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X-Ray Study of the Lattice Dynamics of Sodium Chloride

W. J. L. BUYERS* AND T. SMITH
Department of Natural Philosophy, University of Aberdeen, Aberdeen, Scotland

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Measurements have been made of the thermal diffuse x-ray scattering from sodium chloride. We describe our analysis of these results to give phonon frequencies in the [111] and [100] directions, and discuss the factors limiting the accuracy of the x-ray method. The frequencies are in good agreement with the theory for alkali halides in the dipole approximation, but not with the theory for rigid ions. At long wavelengths they are consistent to 2% with ultrasonic measurements, and also with the longitudinal optic frequency predicted from the Lyddane-Sachs-Teller relation. A new feature in the x-ray diffuse scattering has also been observed which, it is suggested, results from the dependence of the scattering factors of the ions on the nuclear coordinates.

I. INTRODUCTION

IN recent years the study of phonons in solids has been given considerable impetus by the ease with which their dispersion relations may be determined from the inelastic scattering of neutrons. This has led to a relative neglect of the x-ray method. However, as many materials cannot easily be studied by neutrons, it was decided to make a detailed examination of one such material using x-rays, in order to assess the value of the method.

The choice of sodium chloride was influenced by three considerations. Its x-ray properties are good, whereas it has a large absorption for neutrons. Also the theory for the lattice dynamics of alkali halides is sufficiently good for reliable estimates of the multiphonon processes to be made. These are necessary to obtain the one-phonon intensity from the observed intensity. Finally, a material with two atoms per unit cell was chosen, since several monatomic materials have been studied by Olmer,[1] Curien,[2] Jacobsen,[3] Joynson[4] and Walker.[5]

The first attempt to obtain complete dispersion curves for a diatomic material (AgCl) was made by Cole.[6] In his analysis, however, he found it necessary to use results obtained from a linear-chain model and frequencies based on the rigid-ion model of NaCl (Kellerman[7]). The first investigation of an alkali halide, apart from the early measurements by Laval[8] for KCl was the study by Meriel[9] of NaCl and KCl. However, the deduction of accurate frequencies from the intensities was hampered by the lack of a realistic model to estimate the relative vibrational amplitudes of the two ions in a particular mode. The corrections for multiphonon scatter were also very approximate, and the Compton estimate was obtained from room temperature readings by subtracting a theoretical thermal scatter. The resulting Compton curve, in common with other estimates current at that time, lies well below the calculations of Freeman,[10] with which more recent experimental determinations of Walker,[5] Boccara,[11] Corbeau[12] and Buyers and Smith[13] have been in agreement. It may be noted that the long-wavelength frequencies obtained by Meriel did not obey the Lyddane, Sachs, Teller[14] relation.

The only other x-ray investigation of an alkali halide is that of Boccara,[11] who made measurements on KCl at liquid-nitrogen temperatures in order to reduce the contributions of the multiphonon processes to the total scattering. To extract frequencies from the one-phonon intensity he employed a special theoretical model for the interatomic forces, in which the Coulomb interaction and the effects of ionic deformation were together taken into account by considering point ions with a charge less than unity. This "charge" differs from the usual effective charge e^* introduced by Szigeti.[15] It was treated as an adjustable parameter, and a value found so that when the ratio of acoustic to optic scattering predicted by the model was used in conjunction with the observed intensity to find either the acoustic or the optic frequency (assuming the amplitude ratio of the model), then these frequencies were also consistent with the model frequencies. Boccara found the value of e^* to be $0.32e$, where e is the electronic charge. His results do not satisfy the Lyddane-Sachs-Teller[14] relation.

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* Now at Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada.

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[11] N. Boccara, Compt. Rend. **250**, 1025 (1960); thesis, Faculté des Sciences de l'Université de Paris, 1961 (unpublished).

[12] J. Corbeau, Compt. Rend. **253**, 1553 (1961).

[13] W. J. L. Buyers and T. Smith, Acta Cryst. Suppl. **16**, A166 (1963).

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II. EXPERIMENTAL

A. Apparatus and Technique

In the following paragraphs a discussion is given of certain features of experimental technique which are essential for reliable measurements of the thermal cross section.

An x-ray beam with a horizontal divergence of 15 min was produced by reflection of Mo $K\alpha$ x rays from a bent LiF monochromator. This was a modification of the doubly bent moochromator of Chipman[16] and approximately focused the vertically diverging rays (60′) at the detector. The receiving slit on the detector subtended a horizontal angle of 27′ and a vertical angle of 55′ at the sample. This divergence corresponds to a high resolution in reciprocal space. The magnitude of the divergence correction is discussed in Sec. IIC.

The x-ray tube was run at just less than twice the Mo $K\alpha$ excitation potential so that no higher order harmonics were present in the beam. Individual x-ray quanta were detected by a NaI(Tl) phosphor and scintillation counter, followed by an amplifier and single-channel pulse-height analyzer accepting 95% of the signal distribution. The E.H.T. and first dynode voltage were set to minimize the noise which was typically 5 counts/min (Black and Forsyth[17]). Sufficient counts were collected to reduce the standard deviation of each intensity measurement to less than 1%.

The incident beam was continuously monitored by a second scintillation counter which detected the x rays scattered by a thin Melinex foil placed after the last slit and before the sample. Changes in the sensitivity of the apparatus subsequent to the monitor scatter foil (in the electronics or phosphors, for example) were allowed for by frequently measuring the incident beam; the changes seldom exceeded 2% per week.

Since absolute values for the scattering cross section are required, it was necessary to obtain the ratios of incident to scattered intensity. Two independent methods were used to establish the relevant scale factor. One was to measure the high-angle scattering from amorphous paraffin wax, and then calculate the incident beam using the theoretical scattering factors.[18] The other was a direct measurement of the incident beam using a multiple-foil technique. The two methods agreed to within 2%.

Angular settings for any point in one plane of reciprocal space were found relative to the nearest Bragg reflection, the limit being set by the accuracy of ±1′ in the scale carried by the detector.

Air scattering is comparable with the weak phonon scattering if special precautions are not taken. It was eliminated by mounting the crystal in a vacuum enclosure with thin Melinex windows for the x rays. Parasitic scatter from the windows was intercepted by a screen.

The crystal could be cooled to liquid-hydrogen temperatures. These were measured to ±2°K by a thermocouple strapped to the back surface of the crystal.

B. Crystal Preparation

The sodium-chloride specimens were high-purity (6 ppm) single crystals whose mosaic spread never exceeded 15′ arc. They were first ground flat, then etched in distilled water for a few seconds, plunged in water-free alcohol, and finally dried. Crystal surfaces were obtained whose scattering power was the same as that of the cleaved crystal within the experimental error.

C. Divergence Correction

In any measurement of the scattering in reciprocal space, the reading obtained is the integral of the scattering function over the finite volume element arising from the divergences characteristic of the apparatus. Significant error would not be expected from the rather narrow divergences quoted in IIA. We wished to be quite sure on this point, however, due to the appearance in the observations of an unexpected feature which will be discussed in Sec. IID. This is strongest where the scattering function is varying rapidly, and where a divergence correction would be expected to be most important.

To estimate the correction due to the effect of horizontal divergence, the incident beam was analyzed for angular and $K\alpha_1$, $K\alpha_2$ wavelength distribution. Fine slits were used to define 56 rays equally spread through the beam and for each ray the intensity of each wavelength was found by reflection from a crystal. The spread was 3 min within each ray, and the width 0.2 mm. For each of these incident rays, ten rays scattered to different parts of the receiving slit were considered. To each incident scattered pair of rays corresponds a separate point in reciprocal space and a separate value for the intensity function. The apparatus, set at position $\mathbf{K}$ in reciprocal space, records an intensity which is the sum of the intensities produced by each pair of rays in a small domain round $\mathbf{K}$. It was found that the intensity obtained by integration of the contributions from the total of 560 incident scattered pairs of rays never differed by more than 2% from the value of the intensity function at $\mathbf{K}$ itself. This extreme value occurred only near reciprocal lattice points and indicated that the apparatus overestimated the intensity by this amount on both the high- and low-$\mathbf{K}$ side of the points; thus the finite divergence of the beams did not introduce any asymmetry in the observed scatter near Bragg peaks. Elsewhere the correction was negligible. The effect of vertical divergence and mosaic spread was also negligible. These conclusions were

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[16] D. R. Chipman, J. Sci. Instr. **27**, 164 (1956).

[17] P. J. Black and J. B. Forsyth, J. Sci. Instr. **36**, 392 (1959).

[18] *International Tables for X-ray Crystallography*, edited by Kathleen Lonsdale (Kynoch Press, Birmingham, England, 1962).

confirmed experimentally by noting that our readings were not changed by reducing still further the beam divergences.

D. Measurements near Reciprocal Lattice Points

As already noted, the intensities near reciprocal lattice points show features that would not be expected from the normal theory of thermal diffuse scatter given in Sec. III A. It was found that when factors depending on angle have been allowed for, the intensity at a point in reciprocal space on the high-angle side of a reciprocal lattice point is several percent higher than the intensity at the corresponding position below the lattice point. In the normal theory the "angularly independent" intensity in radial symmetry directions should have inversion symmetry in **q** about reciprocal lattice points.

The origin of the observed asymmetry is discussed in Sec. IV D. It can be accounted for by a generalization of the normal theory of diffuse scattering. In this generalized theory, the observed thermal diffuse scattering corresponding to **q** and $-\mathbf{q}$ differs from the intensity of the normal theory by amounts which are, to a first approximation, equal in magnitude and opposite in sign. Thus it is possible to obtain the thermal intensity corresponding to the normal theory by averaging the observed intensity (after being made "angularly independent") at the same **q** below and above reciprocal lattice points. The angular factors can then be put back, to give an averaged intensity which corresponds to Eq. (3). This may then be analysed in the usual way to obtain phonon frequencies.

In practice, the averaged intensity was obtained by an approximate procedure as follows. The percentage difference in intensity between experiment and theory was found for each pair of points, **q** and $-\mathbf{q}$. Any reasonable estimate of phonon frequencies can be used for calculating the theoretical intensity. The algebraic average of the pair of percentage differences for the same q then gives the amount by which the averaged experimental intensity differs from the theoretical intensity. This percentage difference is then applied to our theoretical intensity, to give back the required averaged experimental intensity that corresponds to Eq. (3). It should be emphasized that this procedure does not depend significantly on the phonon frequencies assumed.

III. THEORY

A. The One-Phonon Cross Section

An incident wave described by wave vector $\mathbf{k}_0$ and energy E_0, when scattered by a single phonon $(\mathbf{q},\hbar\omega)$ gives rise to a scattered wave $(\mathbf{k}_1,E_1)$ satisfying the wave vector and energy-conservation equations,

$$E_1-E_0=\hbar c(k_1-k_0)=\pm\hbar\omega\,, \tag{1}$$

$$\mathbf{K}=\mathbf{k}_1-\mathbf{k}_0=\mathbf{q}+\mathbf{G}\,, \tag{2}$$

where **G** is a vector of the reciprocal lattice. For x rays, $\hbar\omega\approx10^{-6}\,E_0$ so that the scattered wave vector $\mathbf{k}_1$ has very closely the same magnitude as $\mathbf{k}_0$. The scattering surface is then the well-known Ewald sphere of reflection and the intensities of processes corresponding to annihilation and creation of phonons [plus and minus signs in Eq. (1)] appear at the same point in reciprocal space **K**. Moreover, since $\omega=\omega(\mathbf{K})$ is a $3g$-valued function of **K** for a crystal with g atoms per unit cell, there are contributions to the intensity at a general point in reciprocal space from the $3g$ branches of the dispersion relations.

The one-phonon x-ray intensity per unit cell may then be written[19] in electron units (e.u.) (that is, the scattered intensity from a single free classical electron under the same conditions) as

$$I\text{ (e.u./cell)}=\sum_{j=1}^{3g}\left(\frac{E}{\omega^2}\right)_{\mathbf{q}j}\times\left|\sum_k\frac{\mathbf{K}\cdot\mathbf{U}_k(\mathbf{q}j)}{(m_k)^{1/2}}f_k\exp(-M_k)\exp(-i\mathbf{G}\cdot\mathbf{r}_k)\right|^2. \tag{3}$$

In this expression

$$E=\hbar\omega\left(\frac{1}{\exp(\hbar\omega/kT)-1}+\frac{1}{2}\right)$$

is the mean energy in thermal equilibrium at temperature T in the mode of frequency ω. $\mathbf{U}_k(\mathbf{q}j)$ is the eigenvector of the kth atom of the unit cell, belonging to the jth branch of the dispersion relation at wave vector **q**. It is normalized according to

$$\sum_k\mathbf{U}_k^*(\mathbf{q}j)\cdot\mathbf{U}_k(\mathbf{q}j')=\delta_{jj'}\,. \tag{4}$$

The eigenvector is related to the displacement $\mathbf{x}(lk)$ of the kth atom (mass m_k) of the lth unit cell from its equilibrium position $\mathbf{r}(lk)=\mathbf{r}(l)+\mathbf{r}(k)$ by the equation

$$\mathbf{x}(lk)=\sum_{\mathbf{q}j}\frac{\mathbf{U}_k(\mathbf{q}j)}{(Nm_k)^{1/2}}\exp[i\mathbf{q}\cdot\mathbf{r}(lk)]Q(\mathbf{q}j)\,, \tag{5}$$

where $Q(\mathbf{q}j)$ is the normal coordinate of mode $(\mathbf{q}j)$. The scattering factor of the free atom f_k and the Debye-Waller factor $\exp(-M_k)$ both depend on position in reciprocal space. N is the number of unit cells in the crystal and does not appear in the intensity per unit cell.

B. Analysis of Results

Since the energy distribution of the scattered radiation is not analyzed, the central problem in using measurements of the thermal diffuse x-ray intensity is that of obtaining the $3g$ frequencies $\omega(\mathbf{q}j)$ and eigenvectors for each atom from the total one-phonon

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[19] M. Born, Proc. Roy. Soc. (London) **A180**, 397 (1942).

expression Eq. (3). The method of doing this along symmetry directions in monatomic crystals is well known (Jacobsen[3]). However, with two atoms in the unit cell, a minimum of two phonon branches contribute to the intensity; this happens when **K** lies along a radial symmetry direction. The one-phonon intensity in a fcc alkali halide then reduces to that due to the longitudinal acoustic (LA) and longitudinal optic (LO) modes.

$$I=\frac{K^2}{\gamma^2 m_1+m_2}\left\{\left(\frac{E}{\omega^2}\right)_{\mathrm{LA}}\left|f_2\,e^{-M_2}\pm\gamma f_1 e^{-M_1}\right|^2+\frac{m_1}{m_2}\left(\frac{E}{\omega^2}\right)_{\mathrm{LO}}\left|\gamma f_2 e^{-M_2}\mp\frac{f_1 e^{-M_1}}{(m_1/m_2)}\right|^2\right\}. \quad (6)$$

In this expression the normalization condition Eq. (4) has been used so that the longitudinal eigenvectors, which are parallel to **K**, appear only through the amplitude ratio

$$\gamma=\frac{U_1(LA)}{(m_1)^{1/2}}\bigg/\frac{U_2(LA)}{(m_2)^{1/2}}. \quad (7)$$

The upper and lower signs apply when **K** lies in an even or odd zone, respectively. This has the consequence that when **K** lies near a reciprocal lattice point **G**, remembering that $\gamma\rightarrow 1$ as $\mathbf{q}\rightarrow 0$, the scattering from acoustic modes is usually favored relative to the optic modes in an even zone and vice-versa in an odd zone. Two well-defined simultaneous equations for ω(LA) and ω(LO) may therefore be obtained from two measurements made at equivalent points in an even and odd zone provided the amplitude ratio is known. It is found that the amplitude ratio in certain directions is not very sensitive to the details of the forces, so that its value may be assumed from a reasonable theoretical model. This is true for modes propagating in the [111] direction in alkali halides, where γ must fall from unity at the origin to zero at the zone boundary by symmetry; in the present experiment the intermediate values of γ were taken from a model allowing for ionic deformation (Karo and Hardy[20]), henceforth called the DD theory.

In this intermediate region the accuracy of the NaCl DD γ is not known experimentally. However, measurements by Buyers, Pirie, and Smith[21] on NaF, where x-ray and neutron results can be combined, have shown no significant deviation from the DD values for this direction. Also, some estimate of the effect of uncertainty in the γ values for NaCl can be obtained from the difference between the DD values and those computed from a rigid ion model. If the error in the DD values are taken as one quarter of this difference, then the corresponding error in the frequencies can be found. They are small for acoustic modes: thus the uncertainty in the acoustic frequencies increases from 0.1% at (0.2, 0.2, 0.2) to 2.0% at (0.4, 0.4, 0.4). At the same time the errors in the optic frequencies vary from 2.9% to 6.9%.

The errors in the frequencies of the (100) transverse acoustic (TA) mode estimated in the same way are negligible (less than 0.02%).

C. The Multiphonon Cross Section

The intensity at any point in reciprocal space also contains a contribution from multiphonon processes which must be subtracted from the observed intensity. Although measurements are always made where this multiphonon intensity is as small as possible, the accuracy with which these processes can be estimated constitutes one of the limitations of the x-ray method. This limitation is not felt to be important in the present work, since the multiphonon scatter at every **K** was obtained directly from a computer calculation, using the theoretical eigenfrequencies and eigenvectors of the DD theory. A mesh of 1000 **q** values distributed uniformly throughout the Brillouin zone[7] was used for the calculation of the two-phonon intensity.

The two-phonon intensity involves a sum over all modes, heavily weighted towards low frequencies. Thus the results of the calculation are relatively insensitive to the details of individual modes and to the most dispersive regions of the spectrum. The results of lattice sums of this type using the DD model are thought to be accurate to 7%. Evidence that the DD model gives answers systematically high by this amount was obtained by comparing the second negative moment μ_{-2} of the DD frequency distribution with a value of μ_{-2} extracted from the specific heat measurements of Barron *et al.*[22] At a typical point such as $\mathbf{K}=(2\pi/d)$ (1.8, 1.8, 1.8), where d is the lattice constant, this leads to an error of 1% in the acoustic frequency, and at an unfavorable point such as $\mathbf{K}=(2\pi/d)$ (2.8, 2.8, 2.8), the error is 3% in the optic frequency.

The three-phonon intensity, involving a double sum over all modes, is even less sensitive to the details of individual modes. It was estimated from a 39-point mesh. The calculation involved contributions to the intensity from more than 300 000 three-phonon frequency combinations, compared with 36 000 for the two-phonon calculation.

Higher order processes were generally negligible, or so small that it was sufficient to obtain a rough estimate from a suitable extrapolation of the ratios of first, second, and third orders.

D. The Compton Cross Section

In addition to the coherent thermal scattering, the x rays are incoherently scattered in processes where the

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

[21] W. J. L. Buyers, J. D. Pirie and T. Smith (to be published).

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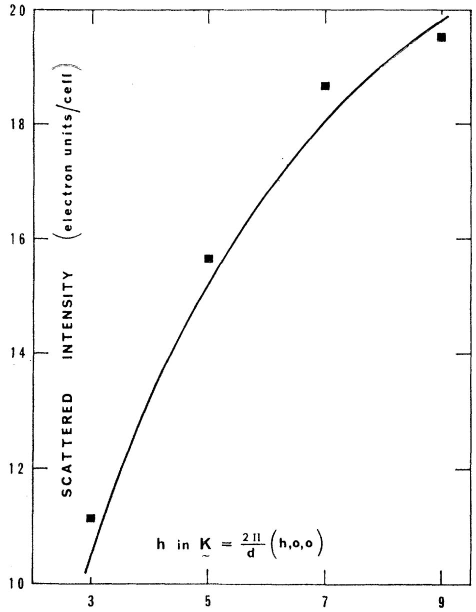

FIG. 1. Compton-scattering measurements from NaCl. The curve represents Freeman's theoretical values. (Ref. 10).

electronic state of the crystal changes. The best available calculations of the intensity of this Compton scattering are those made for a free ion by Freeman[10] who included exchange effects. In a crystal, however, the wave functions will be modified, and several authors (Laval,[23] Curien and Deroche,[24] and Cribier[25]) have suggested that there will be a lowering of the Compton intensity at small angles. However, as already noted, at the angles of interest for diffuse scattering experiments, measurements of the Compton scatter for many materials appear to be in agreement with Freeman's calculations.

In order to test this agreement for sodium chloride, a series of measurements was made at low temperatures. The crystal was cooled to temperatures in the range 40 to 90°K, and the x-ray scattering measured at zone boundaries in the [100] direction. At these points the thermal scattering is much smaller than the total scattering, and so may be subtracted to give an estimate if a realistic theory of the lattice vibrations such as the DD theory is used to predict the thermal scatter. For example, it will be shown later that the frequencies of the DD modes differ by no more than 7% from experiment, so that the one phonon intensity, linear in the frequency at low temperatures is also accurate to 7%. Thus the errors in the Compton estimates are not greater than 3%, since the thermal scattering never exceeds one-third of the total intensity at the points to which we have applied the above method. The results obtained (Fig. 1) agree with the theoretical calculations of Freeman to within this error.

In room-temperature measurements, therefore, the Freeman values for the Compton scattering were subtracted from the total intensity to obtain the thermal intensity.

E. Miscellaneous Parameters

The scattering factors for Na^+ and Cl^- were taken from tables,[18] as was the lattice constant. A linear absorption coefficient of 17.38 cm^{-1} determined by Wagner, Witte, and Wölfel[26] was used. Measurements of the Debye-Waller factors of sodium chloride are uncertain, so these were calculated from the DD theory as described by Buyers and Smith.[27]

IV. RESULTS

Frequencies of phonons propagating in certain symmetry directions have been obtained from an analysis of the one-phonon cross section. The latter was obtained by subtracting from the observed intensity the Compton and multiphonon contributions described in Sec. III.

A. [111] Modes

Measurements of the total x-ray scattering at 295°K along the [111] axis are shown in Fig. 2 with the contributions of Compton and Compton-plus-multiphonon scatter drawn in. It will be seen that in the zone around (222) where the scatter is primarily from the acoustic modes, the multiphonon processes are relatively unimportant.

Our results may be analyzed, as described in Sec. III B by assuming the amplitude ratio γ of the DD theory and combining intensities from two points, one

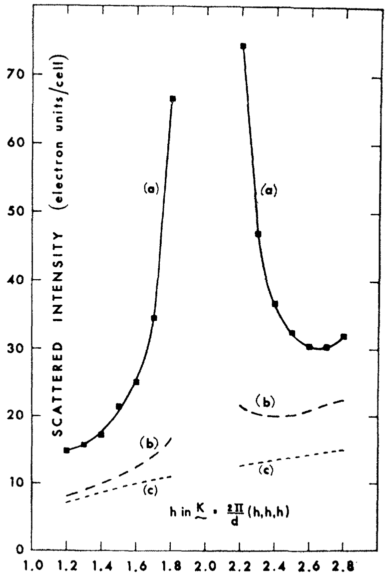

FIG. 2. (a) Measurements of total scattering for NaCl along [111]; (b) theoretical Compton-plus-multiphonon scattering; (c) theoretical Compton scattering.

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[23] J. Laval, Compt. Rend. **215**, 278, 359 (1942).

[24] H. Curien and C. Deroche, Bull. Soc. Franc. Mineral. Crist. **79**, 102 (1956).

[25] D. Cribier, Acta Cryst. **6**, 293 (1953).

[26] B. Wagner, H. Witte, and E. Wölfel, Z. Physik. Chem. (Leipzig) **3**, 273 (1955).

[27] W. J. L. Buyers and T. Smith, J. Phys. Chem. Solids **25**, 483 (1964).

in an even zone and one in an odd zone, but both having equivalent wave vectors **q**. For every wave vector $\mathbf{q}=(\zeta,\zeta,\zeta)(2\pi/d)$, there are four different ways of combining the data in pairs. If the reciprocal space position is denoted by $\mathbf{K}=(2\pi/d)(h,h,h)$, the one-phonon intensity of the even (222) zone may be taken from either $h=(2+\zeta)$ or $h=(2-\zeta)$ and combined with the one-phonon intensity of an odd zone either at $h=(1+\zeta)$ or $h=(3-\zeta)$. Our results for these combinations are given in Table I together with the values of the amplitude ratio taken from the DD theory. The small differences in the frequencies obtained from equivalent points and a common third point are due to the approximate nature of the averaging procedure described in Sec. II D. An iterative procedure was used to obtain acoustic and optic frequencies from each pair of intensities, using the even-zone intensity to refine the acoustic frequency and the odd-zone intensity to refine the optic frequency. This procedure produced values which changed by less than 1 in 1000 after only three or four cycles. However, at the zone boundary, $\zeta=0.5$, the equations are not well defined, and the intensities were more usefully employed in predicting the acoustic frequency only, using the theoretical optic frequency of 4.450×10^{13} sec. The random errors of the experimentally determined frequencies were computed from a 2% standard deviation in each observed intensity, estimated from the repeatability of the readings. The error in each frequency which is therefore related to the separate errors in the two independent intensities from which it was obtained, is shown in Table I.

In Fig. 3 our dispersion curves in this direction are compared with the DD theory and with the earlier rigid ion (RI) theory of Karo.[28]

Our experimental results for the acoustic mode, extrapolated to small wave vector using an even polynomial in **q**, are in good agreement with the ultrasonically determined elastic constants of Overton and Swim.[29] Thus the velocity of sound of 4.10×10^{5} cm/sec as found by the x-ray method is only 2% above the ultrasonic value. The prediction from the DD theory is 4.33×10^{5} cm/sec which is 7.6% above the ultrasonic value.

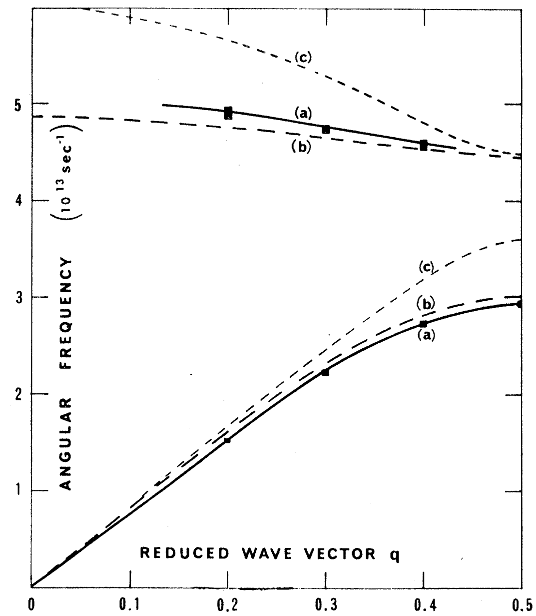

FIG. 3. Longitudinal [111] dispersion curves for NaCl. (a) Measured; (b) predicted by deformation dipole model (Karo-Hardy data); (c) predicted by rigid-ion model (Karo-Hardy data).

Our results may also be compared with independent data in the long-wavelength region of the longitudinal optic branch. Using the measured infrared absorption frequency $\omega_{\mathrm{TO}}=3.09\times10^{13}\ \mathrm{sec}^{-1}$ and the Lyddane-Sachs-Teller[14] relation between the high(ϵ_∞)- and low(ϵ_0)-frequency dielectric constants of Højendahl,[30]

$$\frac{\omega_{\mathrm{LO}}}{\omega_{\mathrm{TO}}}=\left(\frac{\epsilon_0}{\epsilon_\infty}\right)^{1/2}=1.58\,,$$

the LO frequency has a predicted value of 4.88×10^{13} sec^{-1}. These parameters, which were, incidentally, used

TABLE I. Angular frequencies of longitudinal phonons in [111] direction in units $10^{13}\ \mathrm{sec}^{-1}$.

Component of wave vector	0.2		0.3		0.4		0.5	
Amplitude ratio wave vector	0.869		0.690		0.401		0.000	
Reciprocal space positions combined	ω_{LA}	ω_{LO}	ω_{LA}	ω_{LO}	ω_{LA}	ω_{LO}	ω_{LA}	ω_{LO}
$(1+\zeta)$ and $(2-\zeta)$	1.54±0.02	4.95±0.20	2.26±0.04	4.70±0.22	2.79±0.06	4.63±0.25	2.95±0.06	...
$(2-\zeta)$ and $(3-\zeta)$	1.54±0.02	4.80±0.33	2.26±0.04	4.64±0.35	2.80±0.06	4.44±0.37	...	...
$(1+\zeta)$ and $(2+\zeta)$	1.53±0.02	4.96±0.20	2.19±0.05	4.80±0.23	2.70±0.08	4.79±0.27	...	...
$(2+\zeta)$ and $(3-\zeta)$	1.53±0.02	4.81±0.33	2.19±0.05	4.75±0.37	2.70±0.08	4.61±0.40	2.93±0.04	...
Mean frequency	1.54	4.88	2.23	4.72	2.75	4.62	2.94	...

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[28] A. M. Karo, J. Chem. Phys. **31**, 1489 (1959).

[29] W. C. Overton and R. T. Swim, Phys. Rev. **84**, 758 (1951).

[30] K. Højendahl, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **16**, No. 2 (1938).

as input data for the DD model, may slightly underestimate this frequency, for Haussühl's[31] recent value of ϵ_0 leads to the value 4.99×10^{13} sec^{-1}. Our results extrapolated to long wavelengths give 5.09×10^{13} sec^{-1}. The difference of 2% is not significant, since it is covered by the standard deviation.

This satisfactory agreement of our results at long wavelengths with both ultrasonically measured elastic constants and with the Lyddane-Sachs-Teller relation, suggests that the results for the rest of the dispersion curve may be regarded with confidence. It must here be emphasised that there has been no fitting of frequencies or intensities. The results depend throughout on the measurement of scattered intensities on an absolute scale.

From Fig. 3 it may be seen that the RI theory gives a poor descripton of the NaCl frequencies, as its predictions are always too high, by as much as 14% in the acoustic mode and 15% in the optic mode. The DD theory gives much better agreement with experiment, although it is clear that the theoretical acoustic frequency is consistently too high, while the optic frequency is too low. This type of systematic difference in a set of independent points cannot be explained by our random error, and is thought to reflect a real trend in the results of the DD model. The differences do not exceed 5% in either mode.

It is not likely that these differences are due to the uncertainty in the value of the effective charge e^*/e used as a parameter in the DD theory. This uncertainty arises from the determination of the low frequency dielectric constant by Hass,[32] Haussühl[31] and Højendahl[30] whose measurements differ by 4.5%. The resulting variation in e^*/e is 3.5%. A comparison has been made of two predictions based on the DD model which differed only in their effective charge. It appears that the above uncertainty could only lead to a change in the LO mode of 2% at $q=0$, and no change at the zone boundary when all the distortion dipole moment is associated with the chlorine ion, which is at rest. The corresponding changes in the LA mode amount to only 0.5% at the zone boundary and decrease to zero at $q=0$ where again polarization effects play no part. It is possible therefore that the above differences between theory and experiment indicate an inadequacy in the model itself rather than errors in the input parameters.

TABLE II. Comparison of longitudinal [111] phonon frequencies on DD and NNN models (0°K) having $e^*/e=0.7323$.

$\frac{\mathbf{q}d}{2\pi(3)^{1/2}}=\zeta$	ω_{LA} DD	ω_{LA} NNN	ω_{LO} DD	ω_{LO} NNN
0.1	0.853	0.854	4.982	4.978
0.2	1.663	1.666	4.896	4.810
0.3	2.375	2.378	4.778	4.703
0.4	2.901	2.906	4.644	4.577
0.5	3.104	3.114	4.574	4.509

TABLE III. Contributions to one-phonon x-ray intensity in (e.u./cell) along $(6,\zeta,0)$ on DD Theory.

ζ	LO	LA	TO	TA	Total
0.4	0.00	0.11	0.02	99.27	99.40
0.6	0.00	0.12	0.00	55.75	55.88
0.8	0.07	0.10	0.00	41.95	42.12
1.0	0.12	0.13	0.00	38.06	38.31
1.2	0.15	0.22	0.00	40.47	40.84
1.4	0.01	0.64	0.00	51.88	52.54
1.6	0.00	1.60	0.03	89.08	90.71

Hardy and Karo[33] have recently extended their data by including next-nearest-neighbor (NNN) forces. The effect of these forces in NaCl may be found from Table II, where comparison is made of the frequencies of the longitudinal [111] modes predicted by DD and NNN models.

It seems that the effect of next-neighbor forces is quite small. It is zero at $\mathbf{q}=0$ and rises at the zone boundary to +0.3% in the acoustic mode, and −1.4% in the optic mode. The rise in the acoustic mode is in the direction to worsen the agreement with elastic constants, but is insignificant in magnitude. Although NNN data are not available for room temperature, it is likely that the conclusion that the introduction of the next-nearest neighbor interaction in NaCl produces insignificant changes remains valid.

B. [100] Modes

The transverse acoustic dispersion curve for modes propagating in the [010] direction has been obtained from measurements of diffuse scattering carried out at points of the form $(6,\zeta,0)$. This region is at a sufficiently large radius from the origin so that $\mathbf{K}$ is very nearly perpendicular to $\mathbf{q}$. Thus the scattering from longitudinal [010] modes is almost completely excluded. In addition the amplitude ratio γ for the TA mode remains near unity (0.82 at the zone boundary) so that the structure factor for the TO mode is small. The net result is that the observed one-phonon x-ray intensity is nearly all from the TA mode; this is confirmed by the results of calculations of x-ray intensity at points $(6,\zeta,0)$ based on the DD model and given in Table III.

We recall that errors in frequency due to uncertainties in γ are less than 0.02%, so that in this direction a reliable TA dispersion curve may be obtained from the one-phonon intensity when due allowance is made for the small amounts of scattering from other modes.

The frequencies determined from the measured one-phonon intensity are given in Table IV. A very small asymmetry not exceeding 4% of the thermal scatter

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[31] S. Haussühl, Z. Naturforsch. **12a**, 445 (1957).

[32] M. Hass, Phys. Rev. **114**, 633 (1960).

[33] Private communication, and A. M. Karo and J. R. Hardy, Phys. Rev. **141**, 696 (1966).

was present in pairs of experimental intensities of the form $(6,\zeta,0)$, $[6,(2-\zeta),0]$. The one-phonon intensity of Table IV has this asymmetry removed by the procedure described earlier.

Our results when extrapolated to $\mathbf{q}=0$ indicate a velocity of sound equal to 2.44×10^5 cm/sec. This is 0.5% above the velocity deduced from Overton and Swim's[18] value for C_{44}. The excellent agreement serves as a check on the reliability of the x-ray results for the TA[010] branch of the phonon dispersion relations.

In Fig. 4 our experimental values for the [010] TA mode are compared with the theoretical predictions of the RI and the DD model. It is clear that, as before, the introduction of polarizable ions in the DD model leads to a marked improvement in the agreement with experiment, but the DD frequencies are nevertheless low by 3.8% at the zone boundary.

As in all our results there is a 2% standard deviation in the observed intensity, which here leads to 2% in the frequency in the most unfavorable case, namely at the zone boundary. However, the possible effect of systematic errors due to the subtraction of the higher order processes is much greater here than in the [111] measurements, since the observations were made at a greater radius from the origin of reciprocal space. If, as was previously suggested, a 7% overestimate in the multiphonon correction has been made, our zone boundary frequency would be high by 2%. Therefore the differences for the TA[010] mode between the frequencies determined by x rays and the DD model are barely significant.

No appreciable change in the theoretical predictions for this mode results from using the NNN model.

C. The Asymmetry

The averaging procedure for equivalent pairs of points referred to in Sec. II D when used with the theory of Sec. III A, has led to the above results, which agree with frequencies deduced from other techniques. Nevertheless, the asymmetry found in our measurements is a real feature of x-ray scattering, which has not previously been reported. It is not contained in the usual theoretical treatments of the scattering of x-rays by lattice vibrations in crystals, although mentioned by Born.[19] In a forthcoming paper we shall describe further measurements of asymmetry, give an account of the physical nature of the effect, and show how the theory of x-ray scattering has to be generalized. The asymmetry in our measurements is the first evidence that in scattering by phonons, the x rays see not only the nuclear motion, but also the direct effect on the scattering of the mutual deformation of the atoms.

TABLE IV. Experimental one-phonon intensity in (e.u./cell) and angular frequency ω for wave vector $\mathbf{q}=\pm(2\pi/d)(0,\zeta,0)$.

ζ	Intensity at $(6,\zeta,0)$	Intensity at $[6,(2-\zeta),0]$	Frequency $\omega(10^{13}\text{ sec}^{-1})$
0.4	102.3	93.7	0.98
0.6	55.7	52.4	1.32
0.8	38.9	37.8	1.54
1.0	35.1	35.1	1.60

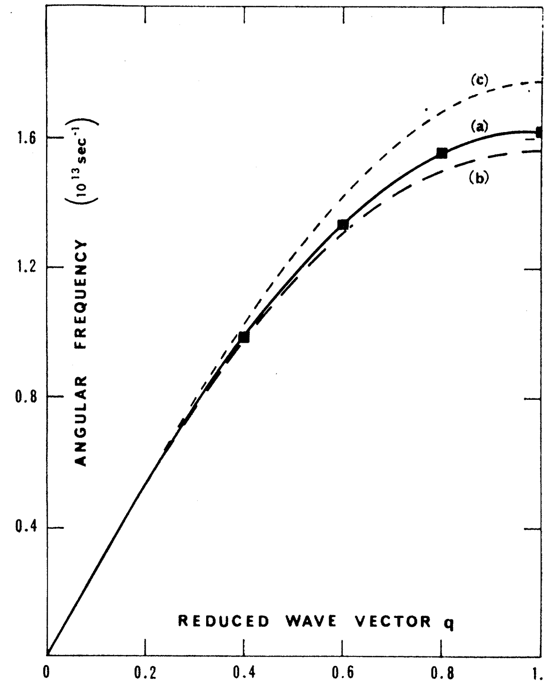

FIG. 4. Transverse [100] dispersion curves for NaCl. (a) Measured; (b) predicted by deformation dipole model (Karo Hardy data); (c) predicted by rigid-ion model (Karo Hardy data).

V. SUMMARY

The x ray thermal diffuse scattering from sodium chloride has been analyzed to yield dispersion relations for the [111] LA and LO modes and the [100] TA mode. Our results are in agreement with the ultrasonically determined elastic constants, and with the LO frequency for small wave vector predicted by the Lyddane-Sachs-Teller[14] relation. The early rigid ion theory of Karo[28] is shown to be in error by as much as 15%, while the deformation dipole model of Karo and Hardy[20] is in agreement with experiment to 5% or better. The remaining differences may reflect an inadequacy in the model rather than uncertainties in its input parameters.

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