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Debye–Waller factors for rubidium halides.

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The mean-square displacements of atoms in RbF, RbCl, RbBr and RbI have been calculated for the temperature range 20 to 300°K utilizing the phonon frequencies determined from neutron-scattering measurements.

Introduction

The mean-square amplitudes of vibration $\langle u^2\rangle_k$ of the different atoms k in a crystal are required for many calculations of crystal properties. The vibrational amplitudes of atoms as determined by X-ray or neutron structure determinations are unreliable unless special precautions have been taken to correct for extinction, diffuse scattering and other systematic errors which have large effects on vibrational parameters. The Debye–Waller factors for most of the alkali halides of the NaCl structure have been calculated (Reid & Smith, 1970). Exceptions to this are rubidium. halides and so far no lattice-dynamical calculations have been reported. Recently, more reliable phonon frequencies have become available from neutron-scattering measurements (Raunio & Rolandson, 1970*a*,*b*; Rolandson & Raunio, 1971) and the shell-model parameters fitted to the measured phonon frequencies have also been published. In addition, two papers have been published (Huiszoon & Groenewegen, 1972; Scheringer, 1973) in which some explicit conclusions about the mass dependence of Debye–Waller factors have been drawn from lattice-dynamics theory based on the harmonic approximation. Further, there are no experimental measurements available for these compounds except for RbCl (Järvinen & Inkinen, 1967). These factors provided the motivation for the present investigation.

Theory

The most familiar effect of temperature on the vibration of ions is the reduction of the intensities of the crystalline reflexions in X-ray diffraction by the well known Debye temperature factor $\exp(-2W)$. For a cubic crystal containing k atoms, the factor W is related to $\langle u^2\rangle_k$, the mean-square amplitude of kth ion, through the relation

$$W_k = \frac{8\pi^2}{3}\cdot\langle u^2\rangle_k\frac{\sin^2\theta}{\lambda^2} \qquad (1)$$
$$= B_k \sin^2\theta/\lambda^2,$$

where λ is the wavelength of the incident radiation and 2θ is the corresponding scattering angle. The mean-square amplitude of an atom is also connected to the fraction of recoilless emission in Mössbauer measurements through the relation

$$2W = \tfrac{1}{3}(2\pi/\lambda)^2\langle u^2\rangle_k\,, \qquad (2)$$

where λ is the wavelength of the transition of the Mössbauer nuclei. The mean-square displacement is related to the eigenfrequencies and eigenvectors of the phonon states by the relation (Dawber & Elliott, 1963)

$$\langle u^2\rangle_k = \frac{\hbar}{NM_k}\sum_{\mathbf{q}j}\frac{|e(k|{}^{\mathbf{q}}_{j})|^2}{\omega_j(\mathbf{q})}\,\{n[\omega_j(\mathbf{q})]+\tfrac{1}{2}\}\,. \qquad (3)$$

$\omega_j(\mathbf{q})$ is the eigenfrequency for the jth phonon branch corresponding to the wavevector $\mathbf{q}$ and $e(k|{}^{\mathbf{q}}_{j})$ is the corresponding eigenvector of the kth particle with mass M_k. The quantity $n[\omega_j(\mathbf{q})]$ is the phonon occupation number defined as

$$n[\omega_j(\mathbf{q})] = \{\exp[\hbar\omega_j(\mathbf{q})/kT]-1\}^{-1}\,. \qquad (4)$$

The sum over $\mathbf{q}$ is performed over an equidistant mesh of N wavevector points in the first Brillouin zone.

3. Results

The best-fit shell-model parameters as determined from neutron-scattering measurements (Raunio & Rolandson, 1970*a*,*b*; Rolandson & Raunio, 1971) were utilized in generating the eigenvalues and eigenvectors for the 262 irreducible wavevector points, the total number of frequencies being 8000. The zero-phonon region was calculated separately by evaluating the summation as an integral and assuming a Debye distribution over the volume of integration which was taken as $\frac{1}{8000}$th of the total Brillouin-zone volume.

Table 1. *Mean-square displacements of the ions in rubidium halides in units of* Å^2

Temperature (°K)	RbF $\langle u^2\rangle_{\rm Rb}$	RbF $\langle u^2\rangle_{\rm F}$	RbCl $\langle u^2\rangle_{\rm Rb}$	RbCl $\langle u^2\rangle_{\rm Cl}$	RbBr $\langle u^2\rangle_{\rm Rb}$	RbBr $\langle u^2\rangle_{\rm Br}$	RbI $\langle u^2\rangle_{\rm Rb}$	RbI $\langle u^2\rangle_{\rm I}$
20	0·00824	0·01675	0·01025	0·01473	0·01092	0·01167	0·01272	0·01058
40	0·01005	0·01799	0·01345	0·01723	0·01482	0·01576	0·01809	0·01582
60	0·01276	0·01991	0·01775	0·02095	0·01753	0·02101	0·02444	0·02181
80	0·01590	0·02224	0·02252	0·02530	0·02519	0·02673	0·03143	0·02856
100	0·01929	0·02538	0·02756	0·03008	0·03092	0·03279	0·03877	0·03505
120	0·02283	0·02868	0·03289	0·03527	0·03681	0·03902	0·04641	0·04211
140	0·02650	0·03223	0·03841	0·04070	0·04291	0·04546	0·05459	0·04869
160	0·03027	0·03599	0·04408	0·04634	0·04942	0·05231	0·06306	0·05755
180	0·03415	0·03991	0·04990	0·05215	0·05592	0·05934	0·07179	0·06566
200	0·03810	0·04397	0·05586	0·05814	0·06299	0·06657	0·08080	0·07405
220	0·04215	0·04815	0·06196	0·06428	0·07004	0·07398	0·09008	0·08270
240	0·04628	0·05245	0·06821	0·07058	0·07732	0·08160	0·09963	0·09162
260	0·05049	0·05686	0·07460	0·07704	0·08479	0·08943	0·10946	0·10081
280	0·05480	0·06138	0·08112	0·08364	0·09243	0·09741	0·11954	0·11043
300	0·05918	0·06599	0·08779	0·09039	0·10030	0·10563	0·12997	0·12005

Table 1 gives the $\langle u^2\rangle_k$ values of the four materials for

Table 2. *Experimental and theoretical* B_k *values for* RbCl *at* 300°K (Å^2)

B_{Rb}		B_{Cl}		
Theoretical	Experimental	Theoretical	Experimental	Reference
2·31	2·28 ± 0·1	2·38	2·44 ± 0·1	Jarvinen & Inkinen (1967)

temperatures in steps of 20°K from 20 to 300°K. In order to check the accuracy of the values we have calculated, comparison is made in Table 2 between the theoretical and the available experimental value of B_k (Jarvinen & Inkinen, 1967) for RbCl at 300°K; the good agreement is highly encouraging. The errors involved and their effect on $\langle u^2\rangle_k$ values (possibly 2%) have been adequately dealt with (Reid & Smith, 1970) and hence no detailed discussion need be made here.

In conclusion, our results are in conformity with the predictions (Scheringer, 1973) namely that for a given fixed number of atoms in the unit cell, the bigger the difference between the masses, the greater the tendency for the heavy (light) atom to have the smaller(larger) amplitude.

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Optimum scanning ratio in neutron diffraction.

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The formula for the optimum scanning ratio, *g* [Werner, S. A. (1972). *Acta Cryst.* A**27**, 665–669] in equatorial-plane, neutron-diffraction experiments has been experimentally verified. This ratio gives the correct coupling between the detector and crystal motions such that the diffracted beam always enters the detector on its centerline.

Introduction

In the course of measuring the Debye–Waller factor of potassium metal at various temperatures, we have encountered difficulties in isolating the elastic Bragg scattering from the thermal diffuse scattering (TDS). Even at liquid-helium temperatures, the contribution of TDS to the integrated intensities of high-index reflections is substantial owing to the large zero-point energy in potassium. From the slope of a plot of $\ln [I_{hkl} . \sin 2\theta_{hkl}]$ *vs.* $(h^2+k^2+l^2)$ (where I_{hkl} is the integrated intensity, and $2\theta_{hkl}$ is the scattering angle corresponding to the *hkl* reflection) our initial measurements at 7·2 °K made with a large detector aperture gave an equivalent Debye temperature about 10 degrees higher than that obtained from the measured frequency distribution (Cowley, Woods & Dolling, 1966).[*] We believe this discrepancy is primarily due to the increasing contribution of TDS to the integrated intensities with increasing scattering vector.[†]

The effects of TDS can be reduced by narrowing the detector aperture. However, it is necessary that the detector accept all of the Bragg-scattered neutrons for every angular setting of the crystal as it is rotated through a given reflection. In order for this to be accomplished the detector and crystal motions must be coupled together in such a way that the centerline of the diffracted beam remains aligned with the centerline of the detector.

A formula for this optimum coupling was given in a paper by one of the present authors (Werner, 1971). Although we have not yet fully resolved the problem of the contribution of TDS to the measurement of the Debye–Waller factor in °K, we have verified that the suggested optimum-scanning prescription is correct.

Under the assumption that the mosaic distributions of both the monochromator (*M*) and the sample (*S*) are Gaussian, and the transmission of the collimator between *M* and *S* is also Gaussian, the optimum scanning ratio is:

$$g=\frac{\alpha_1^2[1+3a+2a^2]+2\eta_M^2a^2}{\eta_S^2+\alpha_1^2(1+a)^2+a^2\eta_M^2}\,, \tag{1}$$

and the width of the rocking curve (FWHM = 2·36σ) is given by

$$\sigma=[\eta_S^2+\alpha_1^2(1+a)^2+a^2\eta_M^2]^{1/2}. \tag{2}$$

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[*] The calculated Debye temperatures based on the neutron measurements of the phonon dispersion in K (Cowley *et al.*, 1966) agree with the specific heat capacity measurements (Martin, 1965) to within about 1·5 degrees at 7·2°K where $\Theta_D \simeq 85$°K.

[†] This effect, of course, is not easily isolated from problems connected with extinction.