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Dynamic Deformation Effects on the Debye–Waller Factor

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Abstract

The effect on the Debye–Waller factors of having scattering factors which depend on atomic motion is developed through the reciprocal-space formulation. The resulting dependence of the Debye–Waller B on the scattering vector is of a simple form when a shell model adequately represents the deformation of the electron distribution. Numerical results are presented, without any serious approximations, for the governing constant appropriate to six alkali halides and explicit results are given for $\Delta B_k / B_k$ for NaF, NaCl and KCl. A comparison with the recent real-space formulation of March & Wilkins [Acta Cryst. (1978), A34, 19–26] suggests that the reciprocal-space approach might be more fruitful.

Introduction

Dynamic deformation refers to the change in the scattering factor of an atom caused by the thermal motion both of the atom itself and of all other atoms in the crystal. The effect on the kth type of atom in the lth unit cell depends on the scattering vector $\mathbf{K}$. Appropriate coupling parameters $\beta(l' - l, kk', \mathbf{K})$ were introduced in slightly reduced generality by Born (1942) and have been discussed in particular by Reid (1974) and March & Wilkins (1978). The latter concentrated on real-space parameters to determine entirely in terms of real-space quantities the resulting changes in the Debye–Waller factors. They showed how the changes were given by an expression which involved all the $\beta(l' - l, kk', \mathbf{K})$ for a lattice but the inevitable lack of knowledge of these parameters forced drastic simplifications before a usable expression could be obtained. Consequently, although they quoted results relevant to typical shell-model distortions (for NaCl and NaF), there is still considerable uncertainty as to the magnitude of the dynamic deformation effect on the Debye–Waller factor shown by current lattice-dynamical models.

The present paper concentrates on the reciprocal-space formulation for the effect of ionic deformation and shows that a simple form is obtained for the modification of the Debye–Waller factor by shell-model distortions. The result is that the effective Debye–Waller factor depends on the scattering vector $\mathbf{K}$ by an amount which can be calculated with a shell model. The size and variation of this effect is illustrated for some alkali halides and a brief comparison made with the results of March & Wilkins (1978).

Deformation effect on the Debye–Waller factor

The freedom of an electron distribution to deform dynamically allows new scattering processes to take place, processes which are not present in a crystal made of atoms which move as rigid units. Buyers, Pirie & Smith (1968) pointed out that these processes can conveniently be represented to first order in β on a scattering diagram in which one (and only one) line from the implicit photon–phonon vertex is associated with a term linear in the β. Fig. 1 shows terms which contribute to the Debye–Waller sum when ionic deformation processes are present. Each additional term involves a similar expression to the corresponding term with rigid ions except that one occurrence of $K(k/\lambda)$ is replaced by β terms, thus:

$$K(k/\lambda) \rightarrow -i\beta(k/\lambda), \qquad (1)$$

where

$$K(k/\lambda) = \mathbf{K}.\mathscr{E}(k/\lambda)\left\{\frac{\hbar}{2Nm_k\,\omega_\lambda}\right\}^{1/2}$$

and

$$\beta(k/\lambda) = \sum_{k'} \beta(\mathbf{q},kk',\mathbf{K}).\mathscr{E}(k'/\lambda) \times \left\{\frac{\hbar}{2Nm_{k'}\,\omega_\lambda}\right\}^{1/2},$$
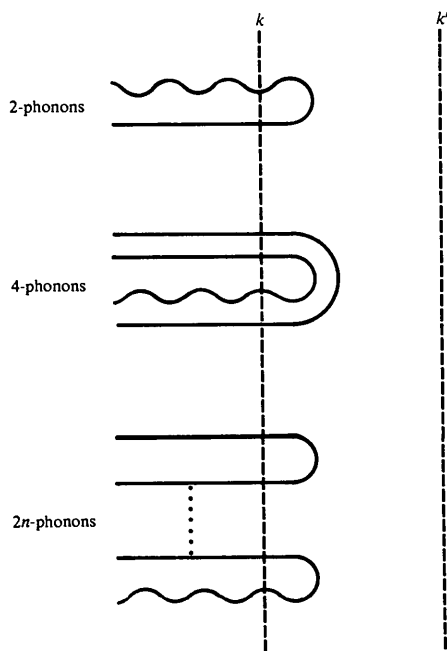
$$(2a)$$

Fig. 1. Examples of dynamic-deformation scattering processes which contribute to the Debye–Waller factor. The wavy deformation line is associated with a term $\beta(k/\lambda)$ while the ordinary straight lines are associated with the terms $K(k/\lambda)$.

with

$$\beta(\mathbf{q},kk',\mathbf{K}) = \sum_{l'} \beta(l' - l, kk', \mathbf{K})$$

$$\times \exp\{-i\mathbf{q}.[\mathbf{r}(lk) - \mathbf{r}(l'k')]\}, \qquad (2b)$$

in a notation almost that of Buyers, Pirie & Smith but with $\lambda \equiv (\mathbf{q}j)$ representing the phonon labels.[†] Since dynamic deformation effects are small, no serious approximations are involved in only considering terms linear in β.

It follows that both the elastic and inelastic scattering cross-sections must include the harmonic Debye–Waller term $\exp(-W_k^D)$ where

$$W_k^D = \tfrac{1}{2}\sum_\lambda (2n_\lambda + 1)[K(k/\lambda)\,K^*(k/\lambda)$$

$$- i\beta(k/\lambda)\,K^*(k/\lambda) + i\beta^*(k/\lambda)\,K(k/\lambda)] \qquad (3)$$

to first order in β. The first term is the usual Debye–Waller exponent

$$W_k = \frac{1}{2N}\sum_\lambda \left(\frac{E}{\omega^2}\right)_\lambda \left|\mathbf{K}.\frac{\mathscr{E}(k/\lambda)}{m_k^{1/2}}\right|^2 \qquad (4)$$

and the other two terms give the effect of ionic deformation.

The $\beta(k/\lambda)$ are derived from the $\beta(l' - l, kk', \mathbf{K})$ through (2). For a material with a centre of symmetry the two β terms in W_k^D either cancel or are equal. This can be seen by noting that

$$\beta(l',kk',\mathbf{K}) = \beta_{\text{odd}}(l',kk',\mathbf{K}) + i\beta_{\text{even}}(l',kk',\mathbf{K}), \qquad (5)$$

where the odd or even refer to the symmetry upon an inversion of $\mathbf{r}(l')$ through the origin atom. The real $\beta(l')$ are associated with even multipole distortions (breathing distortion, quadrupole distortion, etc.) and the imaginary $\beta(l')$ with odd multipole distortions of which the dipole-type shell-model distortion is the obvious archetype. The different symmetry of the $\beta(l')$ directly gives two symmetry options for $\beta(k/\lambda)$ namely

$$\beta(k/-\lambda) = \mp\beta^*(k/\lambda)\begin{cases} - \text{ sign for } \beta_{\text{odd}} \\ + \text{ sign for } \beta_{\text{even}} \end{cases}.$$

Hence, applying this result to (3), one can see that in centrosymmetric crystals all distortions giving real $\beta(l')$ produce zero effect on the Debye–Waller factor whereas all dipole and other distortions giving

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[†] λ is a conventional symbol used to label the phonon states but unfortunately clashes with the even wider use of λ for X-ray wavelength. Although confusion is possible when $\sin\theta/\lambda$ is introduced later, both conventions are kept because the symbols refer to widely different quantities and do not explicitly occur in the same equation.

imaginary $\beta(l')$ give an additional Debye–Waller term of

$$\Delta W_k = W_k^D - W_k = -i \sum_\lambda (2n_\lambda + 1) \beta(k/\lambda) K^*(k/\lambda). \quad (6)$$

In particular, the deformation scattering from the shell model can be given in terms of the relative shell–core displacements $\mathscr{W}(k/\lambda)$, since (Reid, 1974)

$$\beta(k/\lambda) = i \frac{[f_k(\mathbf{K})]_{\text{shell}}}{[f_k(\mathbf{K})]_{\text{atom}}} \mathbf{K} \cdot \mathscr{W}(k/\lambda) \left(\frac{\hbar}{2N\omega_\lambda}\right)^{1/2}. \quad (7)$$

Therefore

$$\Delta W_k = \frac{[f_k(\mathbf{K})]_{\text{shell}}}{[f_k(\mathbf{K})]_{\text{atom}}} \frac{1}{N} \sum_\lambda \left(\frac{E}{\omega^2}\right)_\lambda$$
$$\times \mathbf{K} \cdot \mathscr{W}(k/\lambda) \, \mathbf{K} \cdot \frac{\mathscr{E}^*(k/\lambda)}{m_k^{1/2}}, \quad (8)$$

which simplifies for a cubic crystal to

$$\Delta W_k = \frac{[f_k(\mathbf{K})]_{\text{shell}}}{[f_k(\mathbf{K})]_{\text{atom}}} \frac{K^2}{3N} \sum_\lambda \left(\frac{E}{\omega^2}\right)_\lambda$$
$$\times \mathscr{W}(k/\lambda) \cdot \frac{\mathscr{E}^*(k/\lambda)}{m_k^{1/2}}. \quad (9)$$

In the usual notation,† let

$$W_k = B_k \sin^2 \theta/\lambda^2$$

then the Debye–Waller term with dynamic deformation is given by

$$B_k^D = B_k + \Delta B_k$$

and, for a cubic crystal,

$$\Delta B_k = \frac{[f_k(\mathbf{K})]_{\text{shell}}}{[f_k(\mathbf{K})]_{\text{atom}}} \frac{16\pi^2}{3N} \sum_\lambda \left(\frac{E}{\omega^2}\right)_\lambda$$
$$\times \mathscr{W}(k/\lambda) \cdot \frac{\mathscr{E}^*(k/\lambda)}{m_k^{1/2}}$$
$$= \frac{[f_k(\mathbf{K})]_{\text{shell}}}{[f_k(\mathbf{K})]_{\text{atom}}} S_k, \quad (10)$$

defining S_k independent of $\mathbf{K}$.

The above expressions involve no serious approximations and are amenable to evaluation once a shell model is available. For a cubic crystal ΔB_k depends on $\sin \theta/\lambda$ (and not on the direction of $\mathbf{K}$ unless the shell departs from spherical symmetry) only through the shell/atom scattering-factor ratio. This ratio is likely to

† See previous footnote.

fall off quite quickly with increasing $\sin\theta/\lambda$. The temperature dependence of ΔB_k is similar to that of B_k and hence $\Delta B_k/B_k$ will be only weakly temperature-dependent, as the results in the next section confirm.

Calculations

The basis of the following results rests on the fitted shell models available for the alkali halides. The actual ones used were those which the author previously employed in a detailed evaluation of the harmonic Debye–Waller factors (Reid & Smith, 1970, 1971). With a sample of 64 000 modes uniformly covering the Brillouin zone, the essential constant S_k/B_k was determined for each ion in six alkali halides (Table 1). (Actually, a sample of only 1000 modes gives little loss of accuracy.) Equation (10) shows that this constant is $\Delta B_k/B_k$ without the multiplying scattering-factor ratio term and therefore represents an upper limit to $\Delta B_k/B_k$ considerably in excess of the likely value. Table 1 shows that the term is always negative, the negative ions usually having the larger value. However, the variation across the materials reflects the diversity in the shell models used, as much as the change from one material to another. For example the NaCl model is effectively a one-ion-polarizable model and the NaBr model has zero second-neighbour interactions.

To obtain the absolute magnitude of the deformation effect, ionic scattering factors were obtained for the alkali halides from *International Tables for X-ray Crystallography* (1974). However, to say that the shell scattering factors were derived from the scattering factors given for outer electrons by James & Brindley (1931), which they were, gives them an air of respectability they do not really deserve. The shell of a lattice dynamics model cannot be interpreted literally or even identified exactly with a particular fraction of the electronic charge. To take into account to some extent that the dynamic deformation extends quite far in towards the nucleus, even for an alkali halide, the shell scattering factor was taken as a multiple of the scattering factor for an individual outer p electron for

Table 1. *Values for S_k/B_k at 295 K, see equation* (10)

Multiplying the tabular values by the ratio of shell to atom scattering-factors at any value of scattering vector gives the fractional effect of the dynamic deformation on the Debye–Waller factor.

	Positive ion	Negative ion
NaF	−0·0027	−0·0718
NaCl	−0·0011	−0·1252
NaBr	−0·1598	−0·0780
NaI	−0·0349	−0·0543
KCl	−0·0038	−0·0469
KBr	−0·0469	−0·0644

the materials shown in Fig. 2. The resulting $\Delta B_k/B_k$ as a function of scattering vector $\mathbf{K}$ should be considered as a guide to the kind of behaviour expected and cannot be
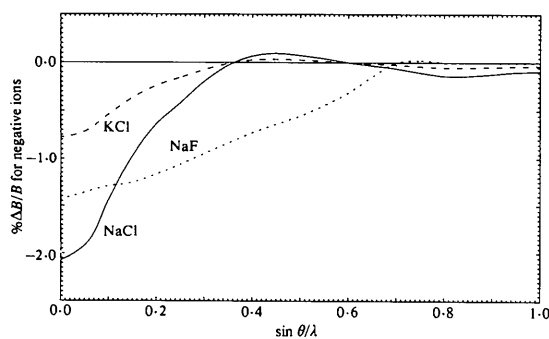

Fig. 2. $\%\Delta B_k/B_k$ values at 295 K as a function of $\sin\theta/\lambda$ for negative ions in NaF, NaCl and KCl. The positive ion values are less than 0·1% everywhere when shell charges 2, 2 and 3 electrons respectively are chosen.
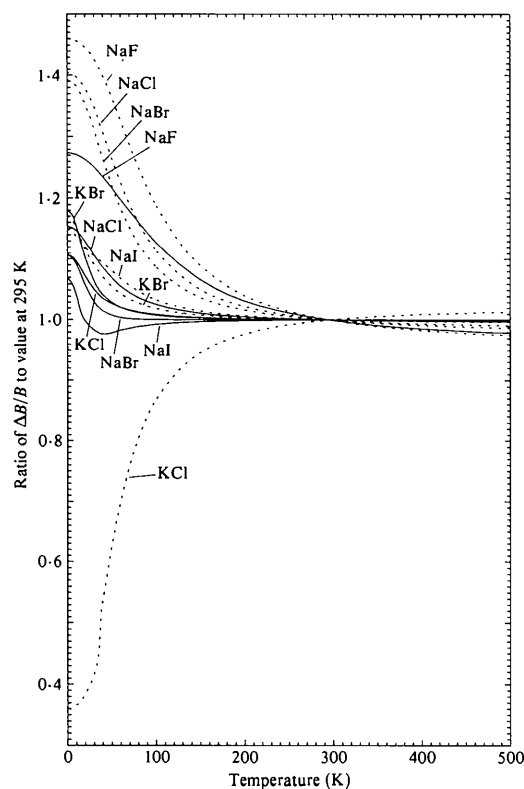

Fig. 3. The variation of $\Delta B_k/B_k$ with temperature relative to the value at 295 K. Solid lines refer to the negative ions and dotted lines to the positive ions for the six alkali halides shown.

relied on quantitatively. In particular, choosing different shell charges simply scales the results correspondingly.

Fig. 3 shows the temperature variations for $\Delta B_k/B_k$. These variations are the same for all scattering vectors $\mathbf{K}$ and hence are independent of the choice of scattering factors. For all the negative ions, the dynamic deformation effect is remarkably independent of temperature, the slight rise at low temperatures showing that the shell-core displacements associated with lower-energy modes are, on the whole, slightly less than those in higher-energy modes. That this is not an inviolable rule for shell models is shown by the positive-ion behaviour, particularly that of K$^+$ in KCl. This greater range of behaviour must to some extent arise from the greater uncertainty in the model parameters for generally small positive-ion deformations.

Finally, a comparison with the $\Delta B_k/B_k$ values quoted by March & Wilkins (1978) is worthwhile because March & Wilkins used the same source of basic data. They give values for NaCl and NaF at $\mathbf{K} = (1\cdot6,0,0)\, 2\pi/d$; their results are of the same sign as those in Fig. 2 but are about three times larger. This discrepancy must surely reflect a failure of their self-deformation approximation which takes account of only the $\beta(l' = 0, kk, \mathbf{K})$ term while effectively discounting other $\beta(l', kk', \mathbf{K})$ of comparable size but opposite sign. The smaller values of the present calculation suggest that for many materials the dynamic deformation effects on the Debye–Waller factors are not going to be of much concern, to the usual accuracy attained by experiments, but in certain favourable circumstances the effects should be quite observable.

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