

## A Charge Density Study of Copper by $\gamma$ -ray Diffractometry on Imperfect Single Crystals†

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### Abstract

19 absolute atomic scattering factors were measured for imperfect copper single crystals with an accuracy of the order of  $\pm 0.05$  electrons for reflections with  $\sin \theta/\lambda \leq 0.7 \text{ \AA}^{-1}$ . This data set is of significantly higher accuracy than those measured earlier with X-rays for imperfect single crystals. The experimental form factors for low momentum transfer are significantly smaller than the free-atom values. The corresponding deformation density shows a small pile up of charge between nearest-neighbour atoms. At the present level of experimental accuracy, none of the available band-structure calculations provides a satisfactory description of the measured form factors over the whole range of momentum transfer where effects due to bonding can be expected.

### Introduction

Crystalline copper has for many years provided a testing ground for the theoretical understanding of the electronic structure of the non-simple elements, *i.e.* metals involving *d* bands. The long-standing and continuing interest in this transition metal is mainly because optical data show clear structure which is unobscured by collective excitations (plasmons); Fermi-surface data of very high precision are available; Cu is light and therefore relatively uncomplicated by relativistic effects; it is nonmagnetic; and its face-centred-cubic crystal structure is tightly packed, which makes the theoretically convenient muffin-tin approximation justifiable.

Recently, Knapp, Himpsel & Eastman (1979) determined the energy band dispersions  $E_n(\mathbf{k})$  for both valence and conduction band states of copper from angle-resolved photoemission data with polarized synchrotron radiation. Since photoemission involves both the initial and the final states, an analysis of such data requires an accurate model for the final-state bands.

Knapp *et al.* (1979) used calculated final bands from a two-parameter, self-consistent calculation proposed by Janak, Williams & Moruzzi (1975). The first parameter in this theory, the exchange coefficient  $\alpha$  appearing in Slater's  $X\alpha$  theory, is adjusted so that the ground-state energy bands generate the measured Fermi surface. The second parameter, the electron–electron contribution to the effective mass  $m^*$  appearing in the Sham–Kohn local density theory of excitations, is adjusted to optical absorption data. Although this band calculation was not fitted to the angle-resolved photoemission data of Knapp *et al.* (1979), the agreement between experimental and theoretical energy-band dispersions is very good.

Based on their more extended angle-resolved photoemission measurements, Thiry, Chandesris, Lecante, Guillot, Pinchaux & Pétroff (1979) reanalysed  $E$  vs  $\mathbf{k}$  for Cu with a free-electron-like model for the final state bands. They found very good agreement between experiment and the band-structure calculation of Burdick (1963), who used the augmented plane wave (APW) method and a potential originally suggested by Chodorow (1939). More recently, Bagayoko, Laurent, Singhal & Callaway (1980) performed a self-consistent calculation of the band structure of copper with a basis of Gaussian orbitals and a local exchange correlation potential. The authors find again very satisfactory agreement with the experimental results of Thiry *et al.* (1979), except for the lowest band.

The agreement between different experimental and theoretical energy-band dispersions for Cu is in general of the order of  $\leq 0.2$  eV, which represents a very satisfactory result. On the other hand, it is well known that, as a general feature of variational band-structure calculations, a first-order error in the wavefunction gives rise to only a second-order error in the energy so that good eigenvalues may be obtained with wavefunctions of somewhat poorer quality. Therefore, an experimental check of theoretical ground-state wavefunctions together with a test of the energy-band dispersions calculated within one and the same theoretical scheme would be very interesting. One way to check the theoretical ground-state wavefunctions  $\psi_0(\mathbf{r})$  of a crystalline solid is to compare the calculated

† Dedicated to Professor Dr H. Maier-Leibnitz, Munich, on the occasion of his 70th birthday.

and the measured structure factor  $F_{\mathbf{H}}$  for various reciprocal-lattice points  $\mathbf{H}$ :

$$F_{\mathbf{H}} = \int |\psi_0(\mathbf{r})|^2 e^{i2\pi\mathbf{H}\cdot\mathbf{r}} d\mathbf{r}.$$

In the free-atom model of a solid the geometrical structure factor  $F_{\mathbf{H}}$  relates the scattering power  $f$  of the individual atoms, which is a continuous function of momentum, to the scattering power of the unit cell. Referring to the usual cubic unit cell, one obtains for a f.c.c. lattice with identical atoms the relationship  $F_{\mathbf{H}} = 4f(\mathbf{H})$ . Following normal practice in the literature, when we compare experimental and theoretical atomic scattering factors or form factors  $f(\mathbf{H})$  we simply mean the quantity  $F_{\mathbf{H}}/4$ . Because the energy of the electromagnetic radiation of 412 keV used in  $\gamma$ -ray diffractometry is much higher than any electron binding energy in the atom the effect of anomalous dispersion need not be considered.

Arlinghaus (1967) recalculated the band structure of Cu along the lines given by Burdick (1963), but he extended his calculations to provide theoretical atomic form factors, which allow an experimental test of the ground-state wavefunctions used in the calculation. The two papers can be considered together and represent a complete study of the electronic structure of Cu. In their band-structure calculations of Cu, Bagayoko *et al.* (1980) went an important step further by calculating the energy-band dispersions, the atomic form factor (Bagayoko, 1980) and the Compton profiles. The latter quantity contains information which is complementary to the atomic form factor and thus the charge density  $\rho(\mathbf{r}) = |\psi_0(\mathbf{r})|^2$ , because it is related to the off-diagonal elements of the spin-free one-electron density matrix (Smith, 1980). Because of the availability of complete band-structure calculations and the experimental  $E$  vs  $\mathbf{k}$  data, Cu is an ideal system for an experimental study of the electron distribution.

Inspection of various theoretical structure factors deduced from different band-structure calculations for a given solid reveals differences in  $F_{\mathbf{H}}$  of the order of 2% or less for Bragg reflections of  $\sin \theta/\lambda = |\mathbf{H}|/2 \leq 0.8 \text{ \AA}^{-1}$  for which one can expect to observe the effects of chemical bonding. Therefore, in order to decide between different theoretical calculations, experimental structure factors with an accuracy of better than 1% are needed.

Aldred & Hart (1973*a,b*) performed absolute measurements of X-ray structure factors of Si by means of the *Pendellösung* method, and the internal consistency of their results indicates that probable errors are of the order of 0.1%. This is the highest accuracy in structure-factor measurements obtained up to the present time. However, the method requires extremely perfect single crystals and unfortunately there are very few systems for which sufficiently perfect crystals exist. In fact, at present there is no other

system which has been studied by the *Pendellösung* method with an accuracy and completeness comparable to the work by Aldred & Hart (1973*a,b*) on Si. Because of the severe sample problems inherent in the *Pendellösung* method, it seems reasonable to develop other experimental techniques to measure absolute structure factors in imperfect single crystals. A method which is fairly insensitive to the actual defect structure of a given sample is of special interest, because one could then study systems undergoing structural phase transitions, which in many cases are accompanied by severe changes in the defect structure of the crystal.

In an earlier paper (Schneider, 1976) it was shown that structure factors measured by means of Bragg diffraction of 412 keV ( $\lambda = 0.0301 \text{ \AA}$ )  $\gamma$ -radiation are, indeed, rather insensitive to changes in the defect structure of the sample. The 220 structure factor was measured independently on an absolute scale in 11 different volume elements of a large Cu single crystal. The mosaic structure, which can be determined accurately by  $\gamma$ -ray diffractometry (Schneider, 1974*b*), varied strongly over the different parts of the crystal. Nevertheless, the structure factors deduced in the first nine volume elements agreed well within the statistical error. The remaining two values, however, were too small by about 1.5%. We have attributed the discrepancy to a possible shortcoming in the applied extinction correction and in the subsequent data analysis we simply excluded the data from these two suspect volume elements. This brief statement unfortunately gave rise to a rather misleading reinterpretation of our measurements by Mackenzie & Mathieson (1979). This work will be discussed below, in the section concerned with sample preparation.

The first  $\gamma$ -ray structure factors were measured on the  $\gamma$ -ray diffractometer installed at the Institut Max von Laue–Paul Langevin in Grenoble (Schneider, 1974*a*). Severe limitations in this work arose from the special design of this diffractometer which was built for the purpose of studying the mosaic structure of large single crystals intended for use as monochromators or samples in neutron scattering experiments. In order to improve the experimental situation we have constructed a new  $\gamma$ -ray diffractometer at the Hahn-Meitner-Institut (HMI) in Berlin, designed for structure-factor measurements.

### The HMI $\gamma$ -ray diffractometer

The  $\gamma$ -ray source is a gold wire of 2 mm diameter and 4 mm length activated in the reactor BER II in a thermal neutron flux of  $8 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1}$ . The best angular resolution which can be obtained on the HMI diffractometer is of the order of 1 minute of arc. The intensity in a  $\gamma$ -ray beam of 3' angular divergence as measured with an intrinsic Ge solid-state detector (30%

photo peak efficiency) is about 6000 counts  $s^{-1}$  for a freshly activated source, compared with the background count rate which is of the order of 0.03 counts  $s^{-1}$ . The way in which the sources are transferred from the reactor to the diffractometer depends very much on such facilities as hot cells available at the reactor station. The transfer procedure used at the Hahn-Meitner-Institut in Berlin, as well as the spectral purity of the primary  $\gamma$ -ray beam, was discussed recently in some detail (Schneider, Pattison & Graf, 1979).

The principal features of the  $\gamma$ -ray diffractometer are shown in Fig. 15 of Schneider, Pattison & Graf (1979). A definition of the quantities measured in  $\gamma$ -ray diffractometry is presented in Schneider (1976). Although it has been shown that multiple Bragg scattering does not play an important role in  $\gamma$ -ray diffractometry (Schneider, 1975; Schneider, Hansen & Pattison, 1980), rocking curves will be measured for, say, three different  $\psi$  settings obtained by rotating the crystal around the scattering vector  $\mathbf{H}$ , in order to check experimentally that the measurements are not affected by multiple scattering.

### Interpretation of $\gamma$ -ray rocking curves

The interpretation of  $\gamma$ -ray rocking curves has already been discussed in the literature (Schneider, 1974*b*; Schneider, 1976; Schneider, Pattison & Graf, 1979) and therefore only additional aspects important for the present determination of Cu structure factors will be discussed.

If  $k$  is the so-called scale factor, the observed and the theoretical structure factors are related by the following equation:

$$k^2 |F_{\text{obs}}(\mathbf{H})|^2 = \exp \left[ -2B_{\text{eff}} \left( \frac{\sin \theta_B}{\lambda} \right)^2 \right] |F_{\text{theor}}(\mathbf{H})|^2$$

$$q_r = \frac{|F_{\text{theor}}(\mathbf{H})|^2}{|F_{\text{obs}}(\mathbf{H})|^2}$$

$$\ln q_r = 2 \ln k + 2B_{\text{eff}} \left( \frac{\sin \theta_B}{\lambda} \right)^2. \quad (1)$$

For reflections with  $\sin \theta/\lambda \gtrsim 0.7 \text{ \AA}^{-1}$ ,  $|F_{\text{theor}}(\mathbf{H})|$  is calculated from relativistic Hartree-Fock free-atom form factors of Doyle & Turner (1968). From a plot of  $\ln q_r$  against  $(\sin \theta/\lambda)^2$  one obtains a value for the scale factor  $k$  and the effective temperature factor  $B_{\text{eff}}$ . ( $B_{\text{eff}}$  is determined without correction for thermal diffuse scattering.)

The extinction length for  $\lambda = 0.0301 \text{ \AA}$  will be much larger than the dimension of the perfect domains which can be expected in mosaic crystals with mosaic spreads of the order of  $10'$ . Therefore, primary extinction can safely be neglected in the extinction correction of  $\gamma$ -ray

rocking curves measured in such mosaic crystals (Schneider, 1977). Following Darwin's theory on secondary extinction we derived the following expression for calculating the structure factor,  $F_{\text{obs}}(\mathbf{H})$  from the measured reflectivity distribution,  $r_m^{\text{obs}}(\omega_\nu)$  (Schneider, 1976).

$$|F_{\text{obs}}(\mathbf{H})| = |F_{\mathbf{H}}| \exp \left[ -B_{\text{eff}} \left( \frac{\sin \theta_B}{\lambda} \right)^2 \right] \quad (2)$$

$$= \left[ \frac{V^2}{r_0^2 \lambda^3} \frac{\sin 2\theta_B \cos \theta_B}{1 + \cos^2 2\theta_B} \frac{1}{T_0} \right. \\ \left. \times \sum_{\nu=1}^N \ln \left( \frac{1}{1 - 2r_m(\omega_\nu)} \right) \Delta\omega \right]^{1/2}.$$

$r_0$  is the classical electron radius and  $V$  is the volume of the unit cell.  $T_0$  represents the thickness of the sample studied in symmetrical Laue geometry. The sum goes over all  $\omega$  steps and  $\Delta\omega$  is the step width.

Formula (2) includes the assumption that the shape of the measured reflectivity distribution,  $r_m(\omega_\nu)$ , is not affected by the instrumental resolution function. The latter function can be measured directly by rocking a perfect single crystal through the angular range where Bragg scattering occurs and can for the present set-up be fitted reasonably well by a Gaussian of FWHM =  $2.8'$ . If the shape of the  $\gamma$ -ray rocking curve,  $r_m(\omega_\nu)$ , measured in the mosaic sample (mosaic spread much larger than FWHM of instrumental resolution function) can also be described by a Gaussian distribution function, the deconvolution of  $r_m(\omega_\nu)$  is straightforward and it is then the deconvoluted reflectivity distribution,  $r_m^*(\omega_\nu)$ , which is used in formula (2).

### Sample preparation

In the first  $\gamma$ -ray measurements of Cu structure factors for imperfect single crystals (Schneider, 1976), certain systematic errors in the applied extinction correction, although unlikely, could not entirely be excluded because of the inhomogeneous mosaic structure of the sample. Therefore an effort was made to produce Cu single crystals which could reliably be described by Darwin's mosaic model. Cu single crystals with very low dislocation densities were plastically deformed by A. Freund, Institut Max von Laue - Paul Langevin, Grenoble (Freund, 1975*a*; Freund & Forsyth, 1979). Reviews on work hardening are given by Seeger (1965) for metals and by Alexander & Haasen (1968) for crystals with diamond structure.

Fig. 1 shows a typical  $\gamma$ -ray rocking curve together with a Gaussian fitted to the experimental data. The structure-factor measurements were performed on three different samples; their dimensions and orientations are indicated in Fig. 2. All  $\gamma$ -ray rocking curves from which we deduced experimental structure factors could be

well described by Gaussians of FWHM varying between 7 and 10 minutes of arc. However, some of the rocking curves measured on these samples showed tails as indicated in Fig. 3. The samples had been cut by spark erosion and chemically etched afterwards. From the relative integrated reflecting powers the thickness of the damaged surface region could be estimated to be of the order of 0.1 mm. Therefore, the sample received an additional surface treatment, namely, they were first

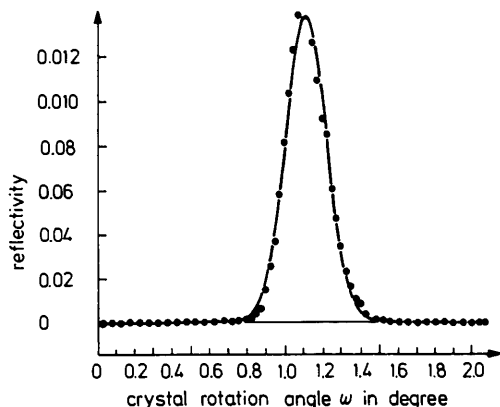


Fig. 1. A Gaussian of FWHM =  $7.5'$  fitted to a  $\gamma$ -ray rocking curve measured at the 220 reflection of crystal CuC. The statistical error is smaller than the symbols in the figure. After deconvolution with a Gaussian of FWHM =  $2.8'$  and correction for secondary extinction one gets a mosaic spread of  $6.8'$ .

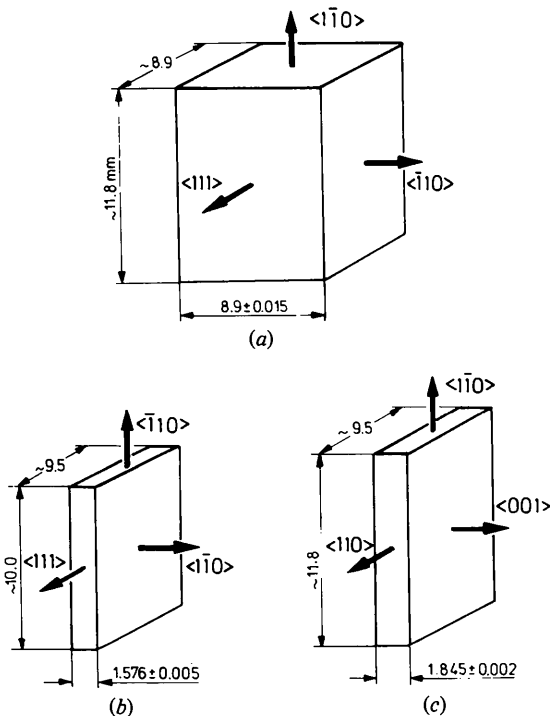


Fig. 2. Dimensions and orientation of the three copper single crystals used in the structure-factor measurements. (a) CuA, (b) CuB, (c) CuC.

polished mechanically and then a standard electrolytical polishing procedure was applied. As a result the tails vanished from the rocking curves as demonstrated in Fig. 3.

On the  $\gamma$ -ray diffractometer installed at the Institut Laue-Langevin where the first  $\gamma$ -ray structure factors were measured, it would have been difficult to observe the tails shown in Fig. 3 since the background count rate was two orders of magnitude higher than the background on the HMI spectrometer. Therefore it is possible that we have unintentionally taken the background in angular ranges still affected by such tails and this would lead to an appreciable error in the measured integrated reflecting power. We believe that the problems with the volume elements 10 and 11 in the earlier structure factor measurements in Cu (Schneider, 1976) resulted from such background problems. The rocking curves of volumes 10 and 11 are rather compact and have an extinction correction comparable to those measured in the new samples shown in Fig. 2. In the present work we experienced no problems in correcting for extinction effects of the order of 10%,

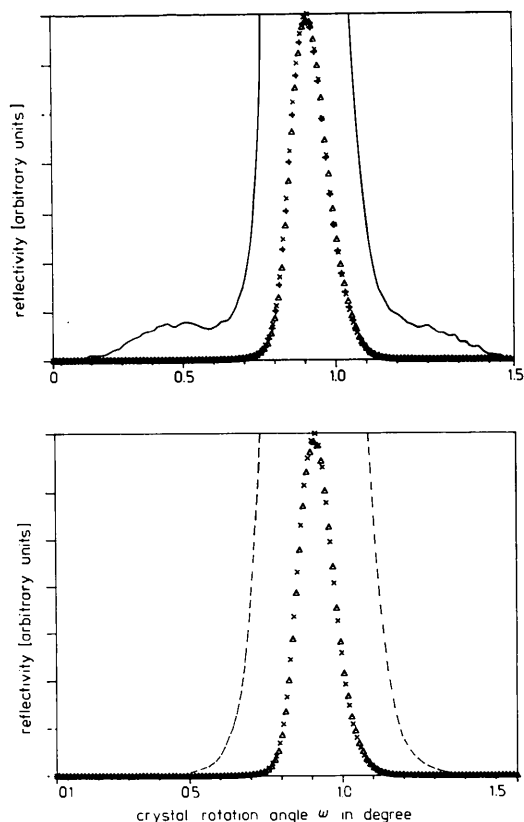


Fig. 3.  $\gamma$ -ray rocking curves measured at the 111 reflection in sample CuC before and after the surface treatment. The solid line represents magnification by a factor of ten of the rocking curve measured before surface treatment; the dotted line represents the same magnification of the rocking curve measured after surface treatment.

with the same formalism as in the earlier paper. We therefore conclude that the comparatively small structure factor values deduced from the measurements in volume elements 10 and 11 are not due to a failure of the applied extinction correction. The confusion probably resulted from the fact that the rocking curves for these two elements were relatively narrow, so that the amount of secondary extinction for which the measured structure factors were corrected was relatively high. On the other hand an extrapolation along a line through two points as performed by Mackenzie & Mathieson (1979) must always be treated with some caution.

### Structure-factor measurements

19 independent structure factors were determined in the range of momentum transfer up to  $\sin \theta/\lambda \approx 1.6 \text{ \AA}^{-1}$ . Because the present measurements are regarded as a test of the accuracy which can be obtained in absolute structure-factor measurements in imperfect single crystals by means of  $\gamma$ -ray diffractometry, we have performed altogether 213 independent measurements on three samples over a period of about 1 year, each individual measurement being on an absolute scale. The effort was concentrated on the low-order reflections for which effects due to chemical bonding are expected and special attention was paid to the extinction correction. The effective temperature parameter,  $B_{\text{eff}}$ , was determined at room temperature and at 50 K, the structure factors which are used for comparison with theoretical values being deduced from the low-temperature measurements.

In order to confirm that the  $\gamma$ -ray rocking curves are unaffected by multiple Bragg scattering, each curve was measured for three  $\psi$  settings, for which the relative rotation around the scattering vector was  $\Delta\psi \approx 0.5^\circ$ . In Fig. 4 such a set of three reflectivity

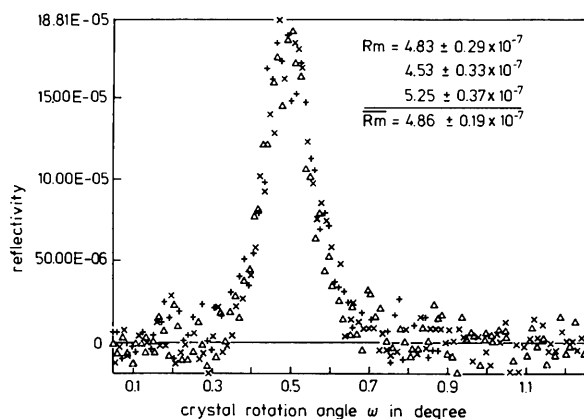


Fig. 4.  $\gamma$ -ray rocking curves measured at the 666 reflection in sample CuA for three  $\psi$  settings (crystal is rotated around the scattering vector).  $R_m$  denotes the integrated reflecting power calculated from each curve,  $\bar{R}_m$  is the mean value.

distributions  $r_m(\omega_\nu)$  measured at the 666 reflection of sample CuA at low temperature is shown together with the values of the integrated reflecting power,  $R_m$ , calculated from each individual rocking curve. If the individual  $R_m$  values agree within their error the mean value of the deduced individual structure factors is considered as the result of that particular structure-factor measurement. As an additional test on possible effects due to multiple Bragg scattering, the transmitted intensity  $P_T^*(\omega)$  was measured as a function of the rocking angle  $\omega$  for all reflections.

Fig. 5 shows a plot of  $\ln q_r$  [for definition see equation (1)] as a function of  $(\sin \theta/\lambda)^2$  for  $T = 50 \text{ K}$  and for room temperature. For intensity reasons the room-temperature data were measured on the thick sample CuA only, while the low-temperature measurements were performed on samples CuA and CuB. Both data sets can be fitted by a straight line, leading to effective temperature factors of  $B_{\text{eff}} = 0.544 (7) \text{ \AA}^2$  for room temperature and  $B_{\text{eff}} = 0.167 (8) \text{ \AA}^2$  for low temperature. Within the error of  $\pm 1\%$  the scale factors turn out to be equal to unity in both cases. Table 3 shows that our temperature factor for  $T = 290 \text{ K}$  is in reasonable agreement with those used in the interpretation of some of the other experiments. A separate

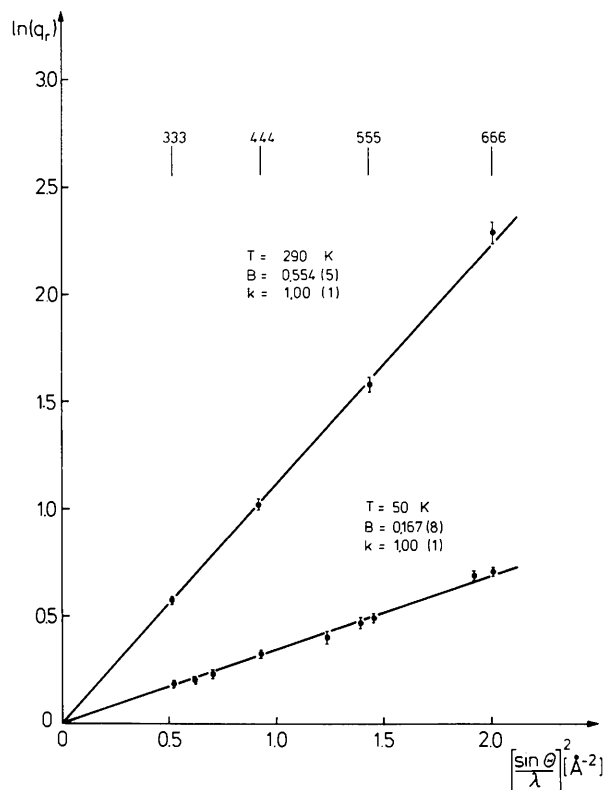


Fig. 5. Wilson (1942) plot of high-order  $\gamma$ -ray data measured at room temperature and 50 K respectively.  $k$  represents the scale factor.  $B_{\text{eff}}$  is the effective temperature parameter. A discussion of the error is given in the text.

study of the temperature factors and the atomic scattering factors of heavy materials such as Au at high values of  $\sin \theta/\lambda$  will be performed in the near future along the lines presented recently (Schneider, Pattison & Graf, 1978).

The room-temperature lattice parameter  $a_0 = 3.61496(2) \text{ \AA}$  was taken from the measurements by Freund (1973*a*). From this value the lattice parameter at 50 K was calculated to be  $a_0 = 3.60350(5) \text{ \AA}$  with the thermal expansion coefficients determined by Hahn (1970). In Fig. 6 we compare series of individual structure factors measured for samples CuA and CuB for reflections 111 and 222 at room temperature and at 50 K. The agreement between room- and low-temperature data is quite satisfactory, which is in support of the used lattice-parameter value. Because of the small Bragg angles for the diffraction of  $0.03 \text{ \AA}$   $\gamma$ -radiation we cannot measure the lattice parameter to sufficient accuracy on our  $\gamma$ -ray diffractometer.

At the beginning and end of each measurement the transmitted intensity  $P_T^*$  was measured with the solid-state detector on both sides of the  $\omega$ -scan range. Additionally, for reflections with  $\sin \theta/\lambda \geq 0.7 \text{ \AA}^{-1}$ ,  $P_T^*(\omega)$  was measured at the same time as  $P_H(\omega)$  as a function of the rocking angle  $\omega$  with the NaI(Tl) scintillation counter. A scaling factor relating the two detectors was established by comparing the measurements of the direct beam intensity with both detectors for each measurement. For reflections with  $\sin \theta/\lambda < 0.7 \text{ \AA}^{-1}$ , the scintillation counter was unfortunately masked by the lead shielding of the solid-state detector. Under these conditions  $P_T^*(\omega)$  was measured with the solid-state detector as a function of  $\omega$  after the measurement of the reflectivity distribution  $P_H(\omega)$ .

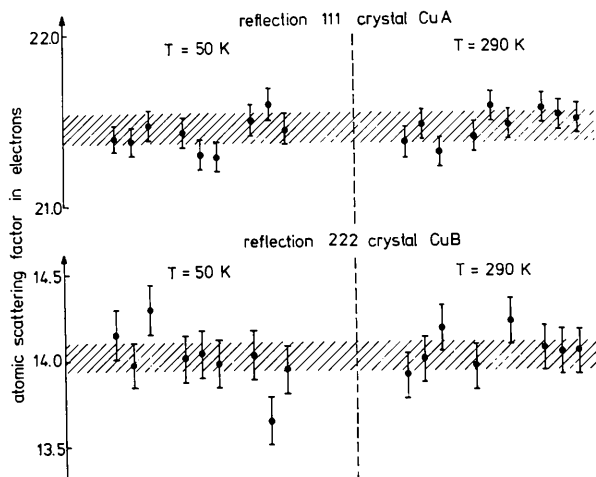


Fig. 6. Series of individual structure factors as calculated from  $\gamma$ -ray rocking curves measured in samples CuA and CuB for reflections 111 and 222 at 50 K and at room temperature. Three neighbouring volume elements were studied and in each case rocking curves for three  $\psi$  settings were measured. The hatched band represents the error of the final structure factors as given in Table 3.

Both intensity distributions can then be related by means of the well known decay constant of  $\lambda = 2.98 \times 10^{-6} \text{ s}^{-1}$  for our 412 keV  $\gamma$ -radiation from radioactive gold.

In Fig. 7 the experimental structure factors are compared with five different free-atom calculations (the numerical values are given in Table 1). In each case we have plotted the difference  $f_{DT} - f$ , where  $f_{DT}$  is the theoretical value of Doyle & Turner (1968).  $f$  represents either the experimental or one of the theoretical values of the form factor. Solid-state effects are expected for reflections with  $\sin \theta/\lambda \lesssim 0.7 \text{ \AA}^{-1}$  and it is obvious that none of the free-atom calculations fits

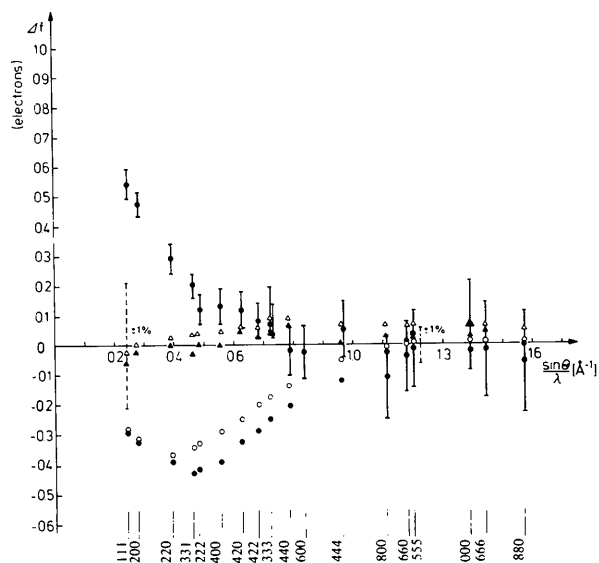


Fig. 7. Comparison of experimental  $\gamma$ -ray form factors with theoretical free-atom scattering factors. The plot shows the difference  $f_{DT} - f$ , where  $f_{DT}$  is the theoretical value of Doyle & Turner (1968).  $f$  represents either the experimental form factor or one of the other theoretical free-atom form factors.  $\Delta$  Cromer & Mann (1968);  $\blacktriangle$  Freeman & Watson (1961);  $\circ$  Hanson, Herman, Lea & Stillman (1964);  $\bullet$  Cromer & Waber (1965).

Table 1. Numerical values of the higher-order atomic form factors

$f_{DT}$  represents the free-atom values calculated by Doyle & Turner (1968),  $f_{exp}$  are the experimental data as measured by  $\gamma$ -ray diffractometry.

$h k l$	$f_{DT}$	Number of independent measurements			$f_{exp}$
		CuA	CuB	CuC	
4 4 0	8.82			3	8.84 (8)
6 0 0	8.35			3	8.37 (9)
4 4 4	7.38	3	12		7.33 (9)
8 0 0	6.64			3	6.75 (14)
6 6 0	6.37			3	6.41 (12)
5 5 5	6.28	3	6		6.29 (13)
10 0 0	5.66			3	5.59 (15)
6 6 6	5.49	3	9		5.51 (16)
8 8 0	5.09			3	5.12 (17)

the experimental data in this range of momentum transfer. On the other hand, the high-order data ( $\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$ ) are in reasonable agreement with the free-atom results obtained by Freeman & Watson (1961), by Cromer & Mann (1968) and by Doyle & Turner (1968) and in somewhat poorer agreement with the free-atom calculations of Hanson, Herman, Lea & Skillman (1964) and Cromer & Waber (1965).

Fig. 8 shows our experimental atomic scattering factors for Cu together with the results of four band-structure calculations. We have plotted the difference between the experimental and theoretical values on one hand and the free-atom results of Doyle & Turner (1968) on the other hand. The lattice parameters used in various solid-state calculations are slightly different and, except for the calculation by Bagayoko *et al.* (1980), clearly differ from our 50 K lattice parameter. In comparing the measured structure factors with the theoretical ones, one must take into account that the  $\sin \theta/\lambda$  value for a given reflexion does change with the lattice parameter; the value of the free-atom form factor for the low-order reflexions is about 0.05 e higher at room temperature than at 50 K owing to a contraction of the reciprocal lattice of about 0.3%. As a consequence, one should compare the difference between superimposed free atoms and experiment with the difference between free-atom model and theory, always with the appropriate lattice constants for the free-atom models. Numerical values of the experimental results are presented in Table 2, which also contains the range of the extinction factor  $y$  for the different reflections, which indicates that the structure-factor measurements were affected by different amounts of extinction. After performing the extinction correction the agreement between the various measurements for samples of different thickness and slightly different mosaic spreads was very satisfying, which demonstrates that the applied correction procedure is suitable in the present case. In Table 2 there are two values for the error in the experimental

atomic scattering factors.  $\sigma_1$  denotes the error of the mean value over all independent measurements for a given reflection calculated from the various sources of error that there are: the statistical error in the measured integrated reflecting power (calculated along the lines given by Lehmann & Larsen, 1974), the uncertainty in the determination of the thickness of the samples and the error in the Debye-Waller factor.  $\sigma_2$  is simply the standard deviation of the mean value

$$\sigma_2 = \left[ \frac{1}{n-1} \sum_{j=1}^n (f_j - \bar{f})^2 \right]^{1/2},$$

which was calculated for those reflections where a reasonable number of independent measurements had been performed. In general  $\sigma_1 \lesssim \sigma_2$ , which demonstrates the good internal consistency of the data.

### Comparison with earlier X-ray experiments

In Table 3 the results of five experimental X-ray structure-factor measurements are compared with

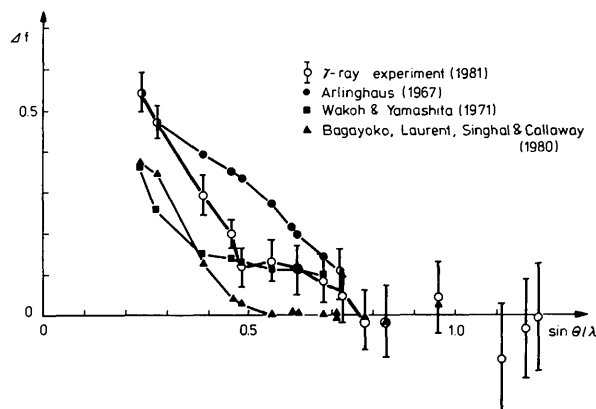


Fig. 8. Comparison of experimental  $\gamma$ -ray form factors with theoretical data from different band-structure calculations. The plot shows the difference  $f_{DT} - f$ , where  $f_{DT}$  is the free-atom value of Doyle & Turner (1968).  $f$  represents either the experimental form factor or one of the theoretical form-factor values.

Table 2. Numerical values of the low-order atomic form factors

$f_{DT}$  represents the free-atom values calculated by Doyle & Turner (1968),  $f_{exp}$  represents the result of the present  $\gamma$ -ray experiment.  $y$  is the extinction factor.  $\sigma_1$  is the error estimated from the individual sources of error and  $\sigma_2$  represents the standard deviation of the mean value.

$hkl$	$f_{DT}$	Number of independent measurements			$y$	$f_{exp}$	$\sigma_1$	$\sigma_2$	$f_{DT} - f_{exp}$	
		CuA	CuB	CuC						
1 1 1	22.05	9	15		0.891	0.976	21.51 (5)	0.05	0.09	0.54 (5)
2 0 0	20.69			18	0.978	0.982	20.22 (4)	0.04	0.06	0.47 (4)
2 2 0	16.74			15	0.986	0.99	16.45 (5)	0.05	0.07	0.29 (5)
3 1 1	14.74			6	0.99		14.54 (4)	0.04	0.06	0.20 (4)
2 2 2	14.19	9	21		0.96	0.994	14.07 (5)	0.05	0.08	0.12 (5)
4 0 0	12.42			9	0.992		12.29 (6)	0.06	0.06	0.13 (6)
4 2 0	11.14			6	0.996		11.02 (6)	0.06		0.12 (6)
4 2 2	10.16			3	0.996		10.08 (6)	0.06		0.08 (6)
3 3 3	9.58	3	15		0.986	0.996	9.49 (6)	0.06	0.09	0.09 (6)
5 1 1	9.58			3	0.996		9.53 (6)	0.06		0.05 (6)

Table 3. *Experimental atomic form factors for copper*

The X-ray measurements were all performed at room temperature.

<i>h k l</i>	Batterman <i>et al.</i> (1961)	Jennings <i>et al.</i> (1964)	Hosoya & Yamagichi (1966)		Temkin <i>et al.</i> (1972)	Freund (1973a)	Schneider (1976)	This experiment
	$B = 0.543 \text{ \AA}^2$ Mo $K\alpha$	$B = 0.550 \text{ \AA}^2$ Mo $K\alpha$	$B = 0.603 \text{ \AA}^2$ Cu $K\alpha$ Mo $K\alpha$		$B = 0.550 \text{ \AA}^2$ Cu $K\alpha$ and Mo $K\alpha$	$B = 0.598 \text{ \AA}^2$ Mo $K\alpha$	(111) $B = 0.584 \text{ \AA}^2$ (110) $B = 0.561 \text{ \AA}^2$ $\lambda = 0.03 \text{ \AA}$	$B = 0.167 (8) \text{ \AA}^2$ ( $T = 50 \text{ K}$ ) $\lambda = 0.03 \text{ \AA}$
1 1 1	21.29 (34)	21.52 (10)	22.08 (9)	22.10 (20)	21.93 (15)	22.63 (20)		21.51 (5)
2 0 0	19.75 (34)		20.70 (18)	20.27 (30)	20.36 (15)			20.22 (4)
2 2 0	16.37 (30)		17.13 (13)	16.85 (39)	16.70 (16)		16.46 (7)	16.45 (5)
3 1 1			14.96 (9)	15.13 (34)	14.71 (17)			14.54 (4)
2 2 2	13.70 (30)	14.01 (10)	14.39 (9)	14.49 (34)	14.18 (17)	14.64 (10)	13.98 (8)	14.07 (5)
4 0 0			12.48 (45)		12.33 (20)			12.29 (6)
3 3 1			11.47 (5)					
4 2 0			11.11 (13)					11.02 (6)
4 2 2	9.69 (38)							10.08 (6)
3 3 3	8.37 (40)	9.41 (10)				9.54 (10)	9.53 (5)	9.49 (6)
5 1 1	8.37 (40)							9.53 (6)
	Powder	Perfect crystal	Powder		Powder	Perfect crystal	Mosaic crystal	Mosaic crystal

those obtained by  $\gamma$ -ray diffractometry. In Fig. 9 we have displayed the various experimental values for the first four reflections. Again, one should consider the effect of the different lattice parameters of Cu for room temperature and 50 K. However, the reduction of 0.05 e of the earlier room-temperature data compared to our present 50 K data is smaller than the error quoted for the earlier measurements and will not affect the discussion below. The agreement between the first powder measurement performed by Batterman, Chipman & DeMarco (1961) and our recent  $\gamma$ -ray results is surprisingly good for small values of  $\sin \theta/\lambda$ , although the quoted experimental error in the powder data is rather large. On the contrary, the later powder measurements performed by Hosoya & Yamagishi (1966) and by Temkin, Henrich & Racciah (1972) clearly disagree with our  $\gamma$ -ray data.

It is also very interesting to note that for small values of  $\sin \theta/\lambda$  the  $\gamma$ -ray results are in very good agreement with early measurements performed by Jennings, Chipman & DeMarco (1964) on perfect Cu crystals. In general, if one works with imperfect single crystals the danger is to underestimate extinction, which gives atomic scattering factors which are too small. On the other hand, if one works with perfect single crystals, the danger is that the crystal may not be sufficiently perfect, which leads to atomic scattering factors which are too high. Any satisfaction about the agreement between these two different types of single-crystal measurements is disturbed by the overall disagreement between the  $\gamma$ -ray results and another set of data deduced by Freund (1973b) from his measurements on perfect Cu crystals. The discrepancy between the results for the 111 reflection deduced from these two perfect single-crystal measurements is dramatic. For the 222 reflection, Freund (1975b) published in a later paper a value of 14.41 (7). By rescaling this result to an

isotropic temperature factor of  $B = 0.55 \text{ \AA}^2$ , one obtains a value of 14.25 (7) which is still in disagreement with the values of 14.01 (10) determined by Jennings *et al.* (1964). The discrepancies between the two measurements performed on perfect single crystals may be due to the different approaches the authors chose to solve the problems caused by the long tail of the diffraction pattern and the important effect of thermal diffuse scattering on the measured quantities.

Another interesting point to note is the good agreement between the two independent  $\gamma$ -ray measurements, particularly because the earlier one (Schneider, 1976) was performed on a Cu single crystal with very inhomogeneous mosaic structure. The shape of the rocking curves measured in the first nine volume elements varied strongly, but, nevertheless, the structure factors calculated from the individual rocking curves agreed within their standard deviations. Therefore, we conclude that accurate structure-factor measurements by means of  $\gamma$ -ray diffractometry should even be possible in systems undergoing structural phase transitions.

### Comparison with solid-state calculations

From a comparison between various solid-state theories and their experimental form factors, Temkin, Henrich & Racciah (1972) found best agreement with a calculation of Wakoh & Yamashita (1971) which is based on the Green-function method with full Slater exchange in a self-consistent procedure. This is a surprising result because in many instances full Slater exchange has proved to be too strong in the valence region. Temkin *et al.* (1972) also compare their experimental results with a self-consistent APW  $X\alpha$  calculation of Snow & Waber (1967) and Snow (1968);



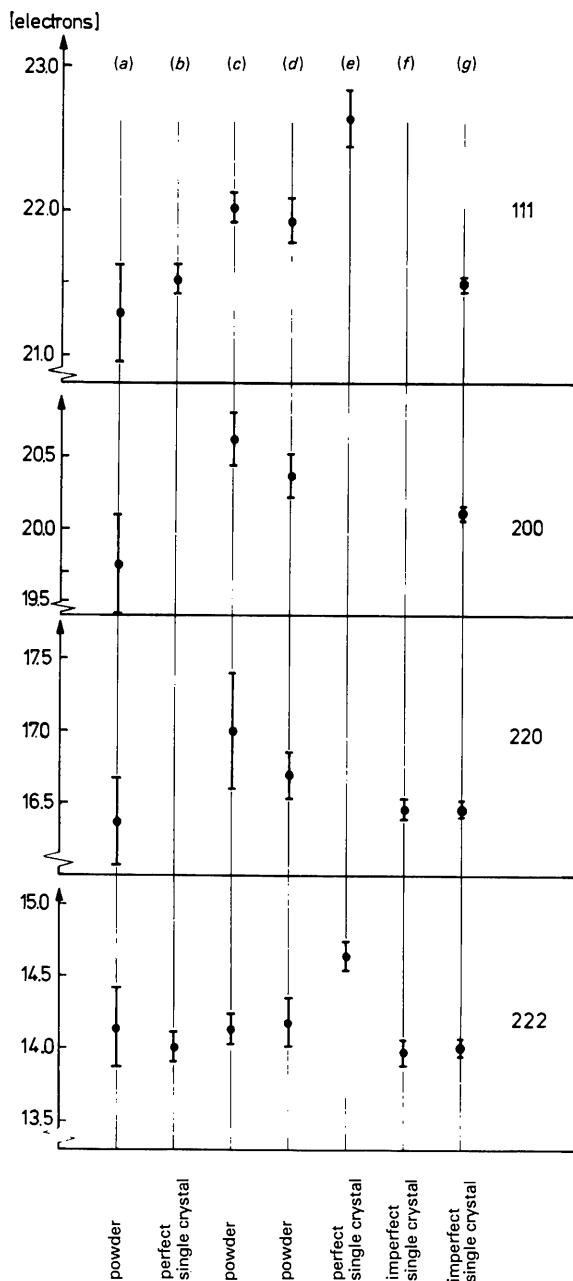


Fig. 9. Experimental X-ray form factors compared with the results obtained by  $\gamma$ -ray diffractometry. References: (a) Batterman *et al.* (1961); (b) Jennings *et al.* (1964); (c) Hosoya & Yamagishi (1966); (d) Temkin *et al.* (1972); (e) Freund (1975a,b); (f) Schneider (1976); (g) Schneider *et al.* (1980).

the corresponding X-ray form factors were taken from a paper by Wood (1967). Snow performed calculations for three different exchange parameters  $\alpha = 1, 5/6$  and  $2/3$  and he obtained best agreement between experimental and theoretical energy band gaps for  $\alpha = 5/6$ . On the other hand, the theoretical form factors are closest to the experimental data of Temkin *et al.* (1972) for  $\alpha = 2/3$ . It is interesting to note that the form

factors calculated by Snow for  $\alpha = 2/3$  are in close agreement with those calculated in a recent self-consistent band-structure calculation of Cu of Bagayoko, Laurent, Singhal & Callaway (1980), who use a basis of Gaussian orbitals and a local exchange-correlation potential. In contrast to Temkin *et al.* (1972) we do not believe that their powder data are of sufficient accuracy to allow for a discrimination between the theoretical form factors of Snow (1968) ( $\alpha = 2/3$ ) and Wakoh & Yamashita (1971). Because of the large errors the experimental form factors seem to be in reasonable agreement with both calculations. On the other hand, there is a net discrepancy between these powder data and the theoretical form factors from the APW calculation of Arlinghaus (1967), and Temkin *et al.* (1972) conclude that the Chodorow potential used by Arlinghaus to describe exchange and correlation is not very suitable for charge density calculations in copper.

In Table 4 we present theoretical form factors from various band-structure calculations, including the most recent data, which are due to Bagayoko, Laurent, Singhal & Callaway (1980). The form factors from this calculation were provided by Bagayoko (1980). The free-atom scattering factors of Doyle & Turner (1968) are presented for room temperature and for 50 K. The calculation by Bagayoko *et al.* (1980) was performed with the 0 K lattice parameter of  $a_0 = 3.6032 \text{ \AA}$ , whereas the other solid-state calculations used the room-temperature lattice parameter. In Fig. 8 we have plotted the differences between the free-atom values and the results from three theoretical calculations, which are also compared with our experimental results. Wakoh & Yamashita (1971) performed their calculations with full Slater exchange as well as the Chodorow potential. In Fig. 8 we have plotted only the Wakoh & Yamashita results obtained for full Slater exchange which fit very well our experimental data in the range of momentum transfer of  $0.5 \lesssim \sin \theta/\lambda \lesssim 0.7 \text{ \AA}^{-1}$ . For the reflections with  $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$  the experimental and the theoretical form factors of Wakoh & Yamashita (1971) clearly disagree. On the other hand, the Arlinghaus (1967) calculation fits perfectly well the experimental values for the reflections 111 and 200, whereas there is a net disagreement for the reflections in the range  $0.3 \lesssim \sin \theta/\lambda \lesssim 0.6 \text{ \AA}^{-1}$ . The most striking difference, however, occurs between our experimental form factors and the results of the most recent band-structure calculation by Bagayoko *et al.* (1980).

The accuracy of the measured form factors allows a study of the deformation density

$$\Delta\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} [F_{\text{obs}}(\mathbf{H}) - F_{\text{theor}}(\mathbf{H})] e^{-i2\pi\mathbf{H}\cdot\mathbf{r}},$$

where  $V$  is the volume of the unit cell. Because of the high symmetry of the f.c.c. lattice and the small

Table 4. *Theoretical atomic form factors for copper*

The free-atom values of Doyle & Turner (1968) are calculated for two temperatures, the other theoretical values are from different solid-state calculations.  $a_0$  represents the lattice parameter.

	$T = 293 \text{ K}, a_0 = 3.615 \text{ \AA}$				$T = 0 \text{ K},$	$T = 50 \text{ K}, a_0 = 3.6035 \text{ \AA}$				
	Doyle & Turner (1968)	$\alpha = 1$	Snow (1968) APW - $x$ $\alpha = 5/6$	$\alpha = 2/3$	Arlinghaus (1967) APW (Chodorow)	Wakoh & Yamashita (1971) (Chodorow)	Bagayoko <i>et al.</i> (1980)	Doyle & Turner (1968)	This experiment	
1 1 1	22.08	22.33	21.90	21.63	21.54	21.72	21.67	21.68	22.05	21.51 (5)
2 0 0	20.72	21.04	20.66	20.40	20.25	20.46	20.39	20.35	20.69	20.22 (4)
2 2 0	16.78	17.12	16.86	16.64	16.39	16.63	16.56	16.62	16.74	16.45 (5)
3 1 1	14.78	15.08	14.87	14.68	14.43	14.64	14.58	14.70	14.74	14.54 (4)
2 2 2	14.23	14.53	14.34	14.16	13.90	14.10	14.04	14.17	14.19	14.07 (5)
4 0 0	12.46	12.72	12.57	12.42	12.19	12.34	12.30	12.42	12.42	12.29 (6)
3 3 1	11.46	11.68	11.55	11.43	11.25	11.35	11.32	11.41	11.42	
4 2 0	11.17	11.38	11.26	11.14	10.98	11.07	11.03	11.13	11.14	11.02 (6)
4 2 2	10.19				10.05			10.16	10.16	10.08 (6)
511/333	9.61				9.51			9.58	9.58	9.53 (6)

number of reflections available in the range of  $\sin \theta/\lambda \lesssim 0.8 \text{ \AA}^{-1}$ , the error in the difference density is appreciable and therefore the map has to be regarded with considerable caution. In Fig. 10 we have plotted the difference density between  $\gamma$ -ray results and the free-atom calculation of Doyle & Turner (1968). The summation only included terms for which  $\sin \theta/\lambda \lesssim 0.8 \text{ \AA}^{-1}$ . This cut-off is justified by the good agreement between experiment and free-atom calculation for the measured reflections above  $\sin \theta/\lambda = 0.8 \text{ \AA}^{-1}$  and, consequently, series terminations effects may be neglected. In the range up to the cut-off a complete set of structure factors was collected with the exception of  $F(331)$  which was estimated by interpolation to be 11.75. At the position of the atoms there is a deficiency of charge of  $-2.77 (25) e \text{ \AA}^{-3}$ , which partly appears as a charge pile up of the order of  $+0.19 (8) e \text{ \AA}^{-3}$  at the midpoint between nearest-neighbour atoms. From the errors  $\sigma_1$  of the measured atomic scattering factors as listed in Table 2, the error in the difference density

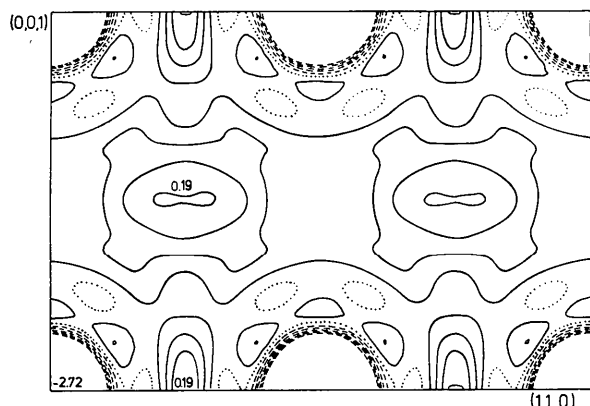


Fig. 10. Difference density between  $\gamma$ -ray results and the free-atom calculation of Doyle & Turner (1968) for copper. The contours are at intervals of  $0.05 e \text{ \AA}^{-3}$ . The density at the positions of the Cu atoms is  $-2.72 e \text{ \AA}^{-3}$ .

$\Delta\rho(\mathbf{r})$  was calculated for a number of points in the asymmetric unit. In Fig. 11 these numbers are displayed for a section of two asymmetric units.

Our deformation density shown in Fig. 10 differs strikingly from another deformation density of copper calculated by Smart & Humphreys (1980) which is based on experimental 111, 200 and 220 form factors deduced from critical-voltage electron diffraction measurements and five theoretical values,  $f(311)$  to  $f(420)$ , from the band-structure calculation of Wakoh & Yamashita (1971). Smart & Humphreys find a concentration of electrons at both the tetrahedral and octahedral interstitial sites; there is no build up of charge in the nearest-neighbour direction in their deformation density. Because of the limited range in  $\sin \theta/\lambda$  of the data points the density maps are strongly affected by series termination errors. If the Fourier synthesis was carried through to convergence the

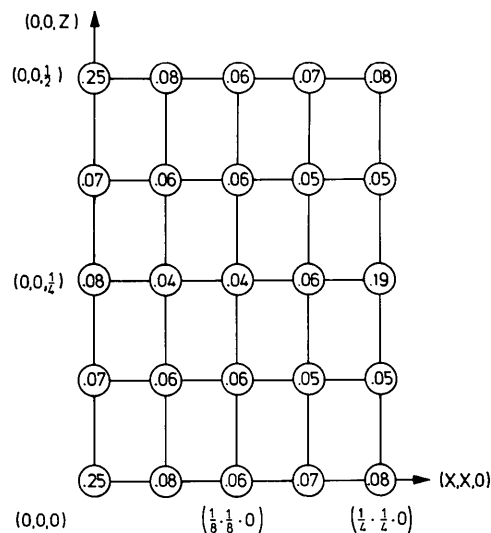


Fig. 11. Standard deviation of the difference density calculated for a number of points in the unit cell.

features would be significantly changed. The actual numbers of the critical-voltage form factors are  $f(111) = 21.786$ ,  $f(200) = 20.454$  and  $f(220) = 16.696$  electrons (Humphreys, 1980). They are about 0.25 e higher than the values deduced from our  $\gamma$ -ray diffraction experiments and about 0.1 e higher than the theoretical values of Bagayoko, Laurent, Singhal & Callaway (1980). At present we cannot offer an explanation of the origin of the marked discrepancy between the two sets of experimental form factors.

### Conclusions

Absolute structure-factor measurements in imperfect single crystals by means of  $\gamma$ -ray diffractometry can achieve significantly higher accuracy than corresponding X-ray measurements, because the X-ray data are subject to a number of important corrections which are not required in the interpretation of the  $\gamma$ -ray data. In  $\gamma$ -ray diffractometry a monochromatic, unpolarized  $\gamma$ -ray beam is obtained without a monochromator. Each individual Bragg reflection is measured on an absolute scale. Absorption of 412 keV  $\gamma$ -radiation in matter is weak and a total attenuation coefficient is measured implicitly for each Bragg reflection. Because of the weak absorption, accurate measurements with samples contained in furnaces, cryostats or high-pressure devices can be performed without causing any additional experimental difficulties. In  $\gamma$ -ray diffractometry rather thick samples are studied, so that the sample surface can be prepared carefully and the determination of the sample thickness is not difficult. Because of the small Bragg angles the scattering geometry is very simple. Possible effects due to multiple Bragg scattering can be avoided. The extinction problem in imperfect single crystals is much easier to handle than in X-ray diffraction experiments. Because for all atoms the  $\gamma$ -ray energy of 412 keV is much higher than the binding energy of even the innermost electrons, anomalous dispersion does not occur.

In the present measurement absolute atomic form factors of copper were measured with an accuracy of the order of  $\pm 0.05$  electrons for reflections with  $\sin \theta/\lambda \lesssim 0.7 \text{ \AA}^{-1}$ . More precisely, the error in the 111 and 200 reflections is of the order of  $\pm 0.2\%$ . Uncertainties in the determination of the thickness of the samples and for higher-order reflections the error in the effective Debye-Waller factor give the main contributions to the final error in the measured form factors. Both effects can be reduced to a certain extent. From the good agreement between our present atomic scattering factors and those obtained in an earlier  $\gamma$ -ray study, where structure factors were measured in a series of volume elements of a large Cu single crystal showing very inhomogeneous mosaic structure (Schneider, 1976), we conclude that structure factors of the present

level of accuracy can be measured by means of  $\gamma$ -ray diffractometry even in systems undergoing structural phase transitions.

None of the available band-structure calculations provides a satisfactory description of the measured form factors over the whole range of momentum transfer where effects due to bonding can be expected, although they do produce energy-band dispersions which agree well with recent angle-resolved photoemission data. In particular, our experimental data do not agree with the theoretical form factors calculated recently by Bagayoko, Laurent, Singhal & Callaway (1980) in an advanced self-consistent band-structure calculation. The authors use a basis of Gaussian orbitals and a local exchange correlation potential. Their energy bands are in satisfactory agreement with the experimental  $E_n$  vs  $k$  data of Thiry *et al.* (1979), except for the lowest band. In the light of these conflicting conclusions, it is helpful that Bagayoko *et al.* (1980) also calculated Compton profiles which they compare with experimental data of Paakkari, Manninen & Berggren (1975) and Eisenberger & Reed (1974). If one considers the result obtained by Zunger & Freeman (1977) for diamond as a measure for good agreement between experimental and theoretical Compton profile anisotropy, the theoretical anisotropy calculated by Bagayoko *et al.* (1980) for copper differs significantly from the experimental data. We have repeated the earlier Compton profile measurements (Pattison, Hansen & Schneider, 1981) and we find excellent agreement in the profile anisotropy with the data of Eisenberger & Reed (1974).

To summarize, the band-structure calculation of Bagayoko, Laurent, Singhal & Callaway (1980) provides energy bands in good agreement with recent angle-resolved photoemission data. However, neither the theoretical form factors nor the Compton profile anisotropies agree so well with the experimental results.

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