

THERMAL EXPANSION OF SOME ALKALI FLUORIDES  
AND MAGNESIUM OXIDE BY X-RAY DIFFRACTION

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*(Received June 23, 1962; Resubmitted September 24, 1962)*

**ABSTRACT** In this paper high temperature X-ray data on the thermal expansion of LiF, NaF and MgO are reported for the first time. The results are compared with the macroscopic observations wherever available. The role of lattice defects is examined and the applicability of Debye-Grimmonson equation to explain the observed variation of thermal expansion with temperature is discussed.

## I N T R O D U C T I O N

The coefficient of thermal expansion  $\alpha$  of almost all ionic crystals increases with temperature. Lawson (1950) assumed that  $\alpha$  should be constant for a perfect crystal lattice and deduced that in such a crystal defects do play a part and contribute to the thermal expansion. He succeeded in proving his point in the case of silver bromide but not for silver chloride. It was pointed out in our previous communication (Pathak and Pandya, 1960 (b)) that in the case of ionic crystals Schottky defects shall predominate and that if defects did contribute to the thermal expansion of a crystal, the value of  $\alpha$  determined by macroscopic methods should be greater than that measured by the X-ray method. On searching the literature it was found that the high temperature X-ray data for the salts examined in the present experiments were not available.

Lithium fluoride has been studied by Adenstedt (1936) in the low temperature region upto about  $-225^{\circ}\text{C}$ . It has also been studied by Eucken and Dannöhl (1934) by the heterodyne beat method and by Sharma (1950) by an interferometric method.

Sodium fluoride has been investigated at low temperatures by Henglein (1925) by the pycnometer method. Room temperature values are quoted by Megaw (1939) and Wooster (1949). It has been recently investigated upto  $254^{\circ}\text{C}$  by Deshpande (1961)

The thermal expansion of magnesium oxide was studied by Fizeau (1867), Goodwin and Mailey (1909) from  $120^{\circ}\text{C}$  to  $270^{\circ}\text{C}$  and Merrit (1926). It has been systematically examined by optical or interferometric methods by Thilonius and Holzmann (1930) upto  $1200^{\circ}\text{C}$ , Austin (1931) upto  $800^{\circ}\text{C}$ , Durand (1936) upto  $85^{\circ}\text{C}$  and Sharma (1950) upto about  $700^{\circ}\text{C}$ . No systematic high temperature X-ray data on this salt are available in the literature.

The observations in the present work were taken by employing a diffractometer, Geiger counter and a ratemeter. The diffractometer had a diameter of 500 mm. and was calibrated in degrees ( $2\theta$ , each degree divided into four parts). The position of the Geiger counter could be read upto one minute of arc and by estimation upto  $\frac{1}{2}$  minute. The error in the measurement of the cell constant  $a_c$  is estimated to be less than  $\pm 0.002$ .

## OBSERVATIONS AND RESULTS

The same small furnace (Pathak and Pandya, 1959) was used in this work which was employed in the earlier measurements on NaCl (Pathak and Pandya, 1959), CsI (Pathak and Pandya, 1960a) and KBr, KI and CsBr (Pathak and Pandya, 1960b). The results of the present measurements are shown in Figs. 1, 2, 3 and Table I.

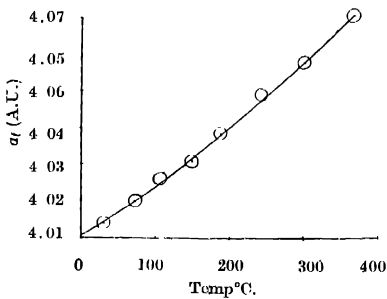


Fig. 1. LiF.

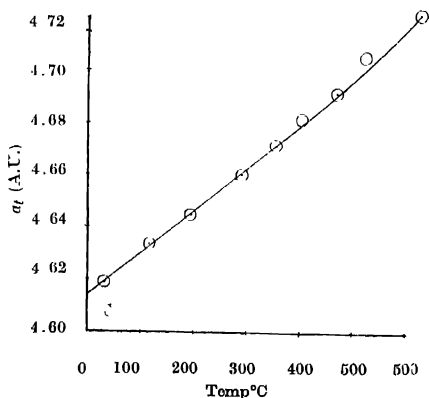


Fig. 2. NaF.

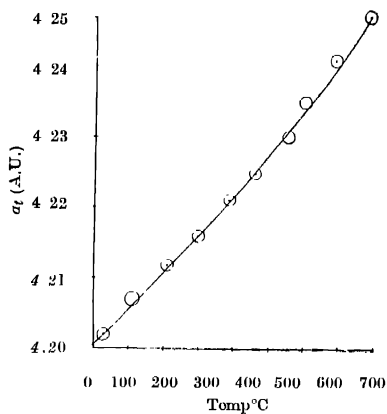


Fig. 3. MgO.

The equations satisfying the smooth curves drawn from the observed points are given below :

$$\text{LiF} \cdot \quad \alpha_t = 4.0102 + 1.312 \times 10^{-4}t + 9.160 \times 10^{-8}t^2$$

$$\text{NaF} \cdot \quad \alpha_t = 4.614 + 1.452 \times 10^{-4}t + 5.595 \times 10^{-8}t^2$$

$$\text{MgO} \cdot \quad \alpha_t = 4.2015 + 4.625 \times 10^{-5}t + 1.392 \times 10^{-8}t^2$$

The coefficient of expansion  $\alpha$  was calculated from the equation  $\alpha = \frac{1}{\alpha_t} \cdot \frac{d\alpha_t}{dt}$ .

The comparison of our results with those of others is shown in Tables II, III and IV.

TABLE I

LiF		NaF		MgO	
Temperature degree C	$\alpha \times 10^6$	Temperature degree C	$\alpha \times 10^6$	Temperature degree C	$\alpha \times 10^6$
30	34.1	30	32.2	27	11.2
72	35.9	72	33.1	208	12.3
160	39.4	116	34.2	386	13.5
187	41.0	195	35.9	552	14.6
242	43.3	288	38.1	691	15.4
301	45.9	351	39.5	788	16.0
307	48.7	400	40.6		
		467	42.1		
		520	43.2		
		625	45.5		

TABLE II  
Lithium fluoride

Temperature degree C	$\alpha \times 10^6$		
	Authors	Sharma	Eucken and Daunohl
0	32.7	33.8	32.2
30	34.1	34.4	33.4
72	35.9	35.5	35.2
150	39.4	37.9	38.4
187	41.0	38.9	40.0
242	43.3	41.6	42.2
301	45.9	44.4	44.6
367	48.7	47.8	47.4

TABLE III  
Sodium fluoride

Temperature degree C	$\alpha \times 10^6$	
	Deshpande	Authors
30	34.0	32.2
72	35.2	33.1
116	36.5	34.2
195	38.8	35.9
288	41.5	38.1

#### DISCUSSION OF THE RESULTS

X-ray data on LiF at high temperatures are not available and hence it is not possible to compare our results with those of other workers. In Table II, however, comparison with the macroscopic data of Sharma (1950) and those of Eucken and Dannöhl (1934) is shown and it is seen that the agreement is fairly good.

Our results on NaF are compared with the X-ray data of Deshpande (1961) in Table III. Our results are slightly lower. Our  $\alpha$  at 0°C viz.  $31.5 \times 10^{-6}$  may also be compared with that of Henglein between -79°C and 0°C viz.  $33.0 \times 10^{-6}$ .

Comparison of our X-ray data on MgO with the macroscopic observations of other workers is shown in Table IV. Our results agree excellently well with those of Sharma (1950). They also agree fairly well with those of Thilenius and Holzmann (1930). Austin's (1931) results are too erratic in the low temperature region with our results at high temperatures.

TABLE IV  
Magnesium oxide

Temperature degree	$\alpha \times 10^6$		
	Literature	Sharma	Authors
40	10.4 <sup>1</sup>	11.2	11.3
120-270	12.1 <sup>2</sup>	12.2	12.3
25-800	13.4 <sup>3</sup>	13.7	13.6
63.7	11.2 <sup>1</sup>	11.4	11.4
153	11.9 <sup>4</sup>	11.9	12.0
246.3	12.8 <sup>4</sup>	12.5	12.6
348.2	13.8 <sup>4</sup>	13.1	13.2
448.4	14.1 <sup>4</sup>	13.8	13.9
546.1	14.6 <sup>1</sup>	14.5	14.5
645.8	12.2 <sup>4</sup>	15.2	15.2
745.5	15.7 <sup>1</sup>	16.0	15.8
20-55	6.7 <sup>5</sup>	11.2	11.3
20-100	9.1 <sup>1</sup>	11.3	11.4
20-150	10.4 <sup>5</sup>	11.5	11.6
20-200	10.9 <sup>5</sup>	11.6	11.7
20-300	11.6 <sup>5</sup>	12.0	12.0
20-400	12.1 <sup>5</sup>	12.3	12.4
20-600	13.0 <sup>5</sup>	13.0	13.0
20-800	13.5 <sup>5</sup>	13.7	13.5

- 1 Fizeau (1867)
- 2 Goodwin and Mailey (1909)
- 3 Merritt (1926)
- 4 Thilonius and Holzmann (1930)
- 5 Austin (1931)

It can be seen from the above discussion that comparison with macroscopic results are possible only in the case of lithium fluoride and magnesium oxide. In the case of the former the X-ray expansions are greater than the macroscopic ones. If lattice defects played any part the reverse should have happened. In

TABLE V  
Grüneisen parameters

Substance	$Q/2R \times 10^3$	$3p$	References
Lithium fluoride	29.01	12.01	Present values
	29.4	11.5	Eucken and Dannohl
	26.2	—	Equation (2)
Sodium fluoride	29.54	8.0	Present values
	29.25	—	Equation (2)
Magnesium oxide	61.15	15.10	Present values
	61.76	—	Equation (2)

the case of magnesium oxide the X-ray data and the macroscopic data agree perfectly. The defects, if any, therefore, affect the X-ray and the macroscopic expansions equally or their contribution to the thermal expansion is negligible.

It can be shown (Pathak and Pandya, 1960b) from the Debye-Grüneisen theory that

$$\frac{a_0}{a_T - a_0} = \frac{Q}{2R} \cdot \frac{1}{TD(\theta/T)} - 3p \quad \dots (1)$$

Where  $a_0$  and  $a_T$  are the cell constants at 0°K. and T°K. respectively,  $D(\theta/T)$  the Debye function and  $Q/2R$  and  $3p$  are constants called the Grüneisen's parameters. The above equation shows that for a crystal obeying Grüneisen's law the graph of  $a_0/a_T - a_0$  against  $1/TD(\theta/T)$  should be a straight line. In the case of substances examined in the present experiments such graphs are found to be straight lines. The Grüneisen's parameters determined from these graphs are compiled in Table V. The value of  $Q$  can also be determined from the relation

$$Q = V_0/\gamma K_0 \quad \dots (2)$$

where  $K_0$  and  $V_0$  are the compressibility and molar volume at 0°K. The values of  $Q/2R$  calculated from this equation are also given in Table V for comparison, the values of  $V_0$  and  $\gamma$  being taken from Born and Huang (1954).

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