Anharmonic phonon response in aluminum: A neutron-scattering test of computer-simulation calculations

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(Received 27 April 1979)

In contrast to the three finite-frequency peaks in the dynamical structure factor $S(\vec{Q},\omega)$ predicted in a recent computer-simulation study of aluminum at 800 K, the line shape observed by means of neutron scattering is smooth and exhibits a single narrow peak at each wave vector. The observed line shape is, however, in agreement with approximate analytical calculations based on self-consistent-phonon theory, using the same interatomic force model as employed in the computer simulation. These comparisons suggest that exact computer simulation on a finite lattice can produce artificial peaks or oscillations not characteristic of the real solid. We find that these artificial peaks are associated with long-time noise in the computer simulation of $S(Q,t)$; their effect on $S(Q,\omega)$ can be minimized by use of a damping function.

I. INTRODUCTION

The study of anharmonic effects in solids, that is, the ways in which the lattice vibrations deviate from harmonic excitations having sharply defined, temperature-independent frequencies, is a subject of continuing interest. These effects are important in solids at elevated temperatures and in materials which exhibit large zero-point oscillations. Up to about 1968, as described in a review by Cowley,[1] work in this field was primarily concerned with the measurement and theoretical calculation of the shift and width of phonon frequencies as a function of temperature. The studies of aluminum[2] and potassium[3] are examples of this work. Subsequently the effect of pressure on phonon modes, for example in Rb,[4] has been studied, and several investigations have been made of a very characteristic anharmonic effect on the one-phonon scattering of both x rays and neutrons—the so-called one-phonon–two-phonon interference effect,[5] which has been reviewed by Glyde.[6] Once again we may cite as examples both aluminum[7,8] and potassium,[9] in addition to the pioneering work on KBr,[5,10] and also the studies of the ^{4}He solids.[11,12]

There is, however, a major problem in comparing theory with experiment; this arises because it is the total density-density response which is measured in a scattering experiment, rather than the one-phonon contribution to that total. It is in principle impossible to distinguish between the one-phonon response and the multiphonon continuum. This difficulty is well known both from theory[5,10,11] and from experiments on classical systems such as KBr.[5] In studies of quantum solids such as helium[12] and neon,[13] there has been a long history[14] of unsuccessful attempts to measure the first moment of the one-phonon part $[S_p(\vec{Q},\omega)]$ of the scattering law $S(\vec{Q},\omega)$ for comparison with the ACB sum rule[15]:

$$M_p^{(1)} = \int \omega S_p(\vec{Q},\omega)d\omega = (\hbar Q^2/2M)\exp(-2W), \quad (1)$$

where $\vec{Q}$ is the momentum-transfer vector, $\hbar\omega$ is the energy transfer, M the neutron mass, and $\exp(-2W)$ the well-known Debye-Waller factor. Since it is impossible to extract only the one-phonon part of the scattering, attempts to derive $M^{(1)}$ from the apparent $S_p(\vec{Q},\omega)$ in the observed one-phonon peak region found that $M_p^{(1)}$ oscillated with $\vec{Q}$. However, the sum rule is correct if all of $S_p(\vec{Q},\omega)$ can be included. In practice, when the experimenter chooses reasonable limits for the integration over the "peak" region, the result is an effective Debye-Waller factor that appears to oscillate as a function of $\vec{Q}$, whereas the "true" Debye-Waller factor does not, even in the presence of strong anharmonicity.[16]

To obviate this problem, one should really calculate the total, all-phonon contributions to $S(\vec{Q},\omega)$, including their mutual interferences. However, this is in general a most complicated computational task[17] especially in the most interesting situations of very large anharmonicity where three-phonon and higher processes are significant.

One way out of these difficulties that is growing in popularity is the use of computer-simulation techniques to calculate the total $S(\vec{Q}, \omega)$ by Fourier transformation of the classical time evolution of the density-density response. These simulations are performed for a finite number of atoms, and in many cases, particularly for liquids,[18,19] they are regarded as the standard against which any approximate analytic theory should be tested. This kind of simulation calculation has recently been performed by Jacucci and Klein[20] for aluminum at 800 K (Al melts at 933 K). The calculations are classical, but this should be satisfactory, since 800 K is more than twice the Debye temperature. A potentially more serious difficulty with these calculations is that only 256 distinct atoms are considered, so that despite the application of periodic boundary conditions, the basic structure corresponds to stacking of only four face-centered-cubic unit cells in each direction in space. In the case of a liquid, where the basic structure is changing dynamically, and is in any case nonperiodic and spherically averaged, the finite cell size does not appear to have led to serious difficulties to date. In the solid, however, the regular periodicity of the static structure when applied to a finite cell might produce resonances in the response, although to date there appears to be no clear evidence for this.[21] Another difficulty concerns the long-time noise in the calculations and its spurious contribution to $S(\vec{Q}, \omega)$ that arises via the Fourier transform of the density-density response.[22]

The solid therefore provides an excellent (i.e., severe) testing ground for state-of-the-art computer-simulation calculations. Moreover, the Jacucci and Klein calculation[20] gave a most surprising result for the phonon response, at least for $\vec{Q} = (2.25, 2.25, 2.25)2\pi/a$. It was unusual in that the response at 800 K consisted of three peaks of comparable strength; the highest-frequency peak corresponded, roughly speaking, to the single-peak one-phonon response at low temperature, but the origin of the two lower-frequency peaks was somewhat obscure. A neutron-scattering experiment was therefore undertaken to examine $S(\vec{Q}, \omega)$ at 800 K for this particularly interesting mode. In addition, the original computer simulation was reexamined for possible problems associated with the Fourier transform. The question of system-size effects was not examined at this time. Perturbation-theory calculations were also undertaken to examine these specific phonons.

II. EXPERIMENT

The single crystal of aluminum, a 1-cm-diameter cylinder, 5 cm long, with the $[1\bar{1}0]$ crystal axis parallel to the cylinder axis, was mounted vertically so that the $[1\bar{1}0]$ axis was perpendicular to the scattering plane of the N5 spectrometer at the NRU reactor, Chalk River. Constant-Q scans were performed at 300 K and 800 K, with fixed scattered neutron energy E_1, for momentum-transfer vectors $\vec{Q} = (\zeta, \zeta, \zeta)2\pi/a$, with values of $\zeta = 1.25$, 1.75, 2.25, and 2.75. The incident monochromatic neutron beam was obtained from the (113) planes of a Ge crystal, and the scattered neutrons were analyzed with the (111) planes of a silicon analyzer. Collimation was 0.6° and 1.0° before and after the crystal. The aluminum-crystal rocking curve was 0.65° wide, consistent with the experimental resolution.

For a fixed number of monitor counts, the single scattering from the crystal for fixed E_1 is proportional to $S(\vec{Q}, \omega)$. Other contributions to the scattering are a small room background (<1 cpm) and also multiple scattering, which affects the data chiefly by permitting observation of the transverse (T) mode in scans of the longitudinal (L) phonon response. In effect, part of the incident neutron beam may be first Bragg reflected and then inelastically scattered by means of a one-phonon process involving the T mode.

This effect was minimized by improving the instrumental resolution and reducing the size of the Ewald sphere (i.e., reducing E_0 and E_1). Almost complete suppression of this T-mode "feed-through" was achieved with $E_1/h = 6$ THz, a value large enough to permit the study of all ζ values except for 2.75, and for the very-low-frequency portions of the other scans. For these, $E_1/h = 7.5$ THz was employed, and the observed intensities corrected for the change in analyzer-detector efficiency between 7.5 and 6 THz.

Test scans at 299 and 800 K with the Al crystal removed from the furnace showed very weak and uniform scattering from the radiation shields, etc. This scattering has been subtracted from the spectra shown below.

III. RESULTS AND DISCUSSION

The results from four scans at equivalent wave vector along the (111) direction are shown in Fig. 1. The chosen reduced wave vector $\vec{q} = (0.25, 0.25, 0.25)2\pi/a$ is the same wave vector for which Jacucci and Klein[20] obtained the most dramatic spectral structure. We specify phonon frequencies by $\nu (= \omega/2\pi)$ in THz units, and in the discussion below we refer to the dynamic structure factor as $S(\vec{Q}, \nu)$.

The scans for 300 K shown are typical of the scattering from essentially harmonic phonons. A well-defined phonon peak whose width is limited by

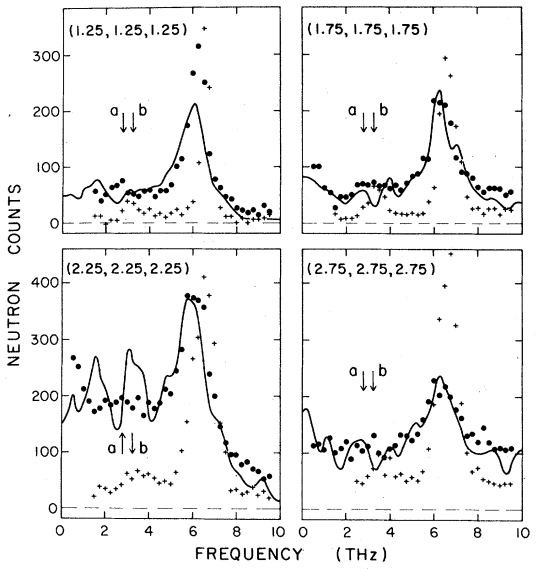

FIG. 1. Constant-$\vec{Q}$ scans at 300K (crosses) and 800K (circles) for longitudinal (L) modes propagating along (111) at reduced wave vector (0.25, 0.25, 0.25)$2\pi/a$. The experimental results at 800K are compared with the computer-simulation results of Jacucci and Klein (Ref. 20) (lines). The weak low-frequency peak close to the T-mode frequency (arrow a for 800K, b for 300K) arises from a double-scattering process described in the text, and is not part of $S(\vec{Q}, \omega)$.

instrumental resolution is observed at 6.59 ±0.06 THz superimposed on a low-intensity multiphonon scattering. In addition there is a small peak near the T mode frequency arising from the multiple-scattering process referred to above. Its origin was confirmed (a) by direct observation of the T phonon at $\vec{Q}$=1.75, 1.75, −2.25)$2\pi/a$ (not shown here) and (b) by observing that the intensity of the T-mode peak was strongly dependent on E_1 and was therefore not part of the desired *single* scattering cross section $S(\vec{Q}, \nu)$.

At 800K the ζ-functionlike part of the response has broadened and shifted to a lower frequency, 6.22 THz. The peak now lies on a large multiphonon background. Anharmonic interference affects the integrated intensity of the peak by subtracting intensity from it at ζ = 1.75 and adding intensity to it at ζ = 2.25. The scaling of intensity from ζ = 1.75 to ζ = 2.25 is more than a factor of 2 greater than the scaling Q^2e^{-2W} that would apply for purely harmonic phonons with θ_D = 360 K.

The most detailed previous measurements on Al at high temperatures are those of Larsson *et al.*[23] These were made by the cold-neutron time-of-flight method and so cannot be compared directly with the present results. Nevertheless, it is clear that for temperatures near 800 K, and in wave-vector regions similar to ours, a single, broadened phonon peak superposed on multiphonon scattering of comparable intensity was observed, in qualitative agreement with our results.

The original computer-simulation results[20] exhibit a somewhat oscillatory line shape, evident at all wave vectors, in Fig. 1, but especially prominent at $\vec{Q}$ = (2.25, 2.25, 2.25)$2\pi/a$. Because the peaks at ν = 1.5 and 3.3 THz are comparable in intensity to the peak at 6.2 THz, it is not clear from the computer-simulation results alone whether the they are pathological features of the simulation or an effect of the extreme anharmonicity present at large wave vector and temperature. From their absence in the observed neutron spectra we conclude that they are spurious. Although their origin is at present not clear, they may be vestiges of the localized resonances associated with the vibrations of a finite collection of atoms. We suggest that the oscillations give, in effect, an estimate of the "error" to be associated with the simulation calculation, which happens to be unusually large at this Q value.

To assess the effect of long-time noise, we have damped away the response beyond 0.5 psec before transforming to $S(Q, \omega)$. The resultant spectrum for $\vec{Q}$ = (2.25, 2.25, 2.25)$2\pi/a$ is then free of the spurious resonances of the original simulation and has the smooth line shape shown in Fig. 2. The new calculations are in good agreement with experiment.

In conventional anharmonic-lattice-dynamics calculations, based on weak perturbation theory,[3,6,9] there is usually no difficulty with spurious satellite peaks analogous to those shown in the full curves of Fig. 1. This is confirmed (see Fig. 2) by our calculations using self-consistent-phonon theory, to which the contributions of three-phonon interactions have been added.[9,24] The calculations were made with the same potential[25] as was used in the computer-simulation study.

The calculations are of the sum of the one-phonon, one-phonon–two-phonon interference, two-phonon, and the three-phonon scattering processes

$$S(\vec{Q}, \nu) = S_1(\vec{Q}, \nu) + S_{1,2}(\vec{Q}, \nu) + S_2(\vec{Q}, \nu) + S_3(\vec{Q}, \nu) \qquad (2)$$

and therefore do not include many other higher-order processes which, though weak, are taken into account in the simulation calculation.

The contribution from terms higher than two-phonon scattering has been estimated from the f-sum rule

$$\int d\nu\, \nu S(\vec{Q}, \nu) = \hbar Q^2/4\pi M. \qquad (3)$$

For example, at $\vec{Q}$ = $(2\pi/a)$(2.25, 2.25, 2.25), the contributions to $S(\vec{Q}, \nu)$ for processes involving up to two phonons given in (2) at T = 800 K exhausts

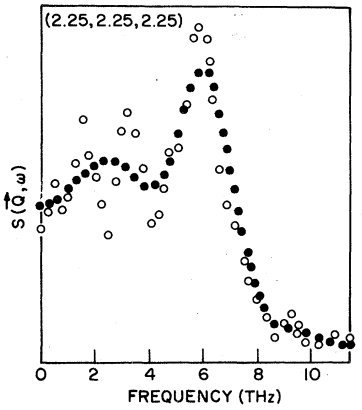

FIG. 2. Computer simulation of $S(\vec{Q}, \omega)$ at $\vec{Q}$ = (2.25, 2.25, 2.25)$2\pi/a$ in Al at 800 K by Fourier transformation with an 0.5 psec damping function (solid circles). For comparison we also show the original undamped response of Ref. 20 (open circles) from the bottom left panel of Fig. 1.

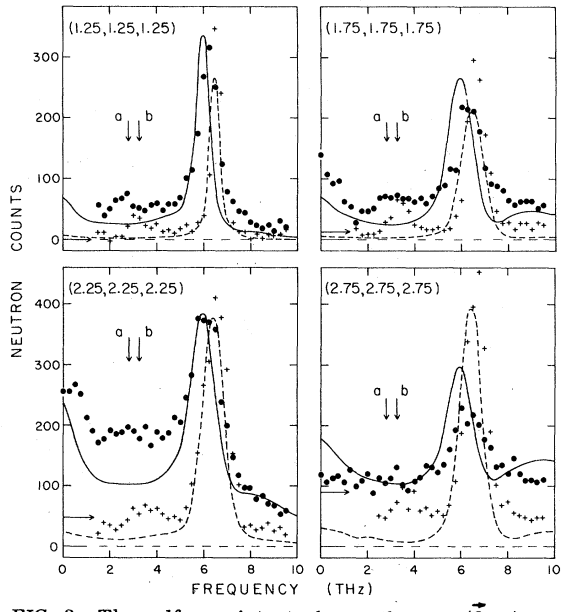

FIG. 3. The self-consistent-phonon theory $S(\vec{Q}, \omega)$, folded with the instrumental resolution function, at T = 800 K (solid lines) and T = 300 K (dashed lines) compared with the observed scattering intensity as in Fig. 1. The horizontal arrows show the part of the theoretical $S(\vec{Q}, \omega)$ estimated to be three-phonon scattering at T = 800 K.

only 53% of the sum rule (3). By assuming that the remaining contribution is essentially three-phonon scattering $S_3(\vec{Q}, \nu)$ and is spread uniformly over a frequency range from zero up to three times the maximum one-phonon frequency, we obtained the magnitude of S_3 at 800 K shown by the horizontal arrows in Fig. 3. It is negligible at 300 K for all $\vec{Q}$ values.

As in the computer simulations in Fig. 1, a single arbitrary scale factor has been applied at all $\vec{Q}$ values and temperatures, in order to achieve the best possible comparison between theory and experiment. The effect of instrumental resolution has been approximately included by folding the theoretical curves with a Gaussian distribution of width [full width at half maximum (FWHM)] 0.5 THz for ζ = 1.25 and 1.0 THz for the other ζ values. At 300 K, the observed widths are dominated by instrumental resolution, but at 800 K, each peak exhibits intrinsic broadening and lies on top of a substantial background arising from multiphonon processes. The theoretical peak frequencies are slightly lower than experiment at both temperatures, and there are some discrepancies in the relative intensities, possibly related to our simplified treatment of instrumental resolution. The results show, however, that there are no spurious satellites or other oscillations of the type seen in the computer simulation.

An interesting aspect of the self-consistent-phonon-theory calculation is the rise in intensity as the frequency tends to zero, which is most marked for $Q = (2\pi/a)(2.25, 2.25, 2.25)$, and which is also observed in the experiments.

IV. CONCLUSION

Neutron-scattering measurements of the density-density response in aluminum at 800 K have highlighted a particular difficulty of current calculations based on the computer-simulation method. For a "computer crystal" of 256 atoms, and for certain values of $\vec{Q}$, these calculations may exhibit satellite structure that does not appear in the experimentally observed spectra. Our calculations based on weak perturbation theory, in the self-consistent-phonon approximation and including explicitly up to two-phonon processes, show no such satellite structure, and confirm the experimental result that the line shape consists of a single peak.

The present experiments provide a set of data which any successful theory of interacting phonons must satisfactorily describe. Broadly speaking, rather good agreement can be obtained between the computer-simulation calculations, conventional perturbation theory, and experiment. For the wave vector of particular interest (2.25, 2.25, 2.25), agreement with experiment is only possible if the long-time tails in the computer simulation are damped out. In future simulation calculations it will be important to verify that the spectrum does not contain quasiresonances associated with the dimensions of the macrocell, and to reduce the statistical noise level.

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