scaled by $F_c(RT)/F_c(100\text{ K})$ yielding a set of $F_{obs}(RT,RS)$.

iv) in order to correct for possible errors in the allocated U_{ij} values and to scale the CUL-data to the RS-data, the $F_{obs}(RT,RS)$ data were then fitted to the isotropic extinction corrected CUL-data by minimizing:

$$[F_{obs}(CUL) - K \cdot F_{obs}(RT,RS) \cdot \exp(-B(h^2+k^2+l^2) - C(hk+hl+kl))]^2,$$

K being a scale factor, and B and C being adjustable parameters which turned out not to differ significantly from zero. However, the corrections which were actually applied, corresponded to $\Delta U = 72 \cdot 10^{-5} \text{ \AA}^2$ for the strong and to $-75 \cdot 10^{-5} \text{ \AA}^2$ for the oxygen reflections. Thus $F_{obs}(RT,RS)$ received an additional correction according to these ΔU . The agreement factors obtained for each of the two reflection groups were $R(F) = 0.0135$ and 0.040 , respectively. The overall agreement for all reflections common to both data sets was 0.020 .

Finally, a joint data set, JOINT, with $s < 1.5 \text{ \AA}^{-1}$ was prepared by weighted averaging of the common reflections. This final data set comprised 170 reflections of which altogether 18 (ooe) and 21 (eoo) were newly observed reflections, and the weights of the averaged (ooe)-reflections were increased considerably.

Al_2O_3

1548 reflections were averaged to 259 unique reflections with an internal consistency $R_{int}(F) = 0.014$ indicating good data quality. None of the reflections was considered as unobserved.

From the literature data deposited by LSF (set II, AgK- α data) a set of corresponding reflections ($s < 1.024 \text{ \AA}^{-1}$) was prepared for comparable refinements.

Data Analysis

a) Independent-atom model (IAM) refinements

The positional and thermal parameters reported by RS and LSF, respectively, were used as starting values for conventional independent-atom (IAM) structure refinements on $|F|$ with weights $w = [\sigma^2(F) + (P \cdot F)^2]^{-1}$. Scattering factors for neutral atoms Al and O were calculated from the Hartree-Fock (HF) wave functions given by Clementi & Roetti (1974). For neutral Cu scattering factors were taken from the International Tables for X-Ray Crystallography, Vol. IV (1974). Anomalous dispersion corrections were taken from Cromer & Liberman (1970), and an isotropic extinction correction (Becker & Coppens, 1974) was included in all refinements. For both crystals type 1 and 2 models with Gaussian or Lorentzian distributions were tested. They all yielded practically identical results with marginal preference for a type 1 Lorentzian distribution. This type of correction was used in all ensuing refinements.

b) Multipole refinements

Full data multipole refinements were carried out with the program VALRAY (Stewart, 1976; Stewart & Spackman, 1981). The total density in the asymmetric unit is assumed to be the sum of localized pseudoatom densities ρ_{at} . The density with respect to its nucleus of each pseudoatom p is given by:

$$\rho_p(\vec{r}_p) = \text{Pop}_p^{\text{sph}} \cdot \rho_p^{\text{sph}}(r_p) + \Delta\rho_p(\vec{r}_p) \quad (4)$$

with

$$\Delta\rho_p(\vec{r}_p) = \sum_{l=0}^l \sum_{m=0}^m [\sum_i \text{Pop}_p(l,m,i) \rho_p(l,r_p)] \cdot Y_{lm\pm}(\vartheta, \Phi) \quad (5)$$

r_p , ϑ , and Φ are polar coordinates of \vec{r}_p , $Y_{lm\pm}(\vartheta, \Phi)$ are Tesseral harmonics, and $\rho_p^{\text{sph}}(r_p)$ is the unperturbed spherical density of atom P, normalized to one electron. The index i in (5) indicates the option of using more than one radial deformation function per multipole order. The radial distribution functions $\rho_p(l,r_p)$ are chosen as Single Exponential Functions (SEF's) of the type:

$$\rho_p(l,r_p) = N_{n,l} \cdot r_p^n \exp(-\alpha_p l r_p) \quad \text{with } n \geq 1 \quad \text{and} \quad (6)$$

$$N_{n,l} = (1/4\pi) \alpha^{n+l+3} / (n+l+3)! \quad (7)$$

Each pseudoatom is considered to be a rigid entity. Therefore, the thermal motion is taken to be the same for all multipole functions assigned to one atom. Each atom was assigned one monopole, and all allowed α_l were treated as variables. Monopolar populations Pop^{Sph} were constrained to ensure neutrality. For Al_2O_3 , correlation of the extinction with the deformation parameters, in particular with the α 's, was obvious. Therefore, the extinction correction factor obtained from the all-data refinement was varied with proper damping throughout the multipole refinements. For Cu_2O the refined extinction corrections were negligible due to the correction on the basis of IAM. Crystallographic standard parameters, multipole populations, and α 's were varied in alternating cycles. This procedure improves convergence of the rather flexible multipole model, but leads to underestimated standard deviations. However, since all refinements were carried out in the same way, the e.s.d.'s can be considered to indicate the significance of the variables achieved for the respective data sets. Details of the refinements are summarized in Table 3.

All refinements were carried out in a straightforward way, systematic studies of the deformation model and/or weighting schemes were not attempted, since they are beyond the scope of this work. However, for both compounds we have also refined the deposited literature data of RS and LSF separately, using the same multipole models in order to avoid interpretation problems that might be caused by different modelling of the density (V.d.Wal, Vos & Kirfel, 1984). Thus, for both compounds the results may be biased by the models, refinement strategy, and reflection weighting. But, since for each compound the refinement conditions were kept constant, differing results may be safely attributed to the data rather than to their handling.

Deformation Properties

With the positional and thermal parameters from the multipole refinements, Fourier maps of interesting sections were calculated according to Stewart (1979). The dynamic deformation density is defined as:

$$\Delta\rho_{\text{dyn}}(\vec{r}) = (2/V) \sum \Delta F(\vec{h}) \cos(2\pi\vec{h}\cdot\vec{r}) \quad (8)$$

with

$$\Delta F(\vec{h}) = [K \cdot |F_o(\vec{h})| - |F(\vec{h})_{\text{IAM}}|] \exp[i\phi(\vec{h})_{\text{c}}^{\text{mult}}] \quad (9)$$

The static deformation density is obtained directly from direct space calculations according to:

$$\Delta\rho_{\text{stat}}(\vec{r}) = \sum_{\text{sym}} \sum_p [\rho_p(\vec{r}-\vec{r}_p) - \rho(\vec{r}-\vec{r}_p)_{\text{IAM}}] \quad (10)$$

where $\rho_p(\vec{r}-\vec{r}_p)$ is a pseudoatom density and $\rho(\vec{r}-\vec{r}_p)_{\text{IAM}}$ is the IAM density at site p.

Results and Discussion

a) Refinement results

Relevant refinement results are listed in Tables 4-6 and are discussed separately for Cu_2O and Al_2O_3 .

Cu_2O

Allowed hexadecapolar deformations on the oxygen atom turned out insignificant and were therefore omitted. All refinements converged readily to the values listed in Table 4. The results can be summarized briefly as follows:

- i) The anisotropy parameter $U_{12}(\text{Cu})$ is always negative indicating a preferred Cu vibration normal to $[11\bar{1}]$, the Cu-O bond axis, in agreement with expectation.
- ii) The "forbidden" (eeo)-reflections are predominantly determined by $U_{12}(\text{Cu})$. This can be seen in Fig. 4 which compares F_{obs} with the F_{c} contributions from both the anisotropic vibration and the deformation functions for some (eeo)-reflections after completion of refinement CULH. A more detailed analysis shows that the U_{12} contribution increases from about 70% for (221) to more than 85% for the high-order reflections. Thus, contrary to expectation the "forbidden" reflections contain only little information about $\Delta\rho(\text{Cu})$. This finding explains why the RS data (without (eeo)-reflections) refine successfully with respect to the Cu deformation. The Cu deformation parameters obtained from both CULH and RSH show a remarkable agreement. This indicates good quality of the synchrotron data as well as successful separation of charge redistribution and thermal smearing for both cases. Thus, we conclude that the (ooo)-reflections carry the main information. Measurement of the "forbidden" (eeo)-reflections is certainly helpful in fixing $U_{12}(\text{Cu})$ and the Cu deformation functions, but it is not decisive for a correct determination of these properties of Cu. In particular the quadrupolar deformation determining the electric field gradient at the Cu site (see below) turned out to be a rather stable property.

iii) The (eeo)-reflections are, however, important for the determination of the oxygen deformation. Table 4 (refinements RSH and RSA) shows that lack of (eeo)-reflections leaves the octapolar deformation on the oxygen atom practically undefined in agreement with RS, whereas inclusion of them yields a significant indication of a weak polarization of electron density towards the Cu atoms in agreement with the theoretical maps.

iv) The refined formal charge transfer from Cu towards oxygen varies between 0.54 and 0.72 electrons and is on average 0.61(9) electrons, the e.s.d. being derived from the scatter. This leads to a formal notation of $\text{Cu}_2^{+0.6}\text{O}^{-1.2}$ in agreement with chemical expectation.

v) The preparation of the joint data set was an attempt to combine the best of the tube and the synchrotron data. The strong reflections were certainly measured with greater accuracy by RS while the weak reflections were much better determined in the synchrotron experiment. In spite of the basic problem of merging data of such different origin, the refinement results indicate a successful combination of the virtues of both data sets, and they show that tube data can be enhanced and improved by additional measurements using synchrotron radiation.

vi) As one of the main results of this study this last point is emphasized in Fig. 5 which shows a F_{obs} vs F_{c} plot for all added (eeo) reflections after refinement CULH. Table 5 contains the corresponding structure factor list. The (eeo) agreement index of 0.068 (0.055 omitting (823)) shows the quality of the very weak reflection intensities which contribute information that could have never been obtained by conventional X-ray tube experiments.

vii) Table 4 contains also results of multipole refinements allowing for anharmonic vibration. The refined parameters are, however, not significantly different from those of the harmonic model. In particular, $U_{12}(\text{Cu})$ remained almost unaffected. An anharmonicity of the Cu vibration as discussed by RS cannot be supported by the present study.

viii) Finally, Table 4 gives refinement results obtained with the CUH data collected during high energy operation of DORIS II. These data are less complete and less accurate than CUL. Nevertheless, the refined parameters indicate the validity of the data reduction procedure and support our opinion that also under less favourable conditions reflection data can be obtained from a

synchrotron source with an accuracy sufficient at least for conventional structure analyses.

Al_2O_3

The conventional refinement (IAMS) (Table 6) converged after a few cycles to a surprisingly low agreement index $R(F) = 0.0107$ indicating only little anisotropic charge redistribution due to chemical bonding. 10 reflections had extinction correction factors $\gamma^{1/2} < 0.9$; the most affected reflections were (300) 0.64, (104) 0.70, and (204) 0.72. In full agreement with LSF the largest discrepancy occurred for reflection (006) as a consequence of the bond induced charge transfer ($F_{\text{obs}}/F_{\text{c}} = 16.20/12.18$ compared to $F_{\text{obs}}(\text{LSF}) / F_{\text{c}}(\text{LSF}) = 16.79/12.18$). The parallel refinement, IAMLSF, yielded $R(F) = 0.0177$ and $\text{GOF} = 3.79$.

The multipole refinements MUSY and MULSF converged readily to $R(F) = 0.0078$ and 0.0128, respectively. Agreement of the refined positional parameters is very good while the vibrational parameters obtained from MULSF are larger by 10(3)%. The formal charge transfer from Al towards oxygen was found different from both refinements; MUSY: 1.17(12) and MULSF 2.12(20) electrons. The first figure is in fair agreement with the charges obtained by LSF as well as by Ngo Thong & Schwarzenbach (1979) for AlPO_4 and SiO_2 .

The very advantage that the use of synchrotron radiation can offer becomes evident when analyzing the observed and calculated structure factors of both data sets after completion of the multipole refinement.

Fig. 6 shows the internal agreement between the observed structure amplitudes, $F_{\text{obs}}^{\text{c}}(\text{Syn})$ and $F_{\text{obs}}^{\text{c}}(\text{LSF})$, and between the corresponding calculated quantities, $F_{\text{calc}}^{\text{c}}(\text{Syn})$ and $F_{\text{calc}}^{\text{c}}(\text{LSF})$, as functions of $|F|$. For both cases the agreement factor is defined as $R_{\text{int}} = \sum |F(\text{Syn}) - F(\text{LSF})| / \sum |F(\text{Syn})|$, $F_{\text{obs}}^{\text{c}}$ being corrected for extinction. Both $R_{\text{int}}(F)$ are nearly equal and close to 0.01 for $10 < |F| < 80$. $R_{\text{int}}(F_{\text{obs}}^{\text{c}})$ for $|F| > 80$ is larger due to extinction. The strongest reflection (300) is omitted in Fig. 6, the respective quantities are $F_{\text{obs}}^{\text{c}}(\text{Syn}) = 138.01$, $F_{\text{calc}}^{\text{c}}(\text{Syn}) = 138.19$, $F_{\text{obs}}^{\text{c}}(\text{LSF}) = 131.3$, $F_{\text{calc}}^{\text{c}}(\text{LSF}) = 137.69$, indicating an insufficient extinction correction in the case of the LSF data. For $1 < |F| < 5$ there are considerable discrepancies expressed by $R_{\text{int}}(F_{\text{obs}}^{\text{c}}) > 0.13$ due to the obvious impossibility of obtaining weak reflection intensities more accurately with tube radiation. For this latter range of struc-

ture amplitudes $R_{\text{int}}(F_{\text{calc}}^{\text{c}})$ is close to 0.02, and less for all other reflections, showing the statistical equivalence of the two refined models. Similar to Fig. 5 an $F_{\text{obs}}^{\text{c}}$ vs $F_{\text{calc}}^{\text{c}}$ comparison for reflections with $|F| < 3$ and for both types of radiation is given in Fig. 7.

b) Deformation properties

Cu_2O

As described by RS, omission of the "forbidden" (eeo) and unobserved (oeo) reflections leads to a pseudo-translation effect (Cu atoms by $1/2, 1/2, 1/2$, O atoms by $1/2, 1/2, 0$) in the difference density maps, i.e. features around Cu and O are repeated at empty sites. On inclusion of calculated structure factors for the missing reflections the effect disappeared, and RS concluded that the combined contribution of those weak reflections is not negligible. The dynamic deformation density obtained after refinement JOIN (Fig. 8a) shows this to be true, no pseudo-translation effects are detectable.

All features of the corresponding residual density (Fig. 8b) are smaller than $0.15 \text{ e}/\text{\AA}^3$ indicating that the observations were well modelled and scaled.

The main result of Fig. 8a is a significant charge depletion at the Cu site. This trough is elongated along the Cu-O bond and accompanied by symmetric charge accumulations off the bond on the [001] direction. The same feature is reproduced in the very similar static deformation density distributions resulting from both CULH and RSH, respectively (Figs. 8c,d). These maps show the model deformation density after deconvolution of thermal smearing. In keeping with the similar refinement results these maps are also very similar. This applies as well to the corresponding maps obtained after the anharmonic refinements CULA and RSA which are omitted since they reveal the same patterns. The prominent features of Figs. 8e,d are a "cross" of charge depletion parallel [111] together with a second "cross" of charge accumulation parallel [001]. This picture becomes clearer upon omission of the monopolar deformation functions as shown in Figs. 8e,f. Exactly those characteristics were obtained from both LAPW band structure calculations by Marksteiner, Blaha & Schwarz (1986) and cluster calculations by Nagel (1985). The main difference between the theoretical maps and Figs. 8e,f is found in the positive lobes. The former show smaller lobes of equal heights while the experimental densities reveal a preferred charge accu-

mulation along [001]. This skewed pattern was already obtained by RS and is reproduced by the completely independent synchrotron data. Consequently, it seems very likely that this is not an artifact, but implies some interaction in the crystal which is not taken into account by the quantum mechanical calculations.

Al₂O₃

Figs. 9 a - d show the static model deformation density distributions resulting from the independent multipole refinements MUSY and MULSF, respectively. The plane (0,1,1,0) of Figs. 9 a and b contains the Al atom in the center and the oxygen atom at x, 0, 1/4 on a diad axis normal to [001]. The symmetry equivalent oxygen atom at z = 5/12 is 0.12 Å out of the plane. The long bond (1.972 Å) points towards the face shared by adjacent oxygen octahedra, the short bond (1.855 Å) towards the unshared face. Both faces can be seen in Figs. 9 c and d, showing the plane (0001) which contains the oxygen atom layer at z = 1/4. The c-axis in the middle of the map runs through the center of the shared face. Thus, the two planes are identical to those published by LSF.

The deformation models obtained from the LSF and synchrotron data possess common features, but show also some disturbing differences which are most likely caused by extinction problems. Common to both models is the charge migration from Al towards O, the polarization of the latter towards Al, especially on the long bond, and the appearance of an oxygen deformation outside the shared face (Figs. 9 c, d). Combining the information of both planes the deformation of the oxygen valence shell takes the form of a sp³ hybrid. While the symmetry related charge accumulations on the long bonds are at most 0.15 e/Å³ and clearly resolved in the MUSY map, they are about twice as large and smeared out to a banana shape in the MULSF map. This latter finding agrees well with the maps published by LSF and is similar to the results of Tsirelson, Antipin, Gerr, Ozerov & Struchkov (1985). This smeared deformation density appears in Fig. 9d as a third density lobe directed towards the center of the shared face, where the deformation density almost vanishes. The lack of such lobes in Fig. 9c is thus due to the resolved density lobes in Fig. 9a rather than to conflicting density models.

A further difference is found for the Al atom. The quadrupolar deformations possess opposite sign and are differently developed for the two data sets.

In order to check whether the observed differences are artifacts introduced by the model, conventional difference density maps were calculated for both data sets. These maps are omitted because they show essentially the same features as Figs. 9 so that correct modelling of the information contained in the respective data sets can be inferred. Hence, the differences must be attributed to the data and their extinction corrections, not to their refinements.

c) Electric field gradient

Cu₂O

The electric field gradient (EFG) tensor at the Cu site is characterized by one component, ∇E_{zz} (z along [111]). From NQR-measurements by Krueger & Meyer-Berkhout (1952) one of the largest known field gradients, $|\nabla E_{zz}| = 134 \cdot 10^{20} \text{ Vm}^{-2}$, is obtained (RS). According to an ionic point-charge model (Hafner & Nagel, 1983) the sign of ∇E_{zz} is positive, whereas the cluster calculation by Nagel (1985) favors the opposite. The EFG results reported by RS are very model dependent with both negative and positive signs, their numerical values were disappointingly off the NQR-result.

Values for the EFG were determined by direct space calculations according to Stewart (1979) and are included in Table 4. All refinements produced EFG's with positive sign and unexpectedly good numerical agreement with the NQR-value of $134 \cdot 10^{20} \text{ Vm}^{-2}$. Even the EFG from the less accurate CUH data is in the vicinity of this figure. The true relative e.s.d. was estimated to be about 60% by performing an additional dummy refinement cycle in which simultaneous variation of all model parameters was allowed. In spite of this large uncertainty it is thus found that the X-ray data do indeed contain information about the EFG at the Cu site.

Al₂O₃

The electric field gradients at both the Al and the oxygen site are known from NQR-measurements. Due to the site symmetry 3, the EFG at Al is determined by one component, $\nabla E_{33}(\text{Al})$. The EFG at the oxygen position can be described by three figures, i.e. the largest eigenvalue $\nabla E_{zz}(\text{O})$, the angle α subtended by the corresponding principal axis z and c₀, and the asymmetry parameter $\eta = (\nabla E_{xx} - \nabla E_{yy}) / \nabla E_{zz}$. From the NQR-results LSF calculated these figures to:

$\nabla E_{33}(\text{Al}) = -6.55 \cdot 10^{20} \text{ Vm}^{-2}$, $\nabla E_{zz}(\text{O}) = +34.9 \cdot 10^{20} \text{ Vm}^{-2}$, $\alpha = 45.85^\circ$, and $\eta = 0.517$.

The corresponding values ($\cdot 10^{-20} \text{ Vm}^{-2}$) obtained from direct space calculations for the models MUSY and MULSF (the latter in parentheses) are: $\nabla E_{33}(\text{Al}) = -27 (+24)$, $\nabla E_{zz}(\text{O}) = -12.5 (+4)$, $\alpha = 50.2^\circ (53.4^\circ)$, and $\eta = 0.67 (0.31)$. For $\nabla E_{33}(\text{Al})$ both moduli are too large, but model MUSY exhibits the correct sign, whereas model MULSF gives the wrong sign similar to results obtained by LSF using an anisotropic extinction correction. For the oxygen atom (with the larger EFG) the situation is reversed: both moduli are too small, and now MULSF gives the correct sign. Common to both data sets is the correct determination of shape and orientation of the EFG tensor. Therefore, the EFG results are inconclusive. Without theoretical calculations there is hardly a basis to extract more information or to discriminate between both refined models.

Summary and Conclusions

This work was intended as a feasibility study in order to assess the accuracy of single crystal reflection intensities measured at a synchrotron radiation source, given the normal beam time allowance of ≤ 7 days. In order to permit a rigorous cross-checking against existing tube data, Cu_2O and Al_2O_3 were chosen due to the availability of high quality electron density analyses, and the data were collected at the same wavelengths as the careful and time consuming tube experiments. Emphasis was put primarily on the experiment and the ensuing data reduction procedure rather than on systematic and thorough electron density studies with their inherent problems. The deformation density properties of both compounds were evaluated in a straightforward manner and yielded in general satisfactory agreement with the reference results. Differences in details are mainly due to the data treatment and in part to the refinement models. The judgement about the electron density results is thus left to the reader, while the following more general conclusions concerning the use of synchrotron radiation can be drawn from the present results:

- i) The specific properties of synchrotron radiation cause no serious problems in single crystal diffractometry. All relevant results indicate that in spite of the relatively fast data collection complete sets of structure amplitudes can be derived whose quality is well comparable with careful tube measurements, provided that there are stable beam conditions, and that proper attention is given to the performance of the experiment and to the data reduction. With respect to experimental strategy and data evaluation one can therefore be confident about the general feasibility of accurate structure analyses using synchrotron radiation. This result is of interest whenever crystals are to be studied at a specific wavelength, or when a short wavelength is deliberately chosen in order to reduce absorption, extinction and polarization effects.
- ii) Compared to tube measurements nothing is gained in the measurement of strong or medium intensity reflections, since for them the signal/noise ratio does not profit from the small beam divergence. Those reflections can be measured more conveniently and at much lower costs in the home laboratory. Using synchrotron radiation, it should also be noted, that any filtering of primary beam intensity means giving away valuable beam time, and simulta-

neously introducing unnecessary errors into the data reduction. These arguments do, however, not hold in the case of

- selected measurements of strong reflections at various wavelengths in order to improve the data by experimental assessment of extinction effects;
- new technical developments like faster counters which may eventually lead to considerable time savings in collection of stronger reflections.

iii) Improvement of data can also be achieved by increasing the reliability of weak reflections. For those, Figs. 5 and 7 give one clear answer to the question when synchrotron radiation may be used most profitably in structure analyses. Since for synchrotron radiation there are virtually no "unobserveds", and since data carry similar uncertainties over a wide intensity range, the keyword is measurement of intensities which - in the home laboratory - are unobservable or close to unobservability because of large statistical errors. More accurately measured weak reflections will not only decrease the statistical noise in the refinements and Fourier maps, but will also alter the weighting scheme in favor of the high-order reflections (giving results closer to a high-order refinement). A data set comprising reflections with similar relative e.s.d.'s will provide an increased effective resolution and an improved determination of the crystallographic standard parameters. This is of special importance for electron density analyses which require unbiased promolecule parameters for a successful separation of bonding effects. Since the collection of weak reflections is possible at a synchrotron radiation source, such measurements are first class candidates for a sensible single crystal X-ray diffraction experiment. With respect to accurate crystal structure analysis we therefore conclude that enhancement of conventionally collected data by synchrotron radiation measurements of selected reflections provides a very economical and promising method for future work.

The financial support for this work, granted by the Bundesminister für Forschung und Technologie is gratefully acknowledged. We are also indebted to D. Schwarzenbach for constructive discussions and to J. Sandoz et fils, SA, CH-1482 Cugy, Switzerland, for the Al_2O_3 samples.

References

- Arndt, U.W. (1978). J.Phys.E, **11**, 671-673.
- Bachmann, F., Kohler, H., Schulz, H. & Weber, H.P. (1985). Acta Cryst., **A41**, 35-40.
- Becker, P. & Coppens, P. (1974 a). Acta Cryst., **A30**, 129-147.
- Becker, P. & Coppens, P. (1974 b). Acta Cryst., **A30**, 148-153.
- Blessing, R.H., Coppens, P. & Becker, P.J. (1972). J. Appl. Cryst., **Z**, 488-492.
- Chipman, D.R. (1969). Acta Cryst., **A25**, 209-214.
- Clementi, E. & Roetti, C. (1974). Atomic Data and Nuclear Data Tables, Vol. **14**, No. 3-4. New York: Academic Press.
- Cromer, D.T. & Liberman, D.A. (1971). J. Chem. Phys., **53**, 1891-1898.
- Dwiggins, C.W. (1975). Acta Cryst., **A31**, 395-396.
- Eichhorn, K. (1987). Program REDUCE: Data Reduction of Step-Scan-Measured Reflection Profiles for both Neutrons and X-Rays. DESY/HASYLAB, unpublished.
- Hafner, S. & Nagel, S. (1983). Phys. Chem. Miner., **9**, 19-22.
- Hallberg, J. & Hanson, R.C. (1970). Phys. Status Solidi, **42**, 305-310.
- International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
- Kirfel, A., Will, G. & Stewart, R.F. (1983). Acta Cryst., **B35**, 2291-2300.
- Kirfel, A. (1987). Acta Cryst., **B43**, 333-343.

Krueger, H. & Meyer-Berkhout, K. (1952). Z. Phys., **132**, 171-178.

Kupcik, V., Wendschuh-Josties, M., Wolf, A. & Wulf, R. (1986). Nucl. Instrum. Methods, **A246**, 624-626.

Kurki-Suonio, K. (1977). Isr. J. Chem., **16**, 115-123.

Landoldt-Boernstein, Ed. Hellwege, K.-H. (1966). Neue Serie III-1, p.13.
Berlin: Springer Verlag.

Lehmann, M.S. & Larsen, F.K. (1974). Acta Cryst., **A30**, 305-310.

Lewis, J., Schwarzenbach, D. & Flack, H.D. (1982).
Acta Cryst., **A38**, 733-739.

Marksteiner, P., Blaha, P. & Schwarz, K. (1986). Z. Phys., **B64**, 119-127.

Merisalo, M. & Kurittu, J. (1978). J. Appl. Cryst., **11**, 179-183.

Mullen, D. & Fischer, K. (1981). Z. Kristallogr., **156**, 85-86.

Nagel, S. (1985). J. Chem. Phys. Solids, **46**, 743-756.

Ngo Thong & Schwarzenbach, D. (1979). Acta Cryst., **A35**, 658-664.

Nielsen, F.S., Lee, P. & Coppens, P. (1986). Acta Cryst., **B42**, 359-364.

Restori, R. & Schwarzenbach, D. (1986). Acta Cryst., **B42**, 201-208.

Smend, F., Schaupp, D., Czerwinski, H., Millhouse, A.H. &
Schenk-Strauss, H. (1984). DESY Internal Report SR-84-003.

Stewart, R.F. (1979). Chem. Phys. Lett., **65**, 335-342.

Stewart, R.F. (1976). Acta Cryst., **A32**, 565-574.

Stewart, R.F. & Spackman, M.A. (1981). VALRAY Users Manual.
Preliminary Draft. Department of Chemistry, Carnegie-Mellon University,
Pittsburgh PA 15213.

Tsirelson, V.G., Antipin, M.Yu., Gerr, R.G., Ozerov, R.P. & Struchkov, Yu.T. (1985).
Phys. Stat. Sol. (a) **87**, 425-433.

Wal, R.J. van der, Vos, A. & Kirfel, A. (1987). Acta Cryst., **B43**, 132-143.

Wulf, R. & Wenschuh-Josties, M. (1989). J. Appl. Cryst., in the press.

Figure Captions

Fig. 1 : Reflection (220) of Cu_2O recorded with both synchrotron radiation (circles) and $\text{AgK}\alpha$ -tube radiation (triangles), on logarithmic scale.

Fig. 2 : Intensity of the Cu_2O check reflection (511) as a function of the monitor counts for a) $t_m = 0$, b) $t_m = 16$, and c) $t_m = 30$ μs effective monitor dead time (counter dead time 8 μs). Note that monitor counts decrease during a fill.

Fig. 3 : Relative error $\Delta P/P$ in the polarization factor for a 10% change in the degree of polarization Q (defined in the text) as a function of the scattering angle 2θ .

Fig. 4 : Structure factors of the low-order "forbidden" (eeo)-reflections of Cu_2O . F_{obs} to the left, F_{calc} to the right, giving contributions from $U_{12}(\text{Cu})$ and $\Delta\rho(\text{Cu}_2\text{O})$ (full black) separately.

Fig. 5 : Plot of F_{obs} vs F_{calc} for all "forbidden" (eeo)-reflections of Cu_2O after refinement CULH (Tables 4,5).

Fig. 6 : Comparison of synchrotron and tube data of Al_2O_3 . Internal agreement of corresponding extinction corrected F_{obs}^c and F_{calc}^c , respectively. The number of contributors is given on top of each column.

Fig. 7 : Plot of F_{obs} vs F_{calc} for weak Al_2O_3 reflections ($|F| < 3$). Crosses: X-ray tube, circles: synchrotron data.

Fig. 8 : Electron density maps for Cu_2O in the plane (110). Horizontal axis: [110], vertical axis: [001]. O-Cu-O bonds along [111] are indicated.

a) dynamic deformation density $\Delta\rho$, from refinement JOIN

b) corresponding residual density, $s_{\text{max}} = 0.85 \text{ \AA}^{-1}$

c, d) static model deformation densities from CULH and RSH, respectively. Monopoles have been included.

e, f) as c and d, monopoles omitted.

Contours at 0.05 e\AA^{-3} (0.1 for a), negative broken, positive full.

Fig. 9 : Static model deformation density maps for Al_2O_3

a, b) plane (010) through Al in (0, 0, z) and O in (x, 0, 1/4)

c, d) plane (001) through oxygen layer at $z = 1/4$

a, c) synchrotron data (MUSY)

b, d) X-ray tube data (MULSF)

Monopoles included; contours at 0.025 e\AA^{-3} , negative broken, positive full lines.

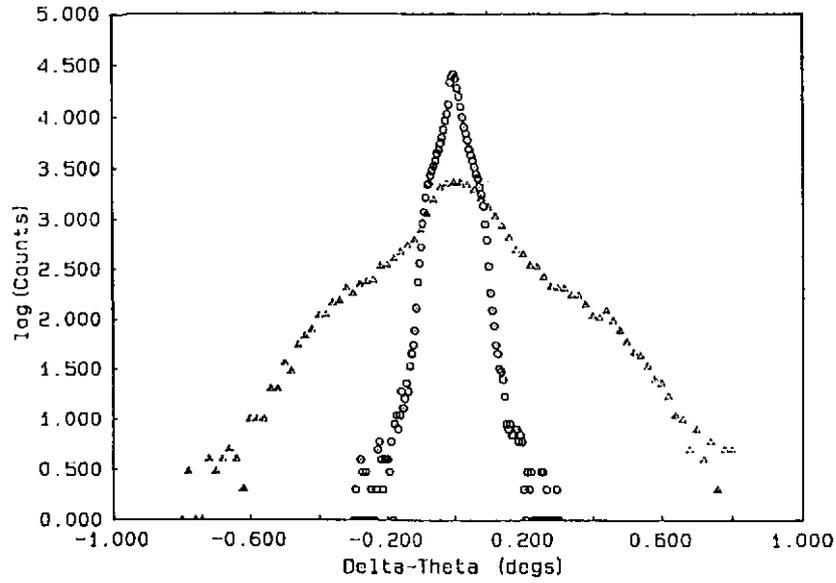


Fig. 1

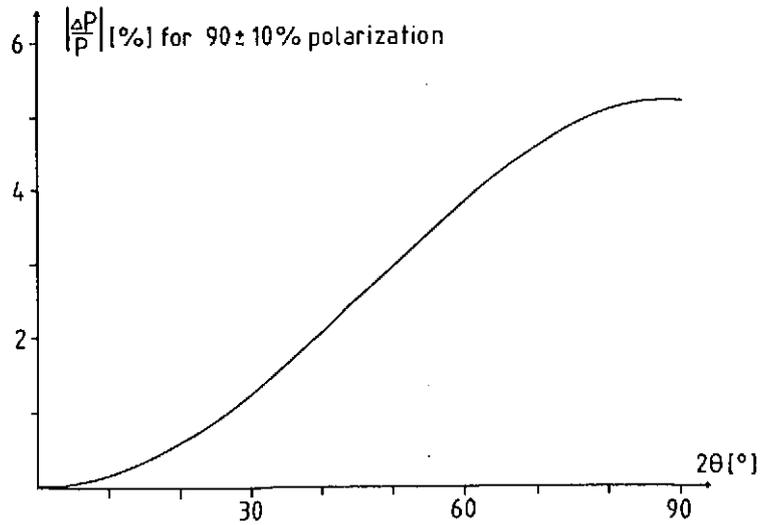


Fig. 3

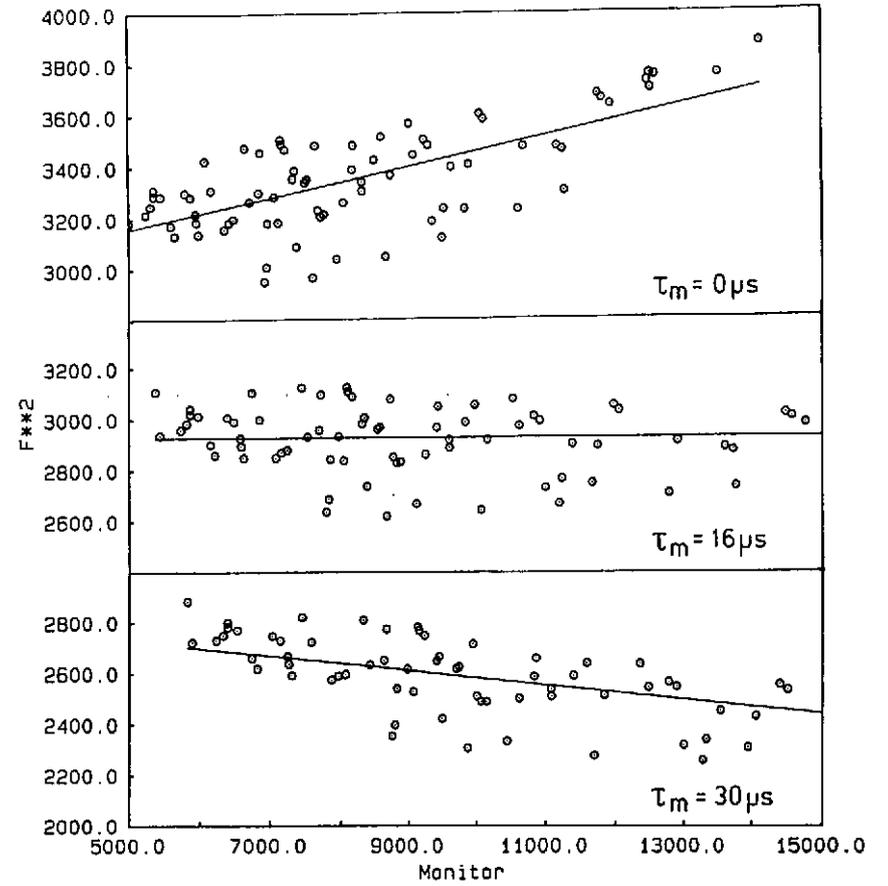


Fig. 2

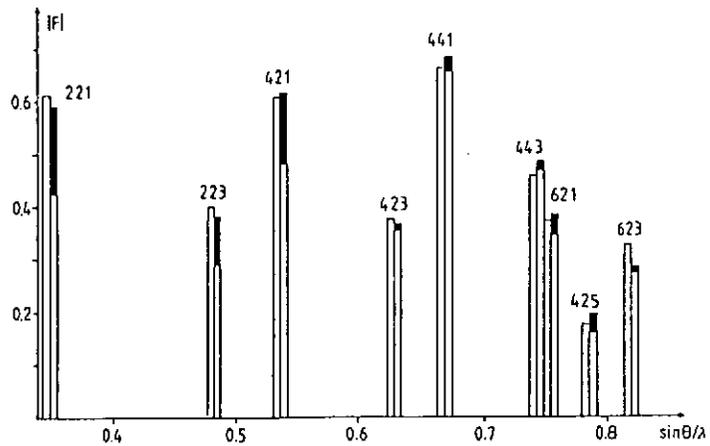


Fig. 4

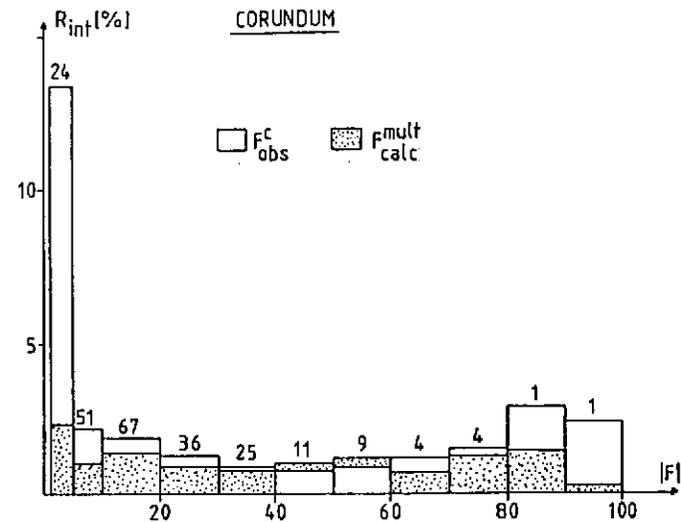


Fig. 6

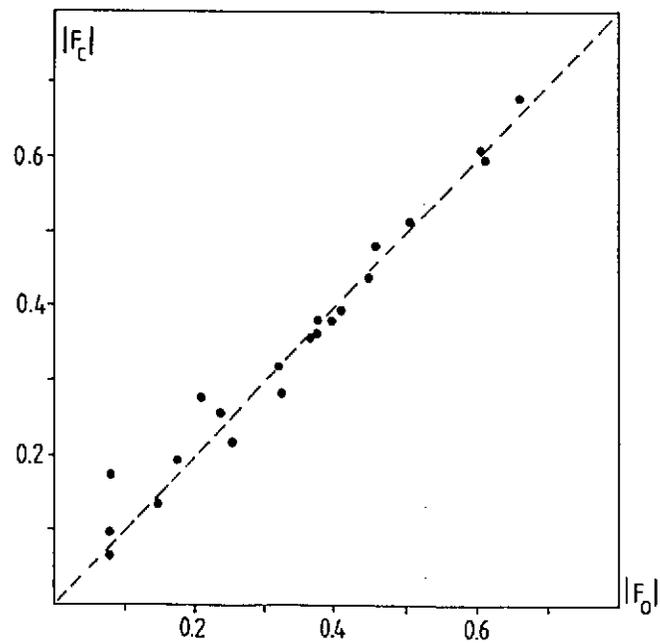


Fig. 5

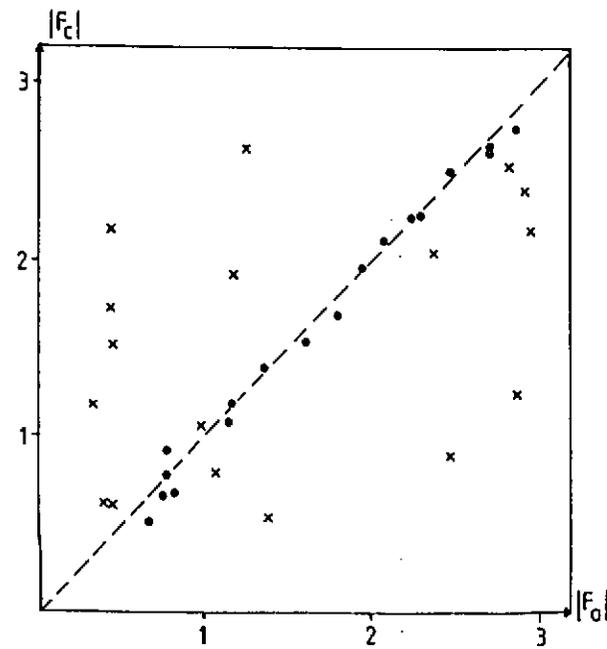
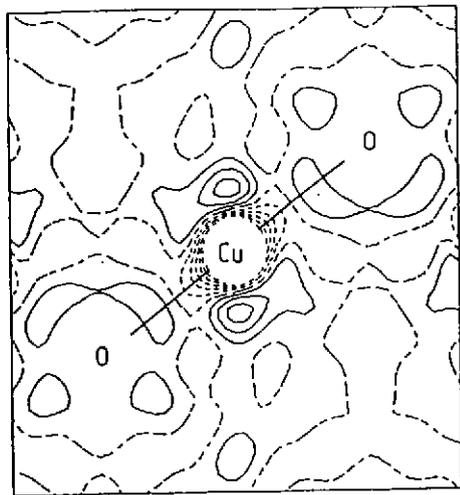
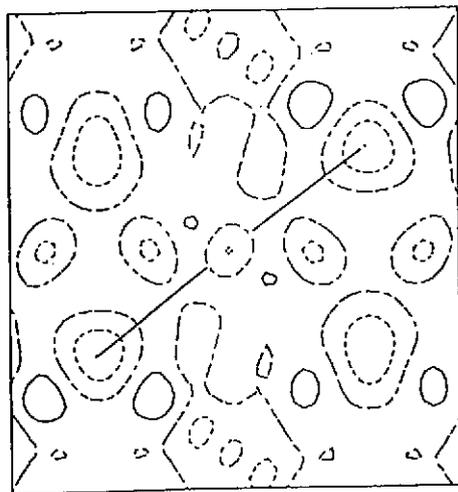


Fig. 7

Fig. 8

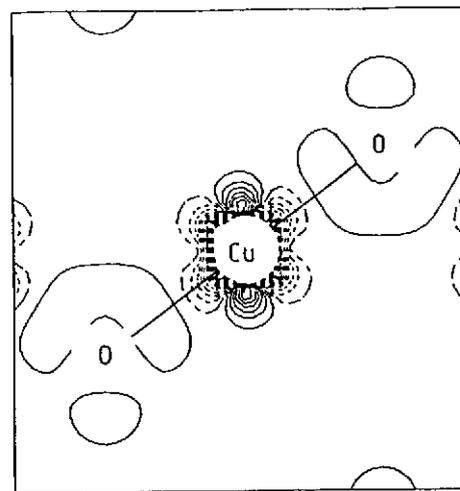


a)

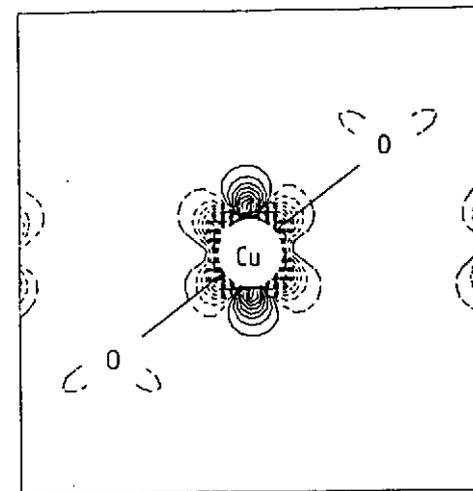


b)

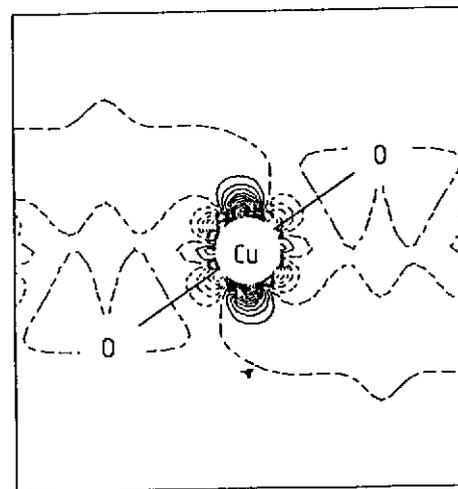
Fig. 8



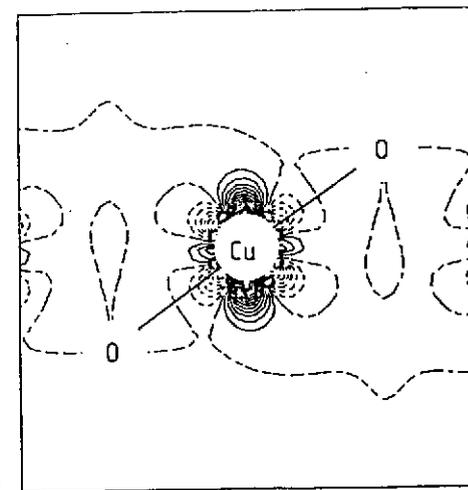
c)



d)

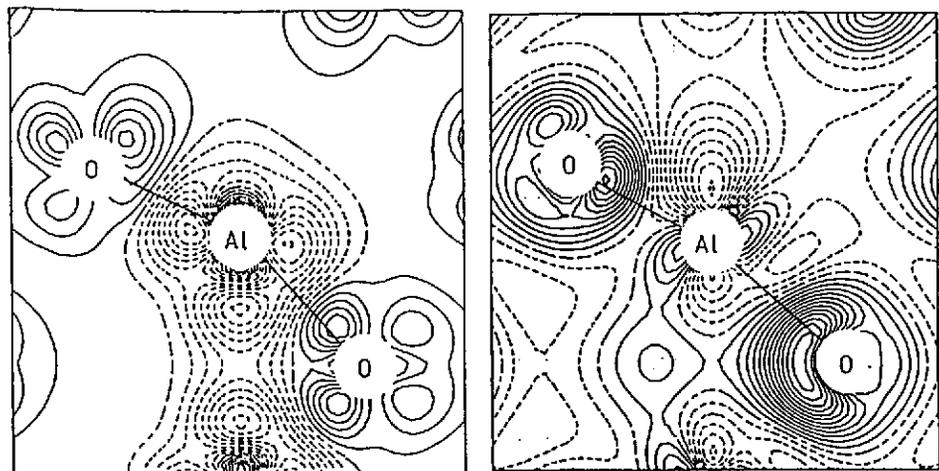


e)



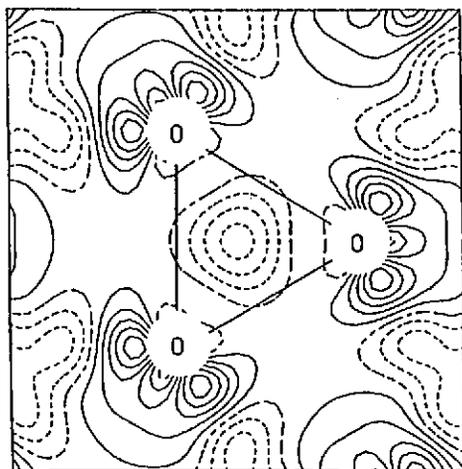
f)

Fig. 9

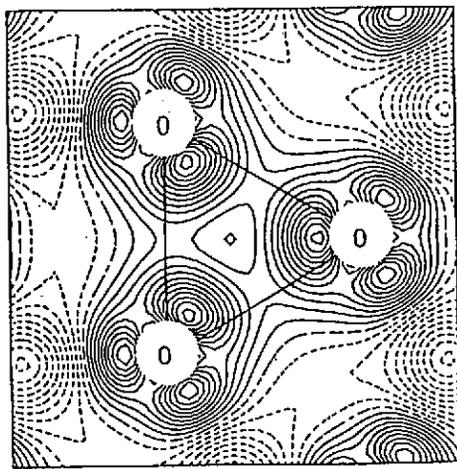


a)

b)



c)



d)

Table 1: Crystallographic data

	Cuprite, Cu_2O	Corundum, $\alpha - \text{Al}_2\text{O}_3$
	cubic	hexagonal
a_0 A	4.2685(5)	4.7570(6)
c_0		12.9877(35)
V_c A^3	77.773	254.52
S.G.	$\text{Pn}\bar{3}\text{m}$ (No. 224)	$\text{R}\bar{3}\text{c}$ (No. 167)
Z	2	6
Atoms	Cu 4b (0,0,0; $\bar{3}\text{m}$) O 2a ($1/4, 1/4, 1/4$; $\bar{4}3\text{m}$)	Al 12c (0,0,z; 3) O 18e (x,0,1/4; 2)
M_r g	143.09	101.96
d_x Mg/m^3	6.104	3.983
$\mu(\text{AgK}\alpha)$ mm^{-1}	13.881	0.657
$\mu\text{-R}$	1.20	0.065

Table 2: Data collection and processing (CUL and CUH refer to dedicated and parasitic modes, respectively)

Instrument	5-circle diffractometer, HASYLAB		
Monochromator	flat double crystal, Ge(111)		
Collimator	1 mm diameter		
Det.-aperture	2 x 2 mm; 3 x 3 mm (CUH)		
Det.-Sample dist.	248 mm		
	<u>Cuprite, Cu₂O</u>	<u>Corundum, Al₂O₃</u>	
Sample	natural, spherical	synthetic, spherical	
Diameter	0.173(2) mm	0.200 mm	
Temperature	ambient (295 K)		
	<u>CUL</u>	<u>CUH</u>	
Wavelength (Å)	0.5599(1)	0.5616(1)	0.5599(1)
(sinθ/λ) _{max}	1.40	1.25	1.024
Scan mode	ω - 2θ step scans		
Steps	121	121	91
Scan angle 2θ (°)	1.2	1.2	0.63
Scan speed (°/min)	0.2-1.2	0.2-1.2	0.277 - 1.40
Check reflections	(5,1,1)		(3,3,+18)
Monitor interval	30 min and begin of a fill		
No. of reflections measured	342	324	1758
No. unique	133	134	259
No. unobs	9 (I < 3σ)	20 (I < 2σ)	none (I < 3σ)
R _{int} (F)		0.017	0.014
R _{int} (I)		0.028	0.032

Table 3: Details of the multipole refinements on Cu₂O and Al₂O₃.

$$\text{Function minimized: } Q = \sum_h w_h [F_o(h) - k \cdot Y(h)^{1/2} \cdot F_c(h)]^2$$

$$F_{\text{obs}}\text{-weights: } w_h = [\sigma^2(F) + (P \cdot F)^2]^{-1}$$

Deformation functions: SEF of type $r^n \exp(-\alpha_l r)$, normalized to 1 electron for $l = 0$

	l-values	0	1	2	3	4
Cu	n	3		2		4
	α _{l,0}	5.0				
Al	n	5	2	2	3	4
	α _{l,0}	4.5				
O	n	3	2	2	3	4
	α _{l,0}	4.5				

Constraints

Cu₂O: Pop(sph,Cu) : Pop(sph,O) = 29 : 8
 Pop(0,Cu) = -0.5 Pop(0,O)

Al₂O₃: Pop(sph,Al) : Pop(sph,O) = 13 : 8
 Pop(0,Al) = -1.5 Pop(0,O)

α_{l,0} are the starting values for all multipole orders.

Table 4: Cu₂O-refinement results, U_{ij} ($\cdot 10^5 \text{ \AA}^2$). See text for details.

	CULH	CULA	CUHH	RSH	RSA	JOIN
Cu U ₁₁	1917(6)	1908(6)	1975(7)	757(1)	757(1)	1900(4)
U ₁₂	-83(1)	-81(1)	-86(2)	-31(2)	-28(2)	-84(1)
Q	-.43(2)	-.46(2)	-.33(7)	-.37(15)	-.33(4)	-.38(2)
$\alpha(2)$	3.95(8)	3.89(6)	3.88(6)	3.67(23)	3.92(20)	4.20(20)
H1	.23(5)	.20(4)	.61(14)	.33(15)	.37(20)	.28(6)
H2	.10(9)	.18(7)	.13(13)	.18(3)	.20(4)	.20(11)
$\alpha(4)$	7.4(4)	7.3(3)	7.3(4)	6.8(2)	6.4(2)	7.0(3)
O U _{iso}	1879(7)	1891(7)	1958(17)	827(8)	828(8)	1880(7)
Oct	-9.4(1.8)	-8.8(1.6)	0(3)	-8.8(8.0)	-2(3)	-9.4(1.9)
$\alpha(3)$	2.46(8)	2.52(8)	4(32)	2.5(5)	3(1)	2.44(8)
CT	.68(14)	.72(14)	.42(22)	.54(4)	.58(4)	.56(11)
∇E_{zz}	135(6)	140(6)	104(22)	127(7)	144(7)	131(7)
P	0.02	0.02	0.02	0.0	0.0	0.02
R	0.0173	0.0168	0.0188	0.0065	0.0065	0.0106
R _w	0.0296	0.0285	0.0523	0.0056	0.0056	0.0281
GOF	1.05	1.05	1.08	0.91	0.91	1.09
NO	123	123	111	129	129	170
NV	15	20	15	15	20	15

Table 5: Structure factors of "forbidden" (eeo)-reflections of Cu₂O, after refinement CULH.

hkl	F _{obs}	F _{calc}
221	0.603(3)	0.590
223	0.398(8)	0.376
225	0.147(37)	0.138
227	0.078(39)	0.068
421	0.600(5)	0.611
423	0.376(16)	0.370
425	0.175(25)	0.198
427	0.078(44)	0.102
441	0.661(5)	0.685
443	0.457(7)	0.487
445	0.208(64)	0.282
621	0.372(4)	0.382
623	0.324(14)	0.283
641	0.506(6)	0.515
643	0.411(15)	0.397
645	0.235(19)	0.258
661	0.447(7)	0.436
663	0.368(12)	0.353
821	0.254(18)	0.218
823	0.078(44)	0.174
841	0.319(14)	0.316

Agreement index R(F) = 0.068 (0.055 omitting (823)).

The temperature factor expression is $\exp[-2\pi^2 \sum \sum U_{ij} h_i h_j a_i^* a_j^*]$.

CT = charge transfer in electrons from Cu towards O,

∇E_{zz} = electric field gradient ($\text{Vm}^{-2} \cdot 10^{-20}$) along Cu-O at Cu site.

CULH = synchrotron data, dedicated operation, harmonic, $s_{\text{max}} = 1.40 \text{ \AA}^{-1}$
 CULA = synchrotron data, dedicated operation, anharmonic, $s_{\text{max}} = 1.40 \text{ \AA}^{-1}$
 CUHH = synchrotron data, parasitic operation, harmonic, $s_{\text{max}} = 1.25 \text{ \AA}^{-1}$
 RSH = 100 K tube data as deposited by RS, harmonic, $s_{\text{max}} = 1.50 \text{ \AA}^{-1}$
 RSA = 100 K tube data as deposited by RS, anharmonic, $s_{\text{max}} = 1.50 \text{ \AA}^{-1}$
 JOIN = room temp. joint data (see text), harmonic, $s_{\text{max}} = 1.50 \text{ \AA}^{-1}$