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Thermal Expansion of Ammonium Bromide, Rubidium Bromide and Rubidium Chloride

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The lattice constants of ammonium bromide, rubidium bromide and rubidium chloride have been determined accurately at different temperatures, using a back-reflection camera, and the coefficients of thermal expansion have been evaluated. The lattice constants of the three compounds at 20 °C. are 4·0587, 6·8908 and 6·5898 Å respectively. The coefficients of expansion of ammonium bromide and rubidium bromide vary parabolically with temperature according to the equations,

$$\alpha = 58{\cdot}96 \times 10^{-6} - 11{\cdot}98 \times 10^{-8}T + 35{\cdot}00 \times 10^{-10}T^2$$

and

$$\alpha = 38{\cdot}00 \times 10^{-6} - 1{\cdot}54 \times 10^{-8}T + 4{\cdot}13 \times 10^{-10}T^2,$$

respectively. The lattice constant of rubidium chloride increases linearly with temperature and the mean coefficient of expansion for the range of temperature 20–190 °C. is $38{\cdot}13 \times 10^{-6}$/°C.

Introduction

The results of the temperature variation of the lattice constants of ammonium bromide, rubidium bromide and rubidium chloride are reported in this paper. Sharma (1950) has studied ammonium bromide by the interferometric method over a range of temperature from 33 to 121 °C. For the rubidium halides, the only available report is that of Baxter & Wallace (1916), who have given mean coefficients of expansion over the ranges 0–25 °C. and 25–50 °C. There also appear to exist some differences in the room temperature values of the lattice constants of the two rubidium salts, as reported by Davey (1923) and Havighurst, Mack & Blake (1924). An accurate determination of these at room temperature and also at elevated temperatures was therefore considered desirable.

The comparison of the results of the X-ray and the macroscopic determinations of the coefficients of expansion appears to be still of some interest. Recently, Visvamitra (1959) has reported the absence of any significant difference between the values obtained by the two methods. On the other hand, Deshpande (1960) has shown, from the existing data on a number of cubic and non-cubic crystals, that the gradients of the α-T curves are, in general, higher in the X-ray determinations than in the macroscopic determinations, and that they appear to agree with each other as a limit. It was, therefore, felt that the collection of more data would be useful in extending the range of this comparison.

Experimental

Flat-film back-reflection photographs were obtained using a Sach-type camera and Cu $K\alpha$ radiation. The experimental set-up and procedure for evaluating the lattice constants was the same as used by Deshpande & Mudholker (1960). As the flat-film camera recorded only two or three reflections, the accuracy of the procedure was checked by determining the lattice constants at room temperature by using a cylindrical Debye–Scherrer camera and comparing these with the values given by the flat-film method. It may be mentioned that accurate lattice parameters were obtained by Nelson & Riley (1945) and Taylor & Floyd (1950) by using only two reflections for extrapolation.

Results and discussion

(1) *Ammonium bromide*

B.D.H. analar grade salt was used for the work. The values of the lattice constant at different temperatures are given in Table 1. The accuracy is estimated to be ±0·0002 Å. The lattice constant at 20 °C., obtained by graphical extrapolation, is 4·0587 ± 0·0002 Å, which is in good agreement with the value 4·059 Å (converted from kX.), quoted by Donnay & Nowacki (1954). The coefficients of expansion evaluated from the experimental data are given in column 2 of Table 2. Least-squares treatment of

Table 1. *Lattice constant of ammonium bromide at various temperatures*

Temperature (°C.)	Lattice constant (Å)
28	4·0603
45·5	4·0644
57	4·0676
71	4·0710
82	4·0740
98	4·0800
112	4·0848
125	4·0899
132	4·0913

these values gives for the coefficient the following equation:

$$\alpha = 58{\cdot}96 \times 10^{-6} - 11{\cdot}98 \times 10^{-8}T + 35{\cdot}00 \times 10^{-10}T^2.$$

Values of the coefficient calculated from this equation are given in column 3 of the table. In column 4 the differences between the experimental and calculated values are given. The last column contains the values obtained from Sharma's (1950) equation. The values

Table 2. *Coefficient of thermal expansion of ammonium bromide*

Temperature in °C.	$\alpha \times 10^6$ (exp.)	$\alpha \times 10^6$ (calc.)	% Difference	$\alpha \times 10^6$ (Sharma)
30	57·90	58·52	−1·0	60·84
40	59·13	59·77	−1·1	63·34
50	62·83	61·72	+1·8	66·24
60	66·52	64·37	+3·3	69·49
70	66·52	67·72	−1·7	73·12
80	71·45	71·78	−0·4	77·11
90	76·38	76·53	−0·2	81·47
100	81·30	82·00	−0·8	86·21
110	87·47	88·13	−0·7	91·31
120	96·09	94·98	+1·1	96·79

obtained in the present work are lower than those given by Sharma over the entire range of temperature.

(2) *Rubidium bromide*

The substance was obtained from Merck, in powder form. The lattice constants corresponding to different temperatures are given in Table 3. Davey (1923) gives the lattice constant of RbBr as 6·849 Å whereas Havighurst *et al.* (1924) give it as 6·886 Å (both converted from kX.). The present value at 20 °C., read from the graph, is $6{\cdot}8908 \pm 0{\cdot}0002$ Å. This is higher than both the values reported earlier. The density of the crystal, calculated from this value of the lattice constant, comes out as 3·353 g.cm.$^{-3}$ and is in good agreement with the value, 3·358 g.cm.$^{-3}$, given by Setterberg (1882). The coefficient of expansion of rubidium bromide follows the equation,

$$\alpha = 38{\cdot}00 \times 10^{-6} - 1{\cdot}54 \times 10^{-8}T + 4{\cdot}13 \times 10^{-10}T^2.$$

In Table 4 the experimentally obtained values are compared with the values calculated from the equation. The mean coefficient of expansion for the range 20–140 °C. is $39{\cdot}54 \times 10^{-6}$/°C. and for the range 25–50 °C. it is $37{\cdot}43 \times 10^{-6}$/°C. Baxter & Wallace (1916) have given for the latter range a lower value of $33{\cdot}66 \times 10^{-6}$/°C.

Table 3. *Lattice constant of rubidium bromide at various temperatures*

Temperature (°C.)	Lattice constant (Å)
27	$6{\cdot}8927 \pm 0{\cdot}0002$
39·5	6·8952
50	6·8988
62	6·9020
82	6·9066
100	6·9121
112	6·9156
140	6·9235

Table 4. *Coefficient of expansion of rubidium bromide*

Temperature (°C.)	$\alpha \times 10^6$ (exp.)	$\alpha \times 10^6$ (calc.)	% Difference
25	38·45	37·88	+1·5
35	37·00	37·97	−2·5
45	39·18	38·15	+2·7
65	38·46	38·75	−0·7
75	39·18	39·18	0·0
85	40·63	39·68	+2·4
105	41·36	40·94	+1·0
125	42·09	42·54	−1·1
135	43·54	43·46	+0·2

(3) *Rubidium chloride*

Merck salt was used for preparing the specimen. Table 5 gives the lattice constant at different temperatures. It is found that within the limits of experimental errors the lattice expands linearly with temperature. The lattice constant at 20 °C. read from the graph, is $6{\cdot}5898 \pm 0{\cdot}0002$ Å. Davey (1923) and Havighurst, Mack & Blake (1924) give the values as 6·548 and 6·584 Å, respectively, both scaled to Ångström units. Donnay & Nowacki (1954) quote two values, namely 6·548 and 6·590 Å. The second of these values is in agreement with the value obtained in the present investigation.

The mean coefficient of thermal expansion over the range 20–190 °C. comes out as $38{\cdot}13 \times 10^{-6}$/°C. This is much higher than the value $27{\cdot}33 \times 10^{-6}$/°C. given by Baxter & Wallace (1916) for the range 25–50 °C.

Table 5. *Lattice constant of rubidium chloride at various temperatures*

Temperature (°C.)	Lattice constant (Å)
28	$6{\cdot}5916 \pm 0{\cdot}0002$
49	6·5972
86	6·6060
102	6·6110
174	6·6296
193	6·6332

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References

Baxter, G. P. & Wallace, C. C. (1916). *J. Amer. Chem. Soc.* **38**, 259.

Davey, W. P. (1923). *Phys. Rev.* **21**, 143.

Deshpande, V. T. (1960). Paper read at the Symposium on Solid State Physics, Indian Institute of Science, Bangalore.

Deshpande, V. T. & Mudholker, V. M. (1960). *Acta Cryst.* **13**, 483.

DONNAY, J. D. H. & NOWACKI, W. (1954). Memoir No. 60, The Geological Society of America.
HAVIGHURST, R. J., MACK, E. & BLAKE, F. C. (1924). *J. Amer. Chem. Soc.* **46**, 2368.
NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc., Lond.* **57**, 477.
TAYLOR, A. & FLOYD, R. W. (1950). *Acta Cryst.* **3**, 285.
SETTERBERG, C. (1882). *Öfvers. Vetensk. Akad. Förh., Stockh.* **6**, p. 23.
SHARMA, S. S. (1950). *Proc. Indian Acad. Sci.* A, **31**, 339.
VISVAMITRA, M. A. (1959). *Proc. Indian. Acad. Sci.* **49**, 326.

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Thermal Expansion of Tetragonal Tin

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Accurate values of the lattice parameters of tetragonal tin have been determined at various temperatures up to 151 °C., using a back-reflection camera and Cohen's analytical procedure. These data have been used to evaluate the two principal coefficients of thermal expansion and their variation with temperature. The room-temperature results agree with those reported in the literature but the rates of increase of the coefficients with temperature are found to be higher.

Values of the mean Grüneisen's constant are found to increase with temperature.

Introduction

Childs & Weintroub (1950) have made the first extensive study of the coefficients of thermal expansion of tetragonal tin, giving their variations from room temperature to the melting point. They found that both $\alpha_\perp$ and $\alpha_\parallel$ increase with temperature. They also observed that large discrepancies existed between their results and the single X-ray values of mean coefficients given by Shinoda (1933) and Kossolapow & Trapesnikow (1936). Lee & Raynor (1954) report a linear variation of the lattice parameter with temperature, (cf. Pearson, 1958), over the range of temperature studied. The present paper reports the results of a similar X-ray study.

Experimental

Tin metal obtained from Johnsons of Hendon was melted and fine filings were taken from the cooled block. These were annealed at 150 °C. for 16 hrs. The experimental set-up used to obtain X-ray diffraction pictures was the same as described by Deshpande & Mudholker (1960). Three or four $\alpha_1\alpha_2$ doublets, all with $\sin^2\theta > 0{\cdot}90$, were used to evaluate the lattice parameters. Cohen's (1935) least-squares method was used, in combination with the error function $f(\varphi) = \cos\varphi - \cos^2\varphi$. The accuracy of the results was checked by (i) comparing the room-temperature values of the parameters obtained by the back-reflection camera with those obtained with the help of Debye–Scherrer photographs, (ii) imposing a deliberate systematic error in the camera radius to test the efficacy of the error function and (iii) taking two photographs at the same temperature and comparing the results. Invariably these checks gave satisfactory results and it is estimated that the uncertainty in both the parameters is not more than 0·0003 Å.

Results and discussion

The lattice parameters at various temperatures are given in Table 1. Their values at 25 °C., obtained by graphical extrapolation, are

$$a = 5{\cdot}8318 \pm 0{\cdot}0003,\ c = 3{\cdot}1819 \pm 0{\cdot}0003\ \text{Å}\ .$$

These are in fair agreement with the values,

$$a = 5{\cdot}8312,\ c = 3{\cdot}1814\ \text{Å}$$

(converted from kX.), given by Jette & Foote (1935). From the cell dimensions the two coefficients of expansion defined by

$$\alpha_\perp = \frac{1}{a_{25}} \cdot \frac{\Delta a}{\Delta t} \quad \text{and} \quad \alpha_\parallel = \frac{1}{c_{25}} \cdot \frac{\Delta c}{\Delta t}\ ,$$

have been evaluated, at different temperatures. Usual methods of curve fitting give for the two coefficients the following equations.

$$\alpha_\perp = 14{\cdot}64 \times 10^{-6} + 6{\cdot}00 \times 10^{-8} t - 0{\cdot}576 \times 10^{-10} t^2$$
$$\alpha_\parallel = 28{\cdot}14 \times 10^{-6} + 9{\cdot}36 \times 10^{-8} t + 0{\cdot}029 \times 10^{-10} t^2\ .$$

Table 1. *Lattice parameters of tin at various temperatures*

Temperature (°C.)	a	c
35	5·8327 Å	3·1825 Å
60	5·8357	3·1854
82	5·8383	3·1882
98	5·8396	3·1897
112	5·8412	3·1921
137	5·8451	3·1954
151·5	5·8461	3·1971