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Electron-Density Studies. I. A Neutron Diffraction Powder Study of Diamond

BY P. F. PRICE AND E. N. MASLEN

Department of Physics, University of Western Australia, Nedlands, Western Australia

AND F. H. MOORE

Australian Institute of Nuclear Science and Engineering, Lucas Heights, New South Wales, Australia

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Neutron powder patterns from two samples have been analysed to provide information on the thermal motion in diamond. The resulting Debye–Waller factor of 0·14–0·17 Å^2 lends support to the lattice-dynamic value of 0·149–0·150 Å^2. The small effect of extinction (less than 4%) is well described by the Becker and Coppens formula but poorly described by that of Zachariasen. The accuracy of the data necessitated a correction for thermal diffuse scattering.

The X-ray diamond powder data of Göttlicher & Wölfel (1959) have been analysed by many workers (Dawson, 1967; McConnell & Sanger, 1970; Kurki-Suonio & Ruuskanen, 1971; Stewart, 1973*a*,*b*; Harel, Hecht & Hirschfeld, 1975; Price & Maslen, 1978) in terms of various charge-density models. The results differ primarily in the determined value of the Debye–Waller factor, or B value. If the charge-density model is based on Hartree–Fock atomic form factors, the resulting B value is 0·20–0·21 Å^2, whereas the valence-density model of Stewart (1973*b*) results in a value of 0·17–0·18 Å^2. When the latter model is amended by an *ad hoc* correction term to satisfy the cusp condition (Kato, 1957; Pack & Brown, 1966) the B value changes to 0·140 ± 0·004 Å^2 (Stewart 1973*b*). Price & Maslen (1978) have shown that this result depends critically on the choice of the 1*s* orbital from the literature and on an arbitrarily chosen exponent in the correction term. In addition, the use of the correction term significantly worsens the fit to the data. The lattice-dynamic B value, calculated (Stewart, 1973*a*) from phonon-dispersion curves measured by inelastic neutron scattering, is 0·149–0·150 Å^2. As the accurate description of the charge density requires a knowledge of the B value, a determination from a neutron powder diffraction experiment was undertaken.

The intensity data were collected at the Australian Atomic Energy Commission's HIFAR reactor on the 4H1 beam hole operated by the Australian Institute of Nuclear Science and Engineering. The incident neutron beam, obtained by reflection from the (111) planes of a copper-crystal monochromator, has a measured mean wavelength of 1·0884 ± 0·003 Å. Data were collected from two samples, with diameters nominally in the ranges 4–8 μm and 0–1 μm. The samples, of about 4 cm^3, were mounted in aluminium tubes. There was no overlap between the lines for diamond and aluminium. The ten lines out to the experimental limit of $\sin\theta/\lambda = 0{\cdot}85$ Å^{-1} were clearly resolved, except for exact overlap of the 333 and 511 lines, and a slight overlap of the trailing and leading edges of the last two lines.

The background was estimated by a variety of methods including analytical representation by a least-squares fit and averaging over wide and narrow ranges. The range of these measurements was used to estimate the standard deviations in the intensities. It was found that an improper treatment of the background could change the determined B value by 0·03 Å^2. The background of the 0–1 μm data was larger and more subject to extremes of data-reduction technique than that of the 4–8 μm data.

Initial refinements indicated the necessity of an extinction correction. The results from the formulae of Zachariasen (1967) and of Becker & Coppens (1974) are shown in Table 1. Since the extinction is weak (the extinction factor, $y > 0{\cdot}96$) the Becker & Coppens formula for primary extinction reduces to that of Zachariasen modified by a factor of $\sin 2\theta$. Although it was not possible to estimate the 'particle size' from the least-squares extinction coefficient, X, they should be proportional. For the extinction-affected data (4–8 μm) the 'goodness-of-fit' (GoF) and weighted R factor (R_w) refinement indices are much lower with the use of the Becker & Coppens formula than with that of Zachariasen.

The GoF index at this stage of analysis was greater than unity, and for the 4–8 μm data, a plot of the residuals showed systematic trends in both data sets, with the observed intensities being too large at the high-angle end of the data. This is consistent with the effect of thermal diffuse scattering (TDS). The evaluation of a TDS correction (Willis, 1969, 1970; Cooper, 1971) is difficult as the sound velocity is greater than the neutron velocity. The transverse and longitudinal velocity ratios, β = sound velocity/neutron

velocity, are $\beta_{TR} = 4{\cdot}8$ and $\beta_L = 3{\cdot}5$. It is sometimes assumed (Willis, 1969) that for $\beta > 1$ there is no TDS correction as the TDS is constant under the Bragg peak and is thus subtracted off with the background. However this is only true for a perpendicular scan for large enough values of β, and even then only if the peak is reasonably sharp (Cooper, 1971). For the powder method, with broad peaks, most of the TDS contribution can be expected to be under the Bragg maximum. The TDS intensity is continuous at $\beta = 1$ and for $\beta < 1$ it is given by the same relation as that for X-rays. Consequently, in this case the X-ray formula will give an upper bound. The X-ray TDS correction of Lucas (1969) was used together with the extinction formula of Becker & Coppens (1974) to generate the results shown under the heading 'BC(TDS)' in Table 1. The GoF and R_w indices decrease and the final residuals show no consistent trends. This TDS correction amounts to a maximum of a 2·4% reduction in the high-angle peak intensities.

The determined B values are quite different for the two samples, 0·160 ± 0·005 Å^2 for the 4–8 μm data and 0·190 ± 0·010 Å^2 for the 0–1 μm data, when the TDS correction is included. As the GoF is 1·07 for the 4–8 μm data and 1·88 for the 0–1 μm data it appears that there are systematic errors in the latter data which have not been taken care of in the analysis. In view of this and the fact that the background for this set of data was larger and more difficult to estimate accurately than that of the 4–8 μm data, we place more reliability on the results of the latter data set. Taking into account the uncertainty in the TDS correction, the B value is determined to be in the range 0·14–0·17 Å^2. This is in good agreement with the lattice-dynamic value of 0·149–0·150 Å^2.

The extinction coefficient [in the Becker & Coppens (1974) formula] should be proportional to the mean particle size. The results are consistent with this. Relative to the Zachariasen treatment, the Becker & Coppens (1974) formula resulted in a decrease of 0·007 Å^2 in the B value of the 4–8 μm data.

The TDS correction resulted in an increase of 0·013 Å^2 in the B value of the 4–8 μm data and 0·016 Å^2 in that of the 0–1 μm data.

Table 1. *Values of the Debye–Waller factor (B), the extinction coefficient (X) and the refinement indices for the two powder samples*

Nominal diameters (μm)	Model correction	B (Å^2)	X	GoF[a]	R_w[b]
4–8	Z[c]	0·154 (8)[f]	10 (3)	1·50	0·0065
	BC[d]	0·147 (6)	12 (3)	1·19	0·0052
	BC(TDS)[e]	0·160 (5)	12 (2)	1·07	0·0047
0–1	Z	0·172 (11)	0 (5)	2·28	0·0102
	BC	0·174 (9)	5 (5)	2·10	0·0094
	BC(TDS)	0·190 (10)	5 (5)	1·88	0·0084

(*a*) GoF = $[\Sigma\omega_i \Delta y_i^2/(n-m)]^{1/2}$, where ω_i is the weight of the ith intensity, y_i, n is the number of intensities (9) and m is the number of parameters (3). (*b*) $R_w = (\Sigma\omega_i \Delta y_i^2/\Sigma\omega_i y_i^2)^{1/2}$. (*c*) Results from the Zachariasen (1967) extinction formula with no TDS correction. (*d*) Results from the Becker & Coppens (1974) extinction formula with no TDS correction. (*e*) Results from the Becker & Coppens (1974) extinction formula with the X-ray TDS correction of Lucas (1969). (*f*) Estimated standard deviations in the last figure quoted in parentheses.

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