J. Phys. C: Solid St. Phys., 13 (1980) 2969–73. Printed in Great Britain

Thermal expansion of β silver iodide at low temperatures

G Harvey† and N H Fletcher
Department of Physics, University of New England, Armidale, NSW 2351, Australia

Received 30 April 1979, in final form 2 January 1980

Abstract. The thermal expansion of β-AgI single crystals has been measured from 4 to 270 K along the c direction, and is found to be negative throughout the range. The results are explained in terms of the negative Gruneisen γ's which have been reported for both transverse acoustic and optic modes in β-AgI.

1. Introduction

The thermal expansion of hexagonal β silver iodide is of interest because it is essentially negative for all temperatures at which this phase exists (0 to 423 K). All measurements to date have been made using powder samples (x-ray) or pressed powder samples (dilatometric). The first reported measurement was by Fizeau (1867) on a sample of unknown structure and history. Thereafter almost all investigators have concentrated their attention on the cubic γ phase or on mixed-phase samples. The preoccupation of workers with the sphalerite (γ or B3) phase is probably for two reasons. Firstly, only a single coefficient needs to be determined. Secondly, γ silver iodide is the most ionic of an isoelectronic series of compounds (α-Sn, InSb, CdTe and γ-AgI in order of increasing ionicity) which have tetrahedrally bonded, open-lattice structures. Each has either the diamond or the related sphalerite structure.

Novikova (1960a, b, 1961a, b) and Novikova and Abrikosov (1963) have shown that as the ionicity increases in this series, both the magnitude of the negative thermal expansion coefficient, and the range of temperature over which it is negative, increase. Novikova (1966) has also calculated the Gruneisen function γ_G for a range of tetrahedrally bonded materials and has attempted to relate the variation of γ_G amongst these materials to the character of the forces acting in the crystal. Appropriate band structure calculations have been made by Smith (1976).

Recently Smith and White (1975) have extended the measurements on these and other materials to lower temperatures. Their results for the Gruneisen parameter γ as a function of T/θ_D^0 (where θ_D^0 is the Debye temperature determined in the zero-temperature limit) show similar behaviour for all materials studied with a negative minimum at $T \sim 0{\cdot}06\,\theta_D^0$. In order to illustrate the behaviour of the thermal expansion with increasing ionicity, Smith and White have plotted γ_0 (the zero-temperature limit of the Gruneisen parameter) against the Phillips fractional ionicity. Their results suggest that a sphalerite

---

† Present Address: Department of Applied Physics, Capricornia Institute of Advanced Education, Rockhampton, Queensland, Australia.

0022-3719/80/162969 + 05 $01·50 © 1980 The Institute of Physics

form of AgI would have a very large negative value of γ_0 and a correspondingly large negative coefficient of thermal expansion.

Majumdar and Roy (1959) have questioned the existence of the sphalerite form. They point out that all of the supposed methods of preparation produce a mixture of γ and β forms, and that the only structural investigations have been made with powder samples. Recently, Prager (1974) has studied the structure of β silver iodide using single crystals grown by the method of Cochrane (1967). The crystals as grown were found to be predominantly of one polytype (4H, stacking sequence ABCB) which has 50 per cent hexagonal packing. Here *n*H designates an *n*-layered hexagonal polytype (Ramsdell and Kohn 1951). On ageing or annealling, the structure transforms through a series of polytypes with increasing hexagonality, until finally the pure wurtzite structure (2H, stacking sequence ABAB) is reached, with 100 per cent hexagonality. In light of this work it is probable that previous workers, using powder samples, were observing these different stacking sequences, and that the γ form does not exist or is at best metastable at room temperature and pressure.

In this paper we report measurements of the thermal expansion of single crystals of β silver iodide along the *c* axis from 4 K to room temperature and propose a model to explain the observed behaviour.

2. Experimental details

The samples used were cleaved from crystals grown by the method developed in this laboratory by Cochrane (1967). When prepared in this way the crystals are predominantly of the 4H polytype and so were annealed at ~370 K for several hours to ensure conversion to the 2H structure. Extended-face x-ray precession photographs of the samples used revealed no evidence of any but the 2H polytype.

Measurements were made using a low-temperature capacitance dilatometer which will be described in detail in a subsequent publication. The principle of measurement is to compare the change in length of an AgI crystal with that of Cer-Vit (Simmons 1967) reference spacers using a capacitive measurement technique (White 1961), though to ensure mechanical stability of the cell, three AgI crystals (each about 12 mm in length) and three Cer-Vit reference spacers were used. A small precision guillotine was constructed to cleave the crystal samples to equal length and great care was exercised in their mounting in order to avoid any possible mechanical deformation.

3. Results

The measured coefficient of thermal expansion, plotted as a function of logarithmic temperature, is shown in figure 1. There is a region of large negative expansion, peaking in the range 0·2 to 0·3 θ_D where θ_D is the Debye temperature (116 K). The magnitude of the coefficient then decreases with increasing temperature until at $T \sim \theta_D$, it again increases in magnitude. Figure 2 shows the variation of lattice parameter with temperature calculated from these measurements.

The particular blank of reference material (Cer-Vit) was calibrated below 100 K (White 1973). The accuracy of the thermal expansion data shown in figure 1 is limited by this calibration, and is indicated by the size of the experimental points. In the range 100 to 300 K the data are based upon an interpolation between the Cer-Vit calibration

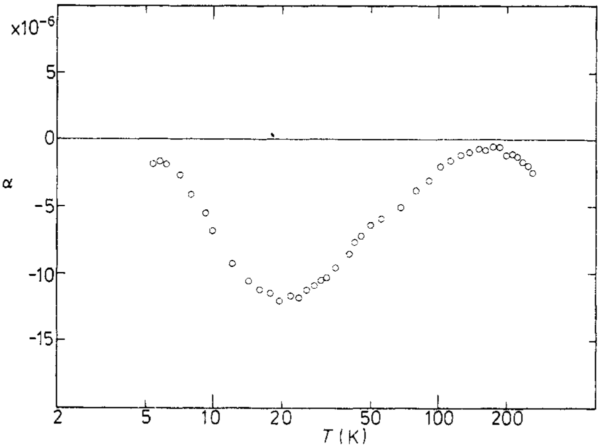

Figure 1. Coefficient of thermal expansion for β-AgI along the *c* direction as a function of logarithmic temperature.

of G K White (1973, private communication), and that of Simmonds (1967). Therefore the accuracy of the data is lower in the above range. Nevertheless the general features described above are present whatever electrode calibration is used. The variation of the lattice parameter as a function of temperature is not very different from that reported for the 'γ phase' of silver iodide by Bienenstock and Burley (1963).

4. Discussion

For axial solids the principal coefficients of the thermal expansion can be written (Munn 1972), for parallel (*c*) and perpendicular (*a*) directions, as:

$$\alpha_a = (C_t/V)[(s_{11} + s_{12})\gamma_a + s_{13}\gamma_c] \quad (1)$$

$$\alpha_c = (C_t/V)(2s_{13}\gamma_a + s_{33}\gamma_c) \quad (2)$$

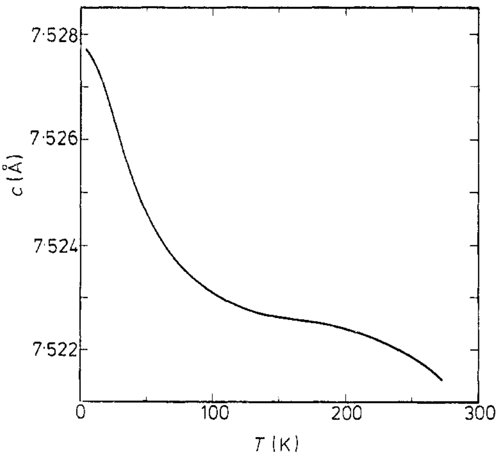

Figure 2. Temperature variation of the lattice parameter (*c*) of β-AgI.

where $s_{\gamma\mu}$ are components of the elastic compliance tensor, C_t is the heat capacity at constant stress, V is the molar volume, and the Gruneisen parameters are given by:

$$\gamma_a = (\tfrac{1}{2}/C_\eta)\left(\frac{\partial S}{\partial \ln a}\right)_{c,T} \qquad \gamma_c = (1/c_\eta)\left(\frac{\partial S}{\partial \ln c}\right)_{a,T} \tag{3}$$

where C_η is the heat capacity under constant strain, a and c are the dimensions of the unit cell, and S is the entropy. Hence in axial solids negative thermal expansion can arise either because of a negative Gruneisen parameter or via the cross compliance term s_{13}. Barron (1955) noted that if sufficient of the modes contribute negative γ_i's then it is conceivable that the thermal expansion coefficient may be negative. The lowest-frequency modes, or the modes most likely to be excited at low temperatures, are the transverse acoustic modes.

The model which we propose is based upon the recent work of Hanson *et al* (1975) in which they report that both transverse optic modes in β-AgI have large negative pressure derivatives and so negative mode gammas. At temperatures less than about 0·2 θ_D, the transverse acoustic modes dominate and give rise to negative thermal expansion. As the temperature increases, the longitudinal acoustic modes become increasingly important, and their positive gamma contributions bring the thermal expansion back towards zero.

As the temperature is further increased, the transverse optic modes begin to add negative contributions to gamma. This starts to take effect below the Debye temperature and dominates at high temperatures right up to the $\beta \rightarrow \alpha$ transition.

Defects may play a part as suggested by Lawn (1964). The positive pressure coefficient of ionic conductivity (Leiser 1956, Hara *et al* 1973, Schock and Hinze 1975) indicates that the formation of Frenkel defects causes a contraction of the lattice. Without a knowledge of the variation of mobility with pressure we are unable to calculate the contraction associated with the formation of each defect.

Finally it is not possible to separate γ_a and γ_c without thermal expansion information

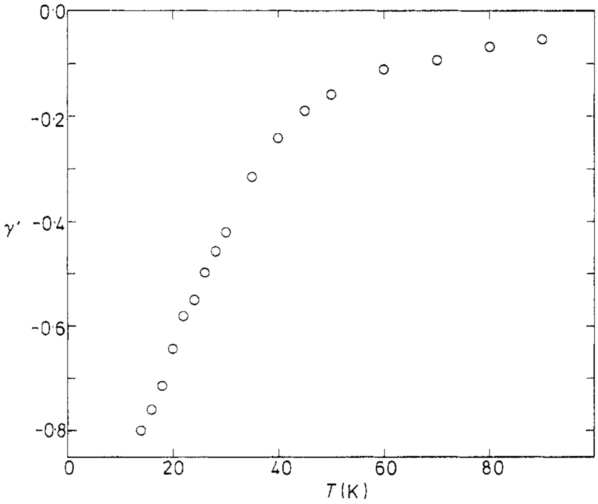

Figure 3. Variation of γ' with temperature.

along both principal axes. A quantity γ' can be calculated however, where, from equation (2),

$$\gamma' = [\gamma_c + (2s_{13}/s_{33})\gamma_a] = (V/s_{33}C_t)\alpha_c. \tag{4}$$

From the heat capacity data of Pitzer (1941), the corresponding values of C_v were calculated using

$$C_p - C_v = VT\beta^2/\chi \tag{5}$$

where $\chi = 2\chi_a + \chi_c$ and β was taken to be $3\alpha_c$. Using the room-temperature values of the elastic compliances, the values of γ' were calculated and are shown in figure 3.

The behaviour of γ' with decreasing temperature is similar to that of γ (Smith and White 1975) in that γ' decreases as if approaching a minimum. If one assumes that γ_a and γ_c are the same and equal to γ_{av}, then because s_{13} is negative, γ_{av} is significantly larger than γ' (by perhaps a factor of four) and so is more in agreement with what would be expected from the relationship between the Gruneisen parameter and the ionicity.

Acknowledgments

The work described was supported by the Australian Research Grants Committee. The authors are also grateful to Dr G K White for advice and assistance.

References

Barron T H K 1955 *Phil. Mag.* **46** 720–34
Bienenstock and Burley 1963 *J. Phys. Chem. Solids* **24** 1271–8
Cochrane G 1967 *Br. J. Appl. Phys.* **18** 687–8
Fizeau H 1867 *C.R. Acad. Sci. Paris* **64** 314–23
Hanson R C, Fjeldly T A and Hochheimer X Y 1975 *Phys. Status. Solidi* (b) **70** 567–76
Hara M, Mori T and Ishiguro M 1973 *J. Appl. Phys. (Japan)* **12** 343–5
Lawn B R 1964 *Acta. Crystallogr.* **17** 1341–7
Lieser K H 1956 *Z. Phys. Chem.* **9** 302–17
Majumdar A J and Roy R 1959 *J. Phys. Chem.* **63** 1858–60
Munn R W 1972 *J. Phys. C: Solid St. Phys.* **5** 535–42
Novikova S I 1960a *Sov. Phys.–Solid St.* **2** 37–8
—— 1960b *Sov. Phys.–Solid St.* **2** 1464–5
—— 1961a *Sov. Phys.–Solid St.* **2** 2087–9
—— 1961b *Sov. Phys.–Solid St.* **3** 129–30
—— 1966 *Sov. Phys.–Solid St.* **7** 2170–3
Novikova S I and Abrikosov N Kh 1963 *Sov. Phys.–Solid St.* **5** 1558–9
Pitzer K S 1941 *J. Am. Chem. Soc.* **63** 2413–8
Prager P R 1974 *Acta. Crystallogr.* **A30** 369–73
Ramsdell L S and Kohn J A 1951 *Acta. Crystallogr.* **4** 111–3
Schock R N and Hinze E 1975 *J. Phys. Chem. Solids* **36** 813–21
Simmons B A 1967 *Opt. Spectra* **1** 25–9
Smith P V 1976 *J. Phys. Chem. Solids* **37** 581–7, 589–97
Smith T F and White G K 1975 *J. Phys. C: Solid St. Phys.* **8** 2031–42
White G K 1961 *Cryogenics* **1** 151–8