

- GELLER, S. (1961). *Acta Cryst.* **14**, 1026–1035.  
 HAMILTON, W. C. (1962). *POWOW*, Brookhaven National Laboratory, Brookhaven, New York.  
 LIPSON, H. & COCHRAN, W. (1966). *The Determination of Crystal Structures*, p. 340. London: Bell.  
 MOOD, A. M. & GRAYBILL, F. A. (1963). *Introduction to the Theory of Statistics*. New York: McGraw-Hill.  
 MORTIER, W. J. & BOSMANS, H. J. (1971). *J. Phys. Chem.* **75**, 3327–3334.  
 MORTIER, W. J., BOSMANS, H. J. & UYTTERHOEVEN, J. B. (1972). *J. Phys. Chem.* **76**, 650–656.  
 OLSON, D. H. (1970). *J. Phys. Chem.* **74**, 2758–2764.  
 SMITH, J. V. (1971). *Advanc. Chem. Ser. No. 101, Molecular Sieve Zeolites*, I, p. 171.

*Acta Cryst.* (1973). **A29**, 477

## Thermal Expansion of NaF, KBr and RbBr and Temperature Variation of the Frequency Spectrum of NaF

BY P. D. PATHAK, J. M. TRIVEDI AND N. G. VASAVADA

*Physics Department, University School of Sciences, Ahmedabad-9, India*

(Received 12 December 1972; accepted 25 January 1973)

Coefficients of thermal expansion of NaF, KBr and RbBr are determined at different temperatures using a diffractometer, Geiger counter, chart recorder and a specially designed furnace. Equations are given for the variation of lattice constants with temperature. The temperature dependence of the thermal expansion at high temperatures is shown to be related to the concentration of thermally generated Schottky defects. The energies of formation of Schottky pairs in the three halides are estimated and are found to be consistent with those deduced from ionic-conductivity studies. The halides are found to obey the 'law of corresponding states' established by Pathak & Vasavada [*Acta Cryst.* (1970), **A26**, 655–658]. The geometric mean of the frequency spectrum of NaF is found to decrease by about 14% between room temperature and 1000°K.

### Introduction

The thermal expansion of NaF, KBr and RbBr has been investigated by many workers both by the X-ray and macroscopic methods, notably by Eucken & Dan-nöhl (1934), Gott (1942), Connell & Martin (1951), Pathak & Pandya (1960), Deshpande (1961), Deshpande & Sirdeshmukh (1961), Pathak, Pandya & Ghadiali (1963).

On examination of the results of the various workers it is found that although the results agree at lower temperatures, there are wide discrepancies at higher temperatures. This can be seen from Tables, 1, 2 and 3.

One of the aims of the present experiments was, therefore, to determine accurate values of the thermal expansion of these salts especially at high temperatures.

### Experimental

The experimental observations were taken with the Philips X-ray unit PW 1009 with an external voltage stabilizer, diffractometer, chart recorder and a specially designed furnace having a large volume of uniform temperature in which the powder specimen was placed. The details of measurements are described in an earlier paper (Pathak & Vasavada, 1970, hereafter called Paper I). The accuracy of the results is estimated to be about ½%.

### Results and discussion

The lattice constants of the different alkali halides were found to vary with temperature according to the follow-

ing equations. The equations were obtained with the help of an IBM 1620 computer.

NaF:

From 0 to 750°C,

$$a_t = 4.6295 + 1.5432 \times 10^{-4}t + 5.727 \times 10^{-8}t^2 + 6.35 \times 10^{-12}t^3 \quad (1)$$

from 700 to 930°C,

$$a_t = 4.7677 + 2.4400 \times 10^{-4}(t - 700) + 7.363 \times 10^{-8} \times (t - 700)^2 + 2.236 \times 10^{-10}(t - 700)^3 \quad (2)$$

KBr:

From 0 to 550°C,

$$a_t = 6.5709 + 2.5138 \times 10^{-4}t + 6.8369 \times 10^{-8}t^2 + 4.892 \times 10^{-11}t^3 \quad (3)$$

from 500 to 700°C,

$$a_t = 6.7198 + 3.5602 \times 10^{-4}(t - 500) + 11.1013 \times 10^{-8}(t - 500)^2 + 6.0796 \times 10^{-10}(t - 500)^3 \quad (4)$$

RbBr:

From 0 to 500°C,

$$a_t = 6.8610 + 2.6423 \times 10^{-4}t + 8.5322 \times 10^{-8}t^2 + 4.143 \times 10^{-11}t^3 \quad (5)$$

from 450 to 650°C,

$$a_t = 7.0010 + 3.6538 \times 10^{-4}(t - 450) + 8.793 \times 10^{-8}(t - 450)^2 + 7.4760 \times 10^{-10}(t - 450)^3 \quad (6)$$

The coefficients of linear expansion, defined by  $\alpha = (1/a_t)(da_t/dt)$ , are given in Tables 1, 2 and 3 along with those determined by other workers.

Table 1. Coefficients of linear expansion  $\alpha$  of NaF

Temperature (°C)	$\alpha (\times 10^6)$		
	Deshpande (1961)	Pathak <i>et al.</i> (1963)	Present work
0	33.1	31.6	33.3
50	34.6	32.7	34.5
100	36.0	33.8	35.7
200	39.0	36.1	38.0
250	40.4	37.2	39.4
300		38.3	40.7
400		40.6	43.2
500		42.8	45.8
600		45.1	48.5
700			51.2
750			52.7
800			55.4
850			58.5
900			62.3
930			64.9

Table 2. Coefficients of linear expansion  $\alpha$  of KBr

Temperature (°C)	$\alpha (\times 10^6)$		
	Eucken & Dannöhl (1934)	Pathak & Pandya (1960)	Present work
0	38.0	38.0	38.3
50	38.7	38.9	39.3
100	39.8	39.9	40.4
150	41.1	40.8	41.6
200	42.6	41.0	43.0
250	44.4	42.6	44.4
300	46.5	43.5	45.9
350	48.8	44.4	47.6
400	51.4	45.2	49.3
450	54.3	46.1	51.1
500	57.4	47.0	53.0
550	60.8	47.8	55.2
600	64.5	48.7	58.7
625	66.4	—	60.9
650	68.4	—	63.5
675	70.5	—	66.4
700	—	—	69.6

Table 3. Coefficients of linear expansion  $\alpha$  of RbBr

Temperature (°C)	$\alpha (\times 10^6)$	
	Deshpande & Sirdeshmukh (1961)	Present work
0	38.0	38.5
50	38.3	39.7
100	40.6	41.0
150	45.0	42.4
200		43.8
250		45.4
300		47.0
350		48.6
400		50.5
450		52.3
500		54.1
525		55.6
550		57.5
575		59.9
600		62.6
625		65.7
650		69.1

It was found, as shown in Fig. 1 for NaF (and similarly for KBr and RbBr) that the thermal expansion  $\alpha$  increases considerably beyond the temperature corresponding approximately to the 'knee' of the electrical conductivity *versus*  $1/T$  plot. It is assumed as in Paper I that (i) equations (1), (3) and (5) hold up to the melting point, (ii) any deviations from them are due to defects (Fig. 1) and (iii) the energy of vacancy formation can be deduced from the slopes of the plots of  $\log \Delta\alpha$  *versus*  $1/T$ . Such plots are shown in Fig. 2. The energy of formation,  $W_s$ , of the Schottky defects, determined from them are given in Table 4 and compared with the values of other workers.

Table 4.  $W_s$  values

Salt	$W_s$ (eV) (from Fig. 2)	$W_s$ (eV)	
		(Experimental or theoretical)	(Pathak & Vasavada, 1970) <sup>f</sup>
NaF	2.42	2.517 <sup>a</sup>	2.59
		2.489 <sup>b</sup>	
		2.399 <sup>c</sup>	
KBr	1.99	2.30 <sup>d</sup>	2.06
		1.985 <sup>a</sup>	
		2.13 <sup>b</sup>	
RbBr	2.14	2.112 <sup>a</sup>	1.96
		2.027 <sup>b</sup>	
		1.99 <sup>e</sup>	

(a) Boswarva & Lidiard (1967)

(b) Schulze & Hardy (1972)

(c) Karo & Hardy (1971)

(d) Barr & Lidiard (1970)

(e) Rao & Rao (1968)

(f) From the equation  $W_s = 2.05 \times 10^{-3} T_m$ , ( $T_m$  = melting point).

It was shown in Paper I that the plot of reduced expansion  $\alpha/\alpha_{m/2}$  *versus* reduced temperature  $T/T_m$  gave a common curve for the alkali halides NaCl, KCl and CsBr. Here  $T_m$  is the melting point and  $\alpha_{m/2}$  is the thermal expansion at  $T = \frac{1}{2}T_m$ . This common curve is shown as the full line in Fig. 3 while points for NaF, KBr and

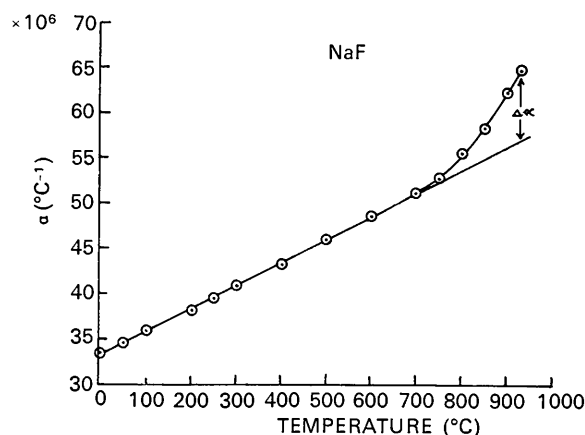


Fig. 1. Plot of coefficient of linear expansion of NaF *versus* temperature.

RbBr are plotted on it. It is seen that these halides also follow the 'law of corresponding states'.

Pathak & Vasavada (1972) have shown that for  $T \approx \Theta$  ( $\Theta^\circ\text{K} = \text{Debye temperature}$ ), the quantity  $(1 - \int_{T_0}^T \gamma \beta dT)$  gave the geometric mean of the frequency

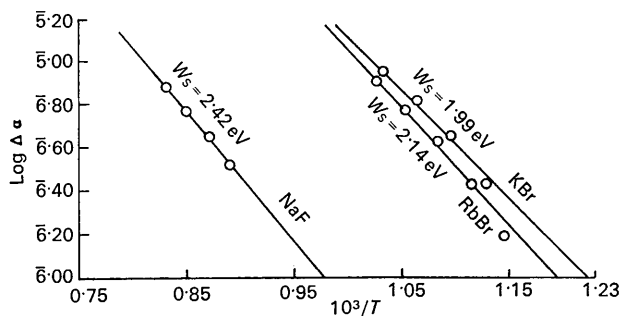


Fig. 2. Plots of logarithm of excess expansion versus reciprocal of temperature.

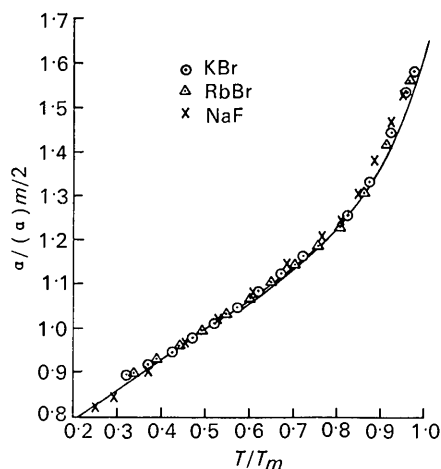


Fig. 3. Common plot of reduced expansion  $\alpha/\alpha_{m/2}$  versus reduced temperature  $T/T_m$  for alkali halides (paper I) with points for KBr, RbBr and NaF superimposed.

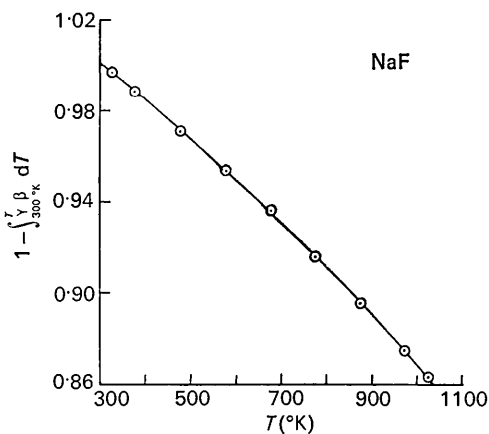


Fig. 4. Plot of geometric mean of frequency spectrum versus temperature.

ratios  $\nu_i/\nu_{i0}$ . Here  $\gamma$  is the Grüneisen constant,  $\beta$  is the volume expansion,  $\nu_i$  is the frequency of mode  $i$  and  $\nu_{i0}$  is the same frequency at some reference temperature  $T_0$ . Fig. 4 shows the plot of  $(1 - \int_{300}^T \gamma \beta dT)$  versus  $T$  for NaF ( $\Theta\text{K} = 430^\circ\text{K}$ ). It is seen that the mean frequency decreases by about 14% between 300 and  $1000^\circ\text{K}$ .

Table 5. The Grüneisen constant  $\gamma$  for NaF

Temperature ( $^\circ\text{C}$ )	$\gamma$
0	1.56
50	1.54
100	1.51
200	1.49
300	1.47
400	1.45
500	1.45
600	1.43
700	1.43
750	1.42

The values of  $\gamma$  at different temperatures are given in Table 5. It is interesting to note that  $\gamma$  decreases with temperature. In calculating  $\gamma$  the values of  $C_p$  used were those of O'Brien & Kelley (1957) while compressibility values were taken from Nikanorov & Stepanov (1963).

Financial assistance to one of us (JMT) by the Gujarat University is gratefully acknowledged.

#### References

- BARR, L. W. & LIDIARD, A. B. (1970). *Physical Chemistry - an Advanced Treatise*. Vol. 10, p. 151. New York: Academic Press.
- BOSWARVA, I. M. & LIDIARD, A. B. (1967). *Phil. Mag.* **16**, 805-826.
- CONNELL, L. F. & MARTIN, H. C. (1951). *Acta Cryst.* **4**, 75-76.
- DESHPANDE, V. T. (1961). *Acta Cryst.* **14**, 794.
- DESHPANDE, V. T. & SIRDESHMUKH, D. B. (1961). *Acta Cryst.* **14**, 353-355.
- EUCKEN, A. & DANNÖHL, W. (1934). *Z. Electrochem.* **40**, 814-821.
- GOTT, A. (1942). *Ann. Phys. Leipz.* **41**, 520-536.
- KARO, A. M. & HARDY, J. R. (1971). *Phys. Rev.* **B3**, 3418-3425.
- NIKANOROV, S. P. & STEPANOV, A. V. (1963). *Sov. Phys. Solid State*, **4**, 1889-1895.
- O'BRIEN, C. J. & KELLEY, K. K. (1957). *J. Amer. Chem. Soc.* **79**, 5616-5618.
- PATHAK, P. D. & PANDYA, N. V. (1960). *Ind. J. Phys.* **34**, 416-423.
- PATHAK, P. D., PANDYA, N. V. & GHADIALI, M. P. (1963). *Ind. J. Phys.* **37**, 293-298.
- PATHAK, P. D. & VASAVADA, N. G. (1970). *Acta Cryst.* **A26**, 655-658.
- PATHAK, P. D. & VASAVADA, N. G. (1972). *Acta Cryst.* **A28**, 30-33.
- RAO, K. J. & RAO, C. N. R. (1968). *Phys. Stat. Sol.* **28**, 157-169.
- SCHULZE, P. D. & HARDY, J. R. (1972). *Phys. Rev.* **B5**, 3270-3276.