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Determination of Elastic Constants of Crystals from Diffuse Reflexions of X-rays. III. Diamond

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The intensity of diffuse X-rays thermally scattered from a Type II diamond has been studied by means of a Geiger-counter spectrometer. To increase the intensity of the diffuse radiation, the crystal was heated to about 300° C. and observations were made in various directions in reciprocal space passing through the reciprocal point 220. Following the method of Ramachandran & Wooster the elastic ratios were determined as $c_{12}/c_{11} = 0{\cdot}30 \pm 0{\cdot}02$; $c_{44}/c_{11} = 0{\cdot}40 \pm 0{\cdot}02$. The absolute values were determined by comparing the intensity of the Compton radiation scattered at an angle of 90° by the crystal, with the intensity of the thermal diffuse X-rays. The values obtained were $c_{11} = 110 \times 10^{11}$; $c_{12} = 33 \times 10^{11}$; $c_{44} = 44 \times 10^{11}$ dyne cm.$^{-2}$ and the accuracy was about $\pm 10\%$. These values are compared critically with those determined by an ultrasonic method by Bhagavantam & Bhimasenachar and it is concluded that their value of c_{12} is too high and their value of c_{11} probably too low.

1. Introduction

In two previous papers Ramachandran & Wooster (1951*a*, *b*, hereafter referred to as I and II) have described a method of measuring the elastic constants of cubic crystals from quantitative measurements of the intensities of the thermal diffuse reflexions appearing in regions of reciprocal space close to a reciprocal-lattice point. Part I contains an exposition of the theory of the method and a description of the experimental apparatus and technique of making the measurements. Part II contains a description of the use of the method to determine the elastic constants of five cubic crystals. The purpose of the present paper is to describe some developments of the technique, and its application to the determination of the elastic constants of diamond.

2. Interest of diamond

Diamond has attracted the attention of both scientists and laymen for centuries because of its remarkable hardness, incompressibility and rigidity. However, because of the great experimental difficulties, quantitative information has remained rather sparse. The bulk compressibility was measured many years ago by Adams (1921) and by Williamson (1922), while, more recently, Bhagavantam & Bhimasenachar (1946) have measured the three elastic constants from the velocities of elastic waves transmitted through crystal plates into a liquid medium. The results of Bhagavantam & Bhimasenachar indicate that there should be a considerable difference between the velocities of the two possible transverse waves travelling along a diad axis. Chandrasekharan (1950) has measured the Doppler shifts in the wavelength of light scattered from a crystal, as predicted by Brillouin (1922), and he finds that there is only one transverse component due to waves travelling along a diad axis. The conditions of his experiments were such that two components ought to have been observed, and he finds the absence of the second one 'very surprising'. In addition to these measurements, Pisharoty (1940) has made a static measurement of the bending modulus of a (111) plate, but his results are not consistent with any of the other available data.

The study of diamond by means of the diffuse-reflexion technique is of further interest because it exhibits two apparently distinct types of 'extra reflexion'. One of these is confined to small regions of reciprocal space along lines passing through lattice points parallel to the cube axes, giving rise to sharp spots on photographs, while the other is spread out all around a lattice point, and gives a diffuse spot similar to the spots which appear on photographs of other crystals owing to the thermal oscillation of the lattice. It has been generally assumed that the sharp 'spikes' are due to some electronic or structural peculiarity, while the diffuse spots are due to the normal diffuse reflexions, but it is desirable to have some further support for the validity of this assumption. A quantitative study of the intensity distribution in these regions of diffuse scattering power gives this support, as well as providing an independent measurement of the elastic constants.

3. Standardization of absolute intensities

As the method used in these experiments to make an absolute determination of the ratio of the diffusely

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scattered intensity to the incident X-ray intensity is different from the method described in Part I, we shall give a brief description of it before proceeding to the details of the experiments. Warren and his associates (see, for instance, Cole & Warren, 1952) have used, with satisfactory results, the intensity of high-angle scattering from paraffin wax as a standard with which to compare the intensities of weak X-ray beams scattered by other processes. They assume that there are two principal contributions to this scattered intensity: the Compton modified scattering and the coherent, or unmodified, scattering, both of which can be evaluated from the atomic scattering factors of carbon and hydrogen, assuming that all of the atoms scatter independently. In diamond the intensity of the Compton modified scattering is comparable with the thermal diffuse intensity, while in a crystalline substance the coherent scattering is negligible except in the neighbourhood of the reciprocal-lattice points. We may therefore assume that the intensity scattered at a point in reciprocal space far from a lattice point is entirely due to the modified component, and use it as a standard with which to compare the thermal diffuse intensities. We may describe this Compton intensity by means of a 'Compton diffuse intensity' defined in a manner analogous to the diffuse structure intensity, which was defined in Part I as the ratio of the intensity scattered by the Compton effect per unit cell of the crystal per unit solid angle to that scattered by a single Thomson electron under the same conditions. This Compton diffuse intensity, D_c, may be written (James, 1948)

$$D_c = 8(6-\Sigma f_{ec}^2)/B^3\,, \tag{1}$$

where Σf_{ec}^2 is a function which describes the effect of the individual carbon atoms scattering incoherently. A table of values of this function may be found in Compton & Allison (1935). B is the Breit–Dirac correction factor, whose value is given by

$$B = 1+\frac{2h\lambda}{mc}\cdot\frac{\sin^2\theta}{\lambda^2}\,. \tag{2}$$

In the present case this correction amounts to about 4%. Using this calculated Compton diffuse intensity, D_c, we may determine the absolute intensity of the incident beam, I_0, from the measured intensity of the diffuse beam, I_c, by a formula similar to (9), Part I, namely,

$$I_0 = I_c\Big/\frac{\varepsilon^2\Omega D_c}{2\mu\tau}\,. \tag{3}$$

Measurements of the absolute intensity of thermal diffuse scattering standardised in this way are accurate to about 5%.

4. Experimental details

The apparatus for the production and measurement of X-rays was identical with that described in Part I, except that a xenon-filled Geiger–Müller tube replaced the previous argon-filled tube and the monitor was somewhat modified (Hargreaves, Prince & Wooster, 1952). Because of the relatively small thermal oscillation in diamond, it was desirable to make the measurements at an elevated temperature. For this reason the crystal was mounted in a small furnace, which was made of copper and heated by an ordinary 210 V., 60 W. soldering-iron element. A control system, consisting of a variac and a controller, manufactured by English Instruments Ltd, Cambridge, employing a copper–constantan thermocouple, gave accurate and stable temperature control within a few degrees Centigrade at temperatures up to about 320° C. The furnace rested on a goniometer head which fitted on the specimen circle of the counter spectrometer.

The specimen, kindly supplied by Mr P. Grodzinski, of Industrial Distributors Ltd, London, was an irregularly shaped lump with a maximum dimension of about 2·0 cm. and a minimum dimension of about 1·0 cm., on which a flat face had been cut and polished parallel to (110). Maximum thermal contact between the heating element and the crystal was obtained by setting the diamond in molten aluminium. When the aluminium solidified, the diamond was set in a mass of metal which fitted its external contours very closely, and the contact was made very tight by differential contraction in cooling from the melting point of aluminium to the operating temperature. The specimen had been previously classified as 'Type II' on the basis of its absorption spectrum, but recent studies of numbers of diamond specimens (Grenville-Wells, 1952) have indicated that there is not the clear distinction between diamond types that was formerly thought to exist. The 220 reflexion was very sharp, and there was remarkably little evidence of mosaic spread. This diamond was, in fact, the only specimen of any substance that has been found in the course of the investigations on which measurements of diffuse scattering could be made along rekhas perpendicular to the rel-vector.

5. Results

In Fig. 1 the total diffuse scattering from the crystal, under the given conditions, is denoted by I. The quantity I_d (see Table 1) is obtained from I by subtracting the general background intensity (given at the top of the same table). The slopes of the curves showing I as a function of $1/|R|^2$ are proportional to the corresponding rekha constants. From the table given in Part II it will be seen that the expressions pertaining to these directions are

$$\left.\begin{aligned} K[110]_{220} &= 2/(c_{11}+c_{12}+2c_{44})\,;\\ K[111]_{220} &= 2/(c_{11}+2c_{12}+4c_{44})+1/(c_{11}-c_{12}+c_{44})\,;\\ K[001]_{220} &= 1/c_{44}\,;\\ K[100]_{220} &= \tfrac{1}{2}(1/c_{11}+1/c_{44})\,;\\ K[1\bar{1}0]_{220} &= 2/(c_{11}-c_{12})\,. \end{aligned}\right\} \tag{4}$$

Table 1

(General background intensity = 90 counts/min.)

Rekha	I_d				
$[ABC]$	$\frac{1}{\lvert R\rvert^2} = 0{\cdot}095$	$\frac{1}{\lvert R\rvert^2} = 0{\cdot}175$	$\frac{1}{\lvert R\rvert^2} = 0{\cdot}250$	Mean slope	$\log_{10}\frac{K[ABC]_{220}}{K[110]_{220}}$
[110]	38	78	104	104	—
[100]	72	140	194	193	0·27
$[1\bar{1}0]$	122	199	290	296	0·45
[111]	68	119	168	171	0·22
[001]	106	183	266	267	0·41

If we put $\chi_1 = c_{12}/c_{11}$ and $\chi_2 = c_{44}/c_{11}$ charts may be drawn, as described in Part II, giving $\log_{10} K[ABC]_{220}/K[110]_{220}$, where A, B, C are the zone indices of any given rekha. In Fig. 2 there are assembled together the curves, obtained from these charts, which correspond to the observed values of this ratio (these are given in the last column of Table 1). To allow for the possible experimental error it would be necessary to replace each of these four curves by a band, the width of which varies from one curve to another but which is roughly equal to half the side of one of the four squares in Fig. 2. The black spot at the centre of the region where the four bands overlap is taken as the best mean value, namely $\chi_1 = 0{\cdot}30$, $\chi_2 = 0{\cdot}40$. The error in each of these determinations is about $\pm 0{\cdot}02$.

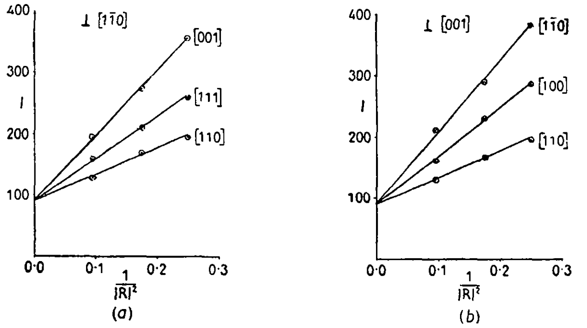

Fig. 1. Plot of the total diffusely scattered intensity I, against $1/|R|^2$, the reciprocal of the square of the distance of the scattering point from the reciprocal lattice point 220, (*a*) for the directions [110], [111], [001], and (*b*) for the directions [110], [100], $[1\bar{1}0]$.

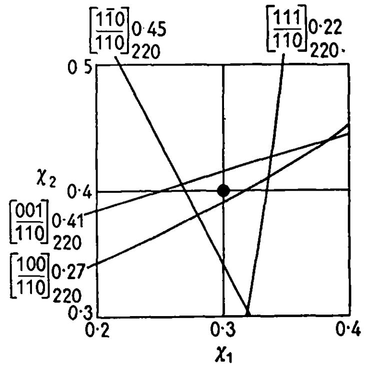

Fig. 2. Plot of one line from each of four K-ratio charts. The value of the K ratio determined experimentally is given on the right-hand side of each symbol. The black dot at the centre gives the mean values of χ_1 and χ_2.

In § 3 the method of standardizing the intensity of the incident beam, I_0, in terms of the calculated Compton diffuse intensity, D_c, was described. The relation between the intensity of the diffuse flux, I_d, and the diffuse structure intensity of first order, D_1, and the corresponding second-order quantity, D_2, are given by the formula (Part I (9))

$$I_d = \frac{I_0 \varepsilon^2 (D_1 + D_2)\Omega}{2\mu\tau}. \qquad (5)$$

In the observations on the 220 reflexion of diamond (using Cu $K\alpha$ radiation) the following values were applicable:

$$\varepsilon^2 = 4{\cdot}49\times 10^{-26}\ \text{ergs sterad}^{-1},$$
$$\Omega = 9{\cdot}65\times 10^{-4}\ \text{sterad},$$
$$\mu = 13{\cdot}5\ \text{cm.}^{-1},$$
$$\tau = 4{\cdot}50\times 10^{-23}\ \text{cm.}^3.$$

From the known value of I_0 and the measured value of I_d the value of (D_1+D_2) could be calculated. From approximate values for the elastic constants the value of D_2/D_1 can be calculated and it is found that D_2 is quite negligible. Using the value of D_1 found from equation (5) and the relation

$$D_1 = \frac{kT}{\tau}|F_T|^2 \frac{q^2}{R^2} K[001]_{220},$$

where

$T = 573°$ K., $|F_T| = 14{\cdot}2$, $q = 61{\cdot}1$ cm.
(scale 1 Å^{-1} = 76·95 cm.), $R = 2$ cm.,

we obtain the value of $K[001]_{220}$. The value of c_{44} is the reciprocal of $K[001]_{220}$ and is thus found to be 44×10^{11} dyne cm.$^{-2}$. Combining this value with the above values of c_{12}/c_{11} and c_{44}/c_{11}, we obtain the following set of values of the elastic constants of diamond

$$c_{11} = 110\times 10^{11};\ c_{12} = 33\times 10^{11};$$
$$c_{44} = 44\times 10^{11}\ \text{dyne cm.}^{-2}.$$

The accuracy of these figures is estimated to be about ±10%. A bulk modulus computed from these constants would be

$$1/\beta = 59\times10^{11} \text{ dynes cm.}^{-2},$$

which is consistent with the published values of Adams (1921) and Williamson (1922).

6. Discussion

These values of c_{11} and c_{12}, and therefore the value of χ_1, differ by an amount that is more than the experimental error from the elastic constants published by Bhagavantam & Bhimasenachar (1946). It is, therefore, of interest to examine the possible reasons for this difference. The method used by Bhagavantam & Bhimasenachar involves measuring the velocities with which vibrations of ultrasonic frequency are transmitted through a crystal plate, in a special direction, into a transparent liquid. Although longitudinal waves are easily transmitted into the liquid, giving an easily observed signal, if the assumptions used in the interpretation of the observations were strictly satisfied, transverse waves would give no signal whatsoever. In practice there is a faint signal transmitted through the crystal at a frequency which is, at least, close to the frequency at which a transverse wave should satisfy the conditions for resonance. This signal is probably produced by the coupling of the transverse modes with certain longitudinal ones, owing to end effects, etc. Bhagavantam & Bhimasenachar assume that the signal so transmitted corresponds exactly to the pure transverse mode of appropriate wavelength. If this assumption were not, in fact, completely justified, a fairly small error in the interpretation could lead to a significant error in the results. With this in mind, let us compare the two sets of measurements.

The absolute values of the elastic constants of diamond, as published by Bhagavantam & Bhimasenachar, are

$$c_{11} = 95\times10^{11};\ c_{12} = 39\times10^{11};$$
$$c_{44} = 43\times10^{11} \text{ dynes cm.}^{-2}.$$

These values are based on the velocities of three particular waves: (1) a longitudinal wave travelling parallel to [211]; (2) a longitudinal wave travelling parallel to [111]; (3) a transverse wave travelling parallel to [111]. The velocity of any wave in a crystal is given by $V = \sqrt{(c_i/\varrho)}$, where c_i is a homogeneous function of the first degree in the elastic constants, and ϱ is the density. For these waves the appropriate forms of c_i are

$$c_1 = \tfrac{1}{2}(c_{11}+c_{12}+2c_{44}),$$
$$c_2 = \tfrac{1}{3}(c_{11}+2c_{12}+4c_{44}),$$
$$c_3 = \tfrac{1}{3}(c_{11}-c_{12}+c_{44}).$$

Table 2 shows the values of these wave velocities as computed from both sets of elastic constants. The density has been taken as 3·51 g.cm.$^{-3}$.

It will be seen from Table 2 that the difference between the two sets of values lies mainly in the velocity of the transverse wave (3) the determination of which is based by Bhagavantam & Bhimasenachar, on a faint signal of doubtful purity. The relative values of c_{11} and c_{12} are determined in the present experiments mainly by the ratio $K[1\bar{1}0]_{220}/K[110]_{220}$, the value of which in terms of χ_1 and χ_2 is given by the expression

$$\frac{K[1\bar{1}0]_{220}}{K[110]_{220}} = \frac{1+\chi_1+2\chi_2}{1-\chi_1}.$$

To indicate what accuracy is obtainable in these measurements a portion of the chart giving $\log_{10}(K[1\bar{1}0]_{220}/K[110]_{220})$ as a function of χ_1 and χ_2 is plotted in Fig. 3. If we suppose the experimentally determined line of this chart goes through the point, $\chi_1 = 0{\cdot}30$, $\chi_2 = 0{\cdot}40$, which corresponds to the mean of several determinations, then the experimental inaccuracy is such that the actual point could lie within the shaded band given in Fig. 3. The values of χ_1 included within this shaded area range over about $\pm 0{\cdot}025$, and since the value of χ_1 for diamond is 0·30 this corresponds to an accuracy of about $\pm 8\%$. The value of χ_1 given by Bhagavantam & Bhimasenachar differs by about 30% from the present value. Finally, the elastic constants of Bhagavantam & Bhimasena-

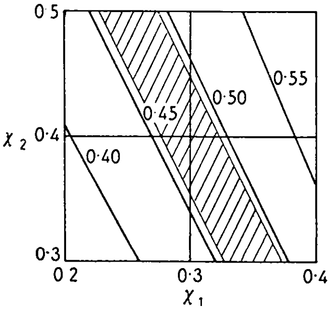

Fig. 3. Portion of the chart for $\log_{10}(K[1\bar{1}0]_{220}/K[110]_{220})$ plotted as a function of χ_1 and χ_2. The experimental error would allow the (χ_1, χ_2) point applicable to diamond to lie anywhere within the shaded area.

Table 2

Direction of wave-normal	Nature of vibration	Velocity of wave determined by: Bhagavantam & Bhimasenachar	Present authors
(1) [211]	Longitudinal	$1{\cdot}76\times10^6$ cm. sec.$^{-1}$	$1{\cdot}81\times10^6$ cm. sec.$^{-1}$
(2) [111]	Longitudinal	1·81	1·83
(3) [111]	Transverse	0·97	1·07

char predict an intensity of diffuse scattering along the rekha $[1\bar{1}0]_{220}$ some 40% greater than was observed during a careful search for this large intensity.

We must note further that the elastic constants as measured from diffuse-scattering experiments predict a much smaller difference between the velocities of the two transverse waves travelling along a diad axis. This is consistent with the observations of Chandrasekharan (1950) that there is only one transverse Brillouin component in the light scattered by waves travelling in that direction.

It may therefore be concluded, concerning the values of the elastic constants published by Bhagavantam & Bhimasenachar, that c_{44} is acceptable, that c_{11} is probably too low, as it differs by more than the experimental value from our value, and that c_{12} is too high.

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An Extension of the 'Difference Patterson' to Facilitate the Solution of Order–Disorder Problems

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In both the ordered and disordered phases of those minerals based upon close packed anions (chalcopyrite, bornite, stannite, etc.) it is often difficult to locate the specific cation positions from among the symmetrically distributed possible sites. Because of the identity of many of the interatomic distance vectors, the Patterson projections, or sections, of such structures cannot be readily solved.

If it can be shown, or assumed, that the non-superstructure, or fundamental, X-ray reflections do not change in intensity when these structures are disordered, then Patterson projections, or sections, made using the superstructure reflections alone, represent vector maps where all the vectors are suppressed except those between like atoms that change position during the disordering process. Positive peaks represent vectors between sites, both of which have gained or both lost in atomic number through disordering. Negative peaks represent vectors between sites where one has gained and the other has lost in atomic number during disordering. Chalcopyrite is used as a known example to show the advantages and shortcomings of the method.

Introduction

The crystallographer often encounters difficulty in attempting to solve structures exhibiting a high degree of symmetry, or pseudo symmetry, that are based upon close-packed anions with two or more species of cations distributed in the interstitial openings. Although anion positions and positions of unspecified cations are relatively easily determined, the determination of the exact distribution of the specific cations among the cationic positions presents a problem.

The major difficulties that stand in the way of the solution of this problem are the similarity in the scattering factor of the different cations involved, and the identity in both direction and magnitude of many of the interatomic distance vectors. Because of this identity, which is brought about by the high symmetry of the close-packed cell, the Patterson projections or Patterson–Harker sections, cannot be readily interpreted.

Perhaps the best example of this is illustrated by some of the highly symmetrical sulphide minerals such