

effects of polarization, absorption, or the variation of each of those quantities with deviation from the exact  $n$ -beam angle. Without detailed discussions of such quantities, the results must be accepted on faith.

It is hard to allocate blame where so many are deserving. Luckily, in this case there is enough for all.

*Acta Cryst.* (1975). A31, 155

**Reply to Post's comments on my paper *Multiple Diffraction of X-rays and the phase problem. Computational procedures and comparison with experiment.*** By R. COLELLA, *Purdue University, Physics Department, West Lafayette, Indiana 47907, U.S.A.*

(Received 8 July 1974; accepted 31 July 1974)

It is shown that the errors in the paper by R. Colella [*Acta Cryst.* (1974). A30, 413–423] pointed out by B. Post [*Acta Cryst.* (1975). A31, 153–155] do not in fact exist.

There is no doubt that the big difference observed between 222–113 and 222– $\bar{1}\bar{1}\bar{3}$  is due in part to the fact that the dispersion equations in the two cases involve structure factors with different magnitudes, such as  $F_{11\bar{1}\bar{1}}$  and  $F_{33\bar{1}\bar{1}}$ , for example.

It is also true, however, that a difference between the two cases would exist *even if the structure factors were all equal*, as it happens to a good approximation in neutron diffraction. One can easily verify this statement by examining the determinantal equation [equation (8) of my paper (Colella, 1974)] and observing that the diagonal terms are essentially different in the two cases.

It is obvious that two reflections with different phases correspond to different Miller indices and therefore to different nodes in reciprocal space. The 'coupling terms' [in Post's (1975) notation] are bound to be different in any case. The intensity differences are affected by the atomic positions, besides the coupling terms. In this respect multiple diffraction can in principle solve the phase problem. The key point is that in dynamical multiple diffraction more than two beams are coherently interacting and the phases do not get lost, as it happens in two-beam diffraction without anomalous dispersion.

Ewald & Héno's (1968) treatment, quoted in the references of my paper, is essentially concerned with the Laue case and considers  $2n$  solutions. As explained in my paper, the transition to the Bragg case is not a trivial one, and  $4n$  solutions must be considered when some of the diffracted beams are parallel to the surface of the crystal. Substantial changes are involved in the boundary conditions.

*Acta Cryst.* (1975). A31, 155

**Schottky defects in KI and RbI.** By P. D. PATHAK and N. M. PANDYA, *Physics Department, Gujarat University, Ahmedabad, India*

(Received 1 July 1974; accepted 14 August 1974)

The temperature dependence of the thermal expansion of KI and RbI at high temperatures is shown to be related to the concentration of thermally generated Schottky defects. The experimental value of the energy of formation of these defects for RbI has been estimated for the first time. The two halides are found to obey the 'law of corresponding states' established by Pathak & Vasavada [*Acta Cryst.* (1970). A26, 655–658].

#### Introduction

The experimental value of the energy of Schottky-pair formation for KI has been determined by Ecklin, Nadler &

#### References

- COLE, H., CHAMBERS, F. W. & DUNN, H. M. (1962). *Acta Cryst.* **15**, 138–144.  
 COLELLA, R. (1974). *Acta Cryst.* **A30**, 413–423.  
 EWALD, P. P. & HÉNO, Y. (1968). *Acta Cryst.* **A24**, 5–15.

My failure to observe Umweganregung effects on the 400 with Co  $K\alpha$  was in fact due to a large vertical divergence (of the order of  $1^\circ$ ). Since these are the conditions in which most of the crystallographic work is done, I felt that it would be of some interest to develop a procedure for predicting whether not Umweganregung effects might be present in given experimental conditions.

As to my statement concerning the ratio (or ratios?) between Umweganregung peaks, it is neither trivial nor incorrect. It is only limited to one particular experiment and its main value is to stimulate further research in this area. That the Umweganregung peaks generally increase upon grinding is a rather obvious result and had been previously reported (Colella & Merlini, 1966).

I do not understand the statement about the different angles formed by the (113) and ( $\bar{1}\bar{1}\bar{3}$ ) planes with (222) in relation to the effects produced by grinding, and I believe that it is not justified.

The other points of Post's paper seem to me irrelevant or inconsequential.

#### References

- COLELLA, R. (1974). **A30**, 413–423.  
 COLELLA, R. & MERLINI, A. (1966). *Phys. Stat. Sol.* **18**, 157–166.  
 EWALD, P. P. & HÉNO, Y. (1968). *Acta Cryst.* **A24**, 5–15.  
 POST, B. (1975). **A31**, 153–155.

Rossel (1964). A similar value for RbI is not available in the literature. Theoretical attempts to estimate these values have been made by Boswarva & Lidiard (1967), Rao & Rao (1968) and others.

The thermal expansion of the two halides at high temperatures has been investigated both by X-ray and macroscopic methods, notably by Eucken & Dannöhl (1934), Connell & Martin (1951), Srinivasan (1955), Pathak & Pandya (1960), Sirdeshmukh & Deshpande (1964) and Rapp & Merchant (1973).

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

One of the aims of the present experiments was therefore to determine accurate values of the thermal expansion of the two halides, especially at high temperatures and to throw light on some interesting phenomena which only occur at those temperatures.

### Experimental

The experimental observations were taken with the Philips X-ray unit P.W. 1009 with an external stabilizer, diffractometer, proportional counter, chart recorder and a specially designed furnace having a large uniform-temperature volume in which the powder specimen was placed. The details of the measurement are described in an earlier paper (Pathak & Vasavada 1970, hereafter called Paper I). The overall accuracy of the results is estimated to be about  $\frac{1}{2}\%$ . The salts used in this investigation were of AnalaR quality from E. Merck.

### Results and discussion

The lattice constants of the two alkali halides were found to vary with temperature according to the following equations. The equations were obtained with the help of an IBM 1620 computer.

KI:

from 0 to 500°C

$$\alpha_t = 7.0465 + 2.5974 \times 10^{-4}t + 9.8343 \times 10^{-8}t^2 + 1.0039 \times 10^{-11}t^3; \quad (1)$$

from 500 to 700°C

Table 1. Coefficient of linear expansion  $\alpha$  of KI

Temperature (°C)	a	b	c ( $\times 10^6$ )	d	Present work
0	35.16	39.8	39.77	39.00	36.86
50	36.48	42.1	40.90	40.72	38.19
100	38.12	44.3	42.15	42.00	39.54
150	40.08	46.5	43.25	43.29	40.90
200	42.34		44.40	45.46	42.28
250	44.93		45.50	48.99	43.66
300	47.83		46.60	52.55	45.06
350	50.05		47.70		46.47
400	54.58		48.87		47.89
450	58.42		50.00		49.32
500	62.52		51.10		50.76
525	64.78		51.60		52.07
550	67.06		52.20		53.62
575	69.41		52.70		55.50
600	71.85		53.20		57.70
625					60.23
650					63.08
675					66.25
700					69.73

(a) Eucken & Dannöhl (1934), (b) Srinivasan (1955), (c) Pathak & Pandya (1960), (d) Rapp & Merchant (1973).

$$\alpha_t = 7.2022 + 3.6620 \times 10^{-4}(t-500) + 1.6164 \times 10^{-7}(t-500)^2 + 6.4417 \times 10^{-10}(t-500)^3. \quad (2)$$

RbI:

from 0 to 400°C

$$\alpha_t = 7.3250 + 2.6952 \times 10^{-4}t + 1.1383 \times 10^{-7}t^2 + 3.1287 \times 10^{-12}t^3; \quad (3)$$

from 400 to 625°C

$$\alpha_t = 7.4512 + 3.6208 \times 10^{-4}(t-400) + 9.3725 \times 10^{-8}(t-400)^2 + 7.3984 \times 10^{-10}(t-400)^3. \quad (4)$$

Table 2. Coefficient of linear expansion  $\alpha$  of RbI

Temperature (°C)	a	b ( $\times 10^6$ )	Present work
0	37.2	37.60	36.79
50	40.4	39.90	38.28
100	44.2	41.47	39.76
150	51.3	42.53	41.24
200		43.84	42.72
250		45.65	44.19
300		45.82	45.66
350			47.13
400			48.59
450			50.46
500			53.79
525			55.99
550			58.55
575			61.47
600			63.80
625			68.35

(a) Sirdeshmukh & Deshpande (1964), (b) Rapp & Merchant (1973).

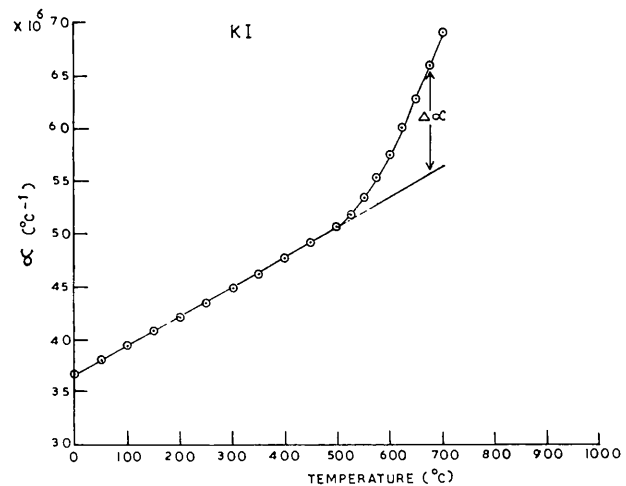


Fig. 1. Plot of coefficient of linear expansion of KI versus temperature.

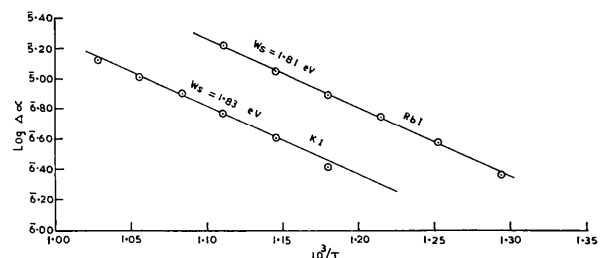


Fig. 2. Plots of logarithm of excess expansion versus reciprocal of temperature.

Table 3.  $W_s$  values

Salt	$W_s$ (eV) (from Fig. 2)	$W_s$ (eV) (Experimental or theoretical)	$W_s$ (eV) (Pathak & Vasavada, 1970)§
KI	1.83	1.60* (Ex) 1.70–1.92†‡ (Th.)	2.04§
RbI	1.81	1.798† 1.88‡	1.88§

\* Ecklin, Nadler & Rosset (1964). † Boswarva & Lidiard (1967). ‡ Rao & Rao (1968).

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

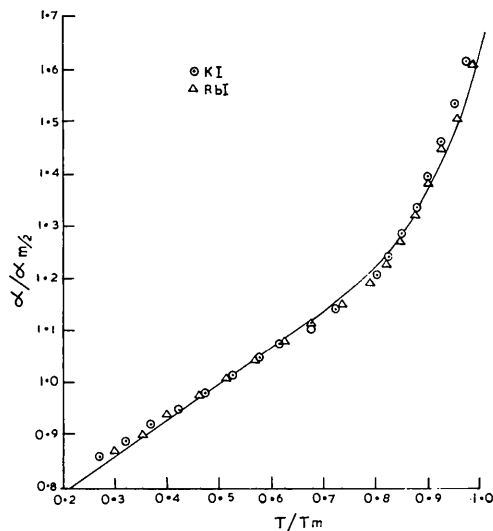


Fig. 3. Plot of reduced expansion  $\alpha/\alpha_{m/2}$  versus reduced temperature  $T/T_m$ .  $T_m$  is the melting temperature ( $^{\circ}\text{K}$ ) and  $\alpha_{m/2}$  is the value of  $\alpha$  at  $T = \frac{1}{2}T_m$ .

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

It was found as shown in Fig. 1 for KI 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) and (3) hold up to 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 3. Since experimental values of  $W_s$  for RbI are not available comparison is made with some theoretical estimates.

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  $T = \frac{1}{2}T_m$ . The common curve is shown as a full line in Fig. 3 while points for KI and RbI are plotted on it. It is seen that these halides also follow the 'law of corresponding states'.

#### References

- BOSWARVA, I. M. & LIDIARD, A. B. (1967). *Phil. Mag.* **16**, 805–826.  
 CONNELL, L. F. & MARTIN, H. C. (1951). *Acta Cryst.* **4**, 75–76.  
 ECKLIN, D., NADLER, C. & ROSSEL, J. (1964). *Helv. Phys. Acta* **37**, 692–696.  
 EUCKEN, A. & DANNÖHL, W. (1934). *Z. Electrochem.* **40**, 814–821.  
 PATHAK, P. D. & PANDYA, N. V. (1960). *Ind. J. Phys.* **34**, 416–423.  
 PATHAK, P. D. & VASAVADA, N. G. (1970). *Acta Cryst.* **A26**, 655–658.  
 RAO, K. J. & RAO, C. N. R. (1968). *Phys. Stat. Sol.* **28**, 157–169.  
 RAPP, J. E. & MERCHANT, A. D. (1973). *J. Appl. Phys.* **44**, 3919–3923.  
 SIRDESHMUKH, D. B. & DESHPANDE, V. T. (1964). *Curr. Sci. India*, **33**, 428.  
 SRINIVASAN, R. (1955). *Proc. Ind. Acad. Sci A* **42**, 255–260.

*Acta Cryst.* (1975). **A31**, 157

### The root-mean-square vibrational displacements of sodium and fluorine ions in sodium fluoride: erratum.

By V. C. SHARMA, *Department of Physics, University of Benin, Ekenwa Road, Benin City, Nigeria*

(Received 8 July 1974; accepted 20 September 1974)

Corrections are given to Sharma [*Acta Cryst.* (1974) **A30**, 299–300].

The following corrections to Sharma (1974) are given:

- Page 299, lines 2 and 3 in the abstract should read: mean-square vibrational displacements of sodium and fluorine ions were determined to be  $0.184 \pm 0.002$  and  $0.186 \pm 0.005$  Å respectively. These values are compared with the values of  $0.202 \pm 0.007$  Å for the two . . . .
- Page 300, lines 14 and 15, column one, should read:
 

$B$ (sodium)	$= 0.893 \pm 0.021$ Å <sup>2</sup>
$B$ (fluorine)	$= 0.912 \pm 0.054$ Å <sup>2</sup>

- Page 300, lines 19 and 20, column one, should read: placements of  $\sqrt{\bar{U}^2}$  (sodium) =  $0.184 \pm 0.002$  Å and  $\sqrt{\bar{U}^2}$  (fluorine) =  $0.186 \pm 0.005$  Å as compared to the values

#### Reference

- SHARMA, V. C. (1974). *Acta Cryst.* **A30**, 299–300.