LATTICE THERMAL EXPANSION OF LEAD IODIDE

LEAD iodide has a structure similar to that of cadmium iodide. Cadmium iodide is hexagonal with a typical 'layer structure', the interatomic forces within the layers being stronger than those perpendicular to the layers; the thermal expansion in a direction parallel to the layers is smaller than that in a perpendicular direction[1]. We have studied the thermal expansion behaviour of lead iodide by the X-ray method.

Analar grade PbI_2 powder was used to obtain X-ray photographs at various temperatures from room temperature to 114° C. With filtered copper radiation, seven $CuK\alpha_1\alpha_2$ doublets could be recorded on a flat-plate back-reflection camera. The experimental arrangement and the procedure for the evaluation of lattice parameters were the same as described earlier[2]. The values of the parameters at different temperatures are given in Table I. The lattice parameters at 25° C are $a = 4{\cdot}5562 \pm 0{\cdot}0004$ Å and $c = 6{\cdot}9830 \pm 0{\cdot}0004$ Å. These values agree well with those given by Swanson *et al.*[3]

TABLE I

Lattice parameters of lead iodide

t °C	a Å	c Å
25·0	4·5562	6·9830
64·5	4·5628	6·9905
86·0	4·5667	6·9964
104·0	4·5693	7·0017
114·0	4·5717	7·0035

The data on lattice parameters have been used to evaluate the directional coefficients of thermal expansion $\bar{\alpha}_a = (1/a_{25})(\Delta a/\Delta t)$ and $\bar{\alpha} = (1/c_{25})(\Delta c/\Delta t)$ over the range 25–100° C. The values are 36·6 and 32·3 (both in units of 10^{-6}/°C). These values lead to $105{\cdot}5 \times 10^{-6}$/°C as the coefficient of cubical expansion. This value compares well with the values 100·8 and 108·6 (in units of 10^{-6}/°C) reported by Fizeau[4] and Klemm *et al.*[5].

We have also evaluated the coefficients defined by $\alpha_a = (1/a_{25})(da/dt)$ and $\alpha = (1/c_{25})(dc/dt)$ at various temperatures. These values are shown in Fig. 1.

The temperature variation of these coefficients can be represented by the equations:

$$\alpha_a = 26{\cdot}36 \times 10^{-6} + 16{\cdot}5 \times 10^{-8}\, t$$
$$\alpha_c = 15{\cdot}69 \times 10^{-6} + 26{\cdot}3 \times 10^{-8}\, t$$

where t is the temperature in °C.

Regarding the anisotropy in thermal expansion, it is seen that the thermal expansion coefficient perpendicular to the layer (α_c). is smaller than that parallel to the layer (α_a). The anisotropy decreases as the temperature increases and at about 100° C, the two coefficients are nearly equal. If the trend continues, the anisotropy will be reversed at higher temperatures. With our technique, we could not record photographs of a measurable quality at higher temperatures.

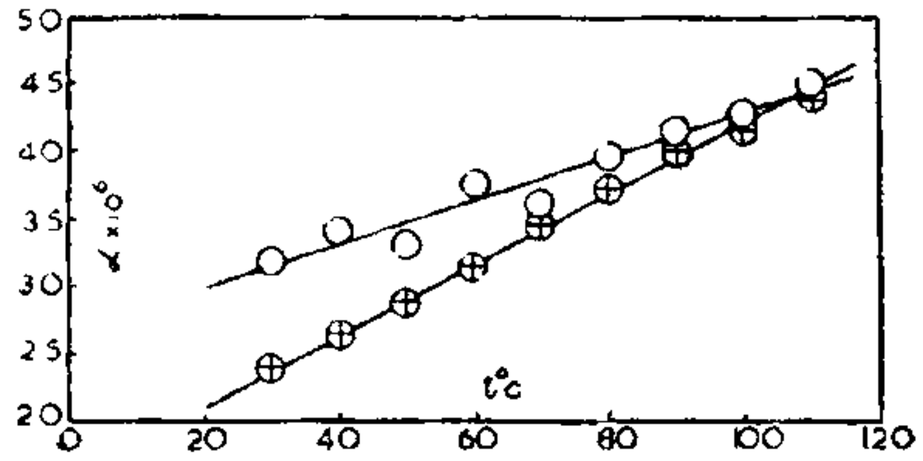

FIG. 1. Principal coefficients of expansion α_a [O] and α_c [⊕] of PbI_2.

In view of the similarity in the structure of CdI_2 and PbI_2, we expected that the thermal expansion will have similar anisotropy. But at room temperature, the anisotropy in the thermal expansion of PbI_2 is the opposite of that in the case of CdI_2. This, however, is not unusual. Wooster[6] and Bredig[1] have given examples of crystals with a layer structure having larger expansion coefficients parallel to the layer than perpendicular to the layer. A better understanding of the difference in the anisotropy of thermal expansion of PbI_2 and CdI_2 would be possible only when the elastic constants of these crystals become available.

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