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Debye Temperature of NaF and RbBr by X-ray Diffraction

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Debye temperatures of NaF and RbBr have been determined by X-ray diffraction from room temperature up to about 800°K using methods due to Paskin [*Acta Cryst.* (1957). **10**, 667–669] and Chipman [*J. Appl. Phys.* (1960). **31**, 2012–2015]. The anharmonic contribution to the Debye Θ is shown to come essentially from thermal expansion. The plot of the reduced thermal expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\Theta^2$ gives a common curve. Here $\alpha_{m/2}$ is the value of α at $T=\frac{1}{2}T_m$, T_m being the melting point, A is the mean atomic weight and a the lattice constant. The energy of vacancy formation is computed using an equation established by Pathak & Trivedi [*Proc. Nucl. Phys. Solid State Phys. Symp. Roorkee, India*, (1969). pp. 50–53].

Introduction

On searching the literature it is found that no systematic investigation of the temperature variation of the Debye temperature Θ_M of NaF and RbBr has been undertaken. Still however, room-temperature values of Θ_M for NaF have been determined by several workers – notably by Brindley (1930), Shonka (1933), Wasastjerna (1946) and Meisalo & Merisalo (1966). Their values are respectively 398, 442, 440 and 400°K.

Experimental

The experimental procedure is fully described by Pathak & Vasavada (1970; hereafter called Paper I). The profiles of lines 420 and 422 were recorded on a chart recorder and planimetered. The background was determined by a method described by Mitra & Misra (1966).

The basic equation from which the X-ray Debye temperature Θ_M is calculated, (Pathak & Trivedi, 1973; hereafter called Paper II), is

$$R=\frac{mK}{12h^2}\,\frac{\lambda^2}{(1-\beta)\sin^2\theta}\left[\ln\frac{I}{I_0}-\ln\frac{B'}{B'_0}\right]$$

$$=\frac{T_0\psi_0}{\Theta^2_{M0}}-\frac{T\psi}{\Theta^2_M}\,\frac{\sin^2\theta}{\sin^2\theta_0}\,, \qquad (1)$$

where I and I_0 are the measured integrated intensities at temperatures T and T_0, and θ is the Bragg angle.

ψ and B' are respectively given by

$$\psi=\frac{1}{x}\int_0^x\frac{u\,du}{e^u-1}+\frac{x}{4}$$

$$B'=Npf^2\,\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}$$

where $x=\Theta_M/T$, N is the number of unit cells irradiated, p is the multiplicity factor and f is the atomic scattering factor.

The quantity $(1-\beta)$ takes into account the one-phonon thermal diffuse scattering (TDS) contribution to the measured intensity according to Chipman &

Paskin (1959). The quantity for f.c.c. crystal is given by

$$\beta=\tfrac{1}{2}\left(\frac{\pi}{3}\right)^{1/3}\frac{a\cos\theta}{\lambda}\Delta\,,$$

where a is the lattice constant and Δ is the length of the straight-line background expressed in radians.

It can be seen from equation (1) that the values of Θ_M at different temperatures can be found only if Θ_{M_0} at some reference temperature T_0 (say room temperature) is known. In this investigation the value of Θ_{M_0} is computed by two methods, *viz.* (i) Paskin's method (ii) Chipman's method.

According to the Paskin's (1957) method, if the temperature variation of Θ_M is due to thermal expansion, the plot of ln (I/I_0) *versus* the reduced temperature T' $[=T(a/a_0)^{6\gamma}]$ should be a straight line and the value of Θ_{M_0} can be obtained from the slope of this line (Paper II).

In the second method Chipman (1960) used the fact that the Θ *versus* T curves as determined from the elastic constants are approximately linear. Hence if one plots a family of Θ-*versus*-T curves with a series of arbitrary values of Θ_0, one can assume that the curve with the smallest curvature is the right one.

Results and discussion

The plots of ln (I_T/I_R) (I_R=intensity at room temperature) *versus* reduced temperature T' $[T'=T(a_T/a_R)^{6\gamma}]$ for line 420 are given in Figs. 1 and 2. Debye Θ_M at different temperatures are presented in Figs. 3 and 4. The values of Θ_M in the plots are averages of those corresponding to the lines 420 and 422.

Since the plots of ln (I_T/I_R) *versus* reduced temperature T' (Figs. 1, 2) are straight lines, it is evident that the anharmonic contribution to the Debye Θ in the range of temperatures examined comes essentially from thermal expansion.

It has been shown in Paper II that the plot of the reduced thermal expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\Theta^2$, in the case of KCl, KBr and RbCl, gives a common straight line whose equation is

$$\frac{\alpha}{\alpha_{m/2}}=0{\cdot}70+0{\cdot}364\times10^{-11}\frac{T}{Aa^2\Theta^2}\,. \qquad (2)$$

Here $\alpha_{m/2}$ is the thermal expansion at $T=\frac{1}{2}T_m$, T_m being the melting temperature, A is the mean atomic weight and a the lattice constant. In Fig. 5 the full line shows the common curve of equation (2) while the points for NaF and RbBr are shown on it. It is seen that NaF and RbBr also follow the 'law of corresponding states'.

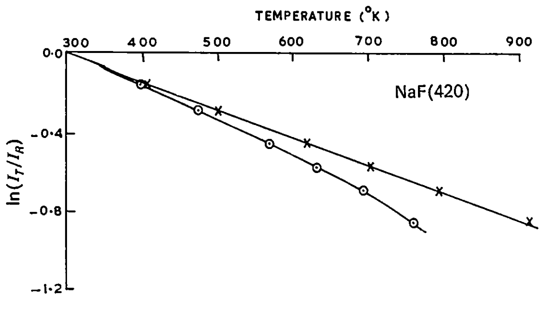

Fig. 1. Temperature dependence of the quantity ln (I_T/I_R) for the 420 reflexion of NaF. ○ ln (I_T/I_R) *versus* absolute temperature. × ln (I_T/I_R) *versus* reduced temperature.

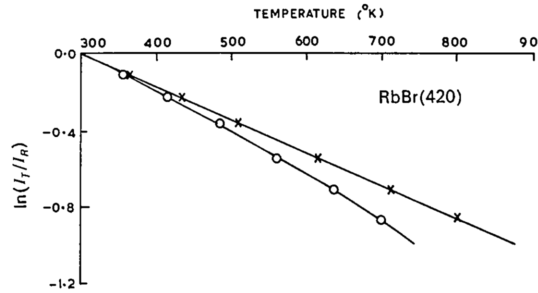

Fig. 2. Temperature dependence of the quantity ln (I_T/I_R) for the 420 reflexion of RbBr. ○ ln (I_T/I_R) *versus* absolute temperature. × ln (I_T/I_R) *versus* reduced temperature.

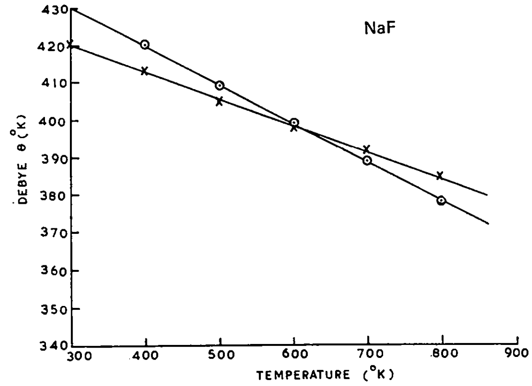

Fig. 3. The Debye Θ (average) *versus* temperature :- NaF. × Paskin's method. ○ Chipman's method.

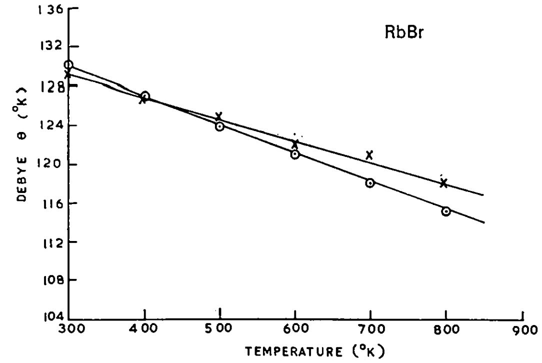

Fig. 4. The Debye Θ (average) *versus* temperature :- RbBr. × Paskin's method. ○ Chipman's method.

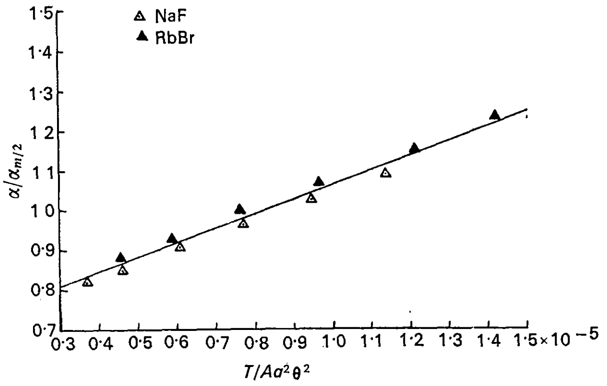

Fig. 5. Common plot of reduced expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\Theta^2$ for alkali halides (Paper II) with points for NaF and RbBr superimposed.

Table 1. E_f (eV) *values*

Substance	From equations (2), (3), (4)	Experimental	Theoretical
LiF	2·50	2·34–2·68^{a,b,c}	2·574^{d}
LiCl	1·89	2·12^{d}	1·557^{d}
LiBr	1·72	1·80^{d}	1·323^{d}
LiI	1·47	1·34^{d}	1·004^{d}
NaF	3·12	–	3·23^{j}
NaCl	2·44	2·4–2·5^{e}	2·36^{j}
NaBr	2·31	1·72^{f}	2·33^{j}
NaI	2·00	–	2·00^{j}
KF	2·73	–	2·514^{d}
KCl	2·36	2·30^{g}	2·259^{d}
KBr	2·23	2·37^{h}	2·124^{d}
KI	2·20	2·21^{i}	2·29^{j}, 1·87^{k}
RbF	2·81	–	2·257^{d}
RbCl	2·21	–	2·198^{d}, 2·17^{k}
RbBr	2·09	–	2·112^{d}, 1·99^{k}
RbI	1·98	–	1·965^{d}, 1·88^{k}

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(*a*) Haven (1950)
(*b*) Barsis, Lilley & Taylor (1967)
(*c*) Stoebe & Praat (1967)
(*d*) Boswarva & Lidiard (1967)
(*e*) Allnatt, Pantelis & Sime (1971)
(*f*) Hoshino & Shimoji (1967)
(*g*) Jacobs & Pantelis (1971)
(*h*) Barr & Dawson (1969)
(*i*) Chandra & Rolfe (1970)
(*j*) Boswarva (1972)
(*k*) Rao & Rao (1968)

For $0\cdot30 < T/T_m < 0\cdot65$ Pathak & Vasavada in Paper I have obtained the equation

$$\frac{\alpha}{\alpha_{m/2}} = 0\cdot65 + 0\cdot70\left(\frac{T}{T_m}\right), \tag{3}$$

which is applicable to all alkali halides. Similarly Pathak & Trivedi (1969) have found the relation

$$\Theta_M = 4183\,(E_f/MV^{2/3})^{1/2} \tag{4}$$

connecting Θ_M and the energy of vacancy formation E_f (in eV) in the case of alkali halides. Here M is the molecular weight and V is the volume.

From equations (2), (3) and (4), the values of E_f are obtained for various alkali halides and are shown in Table 1. The values of E_f so obtained are compared with the experimental and theoretical values of other workers.

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