

- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- GIACOVAZZO, C. (1974). *Acta Cryst.* **A30**, 631–634.
- GIACOVAZZO, C. (1980). *Acta Cryst.* **A36**, 74–82.
- HALL, S. R. (1985). *J. Appl. Cryst.* **18**, 263–264.
- HASEK, J. (1984). *Acta Cryst.* **A40**, 338–340.
- HULL, S. E. & IRWIN, M. J. (1978). *Acta Cryst.* **A34**, 863–870.
- KANTERS, J. A. & VAN VEEN, A. M. (1973). *Cryst. Struct. Commun.* **2**, 261–265.
- KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635–651.
- KARLE, J. & KARLE, I. (1966). *Acta Cryst.* **21**, 849–859.
- MAIN, P. (1985). *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 206–215. Oxford: Clarendon Press.
- OVERBEEK, A. R. & SCHENK, H. (1978). *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 108–112. Delft Univ. Press.
- RYCHLEWSKA, U., BRATEK, M. D. & WIEWIORSKI, M. (1978). *Acta Cryst.* **A34**, S106.
- SCHENK, H. (1973). *Acta Cryst.* **A29**, 77–82.
- SCHENK, H. & KIERS, C. T. (1985). *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 200–205. Oxford: Clarendon Press.
- SHELDRICK, G. M. (1985). *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 184–189. Oxford: Clarendon Press.
- WATSON, G. N. (1952). *A Treatise on the Theory of Bessel Functions*. Cambridge Univ. Press.

*Acta Cryst.* (1987). **A43**, 763–769

## The Electron Density of Beryllium Derived from 0.12 Å $\gamma$ -ray Diffraction Data

BY N. K. HANSEN

*Laboratoire de Minéralogie et Cristallographie, Université de Nancy I, BP 239, F-54506, Nancy CEDEX, France*

J. R. SCHNEIDER

*Hahn-Meitner-Institut, Glienicker Strasse 100, D-1000 Berlin 39, Federal Republic of Germany*

AND W. B. YELON AND W. H. PEARSON

*University of Missouri Research Reactor, Columbia, Missouri 65211, USA*

(Received 9 January 1987; accepted 22 May 1987)

### Abstract

A large set of structure factors for beryllium has been measured with a 0.12 Å  $\gamma$ -ray diffractometer. The present data are in good agreement with other recent X-ray and  $\gamma$ -ray diffraction measurements. Extinction was significant though not very strong. Deformation density maps confirm that the bonding goes through the tetrahedral holes of the hexagonal close-packed structure. Comparisons with band-structure calculations indicate that the local-density approximation to the density functional theory is valid for beryllium. The quality of the data, combined with the earlier experimental results, is sufficient to demonstrate that the structure factors are sensitive to the valence electron hybridization even at high momentum transfer [ $(\sin \theta)/\lambda > 0.75 \text{ \AA}^{-1}$ ]. Core electron deformation is a much smaller effect.

### Introduction

Diffraction of short-wavelength electromagnetic radiation is a powerful tool for the examination of the electronic structure of crystalline solids. Most com-

monly the data are interpreted within the kinematical theory of diffraction, which is valid for small and so-called ideally imperfect crystals. Deviations from this theory are nevertheless more often the rule than the exception when X-rays of wavelengths 0.5–0.7 Å are used, and empirical corrections for secondary extinction must be applied to the experimental data. The method developed by Becker & Coppens (1974) is quite powerful for structure determinations and electron-density analysis of organic crystals. For inorganic materials the degree of perfection is often higher and the task of obtaining structure factors with a precision of better than one percent becomes quite difficult. The use of shorter-wavelength radiation or a decrease in the sample size [which requires a high-intensity source like a synchrotron – e.g. Bachmann, Kohler, Schulz & Weber (1985)] are ways of improving the situation. The former of these possibilities has been successfully applied with  $\gamma$ -radiation from neutron-activated sources; examples are measurements on plastically deformed copper crystals (Schneider, Hansen & Kretschmer, 1981) and on beryllium crystals of quite high perfection (Hansen,

Schneider & Larsen, 1984). In these two cases rather low-intensity 0.03 Å radiation from  $^{198}\text{Au}$  sources was employed which necessitated quite long measuring times. In order to improve on this, we employed a second  $\gamma$ -ray diffractometer using 0.12 Å radiation from a  $^{153}\text{Sm}$  source (Alkire & Yelon, 1981). This intermediate wavelength might be expected to be quite useful for scattering systems with light atoms where intensities at 0.03 Å are too low, but where extinction is still a problem with X-ray measurements.

Beryllium was chosen as a test case since the recent studies by Larsen & Hansen (1984) using the characteristic  $K\alpha$  radiation of molybdenum and of silver, and by Hansen *et al.* (1984) using gold  $\gamma$ -radiation, are judged to have given reliable data against which to compare. Our main effort has therefore been directed to the comparison of these data sets, though we also present the present experimental results in terms of electron-density maps and reconsider the possibility of a core deformation in beryllium. This analysis is completed by a comparison with recent band-structure calculations for beryllium.

### Experimental

The sample used in this study is an almost cubic single crystal of beryllium; it is the larger crystal used by Larsen, Lehmann & Merisalo (1980) for their neutron diffraction measurements, but subsequently etched by us to dimensions  $1.70 \times 1.90 \times 2.16$  mm. Originally it was cut by spark erosion from a larger piece supplied by the Max-Planck-Institut für Metallforschung in Stuttgart.

Diffraction data were obtained on the University of Missouri  $\gamma$ -ray scattering facility (Alkire & Yelon, 1981). The 0.12 Å wavelength radiation is produced by a source of approximately 1000 Ci and 46.27 h half-life. The measurement procedure is much the same as when collecting data on a standard X-ray diffractometer. The diffractometer has a conventional Eulerian cradle; an orientation matrix is determined, and a list of reflections is generated in a standard fashion. The  $\gamma$ -ray beam has been collimated so that the crystal is wholly bathed in it. Throughout the experiment a group of three reference reflections were measured after each 30 regular profiles. The profiles of the Bragg reflections are obtained from step scans in the  $\omega$  mode (bisecting geometry). The  $\omega$ -scan mode can be used safely since the wavelength dispersion of the radiation used is small ( $\Delta\lambda/\lambda \approx 10^{-5}$ ). Furthermore, owing to the low background we chose to operate with a very wide detector aperture ( $0.9^\circ$  seen from the sample) which should be compared with the combined effect of beam divergence and crystal size of about  $0.15^\circ$ . The number of steps per profile is 41, the step width is fixed at  $0.01^\circ$ , and the time spent on counting a reflection is determined from a rapid

prescan in order to obtain good counting statistics for all reflections. All reflections  $hkl$  with  $h - k = 3n$  and  $l$  odd were unobserved, indicating that multiple scattering is weak. The entire procedure is computer controlled and fully automated.

During a period of 36 days, 500 rocking curves were measured, corresponding to 37 symmetry-independent reflections having  $(\sin \theta)/\lambda = 0.85 \text{ \AA}^{-1}$  and 14 reflections were observed above this limit (29 are allowed).

### Data reduction

From the rocking curves, the integrated intensities are obtained by integration and background subtraction. Owing to the very high peak-to-background ratio, this latter correction is almost trivial, the Bragg peaks being well centered in the scanned intervals of  $\omega$ .

Because of the short wavelength of the radiation, the absorption by the sample is very weak. The absorption coefficient  $\mu = 0.241 \text{ cm}^{-1}$  has been determined from the tables compiled by McMaster, Kerr del Grande, Mallett & Hubbell (1969). The absorption correction factors are calculated by a Gaussian quadrature method (Coppens, Leiserowitz & Rabinovich, 1965) using a grid of  $6 \times 6 \times 6$  points. The transmission factors so determined vary between 0.955 and 0.963, and we estimate that the uncertainty of this correction should not be larger than 0.2%.

The intensities were also corrected for one-phonon diffuse scattering. For this purpose the computer program *TDS1/4* (Helmholdt, 1973) was used. The method is described in detail by Helmholdt & Vos (1977). The elastic constants needed were taken from Smith & Arbogast (1960). This correction is not very important. Neglecting it would lead to a decrease of the mean-square amplitudes of thermal vibration of about  $6 \times 10^{-5} \text{ \AA}^2$ , which is of the order of the e.s.d.'s of the thermal parameters as obtained by a least-squares refinement of the beryllium structure.

In addition to these corrections, which are similar to those applied in the analysis of X-ray diffraction data, we must correct the measured intensities for the decay of the radioactive source. Since the full data set has been collected with several sources, it effectively consists of seven subsets of relative measurements which are brought onto a common scale by comparison of repeatedly occurring reflections. After these corrections have been carried out, no systematic variation with time is observed for the structure-factor amplitudes. The scatter of structure factors measured several times or among symmetry-related structure factors does not exceed the acceptable limits based on counting statistics. The averaging of all symmetry-related data results in a set of 37 unique structure-factor amplitudes on a relative scale.

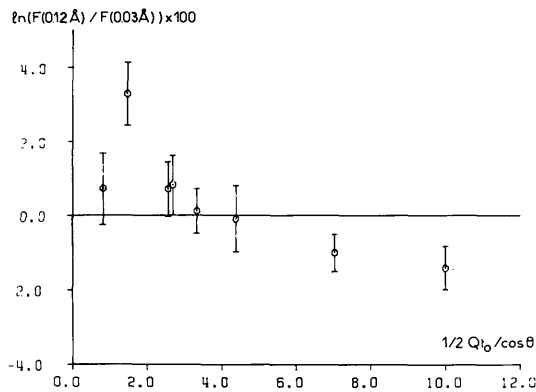
### Determination of an absolute scale for the measured structure factors

The absolute scaled structure factors, *i.e.* the Fourier transform of the electron-density distribution within one unit cell, have been determined by comparison of the present data with the 0.03 Å  $\gamma$ -ray diffraction data which were measured on an absolute scale (Hansen *et al.*, 1984). These data are supposedly free of extinction as discussed by the authors. We determine the scale factor from the equation

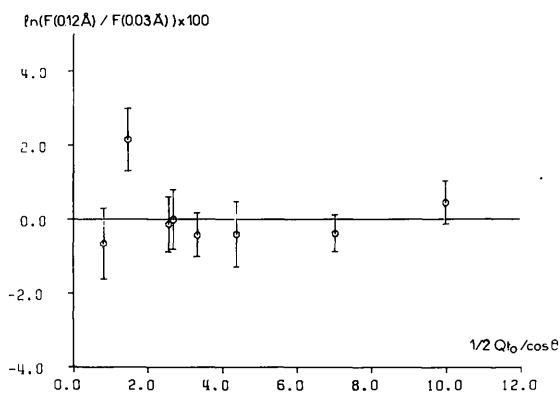
$$F(0.12 \text{ \AA}) = SF(0.03 \text{ \AA}),$$

the absolute structure factors being given by  $F = F(0.12 \text{ \AA})/S$ . The scale factor  $S$  is obtained by a least-squares analysis.

Inspection shows that the structure amplitude so scaled for the 002 reflection is relatively weak. In order to examine whether this could be due to secondary extinction, we show in Fig. 1(a) the magnitude of  $\ln[F(0.12 \text{ \AA})/F(0.03 \text{ \AA})]$  as a function of



(a)



(b)

Fig. 1. Behaviour of  $\ln [F(0.12 \text{ \AA})/F(0.03 \text{ \AA})]$ ;  $F$  denotes a  $\gamma$ -ray structure factor as obtained from measurement with different wavelength radiation (indicated in brackets). (a) Result after a simple scaling of the 0.12 Å data. (b) The 0.12 Å data have been scaled and corrected for secondary extinction. The abscissa,  $\frac{1}{2}Qt_0/\cos\theta$ , is in arbitrary units.

Table 1. Results of the scale-factor refinements

	Scale only	Scale+ext.
Weighted error sum		
$\sum(1/\sigma^2)[F(0.12 \text{ \AA}) - Sy^{1/2}F(0.03 \text{ \AA})]^2$	25	8.5
Scale factor	0.984 (5)	1.000 (6)
Extinction factors:		
$y(002)$		0.93 (2)
$y(101)$		0.96 (1)
$y(hkl)$		>0.975
$g \times 10^4$		0.44 (4)
Mosaic spread(")		7
Correlation coefficient between scale factor and $g$		0.84

$\frac{1}{2}Qt_0/\cos\theta$ , with

$$Q = [r_0(\lambda F(0.03 \text{ \AA})/V)]^2(\lambda/\sin 2\theta)P(\theta),$$

where  $r_0$  is the classical electron radius,  $\lambda$  represents the wavelength,  $V$  the unit-cell volume and  $P$  the polarization factor. If the plotted points all lie on a horizontal line, we deduce that extinction is of no importance, whereas, if they fall close to a line of negative slope, extinction is suspected. Since we are not actually measuring in a symmetrical Laue geometry, Fig. 1(a) should not be used directly for evaluating the possible secondary extinction. The figure certainly indicates that extinction plays a role, and we therefore have modified the expression relating the two  $\gamma$ -ray data sets so that it reads

$$F(0.12 \text{ \AA}) = Sy^{1/2}F(0.03 \text{ \AA}),$$

where  $y$  denotes the secondary-extinction correction factor. We use the model of Becker & Coppens (1974) (type I, isotropic Lorentzian mosaic distribution function). After correction of the 0.12 Å data we display  $\ln [F(0.12 \text{ \AA})/F(0.03 \text{ \AA})]$  in Fig. 1(b). No systematic trend is now observed. The outlier is the 102 reflection. Results of these two refinements are given in Table 1. The scale factor changed by 1.6%, and the extinction correction for the 002 structure factor (the strongest reflection) amounts to 3.4%, *i.e.* a net change of about 2%.

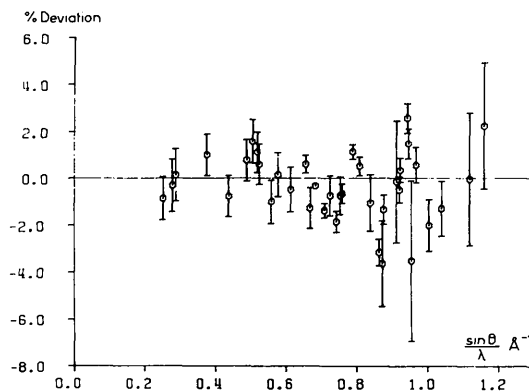


Fig. 2. Percentage deviation of the present  $\gamma$ -ray structure factors from the X-ray structure factors (Larsen & Hansen, 1984) as a function of scattering angle.

In the following discussions we shall use the corrected data and refer to them as the absolute scale data.\* They are in good agreement with the X-ray diffraction measurements (Larsen & Hansen, 1984) showing a random scatter around these values (see Fig. 2). The scatter is only slightly larger than expected from the random errors. The precision of the present low-order data is about equal to that of the X-ray data whereas the high-order data are slightly poorer. No systematic trends are observed in the differences between the two data sets.

### High-order refinements

The amplitudes of thermal vibration in beryllium have been determined from neutron diffraction by Larsen, Lehmann & Merisalo (1980). We can therefore analyse the errors which result when the scale factor of X-ray or  $\gamma$ -ray data and the vibrational parameters,  $U_{ij}$ , are free parameters in refinements of the structure factors. The results of such a procedure with high-order reflections are given in Table 2. The limit is chosen at  $(\sin \theta)/\lambda = 0.65 \text{ \AA}^{-1}$ . The contribution of the valence electrons of beryllium is supposed to be negligible above this limit. All calculations are carried out with free-atom Hartree-Fock (HF) scattering factors (*International Tables for X-ray Crystallography*, 1974). We may safely assume that anomalous dispersion is negligible. Only in the second refinement has the atomic scattering factor been modified:  $f_{\kappa}[(\sin \theta)/\lambda] = f[(\sin \theta)/\lambda\kappa]$  (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979): a value of  $\kappa$  less than one corresponds to an isotropic expansion of the charge density of the atom  $\rho_{\kappa}(r) = \kappa^3 \rho(\kappa r)$ . In practical terms a  $\kappa$  different from one reflects a modification of the core density, since these electrons give the major contribution to the scattering at high angles.

Relatively poor agreement is found when comparing the absolute-scale data with structure factors calculated with  $U_{ij}$  values from the neutron-diffraction study (Larsen *et al.*, 1980) (refinement I). This we attribute to a basic insufficiency of the free-atom model even for high-order data. The introduction of the radial expansion parameter,  $\kappa$ , as a parameter (refinement II) leads to a dramatic improvement, and accords with earlier remarks on a core deformation in beryllium [based on experimental data (Larsen & Hansen, 1984) and on Hartree-Fock band-structure calculations (Dovesi, Angonoa & Causa, 1982)]. The actual value of  $\kappa$  is 0.988 (2), corresponding to a 1.2% linear expansion of the

Table 2. *Results of high-order refinements*

(I) No refined parameters. Absolute scale data,  $U_{ij}$  from neutron diffraction analysis. (II) Refine  $\kappa$  value, otherwise as (I). (III) Refine scale factor and  $U_{ij}$ .

Refinement no.	Scale factor	$U_{11}$ ( $\text{\AA}^2 \times 10^5$ )	$U_{33}$ ( $\text{\AA}^2 \times 10^5$ )	$\Sigma$	G.o.f.
I	1.000 (6)	597 (3)	540 (3)	173	2.63
II	1.000 (6)	597 (3)	540 (3)	63	1.62
III	0.975 (7)	577 (21)	518 (19)	54	1.57

Definitions:

$$\Sigma = \sum_{\mathbf{h}} [F_{\text{obs}}(\mathbf{h}) - F_{\text{calc}}(\mathbf{h})]^2 / \sigma^2 [F_{\text{obs}}(\mathbf{h})].$$

$$\text{G.o.f.} = (\Sigma/\nu)^{1/2},$$

where  $\nu$  is the number of degrees of freedom of the refinement. There are 25 observations for  $(\sin \theta)/\lambda > 0.65 \text{ \AA}^{-1}$ .

electron density. A refinement of the X-ray data due to Larsen & Hansen (1984) leads to the same value of  $\kappa$ , and confirms the good agreement of their data with the present  $\gamma$ -ray measurements at high angles.

Advance lack of knowledge of either the scale factor or the appropriate thermal parameters would have obliged us to use the procedure of refinement II. This gives quite a good agreement with experiment, but the scale factor is in error by 2.5%. Owing to the large estimated errors of the vibrational parameters, their deviations from the neutron values cannot be considered significant. Simultaneous refinement of scale factor,  $U_{ij}$  and  $\kappa$  would be prohibited by very large correlations between these parameters.

### Comparison with recent band-structure calculations

We next examine the agreement of the present experiment with the three most recent structure-factor calculations for beryllium. This is done on the basis of form factors,  $f$ , which for the beryllium crystal are defined by the relation

$$F = 2f \cos \{2\pi[(h-k)/3 + l/4]\} T(hkl),$$

where  $F$  is the X-ray structure factor for a reflection with indices  $hkl$ , and  $T$  is the Debye-Waller factor which takes into account the attenuation due to the thermal vibrations of the atoms.  $T$  is unity for the theoretical data, and for the experimental data we use the amplitudes of vibration determined by neutron diffraction (Larsen *et al.*, 1980).

In all the theoretical studies presented here the free-atom form factors have been calculated as well, and within the same approximations as for the crystal calculations. This allows us to compare differences between the crystal and the free-atom form factors,  $\Delta f$ , with the advantage that a certain cancellation of errors is expected. From the experimental data we subtract free-atom form factors obtained from a correlated wavefunction (Brown, 1970).

Two of the band-structure calculations considered here are of the *ab initio* pseudopotential type. Chou,

\* A list of absolute scaled structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44022 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Lam & Cohen (1983) have obtained the pseudo-valence wavefunctions in the local-density approximation. They find good agreement between their structure factors and the X-ray data of Larsen & Hansen (1984) when they add a core contribution which has been calculated by Dovesi, Pisani, Ricca & Roetti (1982) for the solid. von Barth & Pedroza (1985) have also calculated the pseudo wavefunctions within the local-density scheme, but in addition they have used a non-local-density approximation. For comparison with experiment they not only add a core contribution, but they also apply a correction for the non-orthogonality of the pseudo-valence wavefunctions to the core wavefunctions. This latter correction, which only affects the electron density within the core radius, has an important effect on the structure factors, especially for the high-order reflections.

Pindor, Vosko & Umrigar (1986) have carried out all-electron linearized augmented plane-wave (LAPW) calculations, again within the local-density approximation. They show that a good agreement with the  $0.03 \text{ \AA}$   $\gamma$ -ray data of Hansen *et al.* (1980) can only be achieved if the potential between the muffin-tin spheres is warped. Their calculated structure factors contain a correction which equals the difference between the atomic form factors from a CI wavefunction (configuration interaction, *i.e.* exact exchange and correlation), and from the local-density approximation. As we are considering the differences between solid and atom, this correction is of no importance to our discussion.

It should be stressed that problems with the core electron density are inherent in all of these calculations. The pseudopotential method neglects it; the LAPW method suffers because the local-density approximation gives a poor description when the density is rapidly varying. The HF core wavefunctions are actually more correct.

In Fig. 3 the form-factor differences (between the solid and the free atom),  $\Delta f$ , are shown as a function of  $(\sin \theta)/\lambda$ . In view of the size of the random errors estimated for the experimental data (between 0.5 and 1% for most reflections), the three theories are in satisfactory agreement with each other, and with experiment, especially for the first three reflections (100, 002 and 101). The experimental value of  $\Delta f$  for the fourth-lowest-order reflection, 102, is found to be too large, whereas the measurement with  $0.03 \text{ \AA}$  radiation (Hansen *et al.*, 1984) is in good agreement with theory. This reflection was also an outlier on Fig. 1(b), and has probably been measured as too strong. In the medium range around  $(\sin \theta)/\lambda \approx 0.5 \text{ \AA}^{-1}$  the agreement is poorer. At higher orders, structure factors are only available from the two pseudopotential calculations.

In spite of a rather large scatter, the experimental values of  $\Delta f$  above  $(\sin \theta)/\lambda \approx 0.6 \text{ \AA}^{-1}$  tend to be negative. Low values of the beryllium form factors

have also been observed in earlier studies, and this has been interpreted as due to a core expansion. In this line of thinking we should take the result of the high-order refinement II (Table 2) to indicate a 1% linear expansion, implying a 2% decrease of the kinetic energy of the core electrons, *i.e.* by about 7.5 eV. Dovesi, Angonoa & Causa (1982) have shown on the basis of careful Hartree-Fock band-structure calculations that the change in the kinetic energy of the core electrons (the  $1s$  orbital) compared with the free atom only amounts to 1.5 eV. This result suggests that the major source of the low values observed for the form factors at high scattering angles resides in the modifications to the valence-electron distribution.

What seems to be the right explanation for the effect has been given by von Barth & Pedroza (1985). With a pseudopotential approach they reproduce the observed trend of the form factors quite accurately, although they make no effort to take into account the effects of the crystal field on the core electron density. The good agreement which they obtain is due to correction for the non-orthogonality of the pseudo-valence wave functions. The condition of orthogonality between core and valence states (for the atom as well as for the solid) leads to a core-like cusp in the valence density of the  $s$ -like states, which is absent in the  $p$ -like states. Now, in the solid they find only about 0.6 electrons per atom in valence  $s$  states, in agreement with the other band-structure calculations, whereas the atom which is subtracted (as is commonly done) has two electrons in the  $2s$  orbital. Because of this promotion (hybridization) of electrons from  $2s$  to mainly  $2p$  states in the solid, we observe lower form-factor values for the crystal than for the atom. A comparison of the results of Chou *et al.* (1983) with those of von Barth & Pedroza (1985) in Fig. 3 shows that the orthogonalization effect dominates above  $0.6 \text{ \AA}^{-1}$ . It is to be expected that the latter authors slightly exaggerate the effect, since the free

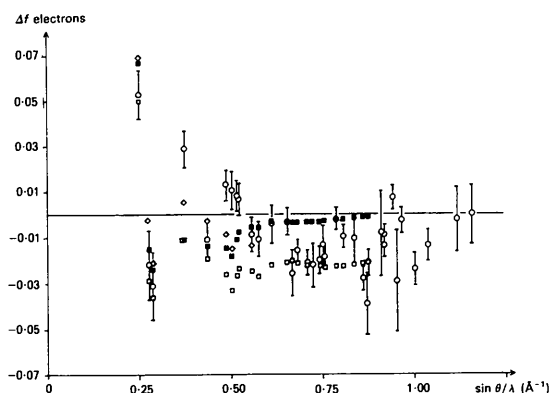


Fig. 3. Differences between beryllium-crystal and free-atom form factors as a function of scattering angle.  $\diamond$  Pindor *et al.* (1986),  $\square$  von Barth & Pedroza (1985),  $\blacksquare$  Chou *et al.* (1983),  $\circ$  the present experiment (the error bar marks  $\pm$  one standard deviation).

beryllium atom actually contains 1.8 electrons in the 2s natural orbital (Bunge, 1968), and not two.

### Electron-density maps

Using the absolute-scale data we may calculate a  $\gamma$ - $N$  deformation density map according to the expression

$$\Delta\rho(\mathbf{r}) = (1/V) \sum_{\mathbf{h}} [F_{\gamma}(\mathbf{h}) - F_N(\mathbf{h})] \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}),$$

where  $F_N$  are the structure factors calculated with free-atom X-ray scattering factors, and the positional and thermal parameters obtained in the neutron diffraction study of Larsen *et al.* (1980). We only extend the Fourier summation over reflections corresponding to a  $(\sin \theta)/\lambda$  value less than  $0.65 \text{ \AA}^{-1}$ . The result for the (110) plane is shown in Fig. 4, and for the (001) plane passing through a layer of beryllium atoms in Fig. 5. Inclusion of higher-order terms mainly modifies the maps within a radius of  $0.9 \text{ \AA}$  from the nuclei. These maps confirm the earlier observations of Larsen & Hansen (1984): Fig. 6 shows an  $X$ - $N$  map based on their data. They show an

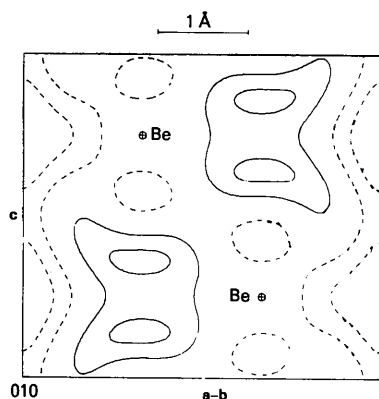


Fig. 4.  $\gamma$ - $N$  deformation map in the (110) plane. Contours are plotted in intervals of  $0.015 \text{ e \AA}^{-3}$ . Negative contours are broken, positive contours are full lines, the zero contours are omitted.

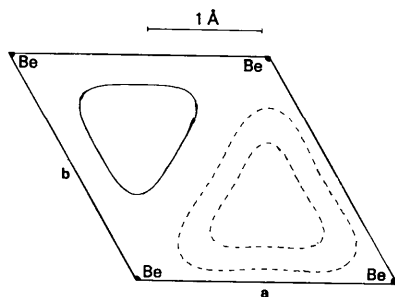


Fig. 5.  $\gamma$ - $N$  deformation map in the section parallel to (001) through a layer of beryllium atoms. Contours as in Fig. 4.

excess density in the tetrahedral holes and a depletion in the columns formed by the octahedral holes parallel to  $c$ .

### Concluding remarks

The present study demonstrates that high-quality diffraction data can be obtained with short-wavelength electromagnetic radiation. The requirements on crystal size are about the same as for neutron diffraction. It should be underlined that secondary extinction cannot be neglected, though the effect is relatively weak for the present data. Nevertheless, in the case of beryllium, it has been impossible to obtain a reliable estimate for extinction using only the  $0.12 \text{ \AA}$  data, since we are not able to separate the effect of valence-electron-density deformation from extinction. A least-squares refinement on all the  $0.12 \text{ \AA}$   $\gamma$ -ray structure factors using free-atom scattering factors leads to negligible corrections. The study of BeO by Downs, Ross & Gibbs (1985) shows that extinction can be much more serious. One might repair this by multi-wavelength experiments [for an example see Schneider & Kretschmer (1985)], or by going to higher-intensity sources like synchrotrons which allow the use of tiny samples, assuming that the conditions of wavelength and intensity stability can be met.

Recent diffraction studies on crystalline beryllium all give a quite consistent picture of the electron-density deformations, and we have seen that these deformations can be reproduced by calculations based on density functional theory. The much discussed core deformation in beryllium needs the comment that the valence density contains a core-like cusp which depends on the state of hybridization. This effect overshadows the modifications of the core itself.

This work was supported by the NATO Scientific Affairs Division (grant No. RG 128.81).

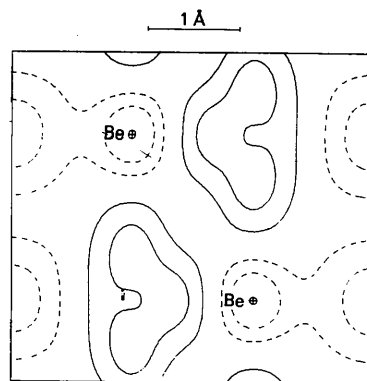


Fig. 6.  $X$ - $N$  deformation map in the (110) plane using the X-ray data of Larsen & Hansen (1984). Contours as in Fig. 4.

## References

- ALKIRE, R. W. & YELON, W. B. (1981). *J. Appl. Cryst.* **14**, 362–369.
- BACHMANN, R., KOHLER, H., SCHULZ, H. & WEBER, H. P. (1985). *Acta Cryst.* **A41**, 35–40.
- BARTH, U. VON & PEDROZA, A. C. (1985). *Phys. Scr.* **32**, 353–358.
- BECKER, P. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 129–147.
- BROWN, R. T. (1970). *Phys. Rev. A*, **2**, 614–620.
- BUNGE, C. F. (1968). *Phys. Rev.* **168**, 92–103.
- CHOU, M. Y., LAM, P. K. & COHEN, M. L. (1983). *Phys. Rev. B*, **28**, 4179–4185.
- COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- DOVESI, R., ANGONOA, G. & CAUSA, M. (1982). *Philos. Mag. B*, **45**, 601–606.
- DOVESI, R., PISANI, C., RICCA, F. & ROETTI, C. (1982). *Phys. Rev. B*, **25**, 3731–3739.
- DOWNES, J. W., ROSS, F. K. & GIBBS, G. V. (1985). *Acta Cryst.* **B41**, 425–431.
- HANSEN, N. K., SCHNEIDER, J. R. & LARSEN, F. K. (1984). *Phys. Rev. B*, **29**, 917–926.
- HELMHOLDT, R. B. (1973). Computer program *TDS1/4*. Univ. of Groningen, The Netherlands.
- HELMHOLDT, R. B. & VOS, A. (1977). *Acta Cryst.* **A33**, 38–45.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- LARSEN, F. K. & HANSEN, N. K. (1984). *Acta Cryst.* **B40**, 169–179.
- LARSEN, F. K., LEHMANN, M. S. & MERISALO, M. (1980). *Acta Cryst.* **A36**, 159–163.
- MCMASTER, W. H., KERR DEL GRANDE, N., MALLETT, J. H. & HUBBELL, J. H. (1969). *Compilation of X-ray Cross Sections*. UCRL-50174 (§2, Rev. 1), Lawrence Radiation Laboratory, University of California at Livermore, CA, USA.
- PINDOR, A. J., VOSKO, S. H. & UMRIGAR, C. J. (1986). *J. Phys. F*, **16**, 1207–1212.
- SCHNEIDER, J. R., HANSEN, N. K. & KRETSCHMER, H. (1981). *Acta Cryst.* **A37**, 711–722.
- SCHNEIDER, J. R. & KRETSCHMER, H. (1985). *Naturwissenschaften*, **72**, 249–259.
- SMITH, J. F. & ARBOGAST, C. L. (1960). *J. Appl. Phys.* **31**, 99–102.

*Acta Cryst.* (1987). **A43**, 769–774

## General Theory of the Effect of Granularity in Powder X-ray Diffraction

BY CARLOS R. GONZALEZ

*Department of Crystallography of Minerals, Centre of Geological Research, Oficinas 154, Havana, Cuba*

(Received 2 December 1985; accepted 21 April 1987)

### Abstract

The effect of granularity in powder X-ray diffraction is reviewed, and the shortcomings of previously developed models in explaining this effect are described. A new physical model encompassing all aspects of this phenomenon is proposed. Mathematical formulae based on the model are derived, and their limit cases are discussed. Values of the theoretical intensities from the model are compared with results from a specially designed experiment.

### Introduction

X-ray diffracted intensities from actual powder samples can be greatly affected compared with the ideal case if the fineness condition  $d(|\bar{\mu} - \mu|) < 0.01$  is not fulfilled (Zevin & Zavyalova, 1974), where  $d$  is the mean size,  $\mu$  is the absorption coefficient of the diffracting phase, and  $\bar{\mu}$  is the absorption coefficient of the matrix.

It is not always possible to reduce the particle size enough to avoid granularity effects in the diffracted intensities, since many crystalline materials will not survive severe mechanical treatment. In such cases, it is more meaningful in quantitative analysis and

structure determination to make mathematical corrections.

The effect of granularity has been studied from the beginnings of X-ray diffractometry. Brindley (1945) gave the first approximation to the problem. His theory, though oversimplified, successfully explained one fundamental aspect of the effect. Wilchinsky (1951) gave a second model which explained the effects of porosity and grain and particle size, although Harrison & Paskin (1964) stated that his statistical treatment of the powder was not rigorous.

These latter authors stated the question from a new point of view. They proposed to explain the effect of granularity in the angular region near  $90^\circ$ . More recently, Shimazu (1967) and Shimazu & Hosoya (1968) returned to Brindley's ideas, considering new aspects not taken into account by him.

None of these models explains all facets of the effect, which, in reality, is a set of effects very closely related to one another (Zevin & Zavyalova, 1974), and no further directly related work was performed in continuance of the cited works.

The effects of granularity depend on the heterogeneity of crystalline powders. An expression for the intensity from ideally homogeneous crystalline