

Elastic X-ray Scattering from Solids Containing Non-Rigid Pseudoatoms

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General methods for treating the elastic X-ray scattering from solids containing non-rigid pseudoatoms are developed. The methods are based on a model which involves the assumption of the adiabatic approximation and the representation of the total electron density as a sum of electron densities from dynamically deformable pseudoatoms. A basic result derived for this model is an expression for the X-ray structure factor in terms of generalized Born β parameters, the calculation being carried out to first order in the strength of the dynamic deformations. If the dynamic-deformation contribution is treated in the harmonic approximation, it is shown that considerable simplification of the expression for the structure factor can be achieved, especially at high temperature (*i.e.* $T > \theta_M$, where θ_M is the Debye temperature). Another, fairly drastic, approximation discussed is that in which only the self-deformation contribution is retained. This latter approximation is used to estimate the effect of dynamic deformation for solid NaCl and NaF, utilizing some β 's calculated from a shell model. Though the calculated effects are small, they are such as to be measurable in highly accurate experiments. Other cases are discussed where the effects of dynamic deformation may be expected to be somewhat larger.

1. Introduction

One of the fundamental assumptions inherent in the conventional treatment of elastic X-ray scattering from solids is the assumption that the ions vibrate rigidly, *i.e.* that each pseudoatom electron density perfectly follows its nucleus. This assumption is sometimes also called the 'perfectly following' or convolution approximation. Its origins in treating diffraction from vibrating atoms may be traced back to the work of Debye (1930). While this approximation is certainly adequate for routine structural work, there is a growing body of evidence (Coulson & Thomas, 1971; Coppens, 1972; Stewart, 1976) to suggest that in certain cases it will have to be transcended when one seeks to obtain the maximum possible amount of positional and bonding-electron-density information from highly accurate X-ray structure-factor measurements.

An important case where the presence of deformable pseudoatoms may be expected to complicate positional and electron-density determinations is that of bonded hydrogen atoms (Stewart, 1976). The large amplitude of vibration (even at low temperature) and the absence of a core structure make hydrogen pseudoatoms particularly susceptible to deformation. Although direct experimental evidence for this effect still seems to be

lacking, there appears to be strong indirect evidence based on the repeated failure of rigid-pseudoatom models to take proper account of the bonded-hydrogen electron density. Stewart (1976) cites an example where use of a single monopole scattering factor for H atoms does not, in general, give the time-averaged proton position. Mair (1978) has found that the assumptions of neutron-measured positional coordinates, together with monopole and dipole static deformation density contributions for H in NH_4F , lead to contradictions involving negative probability density. Price, Varghese & Maslen (1978) found similar difficulties in refining data on melamine.

Additional evidence to suggest that the rigid-pseudoatom model may break down for bonded H atoms is gained from the theoretical calculations of Coulson & Thomas (1971) on the H_2 molecule. They compared the alternative calculations of the H_2 electron density, assuming first the convolution approximation and second the more accurate adiabatic approximation. This comparison indicated a *ca* 2% contraction in the apparent X-ray H–H bond length when the adiabatic approximation is applied. Although small, this effect is still large in comparison with the precision now available from accurate X-ray and neutron diffraction experiments. Moreover, it should be realized that change in apparent bond length is probably not a very sensitive indicator of dynamic deformation.

Further evidence for the failure of the convolution approximation is provided by the recent combined

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X-ray and neutron diffraction results of Roberto, Batterman & Keating (1974) on the 'forbidden' 222 reflexion in Si, as interpreted by Chelikowsky & Cohen (1974). The latter workers found it necessary to introduce different Debye-Waller factors for the core and bond charges, thus implying deformable Si pseudoatoms. More recently, Price, Maslen & Mair (1978) have reported the results of a re-analysis of the extremely accurate *Pendellösung* data of Aldred & Hart (1973) on Si, and their results were also taken to imply the possible presence of dynamic deformation.

Additionally, though from a rather different angle, the inelastic X-ray scattering studies by Buyers, Pirie & Smith (1968) led them to interpret anti-symmetric peaking of the X-ray TDS scattering under a Bragg peak in terms of dynamic deformation of pseudoatoms. This interpretation, however, appears to be complicated by the fact that the anharmonic coupling of one and two-phonon scattering also produces a similar effect (Pirie, Reid & Smith, 1971).

Having briefly outlined the above pointers to the interest in studying deformable pseudoatoms, we shall turn below to a study of the theory of elastic X-ray (Bragg) scattering from a solid with such dynamic deformation. However, it will be helpful first to review earlier treatments of Bragg scattering including such deformability before introducing our own approach.

2. Earlier treatments of Bragg scattering from non-rigid pseudoatoms

The earliest treatment of elastic scattering by non-rigid pseudoatoms was given by Born (1942), who introduced dynamic charge-deformation parameters (β) into the X-ray scattering formulation. These parameters were independent of the scattering vector \mathbf{k} (*i.e.* constants, and so even functions of \mathbf{k}). However, no detailed theory of the effect was worked out. The fact that Born's β parameters were taken as constants implies the over-simplified assumption that the valence and core electrons deform equally. Buyers, Pirie & Smith (1968), working in the language of many-body theory, have given a treatment of elastic and inelastic (TDS) X-ray scattering from dynamically deformable pseudoatoms in the harmonic approximation. Their work appears to contain the implicit assumption that the β 's, although \mathbf{k} -dependent, are real, corresponding to symmetrical (*i.e.* 'breathing shell' type) charge deformation, and this assumption appears to have led them to predict zero effect on the Bragg scattering for the alkali halides (see also §§ 4.1 and 4.2.1 below). Pryor (1966) briefly discussed the possibility of detecting the effect of ionic deformation by comparative X-ray and neutron measurements of the Debye-Waller factor. For the case of NaCl, Pryor estimated the effect of ionic deformation on the basis of anti-symmetrical (odd in \mathbf{k}) charge distortions in a shell-

model calculation, and predicted that the effect for this case was never greater than $\approx 1\%$ of the X-ray scattering factor $f(\mathbf{k})$. Jones & March (1970) introduced a 'tensor charge density' to describe the effect of charge deformation on phonon dispersion as well as X-ray scattering. Their approach, to the order they consider, does not lead to any effect on the Bragg scattering, although it would if taken to sufficiently high order. A null result for Bragg scattering would also obtain with the closely related approach described by Ball (1975).

Another line of approach follows from the work of Melvin, Pirie & Smith (1968) who introduced some generalized β parameters which imply continuous degrees of deformation of the electron density. Recently, Reid (1974) has evaluated the magnitude of these parameters for NaCl and NaF on the basis of a 'rigid' (fixed radius) shell model, in which case the β parameters are imaginary and odd (antisymmetric) in \mathbf{k} . However, he did not estimate the effect on the elastic X-ray scattering intensity.

In the present work, the effect of the dynamic charge deformation on X-ray Bragg scattering (§ 4) is worked out on the basis of a simple physical model for the total electron density (§ 3). For the purpose of assisting in the practical application of the formalism, it is shown that when the deformation contribution is treated in the harmonic approximation (§ 4.1), then, at high temperature, the temperature dependence of this contribution scales as the Debye-Waller factor (§ 4.1.1). As a further helpful step towards practical application of the present formalism, a simple 'self-deformation-only' approximation is developed (§ 4.2). This approximation is illustrated by application to the case of a monatomic solid with a primitive unit cell, for which it is shown (§ 4.2.1) that antisymmetric (rigid-shell) distortion produces an effect on the Bragg intensities which is of first order in the strength of the deformation β , whereas the symmetric ('breathing') component of the deformation only produces an effect of higher order in β [in agreement with the finding of Buyers, Pirie & Smith (1968) for this symmetric case]. For the case of antisymmetric distortion it is shown, within the self-deformation approximation, that the effect on Bragg scattering may be incorporated in the scattering formulae as a modified Debye-Waller factor for inner reflexions. The effect is shown to disappear at high angles if the core density does not deform. In § 5 some shell-model results of Reid (1974) for the effect of ionic deformation on NaCl and NaF are used to help estimate the effect to be expected in the X-ray Bragg scattering. For NaF the effect of charge deformation is such as to produce a reduction of approximately 4% in the anion Debye-Waller factor for low-angle reflexions, while for NaCl the effect is found to be approximately 2%. Since the magnitude of the dynamic deformation of an ion is closely related to its polarizability, it is possible to suggest substances

for which the predicted effect will be somewhat greater than these values.

3. Model for charge density

It is assumed that the adiabatic approximation (see, for example, Born & Huang, 1966) is valid, so that the total electron density in a crystalline solid may be represented, without loss of generality, by the following pseudoatom model:

$$\rho(\mathbf{r}) \equiv \rho(\mathbf{r}, \{\mathbf{u}_{l'\kappa'}\}) = \sum_{l\kappa} \sigma_{\kappa}(\mathbf{r} - \mathbf{R}_{l\kappa} - \mathbf{u}_{l\kappa}, \{\mathbf{u}_{l'\kappa'}\}), \quad (1)$$

where $\mathbf{R}_{l\kappa}$ is the equilibrium position vector of the κ th nucleus in the l th unit cell, whilst $\mathbf{u}_{l\kappa}$ is the small instantaneous nuclear displacement away from that site.* The pseudoatom (or pseudoion) electron density, σ_{κ} , attributed to the κ th type of atom is assumed to be an essentially localized 'atom-like' distribution, the assignment of which, in a solid, is always non-unique to some degree, but which can usually be determined satisfactorily in practice by some additional assumptions such as smoothness or the choice of a particular physical model. It should be noted that σ_{κ} introduced in (1) contains the feature that it is not only a function of the instantaneous nuclear coordinate of the given ion, but also of the instantaneous nuclear coordinates of all the other ions in the solid. Thus it can be seen that (1) transcends the usual rigid-pseudoatom model which, in the present notation, can be expressed as

$$\rho^0(\mathbf{r}) = \sum_{l\kappa} \sigma_{\kappa}(\mathbf{r} - \mathbf{R}_{l\kappa} - \mathbf{u}_{l\kappa}, \{\mathbf{0}\}) = \sum_{l\kappa} \sigma_{\kappa}^0(\mathbf{r} - \mathbf{R}_{l\kappa} - \mathbf{u}_{l\kappa}), \quad (2)$$

the rigid-pseudoatom electron densities, σ_{κ}^0 , being thereby defined.

In the present work we shall assume that $\rho(\mathbf{r})$ is sufficiently well approximated by the expansion of the deformation component in (1) to first order in $\mathbf{u}_{l'\kappa'}$. This approximation gives the total electron density as

$$\rho(\mathbf{r}) = \sum_{l\kappa} [\sigma_{\kappa}^0(\mathbf{r} - \mathbf{R}_{l\kappa} - \mathbf{u}_{l\kappa}) + \sum_{l'\kappa'} \mathbf{u}_{l'\kappa'} \cdot \nabla_{\mathbf{u}_{l'\kappa'}} \sigma_{\kappa}(\mathbf{r} - \mathbf{R}_{l\kappa} - \mathbf{u}_{l\kappa}, \{\mathbf{u}_{l'\kappa'}\})|_{\{\mathbf{0}\}}], \quad (3)$$

where the grad operates only on the second argument of σ_{κ} and is evaluated for $\{\mathbf{u}_{l'\kappa'}\} = \{\mathbf{0}\}$. A useful alternative representation of (3) is obtained by introducing the generalized β coefficients (Melvin, Pirie

& Smith, 1968; Reid, 1974). These coefficients are here defined by the relation

$$\nabla_{\mathbf{u}_{l'\kappa'}} \sigma_{\kappa}(\mathbf{r} - \mathbf{R}_{l\kappa} - \mathbf{u}_{l\kappa}, \{\mathbf{u}_{l'\kappa'}\})|_{\{\mathbf{0}\}} = \beta(l' l, \kappa' \kappa, \mathbf{r} - \mathbf{R}_{l\kappa} - \mathbf{u}_{l\kappa}) \otimes \sigma_{\kappa}^0(\mathbf{r} - \mathbf{R}_{l\kappa} - \mathbf{u}_{l\kappa}), \quad (4)$$

where \otimes denotes the Fourier convolution operation, here carried out w.r.t. the \mathbf{r} -dependent argument. An explicit expression for β can be derived by Fourier-transforming (4) with respect to \mathbf{r} , and this yields

$$\beta(l' l, \kappa' \kappa, \mathbf{k}) = \nabla_{\mathbf{u}_{l'\kappa'}} f_{\kappa}(\mathbf{k}, \{\mathbf{u}_{l'\kappa'}\})|_{\{\mathbf{0}\}} / f_{\kappa}^0(\mathbf{k}), \quad (5)$$

where

$$f_{\kappa}^0(\mathbf{k}) = \int d\mathbf{r} \sigma_{\kappa}^0(\mathbf{r}) \exp \{i \mathbf{k} \cdot \mathbf{r}\} \quad (6a)$$

is the usual rigid-pseudoatom scattering factor, while

$$f_{\kappa}(\mathbf{k}, \{\mathbf{u}_{l'\kappa'}\}) = \int d\mathbf{r} \sigma_{\kappa}(\mathbf{r}, \{\mathbf{u}_{l'\kappa'}\}) \exp \{i \mathbf{k} \cdot \mathbf{r}\} \quad (6b)$$

is the deformable-pseudoatom scattering factor. From (5) it follows that β is well defined except when $f_{\kappa}^0(\mathbf{k})$ is zero – this does not occur in practice, and so no problem arises.

3.1 Properties of Born β coefficients

By use of the present definitions of the deformable pseudoatom charge densities and the fact that the displacements $\{\mathbf{u}_{l\kappa}\}$ are independent variables, subject only to the constraint that they be small relative to the lattice parameters, the following general properties of the β 's may be derived.

(i) Invariance of the individual pseudoatom electron-density distributions to a uniform translation of the whole system leads to the result that

$$\sum_{l'\kappa'} \beta(l' l, \kappa' \kappa, \mathbf{k}) = \mathbf{0} \quad (7)$$

for all κ and \mathbf{k} . As pointed out by Reid (1974), this condition is equivalent to saying that the deformation in acoustic modes of small wave vector must be zero.

(ii) The assumption that there is a rigid core leads to the condition that

$$\beta(l' l, \kappa' \kappa, \mathbf{k}) \rightarrow \mathbf{0} \quad \text{as } |\mathbf{k}| \rightarrow \infty \quad (8)$$

for all l' , κ' , and κ . This result obtains because σ_{κ}^0 is more highly localized in \mathbf{r} space than $\nabla_{\mathbf{u}_{l'\kappa'}} \sigma_{\kappa}$.

(iii) Conservation of the total number of electrons in the system which is undergoing deformation leads to the condition that

$$\sum_{l'\kappa} \beta(l' l, \kappa' \kappa, \mathbf{k}) \rightarrow \mathbf{0} \quad \text{as } |\mathbf{k}| \rightarrow 0 \quad (9)$$

for all κ' . This result may be obtained by successive steps involving integration of (2) and (3) with respect to \mathbf{r} , elimination of the σ_{κ}^0 contribution with the result $\int d\mathbf{r} \rho(\mathbf{r}) = \int d\mathbf{r} \rho^0(\mathbf{r})$, and finally appropriate substitution of (4) and (5) for β .

* To avoid complicating the notation we have not shown the time dependence explicitly. Therefore, we emphasize here that it is the instantaneous positions (*i.e.* relative time $t = 0$) which are relevant to elastic scattering and that time averaging (*i.e.* over the absolute time) will later be achieved by ensemble averaging. A further point of notation is that curly brackets, *e.g.* $\{\mathbf{u}_{l'\kappa'}\}$ in (1), are used to imply the set of all such quantities.

(iv) If, in addition to (iii), the much stronger condition is imposed that no charge is lost or gained from the individual pseudoatom involved in the deformation process, then the more restrictive condition

$$\beta(l', \kappa' \kappa, \mathbf{k}) \rightarrow \mathbf{0} \quad \text{as} \quad |\mathbf{k}| \rightarrow 0 \quad (10)$$

is satisfied for all l', κ and κ' .

With the above representation of the electron density in hand, we now turn to calculating the X-ray scattering.

4. Elastic X-ray scattering

In the present work only the elastic X-ray scattering is considered. The principal quantity involved, therefore, is the coherent X-ray scattering amplitude (neglecting dispersion corrections), which is given by the Fourier inverse of the electron density.

With the above approximation for the total electron density [equations (3), (4), and (5)], the instantaneous unit-cell X-ray scattering structure factor is

$$\begin{aligned} F(\mathbf{k}, \{\mathbf{u}_{l'\kappa'}\}) &= \sum_{\kappa} f_{\kappa}(\mathbf{k}, \{\mathbf{u}_{l'\kappa'}\}) \exp\{i \mathbf{k} \cdot (\mathbf{R}_{l\kappa} + \mathbf{u}_{l\kappa})\} \\ &= \sum_{\kappa} f_{\kappa}^0(\mathbf{k}) [1 + \sum_{l'\kappa'} \mathbf{u}_{l'\kappa'} \cdot \beta(l' l, \kappa' \kappa, \mathbf{k})] \\ &\quad \times \exp\{i \mathbf{k} \cdot \mathbf{u}_{l\kappa}\} \exp\{i \mathbf{k} \cdot \mathbf{R}_{l\kappa}\}, \end{aligned} \quad (11)$$

where the second equality defines the deformable-pseudoatom scattering factor f_{κ} in terms of the undeformed pseudoatom scattering factor f_{κ}^0 (the quantity sought in a conventional electron-density determination). The effect of nuclear thermal motion on the structure factors (11) and (12) is taken account of by ensemble-averaging. For (12), this yields

$$\begin{aligned} \langle F(\mathbf{k}, \{\mathbf{u}_{l'\kappa'}\}) \rangle &= \sum_{\kappa} f_{\kappa}^0(\mathbf{k}) \langle \exp\{i \mathbf{k} \cdot \mathbf{u}_{l\kappa}\} \rangle \\ &\quad + \sum_{l'\kappa'} \beta(l' l, \kappa' \kappa, \mathbf{k}) \cdot \langle \mathbf{u}_{l'\kappa'} \exp\{i \mathbf{k} \cdot \mathbf{u}_{l\kappa}\} \rangle \exp\{i \mathbf{k} \cdot \mathbf{R}_{l\kappa}\}, \end{aligned} \quad (13)$$

where the first term in square brackets in (13) is the usual generalized Debye-Waller factor, while the second, much smaller, term contains both deformation and temperature-dependent factors. Expression (13) provides a basis for extending the Dawson (1967*a,b*, 1975) generalized structure-factor formalism (which presently includes non-spherically symmetric atoms and anharmonic thermal vibrations) to the case of highly polarizable atoms which deform dynamically as they vibrate. It should be noted that (13) is essentially model-independent so far as the precise nature of the thermal vibrations (Buyers *et al.*, 1968) and dynamic deformations goes (Reid, 1974). Unfortunately, the large number of independent parameters in (13) means that it must be simplified still further in order to be useful in structure-factor refinements. It would therefore seem more practical to either: (a) calculate the

deformation terms (and perhaps also some of the vibrational terms) from a particular physical model involving only a few parameters, such as, for example, a shell model, or (b) make some judicious approximations so as to reduce greatly the number of adjustable parameters.

The possibilities under alternative (a) are vast, usually system-specific, often controversial and sometimes largely a matter of taste. Though the shell-model line of approach has been very fruitful to date, we do not have new results to add to it here. Rather, in the following two subsections we consider some possibilities under alternative (b). Since methods of treating the first term in square brackets in (13) are well documented, attention can be focused on the second term.

4.1 Harmonic approximation for dynamic-deformation contribution

Since both the dynamic deformation and anharmonic contributions to $\langle F \rangle$ are expected to be small for most systems, a useful approximation to the dynamic deformation contribution in (13) may be obtained by treating this deformation term in the harmonic approximation (Buyers *et al.*, 1968). The assumption of the harmonic approximation to the vibrational problem for the deformation term enables us to rewrite (13), without further approximation, as

$$\langle F \rangle = \sum_{\kappa} f_{\kappa}^0(\mathbf{k}) [1 + i \cdot \mathcal{B}_{\kappa}(\mathbf{k})] \langle \exp\{i \mathbf{k} \cdot \mathbf{u}_{l\kappa}\} \rangle \exp\{i \mathbf{k} \cdot \mathbf{R}_{l\kappa}\} \quad (14)$$

with

$$\mathcal{B}_{\kappa}(\mathbf{k}) = \mathbf{k}^{\dagger} \sum_{l'\kappa'} \langle \mathbf{u}_{l'\kappa'} \mathbf{u}_{l\kappa}^{\dagger} \rangle \beta(l' l, \kappa' \kappa, \mathbf{k}), \quad (15)$$

where the mathematical result derived in Appendix A has been invoked. In (15) \mathbf{k}^{\dagger} and $\mathbf{u}_{l\kappa}^{\dagger}$ denote the Hermitian conjugates of the vectors \mathbf{k} and $\mathbf{u}_{l\kappa}$, respectively. Thus, for example, $\langle \mathbf{u}_{l'\kappa'} \mathbf{u}_{l\kappa}^{\dagger} \rangle$ is a 3×3 matrix. Also, with regard to (15), it may be noted that $\mathcal{B}_{\kappa}(\mathbf{k})$ is independent of l . This result follows because all unit cells are assumed equivalent so that $\langle \mathbf{u}_{l'\kappa'} \mathbf{u}_{l\kappa}^{\dagger} \rangle$ and $\beta(l' l, \kappa' \kappa, \mathbf{k})$ depend only on $l' - l$. We note also that the deformation term $\mathcal{B}_{\kappa}(\mathbf{k})$ will in general contain a complicated mixture of vibrational and pure dynamic-deformation (*i.e.* β) contributions, and so will not be easily interpretable in physical terms.

At this point it is possible to make direct contact with the work of Buyers *et al.* (1968). We observe firstly that they developed their treatment of dynamic deformation entirely within the framework of the harmonic approximation and used phonon coordinates. By contrast, we have presented much of our general treatment in a form which is independent of the particular vibrational approximation adopted and have used particle coordinates. In the present case, where the dynamic deformation contribution is treated in the

harmonic approximation, we note that our equation (15) translates to Buyers *et al.*'s (1968) equation (13) when the particle coordinates $\mathbf{u}_{l\kappa}$ are expressed in terms of phonon coordinates.

A further point of comparison may be established if we use (14) to calculate the kinematical (*i.e.* first Born approximation) intensity in reduced units, namely

$$I(\mathbf{k}) = N^2 \sum_{\kappa} \sum_{\kappa'} \overline{f_{\kappa'}^0(\mathbf{k})} f_{\kappa}^0(\mathbf{k}) [1 - i \overline{\mathcal{B}}_{\kappa}(\mathbf{k}) + i \mathcal{B}_{\kappa'}(\mathbf{k})] \\ \times \langle \exp\{-i\mathbf{k} \cdot \mathbf{u}_{l\kappa}\} \rangle \langle \exp\{i\mathbf{k} \cdot \mathbf{u}_{l'\kappa'}\} \rangle \\ \times \exp\{i\mathbf{k} \cdot (\mathbf{R}_{l\kappa'} - \mathbf{R}_{l\kappa})\} \sum_{\mathbf{G}} \delta(\mathbf{k} - \mathbf{G}), \quad (16)$$

where an overbar denotes the complex conjugate, and the symbol \mathbf{G} denotes a reciprocal-lattice vector. Some terms which are $O(|\beta|^2)$ have been ignored in obtaining (16). It can now be seen that expression (16) for $I(\mathbf{k})$ largely agrees with the corresponding equation implied by equation (15) of Buyers *et al.* (1968), but with the small difference that \mathcal{B}_{κ} appears in (16), *not* $\mathcal{B}_{\kappa'}$. Whereas in the application of Buyers *et al.* (1968) the implicit assumption that \mathcal{B}_{κ} is real is made; this is not necessarily so, since β may have a non-zero imaginary part (see, for example, § 4.2.1).

Equations (14) and (16) show clearly how the effects of: static deformation of the pseudoatom electron density (contained in f_{κ}^0), dynamic deformation of the electron density (*via* \mathcal{B}_{κ}) and thermal vibration (*i.e.* $\langle \exp\{i\mathbf{k} \cdot \mathbf{u}_{l\kappa}\} \rangle$) appear as distinct factors in each term of the general expressions for the structure factor and intensity. It should be noted that each of these factors is, in general, complex. Equations (14) and (16) can be viewed as a form of the Dawson generalized structure-factor formalism (1967*a,b*; 1975) extended to include non-rigid pseudoatoms. In practice it would also be necessary to include the effects of anomalous dispersion on the f_{κ}^0 's.

Equations (14) and (16) are in a form which makes them suitable for use in analysing experimental data. In order to make a clean separation of the various factors in (14) or (16), one would require, say, combined neutron and X-ray data at a series of temperatures. The neutron data would serve to measure the generalized Debye-Waller factors $\langle \exp\{i\mathbf{k} \cdot \mathbf{u}_{l\kappa}\} \rangle$ so that any residual temperature dependence in the X-ray data analysed *via* (14) or (16) would imply *either* dynamic deformation of the pseudoatoms *or* the presence of intrinsic temperature dependence in the rigid-pseudoatom scattering factors. In principle, it is impossible to separate these two effects if only elastic scattering is used, since this measures the instantaneous electron density averaged over time. However, one can speculate that when one of these two effects is dominant, they may, in practice, be distinguished by the nature of the effect. More specifically, if the measured $\mathcal{B}_{\kappa}(\mathbf{k})$ implied greater localization of the

electron density with increase in temperature, one would tend to infer that it was because of dynamic deformation with the valence charge being 'left behind' in the nuclear motion (see also § 5), whereas if the measured $\mathcal{B}_{\kappa}(\mathbf{k})$ implied delocalization of the electron density with increase in temperature, one would tend to infer that it was because of intrinsic change in the rigid-pseudoatom electron densities. Ultimately, these effects might be distinguished by use of inelastic-scattering data or by recourse to particular physical models (Chelikowsky & Cohen, 1974).

4.1.1. High-temperature form for $\mathcal{B}_{\kappa}(\mathbf{k})$

Concerning the temperature dependence of the deformation factors \mathcal{B}_{κ} in (14) and (16), it should be noted that the β parameters are themselves temperature-independent (by hypothesis) so that all temperature dependence of \mathcal{B}_{κ} 's given by (15) enters *via* the vibrational correlation functions $\langle \mathbf{u}_{l\kappa} \mathbf{u}_{l'\kappa'} \rangle$. It is thus useful to find (see Appendix B) that at high temperatures ($T > \theta_M$, where θ_M is the Debye characteristic temperature), where the effects of deformation will usually be largest, these vibrational correlation functions, evaluated in the harmonic approximation, scale as T ; or put another way, they scale as the elements of the self-correlation function $\langle \mathbf{u}_{l\kappa} \mathbf{u}_{l\kappa}^{\dagger} \rangle$ ($= \mathbf{B}_{\kappa}/8\pi^2$, where \mathbf{B}_{κ} is the thermal-vibration matrix), so that one may write

$$\mathcal{B}_{\kappa}(\mathbf{k}, T) = \mathbf{k}^{\dagger} \langle \mathbf{u}_{l\kappa} \mathbf{u}_{l\kappa}^{\dagger} \rangle \mathcal{B}_{\kappa}^0(\mathbf{k}) \\ = \mathbf{k}^{\dagger} [\mathbf{B}_{\kappa}(T)/8\pi^2] \mathcal{B}_{\kappa}^0(\mathbf{k}), \quad (17)$$

where \mathcal{B}_{κ}^0 is defined by equating individual terms between (15) and (17), and will only be temperature-independent in the high-temperature régime. We note that in the high-temperature régime, application of (17) involves using *only* standard crystallographic thermal-vibration data, and so constitutes a significant simplification of (15).

4.2. Self-deformation approximation for $\mathcal{B}_{\kappa}(\mathbf{k})$

Although the present formalism is in a suitable form to be used to analyse high-temperature X-ray data for the effects of deformation, the values of the $\mathcal{B}_{\kappa}^0(\mathbf{k})$ thus obtained would seem to be difficult to interpret physically, because they involve a complicated mixture of vibrational and pure dynamic deformation contributions (β). For this reason, we present in this subsection a simple, though fairly drastic, approximation to the $\mathcal{B}_{\kappa}(\mathbf{k})$. This approximation is valuable, among other reasons, because it provides a simple picture for the effect of dynamic deformation on elastic X-ray scattering.

The approximation which we now make in (15) is to assume that the main contribution to $\mathcal{B}_{\kappa}(\mathbf{k})$ comes from self-correlations, *i.e.* from the diagonal terms

where $l = l'$ and $\kappa = \kappa'$. This approximation* may be written as

$$\beta_{\kappa}(\mathbf{k}) \simeq \mathbf{k}^{\dagger} \langle \mathbf{u}_{l\kappa} \mathbf{u}_{l\kappa}^{\dagger} \rangle \beta(0, \kappa \kappa, \mathbf{k}). \quad (18)$$

That (18) should be a reasonable approximation for many systems follows from the following considerations. (i) Optic modes, when present, may be expected to produce most of the dynamic deformation,† since for such modes neighbouring atoms tend to move out of phase. Moreover, for optic-mode branches a reasonable first approximation to the phonon dispersion surface is $\omega(\mathbf{q}) = \text{constant}$, suggesting N identical Einstein oscillators which, as shown in Appendix B, would lead to the result

$$\langle \mathbf{u}_{l\kappa} \mathbf{u}_{l'\kappa'}^{\dagger} \rangle = \delta_{ll'} \delta_{\kappa\kappa'} \langle \mathbf{u}_{l\kappa} \mathbf{u}_{l\kappa}^{\dagger} \rangle, \quad (19)$$

and would make (18) exact for the deformation contribution of such branches. In (19) $\delta_{ll'}$ and $\delta_{\kappa\kappa'}$ denote Kröneckers deltas.

(ii) The self-deformation term $\beta(0, \kappa \kappa, \mathbf{k})$ appears, from the limited data available, to be the largest term (see also Reid, 1974, p. 3449). Evidence for this comes from the results of Reid (1974) for NaCl and NaF. First, one can see from Reid's Fig. 5 that the value of $|\beta(l', \kappa \kappa', \mathbf{k})|$ decreases fairly smoothly with increase in distance $R_{l\kappa}$ from the given site. Second, from Reid's Fig. 5 and values of $\beta(0, \kappa \kappa, \mathbf{k})$ given in the text, the ratio of the self-deformation to the nearest neighbour β at $\mathbf{k} = 2\pi/a(1.6, 0, 0)$ is estimated to be approximately 15 for F^- in NaF and 1.5 for Cl^- in NaCl.

In summary, one may reasonably expect that, for many systems, the main contribution to (15) will come from the self-correlation term (with the vibrational average taken only over those modes which contribute significantly to the deformation), since for this term both the vibrational and β contributions may be expected to be largest. The approximation may be expected to be best in the high-temperature régime and also in the zero-point régime, since optic modes will tend to make their greatest relative contribution at these extremes of the temperature range. In

* The referee has pointed out that the approximation (18) does not satisfy the uniform translation condition of (7) exactly (*i.e.* it is probably poor for long-wavelength acoustic modes). In view of (7), this problem can readily be overcome by modifying the approximation (18) to specifically exclude such modes when evaluating $\langle \mathbf{u}_{l\kappa} \mathbf{u}_{l\kappa}^{\dagger} \rangle$; however, we do not wish to further complicate matters by developing this aspect here.

† This conjecture is supported by the shell-model calculations of Reid (1974) for NaCl and NaF (his Figs. 1 and 2, respectively), granted the following interpretation of Reid's curves. First, the quantity plotted is the ratio of relative shell displacement to core displacement for the given anion in various vibrational modes. Second, the portions of the phonon branches where the ratio of displacements goes to infinity are taken to reflect the fact that the anion displacement goes to zero there, rather than indicating any abnormally large relative shell displacement. Third, we suggest that a reasonable estimate of the magnitude of the relative shell displacement can roughly be gauged from Reid's curves, by continuing these smoothly through the apparent singularity.

particular, one may expect the approximation to be useful for terminally bonded hydrogens. Comparison of (17) with (18) suggests that one may regard β_{κ}^0 as an effective self-deformation Born β parameter, *i.e.* as an effective $\beta(0, \kappa \kappa, \mathbf{k})$ 'dressed' to take into account the normal modes of vibration of the system.

4.2.1. Simple cubic lattice

In this subsection we give a particular application of (18) in order to help give some feeling for the nature of β and its effect on $\langle F \rangle$. We consider the case of a monatomic solid with a simple cubic lattice.

From (16) and (18) it follows that the kinematic Bragg intensity for this system is proportional to

$$I(\mathbf{k}) = |f^0(\mathbf{k})|^2 [1 + ik(B/8\pi^2)(\beta(0, \mathbf{k}) - \beta^{\dagger}(0, \mathbf{k}))] \times \exp\{- (B/8\pi^2)k^2\} \sum_{\mathbf{G}} \delta(\mathbf{k} - \mathbf{G}), \quad (20)$$

where some obvious simplification of the notation has been effected. Using some properties of Fourier transforms, it follows from (5), plus the fact that σ is real and σ^0 is centrosymmetric, that

$$\beta(l' - l, \kappa' \kappa, \mathbf{k}) = \beta_e(l' - l, \kappa' \kappa, \mathbf{k}) + i\beta_o(l' - l, \kappa' \kappa, \mathbf{k}), \quad (21)$$

where β_e and β_o are real-even and real-odd functions of \mathbf{k} respectively. Using (21), we can rewrite (20) as

$$I(\mathbf{k}) = |f^0(\mathbf{k})|^2 \exp\{- (B/8\pi^2)k^2\} \times [1 - 2k(B/8\pi^2)\beta_o(\mathbf{k})] \sum_{\mathbf{G}} \delta(\mathbf{k} - \mathbf{G}) \quad (22)$$

so that, to leading order in the deformations, only the imaginary-odd component of β contributes. This anti-symmetric deformation contribution may be visualized as arising in a shell model where the shell radius is fixed (rigid-shell model), and deformation takes place only by rigid motion of the shell charge relative to the core charge. On the other hand, the non-contributing real-symmetric component $\beta_e(\mathbf{k})$ may be visualized as arising from a shell model in which a 'breathing' distortion takes place without any relative motion of the shell and core centroids. Buyers *et al.* (1968) considered only this latter type of term for the alkali halides, which explains why they predicted no effect of deformation on the Bragg scattering [for alkali halides the expression for $I(\mathbf{k})$ is similar to (22)] to first order in the deformations.

Intuitively one might expect dynamic deformation of the pseudoatoms to lead to a difference in the Debye-Waller factor as measured by X-rays relative to that measured with neutrons. Invoking the results developed earlier, a change in the X-ray Debye-Waller factor can be seen to be a reasonable representation of the effect of deformation, because [see also equation (3) of Reid (1974)]

$$\beta_o(\mathbf{k}) \simeq \beta_o \mathbf{k} \quad \text{for small } k, \quad (23)$$

so that one may define an *effective* Debye–Waller factor for X-rays to be

$$B_{\text{eff}}(\mathbf{k}) = B + \Delta B(\mathbf{k}), \quad (24)$$

where

$$\Delta B(\mathbf{k}) = 2B \beta_o(\mathbf{k})/k \simeq 2\beta_o B. \quad (25)$$

Physically, the difference is possible because the X-ray Debye–Waller factor (B_{eff}) relates to the time-averaged electron-density distribution, whereas the neutron-measured Debye–Waller factor (B) relates to the time-averaged nuclear (or rigid-core) distribution.

It should be appreciated that (23) is an approximate representation for $\beta_o(\mathbf{k})$, which is only valid for small k . Higher-order terms in $\beta_o(\mathbf{k})$ than those included in (23) must lead to a departure of B_{eff} from the simple form outlined above, since $\beta(\mathbf{k})$ tends to zero as $k \rightarrow \infty$ [equation (8)]. Note however that (23) has only been introduced to suggest that (24) provides a useful way of representing the effect of deformation, and does not imply the introduction of any additional approximation so far as (24) and the equality in (25) are concerned.

A similar modification of the Debye–Waller factor to that given above would also obtain if the high-temperature result (17) were adopted instead of (18); i.e. if $\beta(0, \kappa\kappa, \mathbf{k})$ were replaced by $\beta_{\kappa}^0(\mathbf{k})$.

5. Results for dynamic deformation in alkali halides

Some estimates of the likely magnitude of ΔB for two alkali halides have been made, by use of the self-deformation approximation with the shell-model calculations of β_o carried out by Reid (1974). For NaCl and NaF, Reid gave values for $\beta_o(0, \kappa\kappa, \mathbf{k})$ at the point $\mathbf{k} = 2\pi/d$ (1.6, 0, 0) in the zone, where d is the unit-cell spacing. These values are presented here in Table 1. Using these values in (25) (which also obtains for the NaCl structure), the values for $\Delta B/B$ recorded in Table

Table 1. *Values for the generalized Born β parameters as calculated by Reid (1974) and the consequent effect on the effective Debye–Waller factor derived via (25)*

All values are for $\mathbf{k} = 2\pi/d$ (1.6, 0, 0).

Case	$\beta_x(l = 0, \kappa\kappa, \mathbf{k})^*$ (\AA^{-1})	$\Delta b/B$
1. NaCl		
Na	0	0
Cl	-0.0218	-0.024
2. NaF		
Na	-0.0019	-0.002
F	-0.039	-0.036

* β_x denotes the x Cartesian component of β .

1 were obtained. From these results, it can be seen that the antisymmetric deformation of the ions leads to a reduction in their effective Debye–Waller factor, corresponding to the outer electrons being ‘left behind’ in the nuclear vibrations. It appears from the present calculations that the magnitude of the effect is such as to be measurable in highly accurate studies (Pryor, 1966), and so should be taken into account in the interpretation of such data.

6. Summary and conclusions

Methods have been developed for treating the elastic X-ray scattering from solids containing deformable pseudoatoms. These methods make use of the generalized Born β parameters introduced by Melvin *et al.* (1968). The present methods may be used to investigate the effect of dynamic deformation either theoretically, by calculation from force models fitted to phonon-dispersion curves, or experimentally, by refining structure-factor measurements at two or more temperatures.

Theoretical estimates for the magnitude of the effect in: some alkali halides (§ 5), H_2 (Coulson & Thomas, 1971), and H_2^+ (Thomas, 1973) suggest that, although small, the effect is measurable in highly accurate studies. Since the magnitude of the dynamic deformation of a pseudoatom is closely related to its electronic polarizability, it is possible to suggest substances for which the effect may be expected to be somewhat greater than for NaCl and NaF discussed above, such as LiH, LiF, and organic solids containing terminally-bonded hydrogens.

In conventional electron-density determinations, the quantity which one attempts to isolate is $f_{\kappa}^0(\mathbf{k})$, giving the static electron density of the κ th pseudoatom when *all* atoms are in their equilibrium positions. The present investigation reveals that conventional analysis more correctly gives a quantity of the form $f_{\kappa}^0 \exp\{-\Delta B(\mathbf{k})/16\pi^2\}$, where for small k , $\Delta B(\mathbf{k})$ resembles a Debye–Waller factor. Thus, residual temperature dependence in conventionally refined scattering factors is an indication that dynamic deformation may be present. Although some hint that the rigid-pseudoatom approximation has broken down may be gained from data at one temperature (*e.g.* presence of extremely sharp dipoles in static deformation-density determination), such effects can always be subsumed into the model for σ_{κ}^0 , physically unrealistic though the result may seem. The present work shows how, by using elastic X-ray scattering measurements at more than one temperature, one may hope to identify the presence of dynamic deformation.

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APPENDIX A

Our aim here is to show that

$$\langle \mathbf{u}_{l'\kappa'} \exp\{i\mathbf{k} \cdot \mathbf{u}_{l\kappa}\} \rangle = i \langle \mathbf{u}_{l'\kappa'} \mathbf{u}_{l\kappa}^\dagger \rangle \mathbf{k} \langle \exp\{i\mathbf{k} \cdot \mathbf{u}_{l\kappa}\} \rangle \quad (A1)$$

in the harmonic approximation.

Proof. We start by considering the one-dimensional case and simplify the notation by taking $X \equiv u_{l'\kappa'}$ and $Y \equiv u_{l\kappa}$. Then, using the method of expanding the characteristic function of a distribution in cumulants (Kubo, 1962), we may write

$$\langle \exp\{ihX + ikY\} \rangle = \exp \left\{ \sum'_{\nu, \lambda} \frac{(ih)^\nu (ik)^\lambda}{\nu! \lambda!} \langle X^\nu Y^\lambda \rangle_c \right\}, \quad (A2)$$

where the prime on the summation indicates that the case $\nu = \lambda = 0$ is to be omitted, while $\langle \rangle_c$ denotes the cumulant average.

Another result which is useful here is the relation

$$\langle X \exp\{ikY\} \rangle = \frac{1}{i} \frac{\partial}{\partial h} \langle \exp\{ihX + ikY\} \rangle_{h=0}. \quad (A3)$$

Now, for the case where X, Y are random variables belonging to a multivariate normal distribution (which occurs when the harmonic approximation obtains), only cumulants up to second order are non-zero, so that (A2) becomes simply

$$\langle \exp\{ihX + ikY\} \rangle = \exp\left\{-\frac{1}{2}(h^2 \langle X^2 \rangle + 2hk \langle XY \rangle + k^2 \langle Y^2 \rangle)\right\}. \quad (A4)$$

From (A3) and (A4) it then follows that

$$\langle X \exp\{ikY\} \rangle = ik \langle XY \rangle \exp\left\{-\frac{1}{2}k^2 \langle Y^2 \rangle\right\} = ik \langle XY \rangle \langle \exp\{ikY\} \rangle, \quad (A5)$$

which when generalized to three dimensions becomes the required result (A1). Note that it may readily be shown that (A5) is valid when $X \equiv Y$.

APPENDIX B

On generalizing equation (7.7.30) of Maradudin, Montroll & Weiss (1963) to the case of many atoms in a unit cell, one finds that at high temperature the instantaneous (*i.e.* relative time $t = 0$) two-particle displacement correlation function in the harmonic approximation is given by

$$\langle \mathbf{u}_{l\kappa} \mathbf{u}_{l'\kappa'}^\dagger \rangle = \frac{kT}{N\sqrt{M_\kappa M_{\kappa'}}} \operatorname{Re} \left[\sum_{\mathbf{q}} \frac{\mathbf{e}(\kappa|\mathbf{q}) \mathbf{e}^\dagger(\kappa'|\mathbf{q})}{\omega_j^2(\mathbf{q})} \times \cos(\mathbf{q} \cdot (\mathbf{R}_{l\kappa} - \mathbf{R}_{l'\kappa'})) \right], \quad (B1)$$

where M_κ denotes the mass of the κ th atom in the unit cell, while $\mathbf{e}(\kappa|\mathbf{q})$ is the eigenvector for the displacement of this atom when vibrating in the phonon mode of wave vector \mathbf{q} in branch j .

From (B1) it follows firstly that the ratio

$$\langle \mathbf{u}_{l\kappa, \mu} \mathbf{u}_{l'\kappa', \mu'} \rangle / \langle \mathbf{u}_{l\kappa, \mu} \mathbf{u}_{l\kappa, \mu'} \rangle$$

is independent of T , and this justifies (18).

Secondly, one can see from (B1) and the closure condition for the lattice functions, that (20) will hold for branches of the dispersion surface for which $\omega_j(\mathbf{q}) = \text{constant}$, at least to the extent that one may make the assumption that $\mathbf{e}(\kappa|\mathbf{q}) \mathbf{e}^\dagger(\kappa'|\mathbf{q})$ is independent of \mathbf{q} (as for example in the Einstein approximation). Examination of equation (7.7.29) of Maradudin *et al.* (1963) reveals that (20) remains valid when the complete range of temperatures is considered.

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