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X-Ray Scattering from Deformable Ions

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Measurements of x-ray diffuse scattering by phonons in three alkali halides show that the usual scattering theory which assumes rigid ions is not adequate. The generalization of the theory to account for the deformation of the ions is given, and leads, in the case of x-ray scattering, to intensities consistent with those observed. The new terms in the scattering are due to the x-ray Raman effect. The measurements indicate that for NaCl a change of about 2% in the scattering factor of the negative ion occurs for a 0.1 Å change in the distance of its nearest-neighbor ion. It is shown that the core-shell displacements of the shell model are too small to explain the observed magnitude of the deformation, and that changes in the radial charge density of an ion are required.

1. INTRODUCTION

THE method of obtaining information on the lattice dynamics of crystals from measurements of x-ray scattering cross sections is well known. It consists in utilizing the relationship between the x-ray thermal cross section and the phonon frequencies and eigenvectors. This method has been applied to many monatomic crystals[1–4] and to a few diatomic materials including Si,[5] NaCl,[6] and NaF.[7] The relationships which have been used by earlier workers are obtained by assuming the form factors of the ions are independent of the nuclear coordinates of their neighbors. This will be called the rigid-ion scattering theory. Our recent measurements[6,8] have shown that this simplification is not justified, and that the use of the simple theory for the analysis of measurements can lead to errors of as much as 10% in the frequencies deduced. The purpose of this paper is to investigate to what extent our experimental results on alkali halides may be described by a scattering theory in which ionic deformation is considered.

Section 2 contains an outline of the general scattering theory for deformable ions, with account taken, to lowest order in the deformation, of the dependence of form factor on neighboring ion positions. The application of the theory to alkali halides is also given. In Sec. 3 our measurements for alkali halides are compared with the generalized theory, and provide an estimate of the form-factor modification. Finally we discuss in Sec. 4 the modification expected for the shell model.

2. SCATTERING THEORY FOR DEFORMABLE ATOMS

A. General Theory

As a function of applied frequency Ω and momentum transfer $\hbar\mathbf{Q}$ the intensity of scattering from a crystal may be written[9]

$$I=\sum_{ll'}\sum_{kk'}\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\psi|W_{lk}^{*}(t)W_{l'k'}(0)$$

$$\times e^{-i\mathbf{Q}\cdot\mathbf{x}(lk,t)}e^{i\mathbf{Q}\cdot\mathbf{x}(1'k',0)}$$

$$\times e^{i\Omega t}|\psi\rangle dt\, e^{-i\mathbf{Q}\cdot[\mathbf{R}(lk)-\mathbf{R}(l'k')]}. \quad (1)$$

The symbol $\langle\psi|\mathrm{O}|\psi\rangle$ denotes the thermal average of the O operator. This expression applies to phonon scattering of both neutrons and x rays. The displacement $\mathbf{x}(lk,t)$ of the kth nucleus within the lth unit cell is measured from its lattice site $\mathbf{R}(lk)$.

To obtain the various orders of scattering the expression (1) is expanded in terms of phonon coordinates $A(\mathbf{q}j,t)$ using

$$\mathbf{x}(lk,t)=\sum_{\mathbf{q}j}\mathbf{U}(k|\mathbf{q}j)e^{i\mathbf{q}\cdot\mathbf{R}(lk)}\left(\frac{\hbar}{2Nm_k\omega(\mathbf{q}j)}\right)^{1/2}A(\mathbf{q}j,t). \quad (2)$$

Usually the scattering factors W_{lk} are assumed to be independent of the nuclear displacements so that only the exponentials in Eq. (1) are expanded. This is the case for neutrons where the scattering is from the nucleus, whose scattering length is characteristic of the nucleus itself. For certain radiation, such as x-rays, however, the scattering factor involves the Fourier transform of the electronic charge density, the outer part of which is known to depend on the position of neighboring atoms. We therefore make the assumption that the scattering factor can be expanded as a power series in the nuclear displacements and a set of atomic deformation parameters. We ignore all but scalar changes in the scattering factor, as it is expected that the off-diagonal elements of the atomic polarizability

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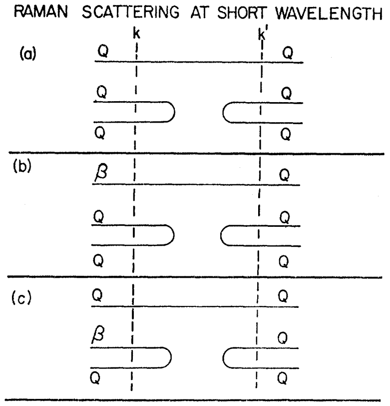

FIG. 1. The diagrams contributing to one-phonon inelastic scattering from a crystal with deformable ions: (a) the scattering from the undeformed ions; (b) the extra scattering due to an atomic deformation in phase with a nuclear displacement; (c) the Debye-Waller type of modification to the scattering from a deformed atom.

tensor will remain small. Retaining only the leading term in the power series for W_{lk}, we write

$$W_{lk}(t)=W_k[1+\sum_{l'k'}\boldsymbol{\beta}(l-l',kk')\cdot\mathbf{x}(l'k',t)]$$

$$=W_k[1+\sum_{\mathbf{q}j}\beta(k|\mathbf{q}j)e^{i\mathbf{q}\cdot\mathbf{R}(lk)}A(\mathbf{q}j,t)], \quad (3)$$

where

$$\beta(k|\mathbf{q}j)=\sum_{l'\mathbf{k}'}\boldsymbol{\beta}(l-l',kk')\cdot\mathbf{U}(k'|\mathbf{q}j)\left\{\frac{\hbar}{2Nm_{k'}\omega(\mathbf{q}j)}\right\}^{1/2}$$

$$\times e^{-i\mathbf{q}\cdot[\mathbf{R}(lk)-\mathbf{R}(l'k')]}. \quad (4)$$

The different β coefficients are different transformations of the atomic deformation parameters. For example, we shall require later the coefficient

$$\boldsymbol{\beta}(\mathbf{q},kk')=\sum_{l'}\boldsymbol{\beta}(l-l',kk')e^{-i\mathbf{q}\cdot[\mathbf{R}(lk)-\mathbf{R}(l'k')]} \quad (5)$$

in terms of which Eq. (4) might have been written.

The scattered intensity may now be written

$$I=\sum_{kk'}\sum_{ll'}e^{-i\mathbf{Q}\cdot[\mathbf{R}(lk)-\mathbf{R}(l'k')]}W_k{}^*W_{k'}$$

$$\times\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\psi|S(ll',kk',t)e^{i\Omega t}|\psi\rangle dt, \quad (6)$$

where

$$S(ll',kk',t)=\{1+\sum_{\mathbf{q}_1j_1}\beta(k|\mathbf{q}_1j_1)e^{i\mathbf{q}_1\cdot\mathbf{R}(lk)}A(\mathbf{q}_1j_1,t)\}$$

$$\times\exp[-i\sum_{\mathbf{q}j}Q(k|\mathbf{q}j)e^{i\mathbf{q}\cdot\mathbf{R}(lk)}A(\mathbf{q}j,t)]$$

$$\times\exp[+i\sum_{\mathbf{q}'j'}Q(k'|\mathbf{q}'j')e^{i\mathbf{q}'\cdot\mathbf{R}(l'k')}A(\mathbf{q}'j',0)]$$

$$\times\{1+\sum_{\mathbf{q}_2j_2}\beta(k'|\mathbf{q}_2j_2)e^{i\mathbf{q}_2\cdot\mathbf{R}(l'k')}A(\mathbf{q}_2j_2,0)\}, \quad (7)$$

and

$$Q(k|\mathbf{q}j)=\mathbf{Q}\cdot\mathbf{U}(k|\mathbf{q}j)\left\{\frac{\hbar}{2Nm_k\omega(\mathbf{q}j)}\right\}^{1/2}. \quad (8)$$

Since Eq. (6) has the form of a spectral density function of the operators occurring within the thermal average we may use a diagram technique[10] to enumerate the various terms occurring in the intensity when the exponentials in Eq. (7) are expanded.

Although the evaluation of Eq. (6) is straightforward for phonon processes of any order, we shall indicate the development only for the case of immediate interest, that of one-phonon processes. The types of diagram contributing to the one-phonon scattering, ignoring terms higher than linear in β, are shown in Fig. 1. Fig. 1(a) shows the usual one-phonon line, 1(b) is the extra scattering due to the modified scattering factors, and 1(c) gives the change in scattering factor of an atom analogous to a Debye-Waller factor. Fig. 1(b) corresponds to the intensity produced when the change in scattering power of atom k, due to its deformation by the phonon $(\mathbf{q}j)$ passing through the crystal, is in phase (for momentum $\hbar\mathbf{Q}$) with the change in scattering from atom k' due to its bodily displacement. Since Fig. 1(c) arises because the scattering factor of an atom is changed by the presence of all the lattice modes, we have described it as analogous to the Debye-Waller factor. However, it is not included in the exact summation of all loops which may be added to (a), (b), (c) to give the exponential form of Debye-Waller factor. Nevertheless, it may be shown that the remaining loops which can be attached to the left side of Fig. 1(c) sum in the same way as those of Figs. 1(a) and 1(b) to give the usual Debye-Waller factor e^{-M_k}.

The one-phonon terms then lead to the following form for the intensity:

$$I=N^2\sum_{kk'}\sum_{\mathbf{q}j}\Delta(\mathbf{Q}-\mathbf{q},\boldsymbol{\tau})W_k{}^*e^{-M_k}e^{-i\tau\cdot\mathbf{R}_k}W_{k'}e^{-M_{k'}}e^{+i\tau\cdot\mathbf{R}_{k'}}$$

$$\times[(n(\mathbf{q}j)+1)\delta(\Omega-\omega(\mathbf{q}j))$$

$$+n(\mathbf{q}j)\delta(\Omega+\omega(\mathbf{q}j))]\times F(kk',\mathbf{q}j). \quad (9)$$

The structure factor $F(kk',\mathbf{q}j)$ consists of contributions from each of the three classes of diagrams of Fig. 1. Class (a) results in the usual structure factor,

$$Q(k|\mathbf{q}j)Q(k'|-\mathbf{q}j). \quad (10)$$

Class (b) introduces the terms

$$i\beta(k|\mathbf{q}j)Q(k'|-\mathbf{q}j)-iQ(k|\mathbf{q}j)\beta(k'|-\mathbf{q}j), \quad (11)$$

while the class (c) diagrams introduce

$$-(iB_k-iB_{k'})Q(k|\mathbf{q}j)Q(k'|-\mathbf{q}j), \quad (12)$$

where

$$B_k=\sum_{\mathbf{q}'j'}\beta(k|\mathbf{q}'j')Q(k|-\mathbf{q}'j')(2n(\mathbf{q}'j')+1). \quad (13)$$

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[10] R. A. Cowley, Advan. Phys. 12, 421 (1963).

When the sum of expressions (10)–(12) are substituted in $F(kk',\mathbf{q}j)$ of Eq. (9) the result is the one-phonon scattering correct to lowest order in the atomic deformation parameters, β.

$$\begin{aligned}F(kk',\mathbf{q}j)=&Q(k|\mathbf{q}j)Q(k'|-\mathbf{q}j)(1-iB_k+iB_{k'})\\&+i\beta(k|\mathbf{q}j)Q(k'|-\mathbf{q}j)-iQ(k|\mathbf{q}j)\beta(k'|-\mathbf{q}j)\,.\end{aligned}\tag{14}$$

The factor $(1-iB_k+iB_{k'})$ is a modification to the normal [class (a)] scattering, and is similar to a modified Debye-Waller factor. The second and third terms give rise to extra scattering.

For elastic scattering it may also be shown that the product of the two Debye-Waller factors is replaced by

$$e^{-M_k}e^{-M_{k'}}(1-iB_k+iB_{k'})\tag{15}$$

in the expression for the intensity. The extra terms are seen to be the same as those occurring in Eq. (14), demonstrating that what we have called the Debye-Waller type of modification to the scattering, is the same for elastic and inelastic processes.

The new terms in the scattering are simply due to the first-order Raman effect at short wavelengths. The effect is analogous to the Raman scattering of infrared radiation, although at these long wavelengths no Debye-Waller terms appear, since the exponentials in Eq. (1) are unity.

Born[11] in 1942 drew attention to the dependence of the atomic scattering factors on nuclear configuration. He suggested a method by which the modified expression for x-ray scattering could be obtained but did not work it out in detail. Cowley[10] also noted the effect but did not evaluate the expression for the scattering. The present treatment, which does not use Born's method, brings out the physical significance of the various terms contributing to the Raman effect, at short wavelengths, and gives detailed expressions for them.

The effect described in this section is relevant to x-ray scattering from solids and liquids, and to the scattering of electrons by the pseudopotential in metals. A similar effect should occur for neutron scattering by magnetic systems. There is also a formal similarity to the effects with an alloy with combined lattice parameter and scattering modulation.[12]

The discussion in this section has assumed the scattering to be caused by transitions between the crystal vibrational levels as in the Raman scattering of visible light. However, because of the greater energy in the x-ray region of the electromagnetic spectrum, Raman scattering may also be caused by transitions between electronic levels. The scattering theory of this section may be modified to include this effect. Evidence for Raman scattering involving electronic levels has been obtained by Das Gupta.[13] In what follows we shall be concerned only with the scattering involving vibrational levels.

B. X-Ray Effect in Alkali Halides

In the usual x-ray experiment the apparatus detects all the scattered frequencies so that Eq. (9) must be integrated over Ω to give a factor of $2n(\mathbf{q}j)+1$.

Let us consider the properties of the atomic deformation parameters in alkali halides. The quantity $\boldsymbol{\beta}(l-l',kk')$ transforms as a vector in a lattice which has cubic point-group summetry at every atom, in which case $\boldsymbol{\beta}(\mathbf{q},kk')$ is a pure imaginary. Thus

$$\beta(k|-\mathbf{q}j)=\beta^*(k|\mathbf{q}j)\,,\tag{16}$$

since

$$\mathbf{U}(k'|-\mathbf{q}j)=\mathbf{U}^*(k'|\mathbf{q}j)\,,$$

and

$$Q(k|-\mathbf{q}j)=Q^*(k|\mathbf{q}j)\,.\tag{17}$$

Since the eigenvectors are real in an alkali halide, it may be shown that

$$B_k=0\,.\tag{18}$$

There is thus no Debye-Waller factor type of correction in an alkali halide, although there may be one in less symmetrical lattices.

Before evaluating the one-phonon terms of Fig. 1, we shall restrict the argument to the case where only nearest neighbors produce changes in the scattering factor of a central atom, k. Application of the symmetry operations of the point group shows that $\boldsymbol{\beta}(l-l',kk')$ lies along the line joining (lk) to $(l'k')$. This leads to the following equations, the second one defining a vector $\mathbf{v}(\mathbf{q})$,

$$\begin{aligned}\boldsymbol{\beta}(\mathbf{q},kk')&=2i\beta(k)[\sin(\pi\eta_x),\,\sin(\pi\eta_y),\,\sin(\pi\eta_z)](1-\delta_{kk'})\\&=2i\beta(k)\mathbf{v}(q)(1-\delta_{kk'})\,,\end{aligned}\tag{19}$$

where

$$\mathbf{q}=\frac{2\pi}{d}(\eta_x,\eta_y,\eta_z)\,.$$

$\beta(k)$ is the fractional change in scattering factor of the kth atom when one of its nearest neighbors is moved radially away from it by unit distance. The terms in expression (11) now become proportional to

$$\begin{aligned}&-2\beta(k)\sum_{k''}\mathbf{v}(\mathbf{q})\cdot\mathbf{U}(k''|\mathbf{q}j)(1-\delta_{kk''})\\&\qquad\qquad\times\mathbf{Q}\cdot\mathbf{U}(k'|\mathbf{q}j)/(m_{k''}m_{k'})^{1/2}\\&+2\beta(k')\sum_{k''}\mathbf{v}(-\mathbf{q})\cdot\mathbf{U}(k''|\mathbf{q}j)(1-\delta_{k'k''})\\&\qquad\qquad\times\mathbf{Q}\cdot\mathbf{U}(k|\mathbf{q}j)/(m_{k''}m_k)^{1/2}.\end{aligned}\tag{20}$$

Since there are only two atoms per unit cell ($k=1,2$), we will now write out the explicit expression for the intensity, after introducing the notation, customary in x-ray work, of $f_k=W_k$ for the scattering factor, $\mathbf{K}=-\mathbf{Q}$ for the scattering vector, and $\mathbf{H}=-\boldsymbol{\tau}$ for a vector of the reciprocal lattice. Thus the extra scatter-

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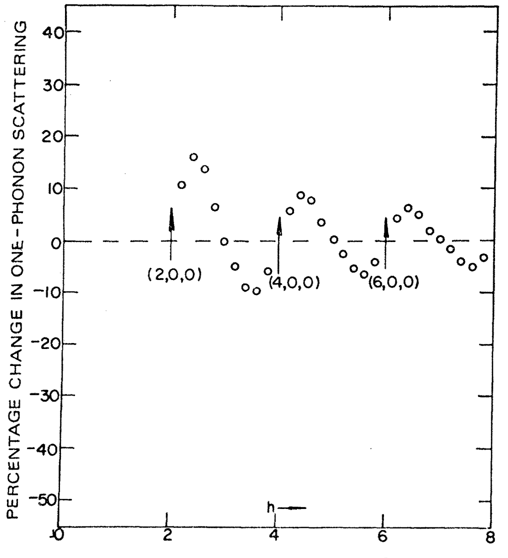

FIG. 2. The computed change in one-phonon scattering in NaCl along [100] when only the negative ion is deformable [β(Na) = 0, B(Cl) = −0.19].

ing is

$$I=N\sum_{\mathbf{q}j}\Delta(\mathbf{K}+\mathbf{q},\mathbf{H})\frac{\hbar}{\omega(\mathbf{q}j)}[n(\mathbf{q}j)+\tfrac{1}{2}]$$
$$\times 4\{f_1e^{-M_1}\mathbf{K}\cdot\mathbf{U}(1|\mathbf{q}j)/m_1^{1/2}$$
$$\pm f_2e^{-M_2}\mathbf{K}\cdot\mathbf{U}(2|\mathbf{q}j)/m_2^{1/2}\}$$
$$\times\{f_1e^{-M_1}\beta(1)\mathbf{v}(\mathbf{q})\cdot\mathbf{U}(2|\mathbf{q}j)/m_2^{1/2}$$
$$\pm f_2e^{-M_2}\beta(2)\mathbf{v}(\mathbf{q})\cdot\mathbf{U}(1|\mathbf{q}j)/m_1^{1/2}\}. \quad (21)$$

The upper (lower) sign is to be used in even (odd) zones. The expression shows that the temperature dependence of the extra scattering is the same as that of the usual one-phonon scattering in the rigid-ion scattering theory.

It is to be noted that the extra scattering is proportional to $\mathbf{v}(\mathbf{q})$, and therefore reverses in sign when $\mathbf{q}\rightarrow-\mathbf{q}$. This is the reason for the success of the averaging procedure used by Buyers and Smith[6] for deducing phonon frequencies from x-ray data.

For scattering in the symmetry directions [100], [110] and [111], interesting features of the scattering are revealed. In this case $\mathbf{v}(\mathbf{q})$ is parallel to $\mathbf{q}$, and $\boldsymbol{\mu}$ is either parallel or perpendicular to $\mathbf{q}$. Thus there is no x-ray Raman effect from transverse modes in symmetry directions. The effect is strongest for longitudinal modes, and takes the form of a harmonic modulation in the extra scattering.

The simplest situation is when only one ion, such as the negative one ($k=2$), deforms. Then the extra scattering from a longitudinal mode is proportional to

$$+4\beta(2)\mathbf{v}(\mathbf{q})\cdot\boldsymbol{\mu}(1|\mathbf{q}j)[f_2e^{-M_2}\mathbf{K}\cdot\mathbf{U}(2|\mathbf{q}j)$$
$$\pm f_1e^{-M_1}\mathbf{K}\cdot\mathbf{U}(1|\mathbf{q}j)]f_2e^{-M_2}. \quad (22)$$

In a radial symmetry direction, on the side of each reciprocal lattice point nearer the origin, the defining equation of wave-vector conservation,

$$\mathbf{K}+\mathbf{q}=\mathbf{H}, \quad (23)$$

results in a positive $v(\mathbf{q})$, so that the extra scattering has the sign of $\beta(2)$.

Cross sections have been computed from Eq. (22) for NaCl and NaF, using the vibrational data of Karo and Hardy for a deformation dipole (DD) model.[14] The calculation was performed for several values of the atomic deformation parameters. For the same values of $\beta(2)$ the percentage change in the two materials was very similar. Figure 2 shows the results in the [100] direction for NaCl. The curve corresponds to a $\beta(2)$ value of −0.19, that is to a change in the scattering factor of 1.9% for a 0.1 Å movement of the nearest neighbors. The curves show extrema, due to the harmonic form of $\mathbf{v}(\mathbf{q})$, at some distance from the Bragg peaks, and the increase above a peak ($\eta_x<0$) is nearly equal to the decrease at the corresponding point below the peak ($\eta_x>0$). The effects are larger at low angles and decrease from 15% near (200) to 5% near (800). If the effect of the deformation polarizability of the positive ion ($\beta(1)$) is also included the curves are similar, but there is some extra structure near the extrema (Fig. 3). The character of the curves is rather different for the [111] direction (Fig. 4). Here even and odd zones alternate, and the effects are only symmetrical about the Bragg peaks for reasonably small $\mathbf{q}$ and are still present at the zone boundary. This lack of symmetry is due to the rapid change of the

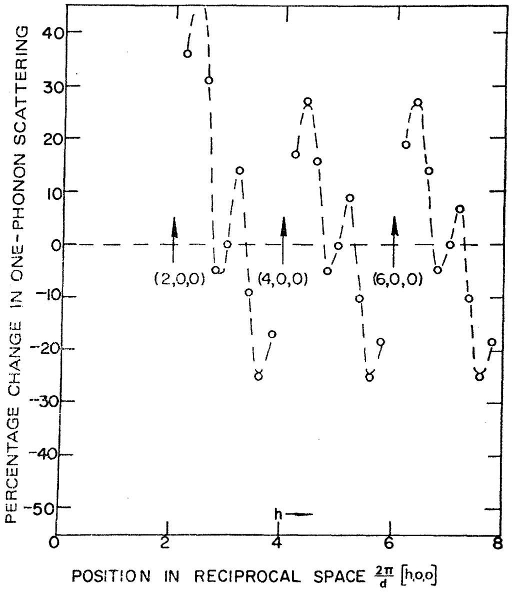

FIG. 3. The computed change in one-phonon scattering in NaCl along [100] when both ions are deformable [β(Na) = 0.19; β(Cl) = −0.19].

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[14] A. M. Karo and J. R. Hardy, Phys. Rev. 129, 2024 (1963).

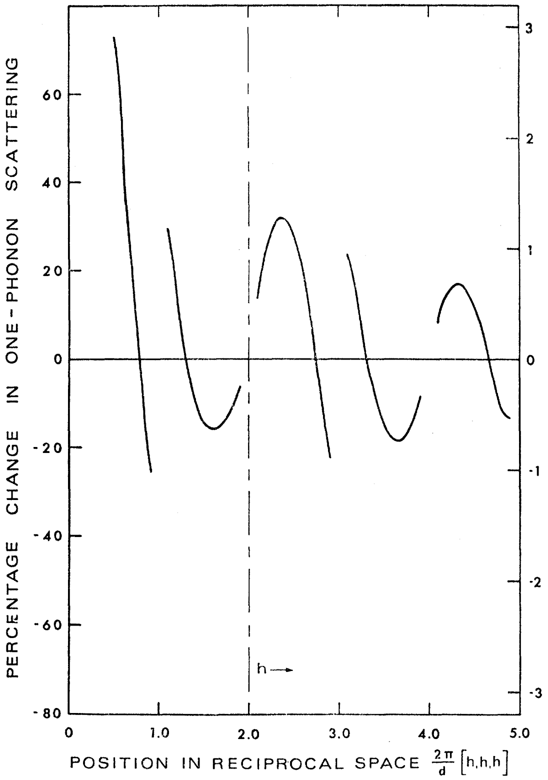

Fig. 4. The computed change in one-phonon scattering in NaCl along [111] when only the negative ion is deformable [β(Na) = 0, β(Cl) = −0.19].

structure factor with scattering vector **K**. This may be contrasted with the zone boundary on [100]. The difference between the changes due to deformation in even and odd zones can be varied by adjusting the atomic deformation parameters of both ions as shown in Fig. 5.

3. MEASUREMENTS ON NaCl, NaF, AND KCl

The measurements described below were made using apparatus which has already been described.[6] A detailed analysis of the angular and wavelength distribution in the incident beam was made, and it was found that the resulting resolution introduced corrections which were never greater than 2%. This relative unimportance of the divergence corrections was confirmed by reducing the incident beam divergence to 4 min of arc.

The total scattering cross section was measured for a particular **K**, and the Compton cross section was subtracted to give the total thermal cross section. This can then be compared with the total thermal cross sections computed[6] from theoretical DD eigenfrequency-eigenvector data using the rigid ion scattering theory. Any difference will result either from errors in the theoretical data, or from approximations in the method of computation of the higher-order processes or from the use of the rigid ion scattering theory. Figure 6 shows that for NaCl along [100], a difference between experiment and theory of up to 30% is found. The difference is not due to errors in computation resulting from the mesh size used for the multiphonon process. (This has been checked by varying the mesh size.) Errors in the dispersion curves of the DD model, or, indeed, of any vibrational spectrum, would result in percentage differences that are the same at **H**+**q** and **H**−**q**. However, it is seen from Fig. 6 that a modulation exists in the results which changes sign between **H**+**q** and **H**−**q**. Thus the measurements show clearly that the rigid-scattering theory is not adequate. This does not exclude the existence of errors in the theoretical dispersion curves, of course, but these errors lead to differences between computed and measured cross sections that are symmetrical in **q**, and smaller in magnitude than the antisymmetric differences observed. In Sec. 2B it has been shown that the extra scattering of the generalised scattering theory contains a modulation which is qualitatively similar to Fig. 6. We therefore associate the observed differences of Fig. 6 with the x-ray Raman effect.

It is now possible to use the observations to deduce approximate values for the atomic deformation parameters. The change between points of the form **H**+**q** and **H**−**q** in the percentage difference between the measured

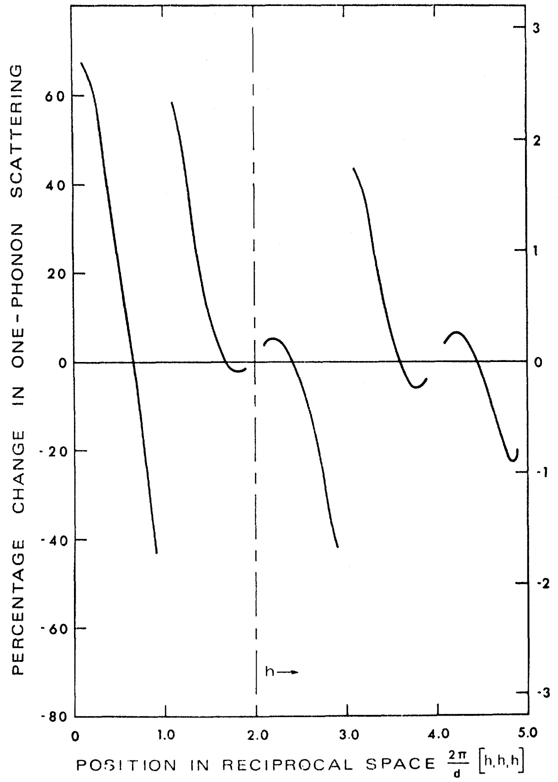

Fig. 5. The computed change in one-phonon scattering in NaCl along [111] when both ions are deformable [β(Na) = +0.19, β(Cl) = −0.19].

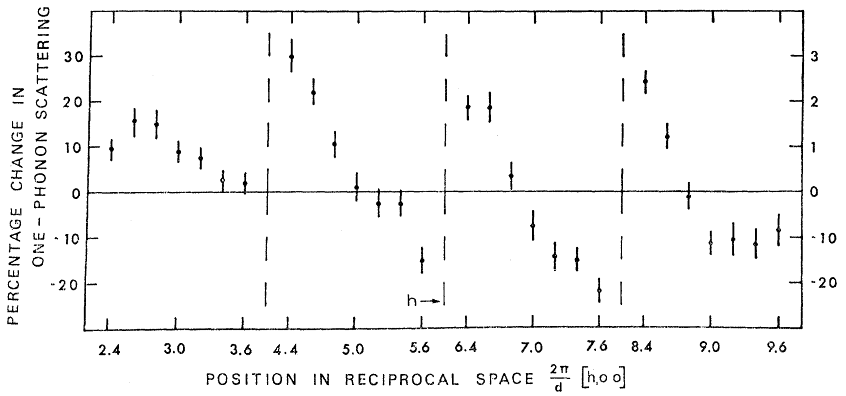

FIG. 6. Percentage difference along [100] in NaCl at 295°K between the total measured thermal scattering and that computed from the rigid atom scattering theory using vibrational data of the deformation dipole theory.

total thermal scattering and the rigid ion scattering predictions will be called the asymmetry for that value of **q**. It is independent of the vibrational data used for making the comparison. The values of the observed asymmetries in NaCl, NaF and KCl are given in Table I. Comparison of the observed asymmetry in NaCl at low scattering vectors with the predictions of Sec. 2B yields

$$\beta(2)=-0.19,$$

if only negative-ion deformation is considered. This corresponds to a 1.9% decrease in the scattering factor of the chlorine ion, where the distance to a neighboring sodium ion is increased by 0.1 Å. The value of $\beta(2)$ is very approximate as no detailed fitting was performed, but it illustrates the magnitude of the effect.

At large scattering vectors comparison with the theory of Sec. 2B is not valid, since the observed thermal scattering consists of a considerable fraction of multiphonon scattering. This may explain the difference between the computed Fig. 2 and the observations of Fig. 6; the magnitude of the modulation falls off less slowly than computed as the scattering vector increases and multiphonon processes begin to dominate. Calculations have not been made of the multiphonon cross section, as it is felt that most of the information on the deformation lies in the low-angle region where multiphonon processes are small.

TABLE I. Asymmetries in NaCl, NaF and KCl.

Material	Position below Bragg peak *h k l*	Position above Bragg peak *h k l*	Asymmetry (as defined in Sec. 3) %
NaCl	3.6 0 0	4.4 0 0	29±3
	3.4 0 0	4.6 0 0	20±3
	3.2 0 0	4.8 0 0	10±3
	5.6 0 0	6.4 0 0	35±3
	5.4 0 0	6.6 0 0	25±3
	5.2 0 0	6.8 0 0	10±3
	7.6 0 0	8.4 0 0	41±3
	7.4 0 0	8.6 0 0	30±3
	7.2 0 0	8.8 0 0	10±3
NaF	3.6 0 0	4.4 0 0	11±5
	3.4 0 0	4.6 0 0	3±5
	3.2 0 0	4.8 0 0	8±5
	5.6 0 0	6.4 0 0	34±5
	5.4 0 0	6.6 0 0	18±5
	5.2 0 0	6.8 0 0	7±5
KCl	3.6 0 0	4.4 0 0	27±5
	5.6 0 0	6.4 0 0	35±5

No asymmetry, outside the experimental accuracy, in the scattering from transverse modes has been observed in any of the crystals studied. This agrees with the prediction of Sec. 2B.

Some of the NaCl measurements were repeated at 120°K to investigate the temperature dependence of the asymmetry. No change was found in the measured asymmetry. This confirms, as predicted in Sec. 2*B*, that the temperature dependence of the extra scattering is the same as that of the usual one phonon expression, since the asymmetry depends on their ratio.

The above measurements show that the rigid ion scattering theory is not adequate for x-ray scattering from the alkali halides. The generalization of the theory for deformable ions must be used, and an atomic deformation parameter of about −0.2 is indicated for NaCl.

4. THE MAGNITUDE OF THE IONIC DEFORMATION

It has been shown above that the analysis of x-ray scattering provides direct evidence for the magnitude of mutual ionic deformation. Previous experimental studies of lattice dynamics have shown that atomic deformations play an important role in determining the phonon frequencies.[15] If one had detailed information on the nature of the deformation it would be possible, using a single set of parameters, to calculate its effect both on the phonon frequencies and on the scattering. One such model of the deformation, for which parameters are known, is the simple shell model.[16] In this section it is shown how the atomic deformation parameters of Sec. 2 are related to the shell-model parameters, and a discussion is given of the failure of the shell model to predict the observed asymmetry.

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[15] W. Cochran, Rept. Progr. Phys. **26**, 1 (1963).

[16] A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

The shell model is interpreted literally, so that the change in the scattering factor of an atom due to the movement of neighboring atoms arises because of the phase shift introduced between the core and the shell. The scattering factor may be written

$$f_k = f_k(c) + f_k(s)\exp\{i\mathbf{K}\cdot\mathbf{W}\}, \tag{24}$$

where $\mathbf{W}$ is the shell displacement relative to the core, $f_k(c)$ is the core scattering factor, and $f_k(s)$ is the scattering factor of the shell (calculated for the shell central about the core). The scattering factor with undisplaced shell is

$$f_k^0 = f_k(c) + f_k(s). \tag{25}$$

If we introduce

$$y_k = f_k(s)/f_k^0, \tag{26}$$

Eq. (25) can be rewritten

$$f_k = f_k^0[1 + iy_k\mathbf{K}\cdot\mathbf{W}], \tag{27}$$

when higher terms in $\mathbf{K}\cdot\mathbf{W}$ are omitted. The displacement of the shell of the (lk) atom can now be obtained from the shell model as

$$W_\alpha(lk) = \sum_{l'k'\gamma} \Phi(l-l',kk'\alpha\gamma)x_\gamma(l'k'). \tag{28}$$

Φ is a known combination of shell-model parameters which may easily be deduced from the simultaneous equations for cores and shells. Thus Eq. (27) becomes

$$f_k = f_k^0[1 + iy_k \sum_\gamma \sum_{l'k'\alpha} K_\alpha \Phi(l-l',kk'\alpha\gamma)x_\gamma(l'k')]. \tag{29}$$

This is similar in form to Eq. (3), and so for the shell model the γ component of $\boldsymbol{\beta}(\mathbf{q},kk')$ is

$$\beta_\gamma(\mathbf{q},kk') = \sum_{l'} iy_k \sum_\alpha K_\alpha \Phi(l-l',kk'\alpha\gamma) \times\exp\{-i\mathbf{q}\cdot[\mathbf{R}(lk)-\mathbf{R}(l'k')]\}. \tag{30}$$

For sodium chloride the values of the asymmetry were calculated from the known $\Phi(l-l',kk'\alpha\gamma)$. The shell scattering factor (and thus y_k) is the only quantity not determined by the shell-model, although the shell charge and atomic radius enable estimates to be made. For any reasonable values of the y_k the computed asymmetry was found to be an order of magnitude less than the measured value. The observations therefore indicate the inadequacy of the shell model in describing the scattering, although it contains most of the features necessary to give a good description of phonon frequencies.

Changes in the radial charge density are suggested by our results, as this will change the scattering factors directly, rather than indirectly through the phase shifts introduced between core and shell in the shell model. An extension of the shell model having this character has recently been proposed by Schroder.[17] It remains to be seen whether such a model is capable of predicting the correct phonon frequencies and the x-ray Raman effect.

5. SUMMARY

Experiments show that x-ray diffuse scattering is not described by the usual scattering theory which assumes rigid ions. A generalization of the theory for inelastic phonon scattering is described which includes the effects of deformation of the ions, and which leads to the x-ray Raman effect. The detailed expression for the one-phonon scattering which is obtained in this way, has almost the same shape in reciprocal space as the measured x-ray scattering in three alkali halides. For NaCl quantitative agreement between theory and experiment is reached when the deformation corresponds to a change of about 2% in the scattering factor of a negative ion for an 0.1 Å radial movement of it snearest neighbor. The form of the extra scattering as a function of wave vector justifies the use of the averaging procedure used by Buyers and Smith[6] to obtain phonon frequencies in NaCl.

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[17] U. Schroder, Solid State Commun. 4, 347 (1966).