THERMAL EXPANSION OF POTASSIUM IODIDE

By R. Srinivasan

(*Physics Department, Indian Institute of Science, Bangalore-3*)

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

A systematic investigation of the variation of thermal expansion coefficient of alkali halides with temperature at low temperatures has been undertaken by the author for the following reasons:—

Because of the simplicity of their structure the alkali halides occupy an important position in any theory of the solid state. Expansion measurements at low temperatures are not present for any of the alkali halides except sodium chloride.

The results of the measurements on sodium and potassium chlorides have already been reported (1955). The results for potassium bromide will be reported elsewhere. As the expansion of potassium iodide exhibits an anomalous behaviour at low temperatures it is reported here separately.

2. Previous Work

The thermal expansion of potassium iodide has been measured by Fizeau (1867–68) with his interference dilatometer He found a value of $42{\cdot}65\times10^{-6}$ for the linear expansion coefficient of potassium iodide at 40° C. The volume expansion eoefficient between 0 to 25° C. was determined by Baxter and Hawkins (1916) employing a pyknometer method. Henglein (1925) measured the volume expansion coefficient of potassium iodide between — 184/— 79° and — 79/0° C. using a gas volumenometer to determine the density of the salt at these temperatures. Eucken and Dannohl (1934) measured the expansion of potassium iodide with the heterodyne beat method. But their values at room temperature are much lower than any of the values mentioned previously, the discrepancy amounting to as much as 20%.

Gott (1942) carried out a series of careful investigations on the macroscopic and lattice expansions of potassium iodide between 20 to 190° C. and found that the former was larger than the latter by about 14%. This discrepancy he attributed to the presence of Schottky defects in the lattice. But the number of such defects in the crystal deduced from other measurements are not sufficiently large to account for the observed discrepancy.

Connell and Martin (1951) have measured the lattice expansion potassium iodide between 20 to 100° and 20 to 190° C. and found that the values of lattice expansion agreed well with the macroscopic values Gott and were larger than the lattice expansion values of the same auth

3. METHOD OF MEASUREMENT AND OTHER DETAILS

The method of measurement both at high and at low temperatu has been indicated in previous papers of the author (1955 *a*, *b*).

Two different sets of spacers of potassium iodide were employed in t investigation. One set of three spacers was prepared from a specim of potassium iodide grown from melt in our laboratory by Dr. Ved and Mr. Gopalakrishnan to whom the author's thanks are due. T substance used for growing the crystal was an extra pure sample suppli by Merck and Co. The crystal was grown in a porcelain crucible a was annealed for two days. The crystal was clear and transparent.

The second set of three spacers was prepared from a specimen pure potassium iodide supplied by Harshaw Chemical Co.

For measurements at high temperatures, the interferometric arrange ment was heated up to 300° C. and cooled back to room temperatur The measurements were then made as the crystals were heated gradual

Low temperature expansion was always measured after the hig temperature experiment was made. This means the specimens were heate up to 300° C. many times before their low temperature expansion wa measured.

On heating up to 300° C. the crystals did not exhibit any visib colouration.

For low temperature measurements, the specimens were first cool to liquid-air temperature and the readings were taken as the specime were heated gradually. The measurements were repeated for specimen after the interferometric arrangement was taken apart and reset for a fres run. Only one run was made for specimen 2. High temperature measure ments were carried out for each set of specimens both before and after the low temperature measurements.

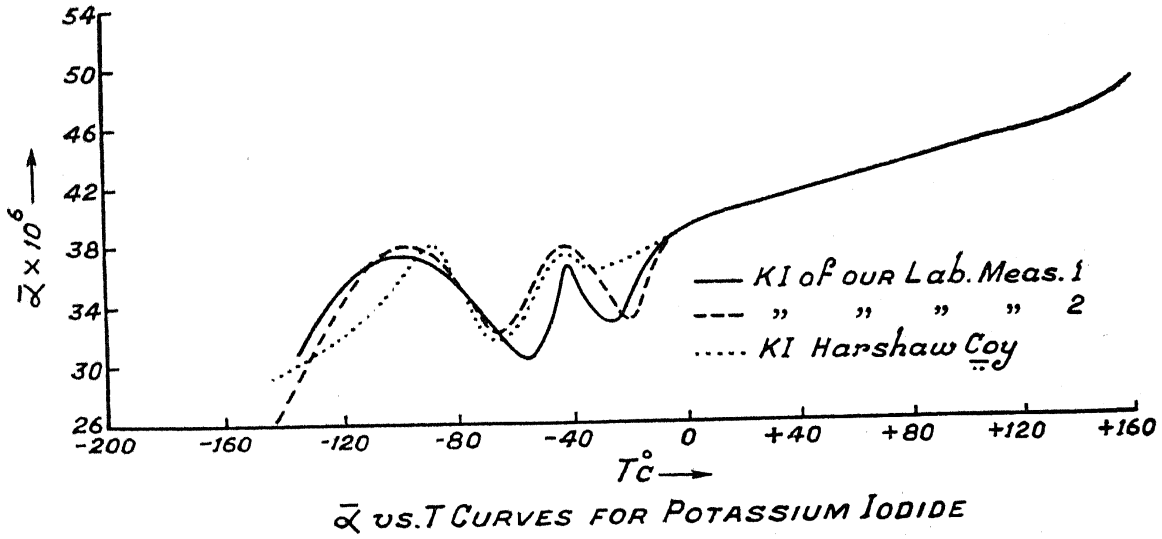
4. RESULTS

The results of these measurements are given in Table I. $\bar{\alpha}$ denotes the mean expansion coefficient over 25° C. intervals. The results are shown graphically in Fig. 1 for specimen 1 (measurements 1 and 2) and specimen 2.

TABLE I

Linear Expansion Coefficient ā of Potassium Iodide at Various Temperatures

Specimen 1 (Grown in our Laboratory) Heating 1		Heating 2		Specimen 2 (Harshaw) Heating 1	
T° C.	$\bar{a}\times10^6$	T° C.	$\bar{a}\times10^6$	T° C.	$\bar{a}\times10^6$
−135·1	30·6	−143·0	26·1	−142·1	29·1
−124·0	34·2	−130·7	30·6	−121·3	32·2
−113·2	36·3	−119·0	34·5	−106·7	34·4
−102·5	37·1	−109·0	36·7	− 96·4	36·5
− 93·3	37·1	− 98·0	37·5	− 88·3	37·2
− 84·4	36·7	− 88·1	37·5	− 80·3	36·2
− 73·2	33·9	− 78·3	35·2	− 69·2	31·9
− 63·5	31·2	− 68·1	32·3	− 57·1	32·9
− 52·0	30·4	− 58·0	33·9	− 46·8	36·7
− 42·2	36·5	− 48·4	37·1	− 32·1	36·5
− 32·3	33·6	− 37·9	37·1	− 21·6	37·7
− 22·5	32·9	− 27·9	34·9	− 12·2	38·7
− 13·0	36·7	− 18·2	33·9	2·1	40·0
− 4·1	38·4	4·0	39·6		
23·0	40·5				
46·4	41·9			46·8	42·0
63·3	43·1			69·2	43·1
88·9	43·5			90·9	44·1
105·4	44·7			112·3	44·8
121·4	45·1			132·9	46·5
133·7	46·9			153·9	47·9
147·7	47·1				



$\bar{\alpha}$ vs. T CURVES FOR POTASSIUM IODIDE

FIG. 1

5. DISCUSSION

An examination of the results given in Table I and the graphs in Fig. 1 reveals the following important features:

1. Below room temperature, the thermal expansion of potassium iodide behaves in an anomalous way. The expansion coefficient *versus* temperature curve for this crystal exhibits two maxima and two minima. The maxima occur at average temperatures of — 95° and — 40° C. The positions of the minima occur at — 60° and — 25° C. The maxima and minima show slight shifts along the temperature axis from one curve to another. The values of these expansion coefficients at these maxima and minima are nearly the same for all the curves. The expansion coefficient ranges from $37{\cdot}5\times10^{-6}$ at the maxima to about $30{\cdot}8\times10^{-6}$ at the minima—a difference of about 20%. The experimental error of these measurements is less than 3%.

All the measurements were carried out as the specimens were heated from liquid-air temperatures to room temperatures. Measurements were attempted on the Harshaw specimen (specimen 2) as it was cooled from room temperature to liquid-air temperature. But because of the initial rapid cooling reliable values were not obtained till about — 50° C. The values of the expansion coefficient while cooling also exhibited a very sharp maximum at — 100° C. coinciding with the maximum at about the same temperature obtained while heating the specimens.

Above 0° C. all the curves merge with the high temperature expansion curve.

The values of α observed by Henglein (1925) between — 185/— 79° and — 79/0° C. were mean values and in view of the present observations do not have any significance.

The specific heat of potassium iodide has been determined by the method of mixtures by Korf (1911) between — 184/— 79° and — 79/0° C. By the nature of the experiment, only mean values of the specific heat over these temperatures could have been obtained by him and so any small anomaly in the specific heat could not be detected. Bronstead (1914) has measured the specific heat of potassium iodide at 10° C. This is a temperature region which is not of any interest to us.

The specific heat of potassium iodide has been measured from 10 to 273° K. by Clusius, Goldmann and Perlick (1949). Unfortunately that paper is not available to us. But from the summary of the paper given in *Chemical Abstracts* (1950) it appears that no anomaly has been reported

between these temperatures. For want of a precise knowledge of their values, we cannot make any comparison between thermal expansion and specific heat values.

2. Above room temperature the macroscopic values of expansion of the two specimens are identical within the limits of experimental error (3%). The high temperature values are completely reproducible and are not affected by cooling the specimens to liquid-air temperatures and heating them back again to room temperature. Also the present experiments on potassium iodide above room temperature and all the other measurements except that of Eucken and Dannohl agree in obtaining a value of over 40×10^{-6} for $\bar{a}$. Eucken and Dannohl's (1934) values are too low and are definitely affected by systematic errors.

Finally from the expansion *versus* temperature curve we see that the length of the spacers do not show any abrupt changes but vary continuously with temperature from -140 to 0° C. This behaviour appears to point to a homomorphous transition (Zwikker, 1954) in this crystal. Bergmann (1942), in his experiments on the variation of the solubilities of potassium chloride, bromide and iodide with temperature, found kinks in the curves at 27, 22 and 11° C. respectively. He postulated a homomorphous transition from α to β type for these salts at these temperatures. But he found no X-ray evidence for any change in the lattice structure at these temperatures. Neither has the present author found any abnormality in the expansion-temperature curves of potassium chloride and bromide at these temperatures. In potassium iodide also the anomalous behaviour in expansion is observed only below 0° C.

Sharma (1952) has observed the change in intensity with temperature of thermoluminiscence bands of a crystal of potassium iodide coloured by cathode-ray bombardment at liquid oxygen temperature. He observed four peaks in the curve at 110 to 120° K., 158° K., 176° K. and 235° K. The last two peaks occur at temperatures almost coincident with the two maxima in the expansion observed by the author at $-95°$ and $-40°$ C. This coincidence appears to be fortuitous.

Further investigations on X-ray diffraction, Raman effect, etc., in potassium iodide at low temperatures, are called for before one could postulate any hypothesis as to the nature of the anomaly.

In conclusion, the author wishes to express his gratitude to Prof. R. S. Krishnan for his interest and encouragement during the course of this investigation and for having provided the specimen of potassium iodide grown by Harshaw Chemical Co.

SUMMARY

The thermal expansion of two different specimens of potassium iodide was measured from liquid-air temperatures to 150° C. One specimen was melt grown in our laboratory and other was supplied by Harshaw Chemical Co.

The expansion coefficient for the two specimens above room temperature are identical with one another. The high temperature expansion was not influenced by heat or cold treatment of the specimens.

Below 0° C. the thermal expansion of potassium iodide exhibits an anomalous behaviour. Two maxima at — 95° and — 40° C. and two minima at — 60° and — 25° C. have been observed. As the length of the specimen varies continuously with the temperature, the transition in this crystal appears to be homomorphous.

REFERENCES

1. Baxter and Hawkins .. *J.A.C.S.*, 1926, **38**, 259.
2. Bergmann .. *C.R.U.R.S.S.*, 1942, **35**, 274; *Chem. Abstr.*, 1943, **37**, 1919.
3. Bronstead .. *Zeit.f. Elec. Chem.*, 1914, **20**, 554.
4. Clusius, Goldmann and Perlick *Zeit. f. Nat. forsch.*, 1949, **4** *a*, 424; *Chem. Abst.*, 1950, **44**, 2839.
5. Connel and Martin .. *Acta Cryst.*, 1951, **4**, 76.
6. Eucken and Dannohl .. *Zeit. f. Elec. Chem.*, 1934, **40**, 814.
7. Fizeau .. *Ann. d. Phys.*, 1867, **132**, 292; *C.R. Acad. Paris*, 1868, **66**, 1005, 1072.
8. Gott .. *Ann. d. Phys.*, 1942, **41**, 520.
9. Henglein .. *Z.f. Elec. Chem.*, 1925, **31**, 424.
10. Sharma .. *Phys. Rev.*, 1952, **85**, 692.
11. Srinivasan *Proc. Ind. Acad. Sci.*, 1955, **41 A**, 49; *J. Indian Inst. of Sci.*, 1955 (under publication).
12. Zwikker .. *Physical Properties of Solid Materials* (Pergamon Press, London), 1954, p. 173.