Thermal Expansion of Silver Iodide

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The linear thermal expansivity of polycrystalline silver iodide has been measured with a "Fused-Quartz Tube" apparatus in the temperature range 170—500 °C, the mean linear thermal expansion coefficient being

$$\alpha_{180}^{t} = (2.607 + 0.00182\, t)\, 10^{-5} \quad (°\mathrm{C}^{-1}) .$$

An irregular change in the thermal expansivity was found close to 432 °C where an order-disorder transition has been reported.

In the high-temperature modification (α-AgI) of silver iodide above 146 °C there exists a high electrical conductivity which is attributed to the high fraction of vacant sites in the cation network[1]. The transition from the ordered (low-temperature) to the disordered (high-temperature) phase is generally assumed to be completed close to the transformation temperature. However, heat capacity measurements on silver iodide by Lieser[2] and by Perrott and Fletcher[3] show an increase in c_p up to about 430 °C followed by a sudden decrease leading to a "lambda" curve. Measurements of electrical conductivity and silver ion diffusion in silver iodide by Josefsson, Kvist, and Tärneberg[4] show a change in the temperature coefficients at this temperature. The Grüneisen theory[5] predicts that a sudden change in the specific heat should be followed by a similar change in the thermal expansivity. Dilatometric measurements by Lieser[6] fail to show any drastic changes in the thermal expansivity around 430 °C. Since such an effect might be small and since evidence for an additional second-order transition at this temperature is accumulating it was decided to re-measure the thermal expansivity of silver iodide in the appropriate temperature interval.

Experimental

Commercially available silver iodide (purum grade) obtained from KEBO AB, Stockholm, Sweden was used after drying in an oven. Since it has been indicated[3] that impurities might obscure the effect, silver iodide was also made from reagent grade potassium iodide and silver nitrate (E. Merck AG, Darmstadt, Germany) according to a method described by Cohen and van Dobbenburg[7]. The salt was cast into cylinders or pressed using a hydraulic ram with a pressure up to 50 kN/cm². A mean sample density of 5.23 – 5.46 g/cm³ was obtained by pressing (tabulated value at room temperature[8] 5.68 g/cm³). The density changed slightly over the length of the samples since they were compressed from one side only. The sample diameter was 11.2 mm and the length waried between 30 and 40 mm.

The experimental arrangement has been described elsewhere[9]. The temperature was changed step-wise every two hours, the steps being 15 °C in the runs intended to cover the whole temperature interval. In the runs covering the expected lambda point the steps were 2 °C between 400 and 460 °C. The plastic flow of the samples which starts somewhat above 400 °C was corrected for graphically as before[9]. A numerical method in which the temperature dependence of the correction terms was calculated was tried in order to minimize the scatter. Satisfactory agreement between the graphical and the numerical methods was obtained.

Results and Discussion

Expansivity readings were made after the samples had been repeatedly cycled between 150 and 450 °C in order to remove stresses which might have been introduced when passing through the phase transition at 146 °C. A plot of $(l-l_0)/l_0$ (l_0 length at room temperature) for a sequence of increasing and decreasing temperatures is shown in Figure 1. Due to plastic deformation above 400 °C, consecutive branches of the curve are displaced downwards. The

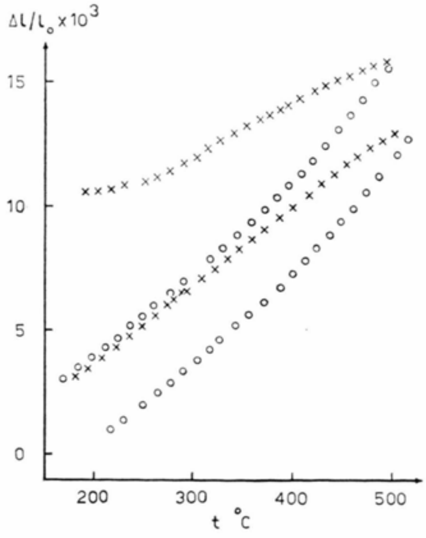

Fig. 1. Relative length change $(l-l_0)/l_0$ versus temperature t of a sample of silver iodide for a series of increasing (×) and decreasing (○) temperatures (l_0 length at room temperature). The first part of the curve shows some remaining stress being annealed out. The following branches are displaced downwards due to plastic deformation of the sample at high temperatures.

mean linear thermal expansion coefficient is defined as

$$\alpha_{t_0}^{t} = \frac{(l-l_0)}{l_0(t-t_0)}$$

where l_0 is the sample length at the temperature t_0. α_{180}^{t} corrected for sample plasticity is plotted in Fig. 2 together with data by Lieser [6]. The agreement between the two sets of data is good. The mean linear thermal expansion coefficient may be represented by a linear equation between 200 and 500 °C:

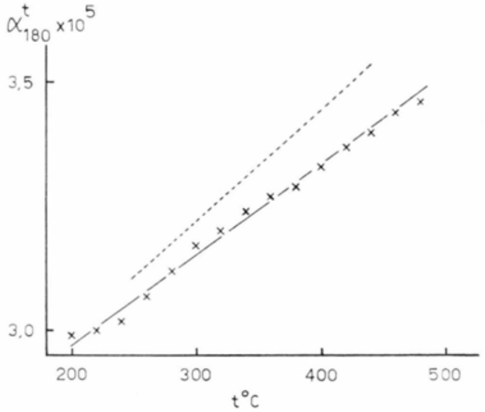

Fig. 2. The mean linear thermal expansivity (α_{180}^{t}) referred to 180 °C as a function of temperature. Full line according to Eq. (1), broken line according to Lieser [6].

$$\alpha_{180}^{t} = (2.607 + 0.00182\, t) \times 10^{-5} \qquad (1)$$

with a standard error of estimate of 0.4%. However, readings taken with a temperature interval as great as 15 °C may fail to show evidence of irregular changes in α occurring within a small temperature range. Thus runs were also made with an average temperature step between readings of 2 °C every two hours in the interval 400 – 460 °C. Corrected plots of l versus t were drawn and the quantity $\mathrm{d}l/\mathrm{d}t$ (approximated as $\Delta l/\Delta t$, $\Delta t = 4$ °C) divided by l is shown as a function of temperature in Fig. 3 for a pressed sample made of commercial silver iodide. In this case the plasticity correction may be comparable to the thermal expansion (particularly above 432 °C where a change in flow properties has been observed [10]) but the corrected plots of l are still resonably smooth over the whole temperature interval and the derivative $\mathrm{d}l/\mathrm{d}t$ shows an appreciable irregularity only at about 437 °C. This irregularity corresponds to a change in thermal expansivity of more than 50% while the scatter in $\mathrm{d}l/\mathrm{d}t$ calculated in this way is lower (about 10%) [11]. Three different samples were studied in this way: 4 runs were made on "commercial" salt, 2 on "pure" salt and an additional check on commercial salt. The irregularity (which might be interpreted as a lambda point) in the thermal expansivity occurs at 437 ± 3 °C.

The present investigation and the plastic flow studies by Jansson and Sjöblom [10] indicate that the mechanical properties of silver iodide change at a temperature slightly above 430 °C, where changes in the temperature dependences of electrical conductivity and silver ion diffusion have been observed by Josefsson, Kvist, and Tärneberg [4]. Specific heat measurements by Lieser [2] show a gradual increase in c_p with t above the phase transition at 146 °C. His measurements were extended by Perrott and Fletcher [3] who found a lambda point in the temperature dependence of c_p at about 430 °C. The corresponding irregularity in the thermal expansivity observed in the present work is smaller than could be expected from their data. They interpreted their observation as due to a gradual disordering (in "pure" AgI only) starting at 146 °C and being completed at 430 °C. This view has been disputed by Widersich and Geller [1] who point out that the entropy of transformation at 146 °C is the same both for "pure" and nonstoichiometric silver iodide. Moreover, even if the mechanism suggested by Perrott and Fletcher [3] does operate, it cannot be responsible for a lambda point in the thermal expansivity.

Acknowledgements

Thanks are due to Mr. Lars Jacobsson for experimental assistance. The work was financially supported by "Adlerbertska Forskningsfonden" which is gratefully acknowledged.

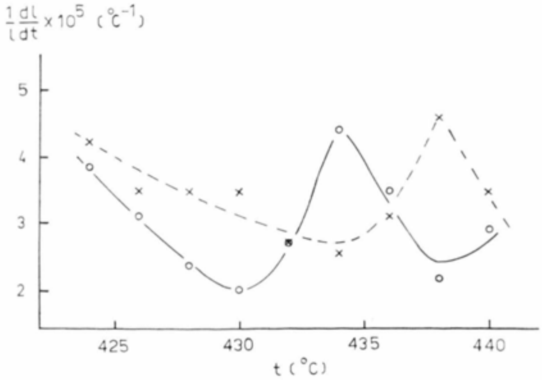

Fig. 3. $(1/l)\,\mathrm{d}l/\mathrm{d}t$ ($\mathrm{d}l/\mathrm{d}t$ approximated by $\Delta l/\Delta t$, $\Delta t = 4$ °C) for a silver iodide sample pressed from commercial salt. (×) = increasing temperature, (○) = decreasing temperature.

[1] H. Widersich and S. Geller, "Properties of Highly Conducting Halide and Chalcogenide Solid Electrolytes", a section of "The Chemistry of Extended Defects in Non-Metallic Solids", North-Holland Publ. Co., Amsterdam 1970, p. 629.

[2] K. H. Lieser, Z. Physik. Chem. (Neue Folge) **2**, 238 [1954].

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[4] A. M. Josefsson, A. Kvist, and R. Tärneberg, "Electrical Conduction and Diffusion of Ag Ions and Na Ions in the Cubic High Temperature Modification of Silver Iodide" in "Atomic Transport in Solids and Liquids" by A. Lodding and T. Lagerwall (ed.), Verlag der Z. Naturforsch., Tübingen 1971, p. 291.

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[9] B. Jansson and C.-A. Sjöblom, Z. Naturforsch. **25 a**, 1115 [1970].

[10] B. Jansson and C.-A. Sjöblom, "Theological Properties of Some Pre-Melting Solid Salts", to be published.

[11] The mean linear thermal expansion coefficient $\alpha^{t}_{\mathrm{iso}}$ (Fig. 2) is smaller than the differential expansion coefficient $\alpha = (1/l)\,\mathrm{d}l/\mathrm{d}t$ (Fig. 3) since α increases with temperature (Cf. Reference 6).

Berichtigungen

G. Petrella and M. Castagnolo, The Conductance of the Alkali Halides IV, **28 a,** 1149 [1973].

The paper contains the following misprints:

p. 1149, Abstract, Line 3: . . . solvent mixtures within . . .

p. 1149 l., Experimental, Line 4: . . . and Nilsson [5] . . .

p. 1150 r., Fig. 1, Line 1: . . . solvents mixtures limiting . . .

p. 1151 l., Line 27: . . . crystallographie radius).

Zu G. Heppke und F. Schneider: Experimentelle Untersuchung des Einflusses der Probengeometrie auf die elektrischen Eigenschaften nematischer Elektrolytlösungen, Z. Naturforsch. **28 a,** 497 [1973].
Formel (8) muß richtig heißen:

$$l/a = I_1{}^{1/\omega_r}(k,\vartheta)/I_1{}^{1/k}(k,\vartheta) = I_{-1}^{-1/\omega_l}\,(k,\vartheta)/I_1{}^{1/k}(k,\vartheta)\ .$$

Jayarama R. Perumareddi, "The d^2 and d^8 Noncubic Field Spectrum. I. The Complete Theory of Quadrate, Trigonal and Cylindrical Ligand Fields." Zeitschrift für Naturforschung **27 a,** 1820 – 1860 [1972].

The paper contains the following misprints:

p. 1821, Line 18 below Eq. (1): 'the' instead of 'te'

p. 1821, Line 20 below Eq. (1): 'scheme of the quadrate fields is more appropriate' instead of 'scheme is applicable in the study of the substituted'

p. 1822, Table 3, last column: 7th row should read $-\frac{1}{2}\,e_{\mathrm{ga}} - e_{\mathrm{gb}}\sqrt{3}/2$

p. 1822, Table 3, last column: 8th row should read $-\frac{1}{2}\,e_{\mathrm{gb}} + e_{\mathrm{ga}}\sqrt{3}/2$

p. 1823, Table 5, $\Gamma_1{}^{\mathrm{Q}}$ Representation: $|6\rangle$ should read

$$i\sqrt{\tfrac{1}{2}}\left\{\left[-\tfrac{1}{2}\,|(z\,x)\,(z^2)| - \frac{\sqrt{3}}{2}\,|(z\,x)\,(x^2-y^2)|\right]\Psi_1 - \left[-\tfrac{1}{2}\,|(y\,z)\,(z^2)| + \frac{\sqrt{3}}{2}\,|(y\,z)\,(x^2-y^2)|\right]\Psi_{-1}\right\}$$

p. 1823, Table 5, $\Gamma_4{}^{\mathrm{Q}}$ Representation:
$|3\rangle$ should read $\ldots + [-\tfrac{1}{2}\,|(y\,z)\,(x^2-y^2)| - \ldots$