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Debye–Waller factors in crystals of the sodium chloride structure.

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Calculation of vibrational properties

In the standard theory of lattice dynamics (*cf.* Maradudin, Montroll & Weiss, 1963) any vibrational property of a lattice can be represented as a sum over the normal lattice modes and, if a reliable model of the interatomic forces is available, may be calculated in a straightforward way by assembling the terms of the 'dynamic matrix' for a mesh of points through the first Brillouin zone and determining the eigenvalues and eigenvectors. This theory is applied here to the calculation of Debye–Waller factors of the individual ions in crystals of the sodium chloride structure. The quantities calculated are the crystallographic B-factors (B_1 for the cation and B_2 for the anion). In the same calculation the lattice specific heat and the two Debye temperatures (Θ_m for diffraction and Θ_c for specific heat) have also been evaluated over a range of temperatures.

Calculations such as this are only possible if a reliable model of the interionic forces is available and, throughout this paper, the 'shell' model (Woods, Cochran & Brockhouse, 1960; Woods, Brockhouse & Cowley, 1963; Cowley, Cochran, Brockhouse & Woods, 1963) has been used exclusively. The above mentioned authors have developed this model and applied it to the interpretation of the dispersion curves of sodium iodide and potassium bromide which they determined experimentally by the method of inelastic neutron diffraction. By using a complex version of the model with nine free parameters they obtained a close fit to the experimentally determined phonon frequencies which were thought to have an accuracy of 1–2 %. For these two crystals it should therefore be possible to calculate the lattice vibrational properties with a similar accuracy. In the case of crystals for which the dispersion curves are not known a simplified version of the 'shell' model can be used for which the parameters can be determined from the elastic and dielectric constants of the material. To assess the accuracy of this derivation it has been applied also to sodium iodide and potassium bromide.

Comparison of calculated and experimental values

Before comparing the calculated B-values with experimental values obtained from diffraction experiments at 300°K an 'expansion correction' was applied to reduce all values to a temperature of 300°K. This correction is described by Paskin (1957). The expansion data of Yates & Panter (1962) were used. (This correction was not applied to the calculated values listed in Table 2.)

Another possible comparison is with the thermodynamic values of Θ_m and Θ_c. The thermodynamic value of Θ_c is, of course, given immediately by the experimental specific heat values; the thermodynamic value of Θ_m is obtainable from the terms of the expansion of the specific heat, C_v, as a power series of the temperature. For this purpose we have followed the theory and the data of Barron, Berg & Morrison (1957) and Barron, Leadbetter, Morrison & Salter (1962).

The comparison of calculated and experimental values of B_1, B_2, Θ_m and Θ_c is shown in Table 1 for sodium iodide, potassium bromide, sodium chloride and lithium fluoride. The B-factors for sodium chloride which were calculated by Buyers & Smith (1964) are also shown. In Table 2 the 'harmonic' values of B_1/B_2, Θ_m and Θ_c are shown as a function of temperature.

The thermal diffuse scattering correction

In assessing the agreement between calculated B-values and those obtained in diffraction experiments it is necessary to take into account the thermal diffuse scattering (TDS) correction. To determine the Debye–Waller factor one must determine the elastic scattering only, at the Bragg positions; but the continuous TDS is peaked at the Bragg positions and one is therefore faced with the problem of subtracting the TDS integrated over that volume of reciprocal space, surrounding the Bragg positions, which is 'seen' by the counter. This is simple enough in principle but laborious in detail (*cf.* Nillson, 1957).

In a simplified approach to this question we have assumed:

(i) that the mode energy is kT and that the modes are acoustic and isotropic with longitudinal velocity c_l and transverse velocity c_t;

(ii) that for single-crystal work the 'seen' volume is a sphere surrounding the Bragg point in reciprocal space, of radius $2\pi\delta\theta/\lambda$, where $2\delta\theta$ is the counter aperture, and that background level lies at the surface of this sphere;

Table 1. *B-factors* ($\times 10^{-16}$) *and Debye temperatures* (°K) *at* 300°K

All values have been adjusted 'quasi-harmonically' for data at 300°K. (Standard deviations of experimental values are shown in brackets where available.)

Substance		B_1	B_2	Θ_m	Θ_c
Potassium-bromide	Calc. from 90°K dispersion curves(1)	2·29	2·35	158	177
	Calc. from 400°K dispersion curves(1)	2·21	2·49	156	176
	Calc. from 300°K physical constants(2)	2·26	2·55	154	174
	Thermodynamic values(3)			160	180
	Observed – single-crystal neutron(4)	2·20	2·28		
		(0·10)	(0·10)		
	Observed – polycrystal neutron (4)	2·17	2·67		
		(0·30)	(0·30)		
Sodium iodide	Calc. from 100°K dispersion curves(1)	2·66	2·16	144	181
	Calc. from 300°K physical constants(2)	2·53	2·42	138	184
	Thermodynamic values(3)			144	184
Sodium chloride	Calc. from 300°K physical constants(2)	1·59	1·63	275	271
	Calc. by Buyers & Smith(5)	1·63	1·58		
	Thermodynamic values(3)			280	279
	Observed – single-crystal X-ray Renninger 1952)(6)	1·25	1·12		
	Abrahams & Bernstein (1964)(6)	1·64	1·33		
		(0·03)	(0·02)		
	Observed – polycrystal X-ray Vihinen (1960)(6)	1·29	1·15		
	Witte & Wölfel (1958)(6)	1·25	1·00		
	Observed – single crystal neutron Levy, Agron & Busing (1963)(6)	1·63	1·42		
		(0·04)	(0·04)		
Lithium fluoride	Calc. from 300°K physical constants(2)	0·91	0·73	617	734
	Observed – X-ray Witte & Wölfel (1958)(6)	1·10	0·67		

(1) Calculated from the dispersion curves and formulae of Woods *et al.* (1960, 1963) and Cowley *et al.* (1963). In all calculations a mesh of 120 points in the irreducible 1/48th of the Brillouin zone was used. Trial calculations had shown that such a mesh was sufficiently fine to give accurate answers.

(2) Calculated from elastic constants of Haussühl (1960) and the dielectric constants of Born & Huang (1954) using the formulae from the references of note (1).

(3) Derived from the specific heat data of Barron *et al.* (1957).

(4) These neutron measurements are preliminary results of experiments carried out at this Establishment. It is intended that these, and further measurements at high temperatures, should form the subject later of publications. These results have been corrected for thermal diffuse scattering.

(5) Calculated by Buyers & Smith (1964) using the data on eigenvalues and eigenvectors, calculated by Karo & Hardy (1963) using a model similar to the 'shell' model.

(6) See *References.*

Table 2. *Calculated values of* B_1/B_2, Θ_m *and* Θ_c *(harmonic values) as a function of temperature, for potassium bromide (based on* 90°K *dispersion curves) and for sodium iodide (based on* 100°K *dispersion curves)*

Temperature	Potassium bromide			Sodium iodide		
(°K)	B_1/B_2	Θ_m	Θ_c	B_1/B_2	Θ_m	Θ_c
7	1·34	164·7	157·1	2·45	154·3	145·1
10	1·33	165·1	151·0	2·42	154·8	135·6
15	1·32	165·5	152·5	2·36	154·9	134·8
20	1·30	165·3	156·5	2·26	154·2	141·7
30	1·24	164·6	166·3	2·03	152·4	156·9
50	1·13	163·7	172·3	1·67	150·8	170·1
70	1·06	163·5	179·8	1·49	150·4	179·9
100	1·02	163·4	182·0	1·27	150·2	184·0
150	0·99	163·3	183·1	1·29	150·2	186·2
200	0·98	163·3	183·6	1·26	150·2	187·0
300	0·98	163·3	183·9	1·23	150·2	187·6
500	0·97	163·3	184·0	1·22	150·2	187·0

(iii) that for powder work the 'seen' volume is a spherical shell passing through the Bragg points in reciprocal space, of thickness $2\pi\delta\theta\cos\theta/\lambda$, where θ is the Bragg angle, and that background level lies at the surface of this shell.

Then, applying the formulae of Cochran (1963) for $\sigma^{(0)}$, the cross-section for elastic scattering, and $\sigma^{(1)}$, the cross-section for 1-phonon TDS, one can show by direct integration over the 'seen' volume, that

$$\frac{\sigma^{(1)}}{\sigma^{(0)}} = \frac{Q^2kT\,.\,4\pi^2}{mv_zc_t^2\lambda}\,\Delta$$

with $\Delta = \cos\theta\,.\,\delta\theta$ for powder patterns

$= \frac{2}{9}\delta\theta(2+c_t^2/c_l^2)$ for single-crystal patterns

where m is the mass per unit cell, v_z the volume of the Brillouin zone and Q the scattering vector. Since this ratio is proportional to Q^2T, and since $1-\sigma^{(1)}/\sigma^{(0)}$ may be approximated by $\exp(-\sigma^{(1)}/\sigma^{(0)})$, the correction may conveniently be expressed as a correction to the B-factor. The velocities c_t and c_l are best obtained by using the Kubic harmonic averaging factors (*cf.* Maradudin *et al.*, 1963). For a complete powder pattern one may take $\cos\theta$ at around two-thirds of the maximum Bragg angle. An actual calculation for sodium chloride at 300°K with $2\delta\theta = 3°$ gave

$$\begin{aligned} \Delta B &= 0{\cdot}055 \text{ for a powder pattern} \\ &= 0{\cdot}037 \text{ for a single crystal pattern .} \end{aligned}$$

The experimental B-factors for potassium bromide, measured at this Establishment, which are quoted in Table 1, have been corrected in this way. Other experimental values have not been so corrected.

Discussion

Consider first the agreement between the thermodynamic values of Θ_m and Θ_c and the calculated values. In the case of potassium bromide and sodium iodide, where the calculations are based on the known dispersion curves, the agreement is very good; and it is quite good also in the case of sodium chloride, where the calculations are based on the elastic and dielectric constants. This is strong supporting evidence for the validity of the calculations.

The agreement between the calculated B-factors and the experimental B-factors is quite good in the case of potassium bromide. For sodium chloride the agreement is also quite good for the most recent determinations by Abrahams & Bernstein (1963) and by Levy, Agron & Busing (1963). The earlier determinations are much too low. The agreement in the case of lithium fluoride is reasonable.

It should be remembered that for sodium chloride and lithium fluoride the calculations are based on the physical constants and the simplified shell model. It is possible that calculations based on a shell model with the constants determined from the experimental dispersion curves would give answers in better agreement with experiment. But for potassium bromide and sodium iodide where this comparison can be made, the simplified shell model gives results which are in quite good agreement with the more exact calculations. It is also encouraging to note that the calculations of Buyers & Smith for sodium chloride are in excellent agreement with those reported here.

It is conceivable that the apparent B-factors for X-rays and neutrons may not be the same. The ions are known to be deformable and therefore the X-rays, being scattered from the electrons, may experience an apparent vibration amplitude different from that of the nucleus. This possibility was examined by direct calculation taking the shell model at its face value. That is to say it was assumed that there really was a shell of electrons which remained spherical and which was displaced from the core, as described in the theory of the 'shell' model. A mean vibration parameter for the shell B_s may therefore be calculated in the same way as the mean vibration parameter of the core was calculated. The shell charge is known and one can therefore propose a radius for the shell and calculate an X-ray form factor *e.g.* for the chloride ion in sodium chloride we have: shell charge = 1·92e, shell radius = 1·2 Å, B at 300°K = 1·63, B_s at 300°K = 1·41. However, if f_t, f_c and f_s are the X-ray form factors for the ion, the core and the shell, and T_c and T_s are the Debye–Waller factors for the core and the shell, then the ratio of f_tT_c to $(f_cT_c+f_sT_s)$ is never more than 1% different from unity at any value of $\sin\theta/\lambda$. That is to say that, in spite of the difference in the core and shell vibration amplitudes, there will never be a detectable difference in the apparent B-factors for X-rays and neutrons. It thus seems safe to take this conclusion as correct in spite of the physical naivety of the above argument.

It may be seen from Table 2 that the harmonic value of Θ_m is constant for $T > 0{\cdot}60$. The actual value decreases owing to the expansion effect. The calculations for potassium bromide based on the 90°K and 400°K dispersion curves can be used to check whether this decrease is correctly described by the quasi-harmonic formula. The agreement (between the first two entries in Table 1) is quite good so that, at least up to 400°K, the quasi-harmonic formulation seems to be adequate to describe Θ_m. Note however, that the ratio of the B-factors appears to change with temperature.

A major difficulty in accurate experimental determinations of the B-factors is the correct form of the thermal diffuse scattering correction.

My interest in this problem arose out of discussions with T. M. Sabine and the work was started while I was attached temporarily to the Physics Department of Monash University, Melbourne. I am greatly obliged to R. M. Mayer for making the results of his single-crystal neutron observations in potassium bromide available before publication, and to B. Dawson for valuable discussions and advice.

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