$$R_1^*(I)=1-\frac{4\sigma_B}{\pi}\int_0^1\frac{y_q^2(1+y_q^2)\mathrm{d}y_q}{[(1+y_q^2)^2-4\sigma_A^2y_q^2]}$$
$$=1-\frac{4\sigma_B}{\pi}\int_0^1\left[1+\sigma_A\left\{\frac{y_q}{(y_q^2-2\sigma_Ay_q+1)}\right.\right.$$
$$\left.-\frac{y_q}{(y_q^2+2\sigma_Ay_q+1)}\right\}$$
$$\left.-\tfrac{1}{2}\left\{\frac{1}{(y_q^2-2\sigma_Ay_q+1)}+\frac{1}{(y_q^2+2\sigma_Ay_q+1)}\right\}\right]$$
$$\times\,\mathrm{d}y_q\,. \qquad \text{(A-26)}$$

Making use of equations (70), (75) and (672) of Peirce & Foster (1966) in (A-26) and simplifying, we obtain

$$R_1^*(I)=2\sigma_B^2-\frac{4\sigma_B}{\pi}\left[1+\frac{\sigma_A}{2}\log_e\left(\frac{1-\sigma_A}{1+\sigma_A}\right)\right]. \qquad \text{(A-27)}$$

Substituting for the p.d.f. of y_q as obtained from Table (1*b*) of SR in (A-25), changing the variable of integration to $x=y_q^2$ and using the result in (A-24) we can show for the *NC* case that

$$R_1^*(I)=1-2\sigma_B^2\int_0^1\frac{(x^2+x)\mathrm{d}x}{[1+2(1-2\sigma_A^2)x+x^2]^{3/2}}\,. \qquad \text{(A-28)}$$

Making use of equations (2.264-6) and (2.264-7) on p. 83 and equation (2.261) on p. 81 of Gradshteyn & Ryzhik (1965) we can show that (A-28) reduces to

$$R_1^*(I)=2\sigma_B\left[1-\sigma_B\log_e\left(\frac{1+\sigma_B}{\sigma_B}\right)\right]. \qquad \text{(A-29)}$$

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Debye Temperatures of KI and RbI and the Anharmonic Parameters of their Potential Functions

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Debye temperatures of potassium iodide and rubidium iodide have been determined by X-ray diffraction from room temperature up to about 800 K with 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 up to about 650 K is shown to arise essentially from thermal expansion. The plot of the reduced thermal expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\theta^2$ is 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 is the lattice constant. The values of the anharmonic parameters γ_0 in the potential energy function of Willis [*Acta Cryst.* (1969), A**25**, 277–300] are found to be $-0{\cdot}065\times10^{-12}$ erg Å^{-4} for KI and $-0{\cdot}116\times10^{-12}$ erg Å^{-4} for RbI.

Introduction

Variation of Debye temperature θ_M with temperature for KI up to about 700K has been investigated by Pearman & Tompson (1967), by Vadets, Giller, Kovich & Fedyshin (1970) and by Geshka & Mikhalchenko (1971). A similar study for RbI from 6K to 370K has been made by Hovi & Pirinen (1972). However, a hightemperature study of RbI has not been reported previously.

Experimental

The experimental procedure is fully described by Pathak & Vasavada (1970) (hereinafter called paper I). The profiles of lines 400 and 420 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; hereinafter called paper II) is

$$R=\frac{mk}{12h^2}\,\frac{\lambda^2}{(1-\beta)\sin^2\theta}\left[\ln\frac{I}{I_0}-\ln\frac{B'}{B'_0}\right]$$
$$=\frac{T_0\psi_0}{\theta^2_{M_0}}-\frac{T\psi}{\theta^2_M}\,\frac{\sin^2\theta}{\sin^2\theta_0} \qquad (1)$$

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

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

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

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 a 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: (i) Paskin's and (ii) Chipman's.

According to 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 correct 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 400 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 lines 420 and 400.

Since the plots of ln (I_T/I_R) *versus* reduced temperature T' (Figs. 1, 2) are straight lines up to about 800 K (reduced), it is evident that the anharmonic contribution to the Debye θ up to this temperature comes essentially from thermal expansion.

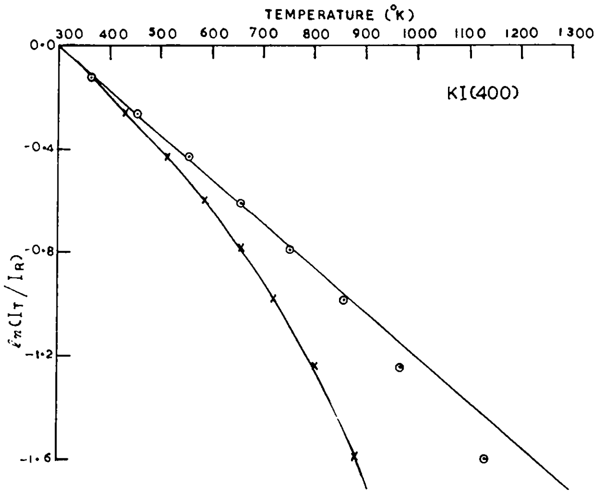

Fig. 1. Temperature dependence of the quantity ln (I_T/I_R) for the 400 reflexion of KI. × ln (I_T/I_R) *versus* absolute temperature. ⊙ ln(I_T/I_R) *versus* reduced temperature.

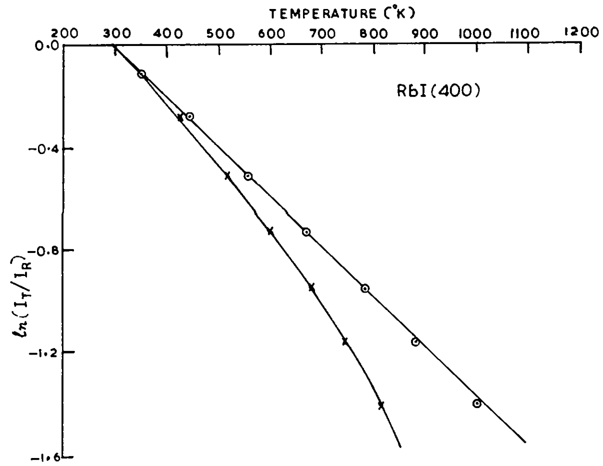

Fig. 2. Temperature dependence of the quantity ln(I_T/I_R) for the 400 reflexion of RbI. × ln (I_T/I_R) *versus* absolute temperature. ⊙ ln (I_T/I_R) *versus* reduced temperature.

The plot of the reduced thermal expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\theta^2$ (Fig. 5) was found to give a common straight line whose equation is

$$\alpha/\alpha_{m/2}=0{\cdot}75+0{\cdot}25\times 10^{-11}\;T/Aa^2\theta^2. \qquad (2)$$

Here $\alpha_{m/2}$ is the thermal expansion at $T=\frac{1}{2}T_m$, T_m being the melting temperature, A the mean atomic weight and a the lattice constant. Thus it can be said that the two halides follow the 'law of corresponding states'.

The general expression due to Willis (1969) for the potential of the Kth atom in a cubic crystalline field is given by

$$V_K(U_1U_2U_3)=V_0+\tfrac{1}{2}\alpha_K r^2+\beta_K U_1U_2U_3 + r_K r^4+\delta_K(U_1^4+U_2^4+U_3^4-\tfrac{3}{5}r^4) \qquad (3)$$

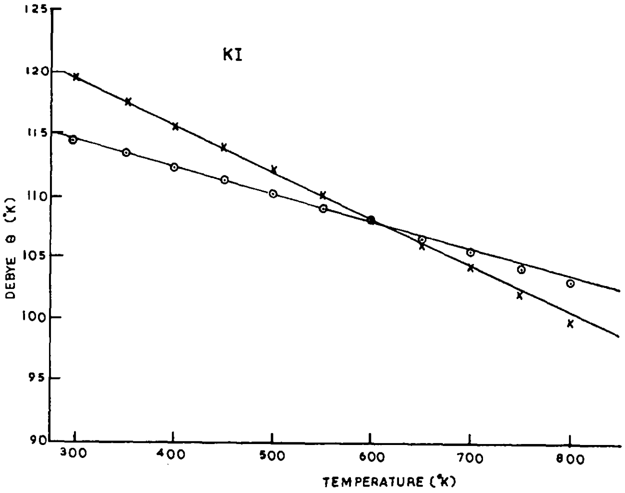

Fig. 3. Debye θ (average) *versus* temperature: KI. ⊙ Paskin's method. × Chipman's method.

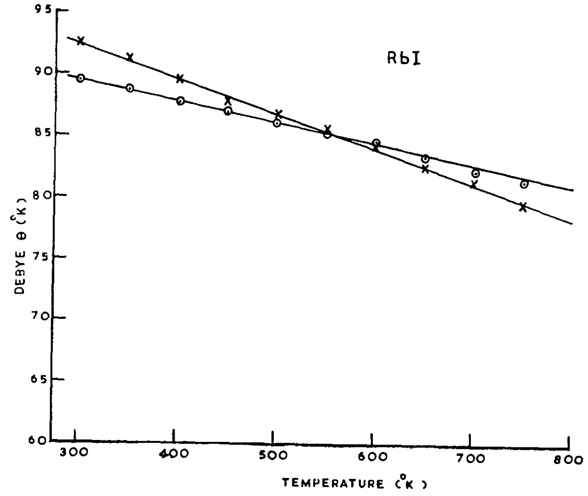

Fig. 4. Debye θ (average) *versus* temperature: RbI. ⊙ Paskin's method. × Chipman's method.

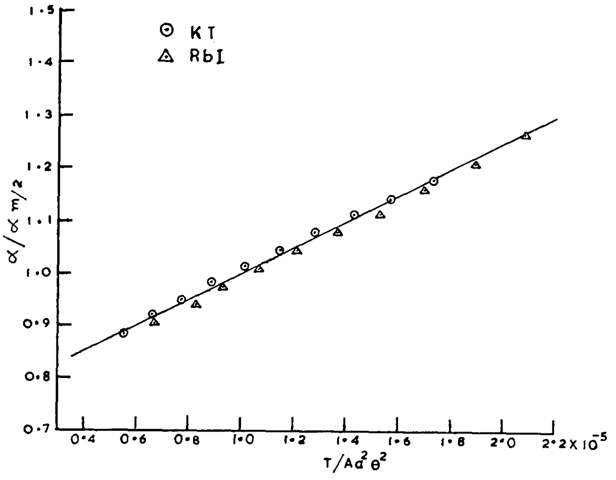

Fig. 5. Common plot of reduced expansion $\alpha/\alpha_{m/2}$ *versus* $T/Aa^2\theta^2$ for KI and RbI.

where $r^2=U_1^2+U_2^2+U_3^2$. $\beta_K=0$ when the atomic site coincides with the centre of symmetry. δ_K is the anisotropic term taken to be zero in the present case.

The potential parameters α and γ are temperature-dependent, their relations with temperature being given by

$$\frac{1}{\alpha}=\frac{1}{\alpha_0}(1+2\gamma_G\chi T)$$

or

$$\alpha=\alpha_0(1-2\gamma_G\chi T)$$

with a similar expression for γ. Here α_0 is the value of α in the absence of expansion and it is assumed that $2\gamma_G\chi T\ll 1$. γ_G is the Grüneisen constant and χ the volume coefficient of expansion.

Now

$$\left(\frac{\lambda}{\sin\theta}\right)^2 \ln\,(I_T/I_R)=2[B(T)-B(T_R)]\,. \qquad (4)$$

$B(T)$ is the Debye–Waller factor at temperature T and T_R the room temperature. Willis (1969) has shown that

$$B(T)=B^h(T)\left[1+T\left(2\chi\gamma_G-20k_B\frac{\gamma_0}{\alpha_0^2}\right)\right] \qquad (5)$$

where k_B is the Boltzmann constant and $B^h(T)$ the harmonic B factor given by

$$B^h(T)=\frac{8\pi^2k_BT}{\alpha_0}\,. \qquad (6)$$

Figs. 6 and 7 represent the plots of $(\lambda/\sin\theta)^2\ln\,(I_T/I_R)$ *versus* T.

Experimental points are plotted as circles. The curve A corresponds to the harmonic Debye–Waller theory.

Curve B is drawn using equation (5) in its quasi harmonic form, that is by retaining the thermal expansion term but writing $\gamma_0/\alpha_0^2=0$. Curve C represents the anharmonic form of equation (5) with $\gamma_0/\alpha_0^2=-0{\cdot}0498\times10^{12}\ \mathrm{erg}^{-1}$ for KI and $\gamma_0/\alpha_0^2=-0{\cdot}116\times10^{12}\ \mathrm{erg}^{-1}$ for RbI. These values were chosen so as to make the anharmonic curve pass through the experimental points at the highest temperature where the influence of anharmonicity is greatest.

The harmonic parameters α_0 were calculated from equation (6) and were found to be $1{\cdot}142\times10^{-12}\ \mathrm{erg\,Å}^{-2}$ for KI and $1{\cdot}001\times10^{-12}\ \mathrm{erg\ Å}^{-2}$ for RbI. These values give

$$\gamma_0=-0{\cdot}065\times10^{-12}\ \mathrm{erg\ Å}^{-4}\ \text{for KI}$$

and

$$\gamma_0=-0{\cdot}116\times10^{-12}\ \mathrm{erg\ Å}^{-4}\ \text{for RbI}\ .$$

The value of $B^h(T)$ for KI was obtained from Pearman & Tompson (1967) and that for RbI from Govindarajan (1973). The Grüneisen constants were taken from Born & Huang (1954) and the expansion coefficients from Pathak & Pandya (1975).

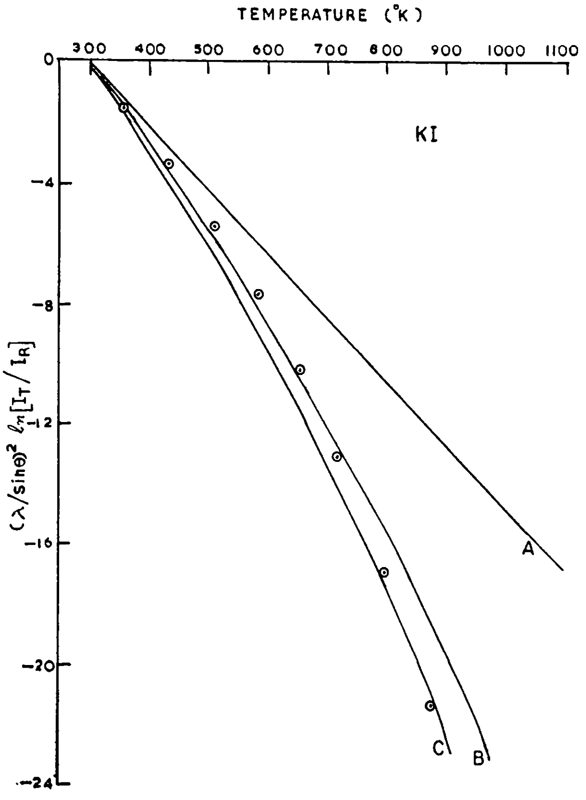

Fig. 6. The logarithm of the integrated intensities from KI plotted against temperature. Experimental points are shown as circles. Curve A was calculated using the harmonic Debye–Waller theory; curve B was calculated using the quasiharmonic theory to include the effect of thermal expansion; curve C was calculated using the anharmonic theory accounting for both thermal expansion and quartic anharmonicity.

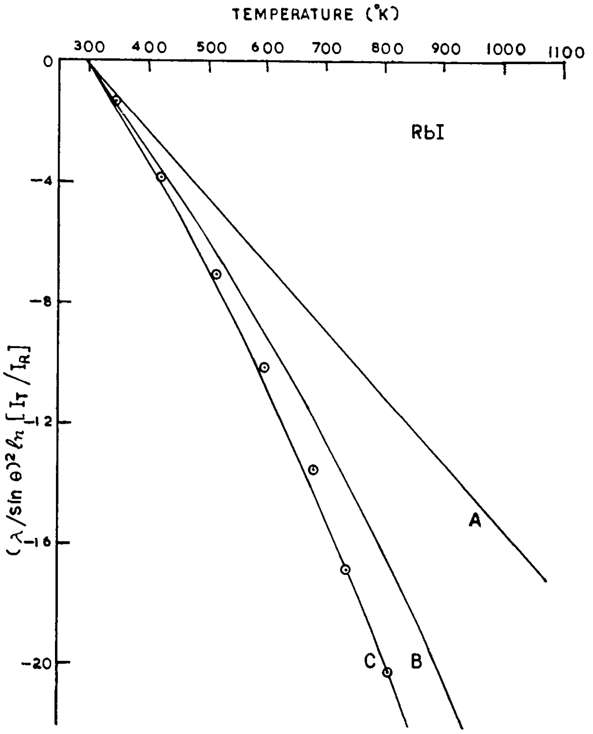

Fig. 7. The logarithm of the integrated intensities from RbI plotted against temperature. Experimental points are shown as circles. Curve A was calculated using the harmonic Debye–Waller theory; curve B was calculated using the quasi-harmonic theory to include the effect of thermal expansion; curve C was calculated using the anharmonic theory, accounting for both thermal expansion and quartic anharmonicity.

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