INTERFERENCE BETWEEN ONE- AND MULTIPHONON PROCESSES IN THE SCATTERING OF NEUTRONS AND X RAYS BY CRYSTALS

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We show that the intensity of x-ray and neutron scattering by anharmonic crystals is markedly affected by the interference between one- and multiphonon scattering processes. The previously unexplained intensity modulation in the x-ray diffuse scattering from NaCl is shown by calculations to be largely of this origin. We have also observed the effect of the interference in neutron inelastic scattering from KBr; calculations give quantitative agreement with the experimental results.

The inelastic scattering of neutrons[1] and x rays[2] are well established techniques for obtaining information about the normal modes of vibration in crystals. It is usually assumed that the scattering consists of independent one- and multiphonon contributions. The intensity of the one-phonon scattering then gives information about the phonon frequencies and eigenvectors. In an anharmonic crystal, however, the one- and multiphonon contributions are not independent.[3] In this Letter we show that the interference between these contributions produces a marked change in the intensity of the scattering. We propose that the difference between the intensity of the x-ray scattering recently observed for alkali halides[4] and that calculated using the normally accepted harmonic theory is largely of this origin. Detailed calculations for NaCl support this proposal. We have also observed the effect of the interference in neutron inelastic scattering from KBr where it makes an important contribution to the intensities of the one-phonon groups. Calculations of the interference between the one- and two-phonon scattering processes give quantitative agreement with the observations.

Although the results of calculations for the alkali halides will be discussed later, we will, for simplicity, give the theoretical expressions appropriate to a monatomic crystal. The extension is given in a paper by Cowley and Buyers.[5] The scattering by a single phonon of particular symmetry, wave vector $\vec{q}$, label 0, frequency ω_0, and eigenvector $\vec{e}(0)$ may be evaluated by using standard methods.[6] For a wave vector transfer $\vec{Q}$, and a frequency transfer ω, the result is

$$S(\vec{Q},\omega)=\sum\frac{b^2\hbar N}{\pi}[n(\omega)+1]\delta(\vec{Q}+\vec{q}-\vec{\tau})\,\mathrm{Im}[F(\vec{Q})F(-\vec{Q})G_0], \tag{1}$$

where b^2 is the product of the Debye-Waller factor and the square of the coherent scattering length (for neutrons) or form factor (for x rays), $n(\omega)$ is the Bose distribution function, and the summation is over all reciprocal-lattice vectors $\vec{\tau}$. The one-phonon response function G_0 is given by

$$G_0=[\omega_0{}^2+2\omega_0(\Delta+i\Gamma)-\omega^2]^{-1}, \tag{2}$$

where Δ and Γ are the real and imaginary parts of the anharmonic self-energy. The one-photon structure factor $F(\vec{Q})$ can be written as

$$F(\vec{Q})=i\vec{Q}\cdot\vec{e}(0)-\sum 3i\left(\frac{\omega_0}{2N\omega_1\omega_2}\right)^{1/2}V(-1,-2,0)[\vec{Q}\cdot\vec{e}(1)][\vec{Q}\cdot\vec{e}(2)]$$
$$\times\left(\frac{n_1+n_2+1}{\omega_1+\omega_2+\omega_+}+\frac{n_1+n_2+1}{\omega_1+\omega_2-\omega_+}+\frac{n_2-n_1}{\omega_1-\omega_2+\omega_+}+\frac{n_2-n_1}{\omega_1-\omega_2-\omega_+}\right)+\cdots, \tag{3}$$

where the first term is the normal harmonic structure factor, and the second term, which increases with increasing temperature, results from the interference between one- and two-phonon processes. The summation is over all the phonons within the Brillouin zone, and $\omega_+=\omega+i\epsilon$, where ϵ tends to zero. The cubic anharmonic interaction $V(-1,-2,0)$ may be shown to change sign when all the wave vectors $\vec{q}$ reverse in sign.

From Eq. (1) it is seen that the interference between one- and two-phonon processes gives rise to two types of contributions to the cross section. The first is of the form $\mathrm{Im}[F(\vec{Q})F(-\vec{Q})]\mathrm{Re}[G_0]$. This term is asymmetric with respect to ω about the frequency ω_0 and will consequently alter the shape of the cross section in this region as first discussed by Ambegaokar, Conway, and Baym[3] and shown by later calculations[7] to give only a small effect. The second contribution is of the form Re[$F(\vec{Q})F(-\vec{Q})$]Im[G_0]. This contribution, which is roughly Lorentzian in shape about ω_0, was not discussed in detail by the earlier authors although it markedly modifies the scattered intensity. Since the anharmonic coefficient changes sign when $\vec{q}$ changes sign, the effect of this interference on both the intensity and shape will change sign when $\vec{q}$ is reversed, if $\vec{Q}$ and $\vec{q}$ are almost parallel. Consequently the results of measurements carried out along radial directions with momentum transfers $\vec{Q}_1=\vec{\tau}+\vec{q}$ and $\vec{Q}_2=\vec{\tau}-\vec{q}$ can be used to determine the magnitude of this interference. (The higher-order interference terms which give contributions of opposite sign at $\vec{Q}_1$ and $\vec{Q}_2$ involve at least five phonons and have therefore been ignored in the calculations.)

The cross section for x-ray diffuse scattering is obtained by integrating Eq. (1) over frequency, ω. Detailed calculations of the contribution to the intensities from the interference between one-phonon and two-phonon processes have been carried out using the same techniques and approximations as were used in earlier calculations[8] of anharmonic effects in alkali halides. No adjustable parameters are employed. The results of the calculations for momentum transfers along the [ξ00] direction in NaCl are shown in Fig. 1. The experimental measurements also shown in Fig. 1 were obtained from the results given in Ref. 4. They are the part of the percentage difference between the observed intensity of the x-ray scattering and that computed on a harmonic model that is antisymmetric in $\vec{q}$. In view of the uncertainties in the anharmonic calculations and the errors on the measurements the agreement between the two is very reasonable. We conclude that most of the observed deviation is caused by the interference effect, although we cannot rule out the possibility of a smaller contribution caused by changes in the form factors[4,9] of the ions resulting from their motion.

By means of measurements on a single crystal of KBr, we have also demonstrated that the interference effect markedly modifies the intensities of one-phonon groups in typical neutron-inelastic-scattering experiments. These measurements cannot be affected by form-factor changes since neutron scattering is a nuclear process. The measurements were carried out using a triple-axis crystal spectrometer controlled so that the energy transfer was varied while the momentum transfer was held constant.[1] The (002) planes of a beryllium cyrstal were used for the monochromator, and, to help avoid spurious scattering processes, the (111) planes of a germanium crystal (second-order Bragg scattering absent) were used for the analyzer. Longitudinal optical (LO) phonons propagating along the ($\xi\xi\xi$) direction were chosen for study since the interference effect was calculated to be large for these modes; also, corrections for the effects of focusing and resolution are unnecessary for this almost flat LO branch.[10] The crystal was mounted with a (1$\bar{1}$0) axis vertical, and the measurements were carried out in the Brillouin zone about the reciprocal-lattice point (333) at temperatures of 94, 298, and 450°K. To further guard against spurious scattering processes, two scattered-neutron energies, $E'=5.126$ and 5.746 THz, were employed.

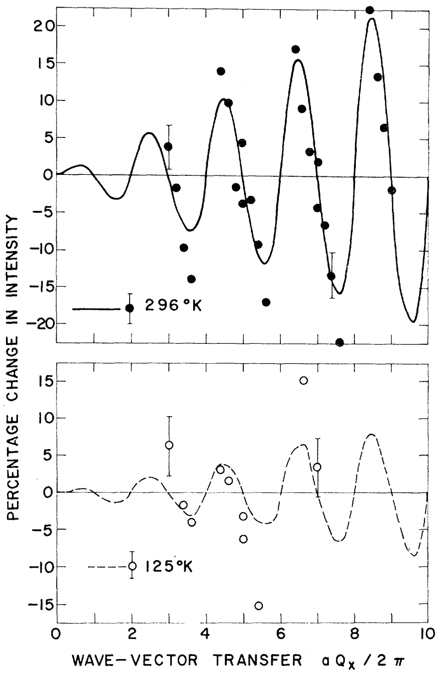

FIG. 1. The calculated relative contribution of the interference effect to the one-phonon x-ray scattering along the [ξ00] direction in NaCl as compared with experimental results (see Ref. 4). Typical error bars are shown.

The background under the observed neutron groups was a substantial fraction of the total scattering especially at the higher temperatures. Since the background consisted mainly of one-phonon incoherent and two-phonon coherent scattering, it was necessary to calculate these cross sections in detail as functions of frequency, wave vector, and temperature. These were normalized to the one-phonon coherent scattering by a scale

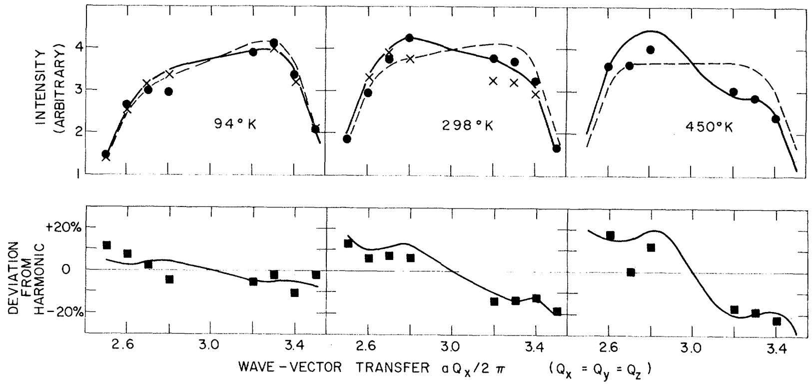

FIG. 2. The experimental intensities of the neutron groups for (ζζζ) LO modes in KBr, and the results of calculations based on harmonic theory (dashed curves) and our anharmonic theory (solid curves). Closed circles and crosses indicate measurements performed with $E' = 5.126$ and 5.746 THz, respectively. The lower part of the figure shows the deviations from harmonic theory of our averaged experimental results (closed squares) and our anharmonic theory (solid curves).

factor obtained by fitting to the total scattered intensity at 94°K, and it was found that the same scale factor was appropriate to the measurements at 298 and 450°K. The integrated intensities of the one-phonon groups obtained after subtraction of the background are compared in Fig. 2 with the results of calculations based on harmonic theory and on our anharmonic theory which includes the interference effect. The deviation of the observations from harmonic theory clearly demonstrates the presence of the interference effect. The rms differences between the experimental intensities and those calculated using harmonic theory are $(13 \pm 6)\%$ at 298°K and $(17 \pm 7)\%$ at 450°K in excellent agreement with the values 14 and 20% predicted by our anharmonic theory. The measurements showed no significant difference in the phonon frequency on opposite sides of the reciprocal-lattice point in agreement with the calculated magnitude of the frequency difference caused by the interference effect. These results confirm the existence of the interference effect in neutron-scattering measurements, and hence support our contention that it is the probable explanation of the intensity modulation observed in the x-ray scattering measurements.

The same interference mechanism will also affect the results of measurements by optical techniques. In this case (very small $|\vec{Q}|$), however, effects caused by the interference are very difficult to distinguish from those arising from a frequency dependence of the phonon self-energy in Eq. (2). In neutron and x-ray scattering measurements, the self-energy effects, which are the same on opposite sides of a reciprocal-lattice point, may readily be distinguished from the effects of the interference between one- and two-phonon processes by the methods described above.

In conclusion, we have demonstrated that the interference between the one-phonon and two-phonon scattering processes in an anharmonic crystal has a marked effect on the intensities observed in both x-ray and neutron-scattering measurements. Our results show that the interference effects are sufficiently large that they must be allowed for when extracting phonon eigenvectors from neutron group intensities,[11] or phonon frequencies from the intensity of x-ray diffuse scattering.[2] The usual procedures based on harmonic theory can only be employed with data obtained either at low temperatures or small $|\vec{Q}|$. In an anharmonic crystal, either the interference effect must be calculated in detail, or the intensities observed at $\vec{Q}_1 = \vec{\tau} + \vec{q}$ and $\vec{Q}_2 = \vec{\tau} - \vec{q}$ must be appropriately averaged to minimize the effects of the interference as far as possible.

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MEASUREMENT OF THE ANOMALY AT THE $L_{\mathrm{II,III}}$ EDGE OF SODIUM

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The absorption structure of sodium metals has been measured in the vicinity of the onset of $2p$ electron absorption. The results agree with theoretical investigations which claim a sharp absorption peak at the edge.

Recently interest in the absorption and emission structure near the onset of inner-shell transitions in simple metals has been revived in a series of theoretical papers.[1-9] Previously absorption at the edge was regarded as being due to transitions of core electrons into empty states just above the undisturbed Fermi level. This would explain a step in the absorption coefficient. The influence of the potential due to the deep-state hole was considered to be negligible because of immediate shielding by the conduction electrons. A more refined theoretical analysis yields the result that electron states in the vicinity of the Fermi surface are affected by the core potential in such a way that a singular behavior of the absorption and emission occurs at the edge[1-9]:

$$\mu \propto |\Delta E|^{-\alpha}, \tag{1}$$

where ΔE is the distance from the edge to higher (lower) energies in absorption (emission), μ is the absorption coefficient, respectively emission probability. α is expected to be positive for $L_{\mathrm{II,III}}$ transitions whereas it can also achieve negative values for K transitions. In the latter case a smoothing of the edge instead of a peak should be observed.

We have considered Na as being an ideal metal to test these predictions because a peak near the onset could not be caused by a band singularity. Emission spectra of Na show a peak near the $L_{\mathrm{II,III}}$ edge.[10] The only older absorption measurements which came to our attention are those of O'Bryan.[11] Though some peaking near the edge was observed we felt that a remeasurement with better techniques was desirable.

Synchrotron light from the Deutsches Elektronen-Synchrotron accelerator served as the source of radiation. The Na films were evaporated from nickel boats onto substrate films of Mg and Al which were surrounded by surfaces cooled to 77 °K. The base pressure in the system outside the cool trap was 10^{-6} Torr. The cooling served to lower water vapor pressure and has been proved to be a good means[12] to get good metallic Na films without ultrahigh vacuum. The samples themselves were maintained at 77°K. Absorption was measured immediately after evaporation and it was verified that none of the observed structures are caused by oxide.

Figure 1 shows our results. The absorption coefficient μ is given in arbitrary units since the film thicknesses were not determined. The reproducibility of curves from different samples which were fitted at two points was within 3 % of the total edge discontinuity. The accuracy of absolute energy calibration is ±0.05 eV.

A peaking of the absorption towards the edge is clearly recognized. The structure is somewhat complicated by the spin-orbit splitting of the edge showing up as a separation of 0.17 ± 0.02 eV. The observed intensity ratio of these two contribu-