whose prototypes are provided by methane and benzene respectively. The *Pbca* family is predominant. The isotranslational subgroup relation serves as the route of descent or ascent in symmetry of the crystal structures by chemical (atomic, group and homologous) substitutions, and constitutes the pedigree of organic crystals. Elucidation of the physical significance of the descent and ascent in symmetry will give a powerful clue to the better understanding of the mechanism of polymorphic transition and the systematization of organic molecular crystals.

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Debye–Waller Factors of CuBr by Powder Neutron Diffraction at 295 K

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Zinc blende structures are of interest because of their semiconducting properties. Lattice dynamical properties of copper halides which belong to this class of structures have recently been studied. A powder neutron diffraction study of the Debye–Waller factors of the cubic (zinc blende) γ phase of CuBr is reported here. The diffraction pattern was obtained on the high-resolution diffractometer PANDA installed at the PLUTO reactor, Harwell. A neutron wavelength of 1·524 Å was used in the experiment. The B factors determined were $B_{\rm Cu} = 2{\cdot}85 \pm 0{\cdot}33$ and $B_{\rm Br} = 2{\cdot}71 \pm 0{\cdot}33$ Å^2. A mean value $\bar{B} = \sum m_iB_i/\sum m_i = 2{\cdot}77$ Å^2, $i =$ Cu, Br, gives the corresponding Debye temperature of 131 ± 8 K.

Introduction

Crystals of zinc blende structure have been the subject of investigations in recent years. One of the reasons for the interest is their semiconducting properties. Copper halides CuI, CuCl and CuBr belong to the above class of structures. Investigations on the crystal structure and the temperature-dependent phase transitions have been made on CuI (Miyake, Hoshino & Takenada, 1952) and on CuBr (Hoshino, 1952). Recent studies of the anharmonicity of atomic vibrations of these substances have been made by the method of neutron diffraction on single-crystal samples (Sakata, Hoshino & Harada, 1974; Hoshino, Fuji, Harada & Axe, 1975). Results of these experiments similar to that for fluorite

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structures, such as UO_2, ThO_2 (Willis 1963*a*,*b*), BaF_2 (Cooper, Rouse & Willis, 1968), SrF_2, CaF_2 (Cooper & Rouse, 1971) and the zinc blende structures ZnS, ZnTe (Cooper, Rouse & Fuess, 1973), have been reported. The phonon dispersion relations of CuI (Hennion, Moussa, Prevot, Carabatos & Schwab, 1972) and CuBr (Prevot, Carabatos, Schwab, Hennion & Moussa, 1973) have been reported using the inelastic neutron scattering technique, while some theoretical models have been discussed by Pandey & Dayal (1974). No explicit investigations of the Debye–Waller factors and the Debye temperature of CuBr have been reported. We therefore took up the study of these parameters for the cubic γ phase (at room temperature) of this material by the method of powder neutron diffraction. The two other phases of CuBr are, however, a β phase (hexagonal) beyond 385 °C and an α phase (cubic) beyond 470 °C.

Theory

The space group of the cubic (zinc blende) γ phase is $F\bar{4}3m$. The structure factors in this case can be expressed in three forms, depending upon the sum $h + k + l$ being expressed by $4n$, $4n \pm 1$ or $4n + 2$, n being an integer. With Cu atoms at (0,0,0) and equivalent positions and the Br atoms at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and equivalent positions, the structure factors are given by:

$$F^2_{4n} = 16[b_{\text{Cu}} \exp(-M_{\text{Cu}}) + b_{\text{Br}} \exp(-M_{\text{Br}})]^2 \quad (1)$$

for $h + k + l = 4n$, *i.e.* 220, 400, 422 *etc.*,

$$F^2_{4n+1} = 16[b_{\text{Cu}} \exp(-M_{\text{Cu}})]^2 + 16[b_{\text{Br}} \exp(-M_{\text{Br}})]^2 \quad (2)$$

for $h + k + l = 4n \pm 1$, *i.e.* 111, 311, 331 *etc.*,

$$F^2_{4n+2} = 16[b_{\text{Cu}} \exp(-M_{\text{Cu}}) - b_{\text{Br}} \exp(-M_{\text{Br}})]^2 \quad (3)$$

for $h + k + l = 4n + 2$, *i.e.* 200, 420, 442 *etc.* Here $M = B(\sin\theta/\lambda)^2$, B being the Debye–Waller coefficient, b_{Cu} and b_{Br} are the neutron scattering lengths of Cu and Br, respectively. The reflections of the last type are rather weak; however, the observations of the $h + k + l = 4n$ and $h + k + l = 4n \pm 1$ type reflections enable one to determine the B values for Cu and Br atoms separately.

From the above three expressions one can write

$$\ln(\alpha + \beta) = \text{constant} - B_{\text{Cu}} \left(\frac{\sin\theta}{\lambda}\right)^2 \quad (4)$$

and

$$\ln(\alpha - \beta) = \text{constant} - B_{\text{Br}} \left(\frac{\sin\theta}{\lambda}\right)^2, \quad (5)$$

where

$$\alpha \equiv [F^2_{4n}]^{1/2} \quad \text{and} \quad \beta \equiv [2F^2_{4n\pm1} - F^2_{4n}]^{1/2}.$$

The slopes of the straight lines obtained by the plots of $\ln(\alpha + \beta)$ and $\ln(\alpha - \beta)$ against $(\sin\theta/\lambda)^2$ would yield, respectively, B_{Cu} and B_{Br}.

Experiment

Fine powder of CuBr of purity greater than 99%, supplied by Koch-Light Laboratories Ltd, UK, was used in the experiment. The powder was contained in a vanadium cylindrical can of 1 cm diameter and 5 cm length. A neutron wavelength of 1·524 Å obtained using a germanium monochromator was used for these measurements. The diffraction pattern was obtained on the diffractometer PANDA installed at the PLUTO reactor. A bank of three BF_3 detectors was used to collect the neutron data. The Bragg peaks were scanned over a 2θ range of 100° and the counts were printed at an angular interval of 0·1°. All the measurements were taken at room temperature (295 K).

Data analysis and discussion

The observed intensities were corrected for thermal diffuse scattering (TDS) by the method of Chipman & Paskin (1959) originally applied in the X-ray diffraction experiments. The same procedure could be used in neutron diffraction, as the neutron velocity ($0·26 \times 10^6$ cm s^{-1}) was found to be larger than the elastic-wave velocity ($0·2 \times 10^6$ cm s^{-1}), the average of the transverse and longitudinal components. In calculating the elastic-wave velocity, the theoretical values of the elastic constants, $c_{11} = 0·488 \times 10^{12}$ dyn cm^{-2}, $c_{12} = 0·354 \times 10^{12}$ dyn cm^{-2} and $c_{44} = 0·065 \times 10^{12}$ dyn cm^{-2} (Prevot, Carabatos, Schwab, Hennion & Moussa, 1973) were used. Since only the acoustic modes contribute to the TDS, whereas both the acoustic and optic modes contribute to the Debye–Waller factor, the value of B used in the calculation of the TDS correction was $\frac{2}{3}\bar{B}$ (Suortti, 1967), where $\bar{B}$ is the average value of the two atoms. $\bar{B}$ is calculated from the expression $\bar{B} = \sum m_i B_i / \sum m_i$, $i = \text{Cu}, \text{Br}$.

Table 1. *The observed and calculated intensities for* CuBr *at room temperature*

$\lambda = 1·524$ Å, $a = 5·679$ Å.

h k l	I_o	I_c
1 1 1	4170	4179
2 0 0	0	13
2 2 0	3970	3971
3 1 1	2645	2628
2 2 2	0	4
4 0 0	775	771
3 3 1	1174	1189
4 2 0	0	5
4 2 2	1629	1629

Harwell's *TAILS* computer program (Rouse, 1977) was used to refine a scale factor and the two isotropic temperature factors B_{Cu} and B_{Br}. The scattering lengths $b_{\mathrm{Cu}} = 0{\cdot}76 \times 10^{-12}$ cm and $b_{\mathrm{Br}} = 0{\cdot}679 \times 10^{-12}$ cm used for the calculated intensities were from Bacon (1972). The observed and calculated intensities are given in Table 1.

The R factor $= \sum (I_O - I_C)/\sum I_O$ was found to be 0·5%, which shows a very good agreement between the observed intensities I_O and the calculated intensities I_C.

The experimental results obtained from the above refinement were: $B_{\mathrm{Cu}} = 2{\cdot}85 \pm 0{\cdot}33$, $B_{\mathrm{Br}} = 2{\cdot}71 \pm 0{\cdot}33$ Å^2, $R = 0{\cdot}005$. The Debye temperature obtained was $\theta = 131 \pm 8$ K, corresponding to the average $\bar{B} = 2{\cdot}77 \pm 0{\cdot}33$ Å^2. This value is in agreement with a recent value of $\bar{B} = 2{\cdot}54$ derived from single-crystal neutron diffraction measurements (Harada, Suzuki & Hoshino, 1976).

In the above experiments we have not considered the possible effect of anharmonicity on the B values, which could modify them slightly. However, it would be interesting to find these parameters at low temperatures, such as 4·2 K, where the TDS and anharmonic corrections could become very small.

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The van der Waals Criterion for Hydrogen Bonding

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Existing neutron diffraction data for hydrogen-bonded solids have been studied in the light of the van der Waals criterion for hydrogen bonding. It was found that for the formation of A—H$\cdots B$ bonds the distance $A \cdots B$ should be less than the sum of the A—H covalent bond distance, the van der Waals radius of H and that of B. It has also been shown that with decrease in $A \cdots B$ distance, the A—H bond extends in a quantitative manner irrespective of what atoms A and B are. Particularly, for A—H$\cdots A$ bonds when the overlap of the van der Waals radii of two A atoms exceeds a certain high value, the A—H bond is extended so much that the H atom is placed at the midpoint between A and A resulting in a symmetrical hydrogen bond.