References

BLERIS, G. L., NOUET, G., HAGÈGE, S. & DELAVIGNETTE, P. (1982). *Acta Cryst.* A38, 550–557.
BONNET, R. & COUSINEAU, E. (1977). *Acta Cryst.* A33, 850–856.
BONNET, R., COUSINEAU, E. & WARRINGTON, D. H. (1981). *Acta Cryst.* A37, 184–189.
BONNET, R. & DURAND, F. (1975). *Philos. Mag.* 32, 997–1006.
DONI, E. G., FANIDES, CH. & BLERIS, G. L. (1986). *Cryst. Res. Technol.* 21, 1469–1474.
ECKERLIN, P. & KANDLER, H. (1971). *Landolt-Börnstein, New Series*, Group III, Vol. 6. Berlin: Springer.
EROCHINE, S. & NOUET, G. (1983). *Scr. Metall.* 17, 1069–1072.

GRIMMER, H. (1974). *Acta Cryst.* A30, 685–688.
GRIMMER, H. (1989a). *Helv. Phys. Acta,* 62, 231–234.
GRIMMER, H. (1989b). *Acta Cryst.* A45, 320–325.
GRIMMER, H. (1989c). *Scr. Metall.* 23, 1407–1412.
GRIMMER, H. (1989d). *Acta Cryst.* A45, 505–523.
GRIMMER, H. & WARRINGTON, D. H. (1985). *J. Phys. (Paris) Colloq.* 46, C4, 231–236.
GRIMMER, H. & WARRINGTON, D. H. (1987). *Acta Cryst.* A43, 232–243.
LARTIGUE, S. (1988). *Doctoral thesis.* Univ. de Paris-Sud, France. Unpublished.
WAERDEN, B. L. VAN DER (1966). *Algebra,* Vol. 1. Berlin: Springer.
WARRINGTON, D. H. (1975). *J. Phys. (Paris) Colloq.* 36, C4, 87–95.

Measurement of the Structure Factors of Diamond

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Abstract

The absolute values of the structure factors of diamond are determined for nine low-order reflections by measuring the X-ray *Pendellösung* beats on the wavelength scale. Parallel-sided wafers of synthetic diamond single crystals are used for specimens. The deformation charge density and the Debye-Waller B factor are evaluated from the structure factors. The charge density of pile-up electrons is estimated to be $0.44\,(17)\,\mathrm{e\AA^{-3}}$ at the midpoint between the nearest-neighbour atoms. The density is slightly smaller than that determined by the powder diffraction method. The obtained B factor, $0.142\,(9)\,\mathrm{\AA^2}$, is in good agreement with that evaluated to date from neutron diffraction measurements.

1. Introduction

Diamond is a typical covalent crystal in which each atom is linked tetrahedrally to four neighbouring atoms. The charge distribution is modified in the crystal so as to reflect the site symmetry $(\bar{4}3m)$ of the atomic positions. A weak X-ray intensity measured for the forbidden 222 reflection (Renninger, 1955) is clear evidence of this modification. The structure factors of diamond were determined by Göttlicher &

Wölfel (1959) (hereafter GW). They carried out an X-ray measurement of integrated intensity diffracted from a fine-powder sample and evaluated the structure factors using kinematical diffraction theory.

Lang & Mai (1979) (hereafter LM) observed the *Pendellösung* fringes in the Bragg case from natural diamond crystals. They determined the structure factor of the 311 reflection from the fringe spacing based on dynamical diffraction theory. The advantage of the *Pendellösung*-fringe method is that no absolute intensity measurement is required but only the extremum positions need to be determined. However, as far as diamond is concerned, no data from the *Pendellösung*-fringe method are available except the value for the 311 reflection by LM.

The present authors have developed a technique of measuring the *Pendellösung* beats on the wavelength scale and determined the structure factors of various substances (Takama & Sato, 1988; Kobayashi, Takama, Tohno & Sato, 1988). In the present study, the technique is applied to determine the structure factors of diamond. The structure factors for the nine low-order reflections are used to evaluate deformation charge density as well as the temperature factor.

2. Measurements

The synthetic diamond crystals were grown under a pressure of 5.0–$5.5\,\mathrm{GPa}$ at 1700–1800 K with the help of a metal solvent. Granular crystals were cut to parallel-sided wafers having a {110} surface and about

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0·2–0·6 mm thickness. A topographic examination revealed that there existed regions inside some wafers in which almost no dislocations were detected. Four wafers with low dislocation density were selected from among 19 specimens. Fig. 1 is a transmission white X-ray topograph showing an example of a defect-free region, the area used for data collection.

A collimated beam of white radiation from a high-power X-ray generator (RU-1000 C2, Rigaku Denki Co.) was used to irradiate the defect-free region. The integrated intensity J_g of a Laue spot in the Laue case was measured at an angle 2θ using a germanium solid-state detector. The measurement was carried out for a fixed time, and then the position was changed for the next measurement. The variation of J_g with wavelength was measured by repeating similar measurements at different 2θ settings. The detail of the method of measurement has been described elsewhere (Takama & Sato, 1988).

3. Experimental results

Dynamical diffraction theory (Kato, 1968) predicts that the integrated intensity J_g in the Laue case can be expressed as a function consisting of two terms for each polarization of the X-ray beam. One term is the Waller integral which shows an oscillation with respect to the upper limit of integration. The upper limit is a function of $\lambda t/\cos\theta$ and $|F_g|$ where λ, t, θ and $|F_g|$ are the wavelength of the X-rays, the thickness of the specimen, the Bragg angle and the real part of the structure factor of the g reflection, respectively. Hence, measurement of beat variation with wavelength can give us the absolute values of $|F_g|$

with its wavelength dependence if we know the thickness t. The other term, related to Borrmann absorption, is less important, because the wavelength used was much smaller than the K absorption edge of carbon.

Fig. 2 shows an example of the measured intensity oscillations of J_{111}. The experimentally determined curve was subjected to three corrections which are associated with incident-beam spectrum, absorption and geometrical factors. The structure factors were determined by comparing the extremum positions in the beats with the positions calculated by dynamical theory. The resulting values of the structure factors for the 111 reflection are shown in Fig. 3. Wavelength dependence is not obvious, in contrast to previous results for materials composed of heavy atoms (Takama & Sato, 1988; Kobayashi, Takama, Tohno & Sato, 1988). According to the calculation by Cromer & Liberman (1970), the real part of the anomalous-dispersion term is less than 0·006 for the present wavelength range which is less than 1·0 Å. Therefore, we may neglect this effect and take the simple arithmetic average of the measured values at different wavelengths. The obtained values of the structure factors at 294 K are listed in Table 1.

4. Analysis of deformation charge density

Dawson (1967) proposed a model to describe the deformation charge density and tried to determine the density in diamond from the structure factors measured by Göttlicher & Wölfel (1959). A similar
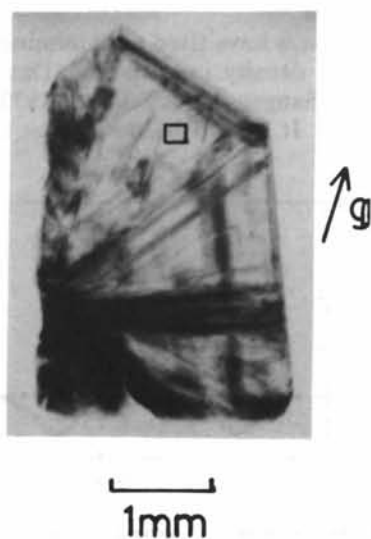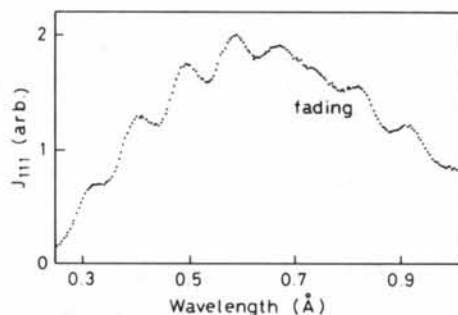

Fig. 1. White X-ray transmission topograph showing grown-in defects in a synthetic diamond wafer. The square indicates the region used for the *Pendellösung* beats measurements. g = 422.

Fig. 2. *Pendellösung* beats measured in the 111 reflection of diamond. Fading is seen at 0·75 Å.
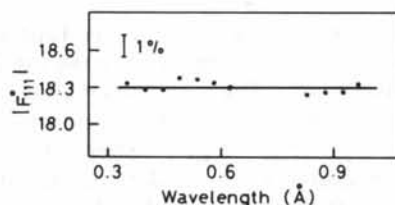

Fig. 3. Obtained structure factors $|F^\circ_{111}|$ of diamond for the 111 reflection.

Table 1. *Structure factors of diamond determined at 294 K*

The values reported by Göttlicher & Wölfel (1959) and by Lang & Mai (1979) are listed for comparison.

h k l	Present results	Göttlicher & Wölfel	Lang & Mai
1 1 1	18·37 (6) [6]	18·566 (40)	
2 2 0	15·36 (4) [5]	15·288 (72)	
3 1 1	9·32 (2) [3]	9·006 (40)	9·22 (17)
4 0 0	11·93 (5) [3]	11·112 (72)	
3 3 1	8·39 (4) [3]	8·287 (28)	
4 2 2	10·90 (8) [3]	10·504 (16)	
5 1 1	7·41 (1) [3]	7·212 (28)	
3 3 3	7·28 (3) [2]	7·212 (28)	
4 4 0	9·58 (2) [2]	9·080 (72)	

The figures in square brackets are the number of measurements made for different irradiated regions.

evaluation of the charge density is performed following Dawson's treatment on the basis of the present structure factors.

Dawson expressed the charge density $\rho(\mathbf{r})$ of a C atom in diamond as

$$\rho(\mathbf{r}) = \rho_c(\mathbf{r}) + \rho_a(\mathbf{r}) + \delta\rho_c(\mathbf{r}), \qquad (1)$$

in which $\rho_c(\mathbf{r})$ is the spherically symmetric component and the two terms $\rho_a(\mathbf{r})$ and $\delta\rho_c(\mathbf{r})$ represent the antisymmetric and the centrosymmetric component, respectively. He expanded the non-spherical components to the fourth-order terms in the cubic harmonics as

$$\rho_a(\mathbf{r}) = F_3(r)[(xyz)/r^3] \qquad (2)$$

and

$$\delta\rho_c(\mathbf{r}) = G_4(r)\{[(x^4 + y^4 + z^4)/r^4] - 3/5\}. \qquad (3)$$

The Fourier transform of (1) gives the atomic scattering factors for the model charge density. Dawson set the radial distribution functions $F_3(r)$ and $G_4(r)$ to

$$F_3(r) = K_{22}r^2 \exp(-\alpha r^2) \qquad (4a)$$

and

$$G_4(r) = L_{22}r^2 \exp(-\alpha r^2), \qquad (4b)$$

and set α, *a priori*, to 2·2 Å^{-2} with an isotropic temperature factor B of 0·20 Å^2. He determined suitable values for the two parameters K_{22} and L_{22} which made the model structure factors fit the experimental data by GW.

In the present treatment, we set the four unknown parameters (*i.e.* α, B, K_{22} and L_{22}) in the model structure factors of F_g^c. The optimum values of these parameters were determined by minimizing the residual $\delta = \sum_g (|F_g^o| - |F_g^c|)^2$, where $|F_g^o|$ is the observed structure factor. In the calculation of F_g^c, the atomic scattering factors tabulated by Cromer & Waber (1974) were used for the scattering factors which arise from the spherically symmetric com-

Table 2. *Values of the four parameters determined in the deformation density model*

The values by Dawson are also shown.

	Present results	Dawson
$B(\text{Å}^2)$	0·142 (9)	0·20
$\alpha(\text{Å}^{-2})$	2·10 (26)	2·2
$K_{22}(\text{Å}^{-5})$	5·9 (23)	7·5
$L_{22}(\text{Å}^{-5})$	−0·58 (34)	−2·0

ponent $\rho_c(\mathbf{r})$. The values of the four determined parameters are given in Table 2. The agreement factor $R = \sum_g \|F_g^o| - |F_g^c\|/\sum_g |F_g^o|$ was 0·6%. Fig. 4 shows the profile of the resultant deformation charge density at 0 K calculated from (2) and (3).

5. Discussion

Göttlicher & Wölfel determined the absolute structure factors by measuring the integrated intensity diffracted from powdered diamond. In order to obtain the absolute structure factors, the measured intensities are to be corrected for several effects such as intensity of incident beam, preferred orientation, thermal diffuse scattering, extinction, absorption of X-rays *etc.* Accordingly, the accuracy of the structure factors is strongly and directly influenced by such corrections to the method.

The structure factors obtained in the present experiment are compared with those derived by GW and LM in Table 1. One sees fairly good agreement between our result and that of LM for the 311 reflection. However, our values are larger than those obtained by GW except for the 111 reflection. The discrepancy might be partly attributed to inaccurate corrections made for the measured intensity in the powder method.

Several workers have tried to determine the deformation charge density in diamond (Dawson, 1967; McConnell & Sanger, 1970; Stewart, 1973a; Price & Maslen, 1978). It should be noted that all of these
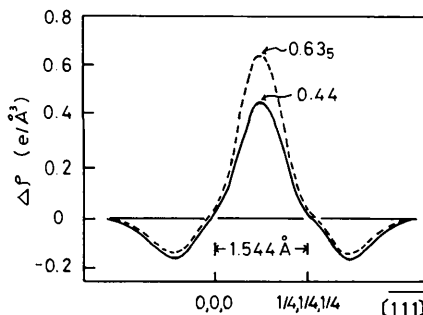

Fig. 4. Distribution of deformation charge density $\Delta\rho$ plotted along the [111] direction through two nearest-neighbour atoms located at $(0, 0, 0)$ and $(1/4, 1/4, 1/4)$. The solid line is obtained from the present data and the broken line from the Göttlicher & Wölfel data used by Dawson.

analyses have utilized the experimental data of GW. In the present study, the four parameters in the Dawson functions were determined from the present experimental data. The exponent α of the radial distribution functions in (4) was found to be $2 \cdot 10\,(26)$ Å^{-2}. This value is almost the same as that assumed by Dawson as shown in Table 2. However, the values of the parameters K_{22} and L_{22} which were obtained are slightly different from those of Dawson. One can calculate the deformation charge density using these parameters. The maximum deformation density at the midpoint between the nearest-neighbour atoms is $0 \cdot 44\,(17)$ eÅ^{-3}, which is smaller than Dawson's value of $0 \cdot 63_5$ eÅ^{-3} as shown in Fig. 4.

In order to study the thermal vibration, the GW data have been recalculated for several charge density models (McConnell & Sanger, 1970; Stewart, 1973a; Price & Maslen, 1978). The B values obtained in the recalculations range from $0 \cdot 14$ to $0 \cdot 22$ Å^2 depending on the models used. On the other hand, the neutron diffraction studies have concluded that the values lie between $0 \cdot 14$ and $0 \cdot 17$ Å^2. The present value of $0 \cdot 142\,(9)$ Å^2 is in good agreement with the value calculated from the phonon dispersion curves measured by inelastic neutron scattering, $0 \cdot 149$–$0 \cdot 150$ Å^2 (Stewart, 1973b), and also with that from neutron diffraction of the powdered sample, $0 \cdot 14$–$0 \cdot 17$ Å^2 (Price, Maslen & Moore, 1978).

Synthetic diamond crystals were used as the specimens and these contained grown-in dislocations to a certain extent as shown in Fig. 1. The *Pendellösung* beats were measured only in the defect-free regions. However, it is inevitable that there are some effects resulting from the strain field around the dislocations near the region used. Nevertheless, the effects are thought to be small, because the values of the structure factors obtained differ only slightly from each other in the different regions.

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography.* Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
DAWSON, B. (1967). *Proc. R. Soc. London Ser. A,* **298**, 264–288.
GÖTTLICHER, S. & WÖLFEL, E. (1959). *Z. Elektrochem.* **63**, 891–901.
KATO, N. (1968). *J. Appl. Phys.* **39**, 2225–2237.
KOBAYASHI, K., TAKAMA, T., TOHNO, S. & SATO, S. (1988). *Jpn. J. Appl. Phys.* **27**, 1793–1797.
LANG, A. R. & MAI, Z.-H. (1979). *Proc. R. Soc. London Ser. A,* **368**, 313–329.
MCCONNELL, J. F. & SANGER, P. L. (1970). *Acta Cryst.* A**26**, 83–93.
PRICE, P. F. & MASLEN, E. N. (1978). *Acta Cryst.* A**34**, 173–183.
PRICE, P. F., MASLEN, E. N. & MOORE, F. H. (1978). *Acta Cryst.* A**34**, 171–172.
RENNINGER, M. (1955). *Acta Cryst.* **8**, 606–610.
STEWART, R. F. (1973a). *J. Chem. Phys.* **58**, 4430–4438.
STEWART, R. F. (1973b). *Acta Cryst.* A**29**, 602–605.
TAKAMA, T. & SATO, S. (1988). *Aust. J. Phys.* **41**, 433–448.

The Use of Structural Information in Phase Determination

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Abstract

The procedure adopted by Heinerman [*Acta Cryst.* (1977). A**33**, 100–106] to incorporate structural information in phase determination is combined with that of Giacovazzo [*Acta Cryst.* (1983). A**39**, 685–692]. The resulting joint probability distribution of three structure factors is a generalization of the corresponding distributions of the previous authors. This distribution is used (i) to calculate the phase of a triple product given *a priori* structural information, (ii) to resolve the sign ambiguity in single isomorphous replacement if the replacement structure is known. The latter application for the incorporation of partial structure information is more general than that proposed by Fan Hai-fu & Gu Yuan-xin [*Acta Cryst.* (1985). A**41**, 280–284].

Introduction

In the generalized Cochran formula proposed by Main (1976), four different types of *a priori* informa-