

Evaluation of the Elastic Constants of 1,3,5-Triphenylbenzene from Thermal Diffuse Scattering of X-rays

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From the measurements of the intensities of thermal diffuse scattering observed in the stationary-crystal photographs taken with monochromatic Cu $K\alpha$ radiation, all the nine elastic constants of orthorhombic 1,3,5-triphenylbenzene single crystals have been determined by the photographic method. Each constant is evaluated from two or more directions of thermal wave vectors. The reciprocal nodes involved for the determination of all the constants were 200, 206, 002, 015 and 006. Diffusely scattered intensities were corrected for general scattering, polarization and skew factors. Corrections for absorption, divergence and second-order diffuse scattering were found negligible. The values of elastic constants in units of 10^{10} dynes.cm $^{-2}$ are $C_{11}=0.31$, $C_{22}=1.36$, $C_{33}=2.33$, $C_{44}=5.02$, $C_{55}=0.34$, $C_{66}=3.69$, $C_{12}=-1.78$, $C_{13}=0.92$ and $C_{23}=0.80$. Correlation of the elastic data with the structure have been attempted.

Introduction

The method of determining the elastic constants of single crystals from a quantitative study of the thermal diffuse scattering of X-rays has been successfully applied by Ramachandran & Wooster (1951*a, b*), Chakraborty & Sen (1958), Wooster (1962) and Joshi & Kashyap (1964). This method is suitable for soft substances for which only small crystals are available and requires only a small amount of material. Two methods are available for studying diffuse reflexions; one uses Geiger counters, the other uses the photographic technique. A specially developed photographic method has been preferred because of its simplicity and practicability for studying diffuse scattering due to low values of the thermal wave vector and high angular resolution. Other advantages of the present method are that stabilization of the output of X-rays is not essential and that only very small crystals, which can be easily grown, are required. In this paper the results of the determination of elastic constants of 1,3,5-triphenylbenzene, belonging to the orthorhombic system, are presented. Its structure was completely solved by Farag (1954) who also revealed the elastic waves of thermal origin (Farag, 1959).

Theory

The diffuse scattered X-ray intensity, I'_d (1st order only) from a thermally vibrating crystal of volume δV , is given in terms of the incident intensity I_0 , by

$$I'_d = I_0 \frac{\varepsilon^2 k T}{V^2} F_T^2 \delta V \frac{Q^2}{q^2} K[uvw]_{hkl}. \quad (1)$$

Here ε^2 is the intensity scattered by a free electron and is given by Thomson's formula, k is Boltzmann's constant, V is the volume of the unit cell, F_T is the observed structure factor at the temperature T for the plane (hkl), Q is the reciprocal lattice vector, q , the

thermal wave vector and

$$K[uvw]_{hkl} = P^2 A_{11}^{-1} + Q^2 A_{22}^{-1} + R^2 A_{33}^{-1} + 2PQ A_{12}^{-1} + 2PR A_{13}^{-1} + 2QR A_{23}^{-1}, \quad (2)$$

where P , Q , R and u , v , w are the direction cosines of Q and q respectively. A_{ij}^{-1} are the elements of the inverse of the matrix A_{ij} , given for orthorhombic crystals by

$$\begin{bmatrix} A_{11} \\ A_{22} \\ A_{33} \\ A_{23} \\ A_{31} \\ A_{12} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{66} & c_{55} & 0 & 0 & 0 \\ c_{66} & c_{22} & c_{44} & 0 & 0 & 0 \\ c_{55} & c_{44} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{23} + c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{13} + c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{12} + c_{66} \end{bmatrix} \begin{bmatrix} u^2 \\ v^2 \\ w^2 \\ vw \\ wu \\ uv \end{bmatrix}. \quad (3)$$

For a particular direction of propagation of the thermal wave, the value of q is calculated from the known orientation of the crystal with respect to the incident beam. Hence from a measurement of I'_d/I_0 , the value of $K[uvw]_{hkl}$ can be evaluated from equation (1) and from it the elastic constants. In general the explicit expression for $K[uvw]_{hkl}$ involves many constants. For some simple direction of propagation of the thermal wave, the intensity depends on one or two constants only. But to determine all the elastic constants, some complex directions of propagation of the thermal waves had to be used.

Experimental technique

1,3,5-Triphenylbenzene crystals were grown by slow evaporation of a solution in ether+alcohol at room temperature (25–30°C). The crystals are stable during the whole experiment. A suitable crystal of linear dimensions, roughly 0.5 mm, examined under a polarizing microscope, was mounted on the tip of a thin aluminum fitted on the top of the goniometer. In order to increase resolution stationary-crystal photographs were taken on an Universal Unicam camera converted

to diameter 10 cm and having a collimator of 6.5 cm length. Powder diffraction lines of aluminum in the photographs were used for (a) determination of the correct orientation of a particular plane with respect to the incident beam, (b) standardization of the camera radius and (c) calibration of the angle of diffraction to a high degree of accuracy.

The monochromated X-ray beam (Cu $K\alpha$), obtained by reflexion from a calcite crystal was collimated and allowed to fall on the crystal at the correct orientation, known from the Laue photograph taken earlier with polychromatic radiation. The undeviated incident beam was recorded on the film after reduction in intensity by a factor of about 10^6 , by nickel foils placed in between the experimental crystal and the film. The thickness of the nickel absorber is adjusted so that the intensity of the transmitted beam is nearly equal to the intensity of diffuse reflexion. The average time of exposure was about 25–40 h. The X-ray tube was operated at 17 kV and 25–30 mA, so that $\lambda/2$ was practically, and the higher harmonics totally, absent from the monochromatic beam. Each photograph thus taken contained the diffuse reflexion, the image of the direction beam and the powder diffraction lines of aluminum. A number of such photographs for different diffuse reflexions with various mis-setting angles from the Bragg position were taken. A small angle of mis-set was taken, as we were interested in the long-wave approximation with small q values only. Each photograph was developed in fresh developer at a controlled temperature together with a calibration strip, cut from the same sheet of film as used in the monochromatic photograph.

The intensity distribution of the diffuse spot along φ , the angle of diffraction and intensity of the direct beam were scanned with a Moll Recording Photometer. Photographs were scanned by an exploring spot of light of dimensions about 0.02×0.005 cm along the equatorial line passing through the diffuse spot as well as the direct beam image and recorded in the photometric curve. The intensities were computed from the ordinates of the photometric curve by comparison with the calibration wedge, following the method of Robinson (1933). Measured intensities were corrected for general scattering, polarization and skew factors. Corrections for absorption, divergence and second-order diffuse scattering were not carried out, in view of the limits of accuracy of the intensity measurements by the photographic method.

Results and discussion

Crystals of 1,3,5-triphenylbenzene are orthorhombic with axial parameters $a=7.47$, $b=19.66$ and $c=11.19$ Å and space group $Pna2_1$. The reciprocal-lattice points used for the evaluation of all the elastic constants are of the type $h00$, $00l$, $h0l$ and $0kl$ in different reciprocal planes. Table 1 gives the planes studied and their structure-factor values.

Table 1. Reciprocal-lattice planes with their structure factors

Index of plane	Structure factor
200	160.3
002	140.0
006	178.6
206	90.4
015	70.0

The value of wave vector q and the angle of scattering φ for a particular direction of propagation of the thermal wave can be calculated by establishing trigonometrical relations from the considerations of the geometrical position of the circle of reflection in the reciprocal lattice net for a particular setting of the crystal. The position of the circle is completely determined by the knowledge of the correct orientation of the crystal with respect to the incident beam.

The observed intensities (arbitrary scale) of the undeviated beam in the film multiplied by the factor $e^{-\mu t}$, where μ is the linear absorption coefficient of nickel for Cu $K\alpha$ and t is the thickness of the absorber, gives the intensity of the incident energy at the film. Let it be I'_0 ; then I_0 , the intensity at the crystal = $I'_0 \cdot S'/S$, where S is the area of cross section of the beam intercepted normally by the crystal and S' is the projection of the area S on the film along the direction of the undeviated beam.

The intensity I_d (uncorrected for any factor) of diffuse scattering at a point in the diffuse spot corresponding to certain φ was also evaluated on the same arbitrary scale from the photometric curve of the diffuse spot. I_d/I_0 was plotted against φ for each case and these curves used for determining the value of I_d/I_0 corresponding to a certain φ , which corresponded to a certain wave vector. Curves showing the relation between the intensity of diffuse scattering and the square of the wave length of the thermal waves ($\lambda^2 = 1/q^2$) for points lying in reciprocal lattice planes were drawn as in Fig. 1. Since I'_d/I_0 values have already been corrected, the curves I'_d/I_0 versus λ^2 are straight lines passing through the origin. The average value of $K[uvw]_{hkl}$ was determined from the slopes of these curves. It will be seen that the six constants C_{11} , C_{22} , C_{33} , C_{44} , C_{55} and C_{66} may first be determined by suitable choice of planes and the directions of the q vectors. The value of $K[uvw]_{hkl}$ then depends on one or two constants only. After finding the above constants it is possible to determine the other three constants, namely C_{12} , C_{13} and C_{23} . For example C_{12} requires the knowledge of $K[1\sqrt{2}, 1/\sqrt{2}, 0]_{0k0}$ and is related to the other constants by the relation

$$C_{12} = -C_{66} + \left[C_{66}^2 + C_{11}(C_{22} + C_{66}) + C_{22}C_{66} - \frac{2(C_{11} + C_{66})}{K \left[\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right]_{0k0}} \right]^{1/2}$$

The wave vector \mathbf{q} having the same direction cosines as reciprocal lattice vector \mathbf{Q} cannot ordinarily be employed for the evaluation of elastic constants, as

for such wave vectors the geometry of reflexion is such that even for the smallest angle of mis-setting from the Bragg position, the value of $K[uvw]_{hkl}$ becomes very

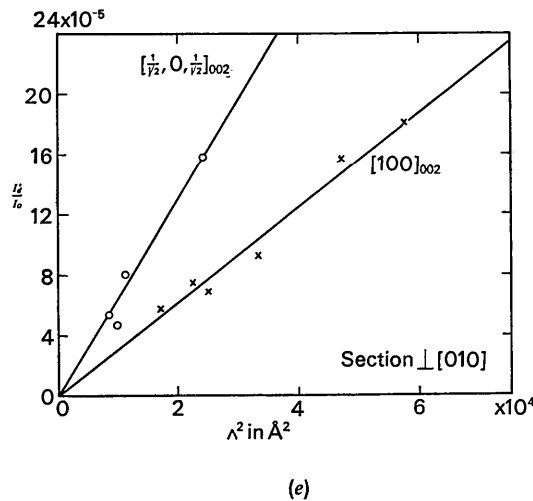
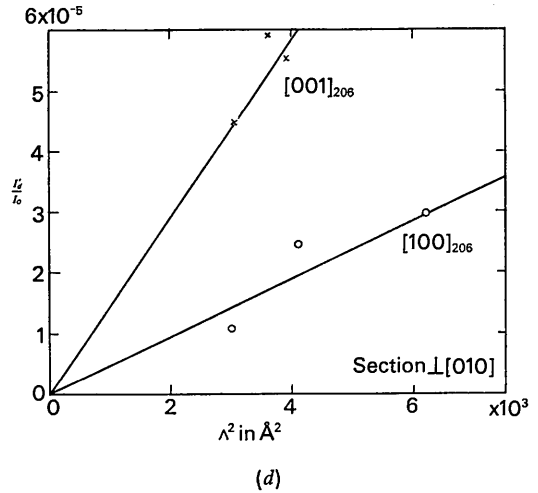
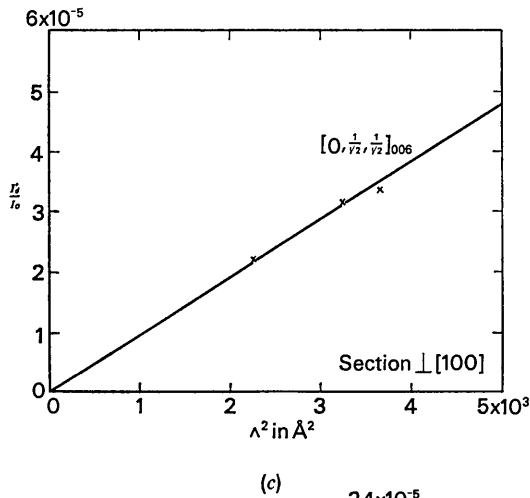
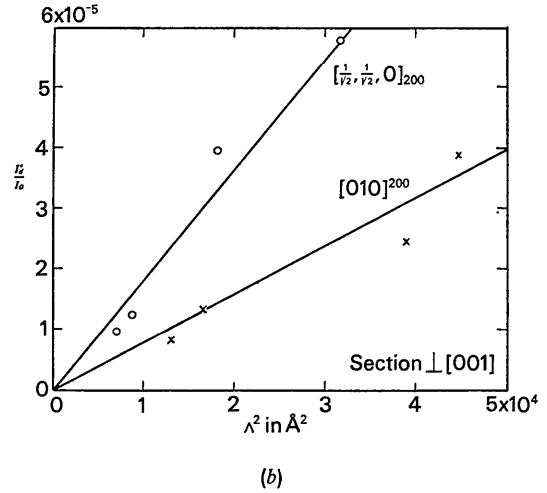
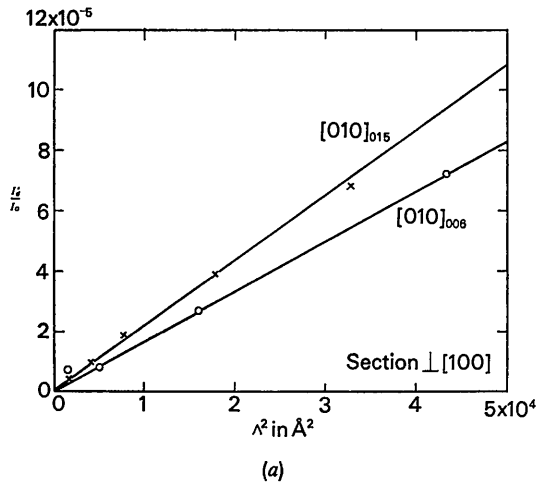


Fig. 1. Variation of diffuse scattering intensity with the square of the wavelength of thermal waves, ($\lambda^2 = 1/|q|^2$) for various directions of propagation vector and various reciprocal-lattice points.

high and therefore the value of I_d/I_0 falls to a low value and can hardly be distinguished from the background intensity.

Each elastic constant is evaluated from at least two different directions of the thermal wave vector. The values of the elastic constants are presented in Table 2 along with the corresponding $K[uvw]_{hkl}$. It is estimated that because of the inherent errors in the measurement of the intensity of diffuse reflexion and the direct beam, use of absorption screens and the uncertainty in the estimation of correction factors, elastic constants C_{44} , C_{55} , and C_{66} may have errors up to 5%. Evaluation of the remaining constants depends upon the accuracy of the other constants, so error may be up to 8%.

A correlation of the elastic data (Table 2) with the structure of 1,3,5-triphenylbenzene has been attempted. The crystal structure analysis shows that the molecules are arranged in two layers at approximately $x = \frac{1}{4}$, $\frac{3}{4}$ and are nearly parallel to the (200) planes. The diffuse spots corresponding to thermal vibrations affecting these planes signify that all the bonds in planes (200) are stronger than those normal to them. This means that C_{22} and C_{33} , a measure of resistance to expansion in layers, are greater than C_{11} , which corresponds to separation of the layers. Thermal diffuse scattering pictures also revealed transverse elastic waves of large amplitude travelling along the [100] axis such that (001) planes are strongly affected. This gives a large diffuse intensity for the reflexion 002, when the X-ray beam is parallel to [100] axis: which is presumably the cause of the small value of C_{55} .

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Table 2. Elastic constants of 1,3,5-triphenylbenzene

Elastic constant	$K[uvw]_{hkl}$ from which the elastic constant is evaluated	Value of the elastic constant in unit of 10^{10} dynes. cm^{-2}
C_{11}	$K[100]_{206}$	0.31
C_{22}	$K[010]_{015}$	1.36
C_{33}	$K[001]_{206}$	2.33
C_{44}	$K[010]_{006}$	5.02
C_{55}	$K[100]_{002}$	0.34
C_{66}	$K[010]_{200}$	3.69
C_{12}	$K[1/2, 1/2, 0]_{200}$	-1.78
C_{23}	$K[0, 1/2, 1/2]_{006}$	0.80
C_{13}	$K[1/2, 0, 1/2]_{002}$	0.92

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On the Relation Between Molybdenum Trioxide and Rhenium Trioxide Type Crystal Structures

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The structural relation between MoO_3 -type and ReO_3 -type is clarified by considering layers of anions parallel to $(1\bar{3}\bar{1})_{\text{MoO}_3}$ and $(111)_{\text{ReO}_3}$. MoO_3 is then seen to be approximately cubic close-packed anions while ReO_3 is cubic close-packed anions but with one-quarter of the anion sites unoccupied. The two structures may then be interconverted by a rotation operation resembling that which links ReO_3 - and PdF_3 -type structures. Photographs of ball models are used to illustrate the relations. No compounds are known which exhibit direct transition from ReO_3 -type to either MoO_3 - or PdF_3 -type. This is probably because of the large change in volume per anion. The interface between ReO_3 and the close packed structures may be described as a *dilation* fault.

Introduction

Two groups of higher molybdenum oxides may be distinguished. The first includes MoO_3 and the structures $\text{Mo}_n\text{O}_{3n-2}$ ($n = 18$ to 22) derived from it by crys-

tallographic shear (Kihlberg, 1963a; Bursill, 1972). These occupy the composition range MoO_x ($2.8 \leq x \leq 3.00$). The second contains three subgroups, each derived from the ReO_3 structure type (Kihlberg, 1963a): Mo_4O_{11} , by the ordered omission of oxygen; Mo_8O_{23}