PHYSICAL REVIEW B VOLUME 11, NUMBER 2 15 JANUARY 1975

Temperature dependence of far-infrared absorption in GaAs

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(Received 1 August 1974)

The temperature dependence of the far-infrared absorption in GaAs has been measured. The results show that both two- and three-phonon difference processes contribute to the absorption. The two-phonon part of the absorption is dominated by processes which involve optical and longitudinal-acoustic phonons (O-LA) rather than longitudinal- and transverse-acoustic phonons (LA-TA). Since density-of-states arguments imply that the absorption from LA-TA should be an order of magnitude larger than O-LA the implication is that there is a considerable difference in the coupling coefficients. This result is consistent with the approximation selection rules proposed by Nedoluha.

I. INTRODUCTION

In crystals the infrared absorption on either side of a fundamental resonance arises from various multiphonon processes.[1–3] On the long-wavelength side of this resonance the absorption is usually dominated by two-phonon difference processes in which one phonon is absorbed and another emitted with higher energy. In addition, there will be a background absorption from similar processes involving three phonons.[1] In this work the temperature dependence of the far-infrared absorption in GaAs in the 50–110 cm^{-1} frequency range has been measured between 60 and 480 °K. At higher temperatures the absorption is observed to vary as $AT+BT^2$ where A and B are constants. The high-temperature absorption from a two-phonon process varies linearly with temperature while that from a three-phonon process varies as T^2 so that this is the form expected for a mixture of two-phonon and three-phonon difference processes. More detailed analysis of temperature dependence at low temperatures shows the dominant two-phonon difference process to involve optical and longitudinal-acoustic phonons (O-LA) rather than longitudinal- and transverse-acoustic phonons (LA-TA). Neither of these processes is forbidden by symmetry arguments.[4] Since arguments based on densities of states and phonon occupation numbers imply that the absorption from LA-TA should be an order of magnitude larger than O-LA the implication is that there is a considerable difference in the coupling coefficients. These observations are consistent with the results of a theoretical approach in which the anharmonic part of the Hamiltonian is limited to interactions between nearest-neighbor ions. Nedoluha has shown that in this approximation the number of possible two-phonon combinations is considerably reduced. The most striking prediction is that all combinations involving the transverse-acoustic branch will be weak.[5]

The absorption coefficient from two-phonon difference processes will be a sum over contributions of the form,[1–3]

$$\alpha(\omega) \sim \omega \sum_{\omega_1, \omega_2} C_{12} \frac{n_1 - n_2}{\omega_1 \omega_2}, \qquad \omega_1 < \omega_2, \quad \omega = \omega_2 - \omega_1, \tag{1}$$

where ω_1 is the frequency of the phonon which is absorbed and ω_2 is the frequency of a phonon which is emitted with the same momentum on a higher branch of the phonon dispersion curves. The difference in energy is supplied by the absorbed infrared quantum. C_{12} is the coupling coefficient which is assumed to be temperature independent. The temperature dependence is contained in the term $n_1 - n_2$, where n_1 and n_2 are the Bose-Einstein occupation numbers $1/n_i = \exp(\hbar\omega_i/kT) - 1$. At high temperature $n_1 - n_2$ becomes linear in temperature with the transition to linear behavior occuring around a temperature T_L, where $\hbar\omega_1/kT_L = 1$. Thus, if the absorption is dominated by phonons from only one pair of branches it is possible to relate T_L to the frequencies of the phonons involved.

If we include three-phonon effects, the high-temperature ir absorption will be of the form $AT + BT^2$ because the three-phonon processes show a T^2 temperature dependence.[1] A plot of the absorption divided by temperature will then be a straight line at high temperature. It will begin to drop below this line at temperatures below T_L, where T_L depends on the frequency ω_1 of the phonon involved in the two-phonon absorption process. As we show below, the three-phonon contribution shows a fairly small deviation from T^2 behavior at low temperatures.

II. EXPERIMENTAL PROCEDURE AND RESULTS

In Fig. 1 experimental measurements of α/T for GaAs are plotted vs T, where α is the absorption per centimeter and T is the sample temperature in °K. Transmission measurements were made at fixed frequencies of 50.0, 80.0, and

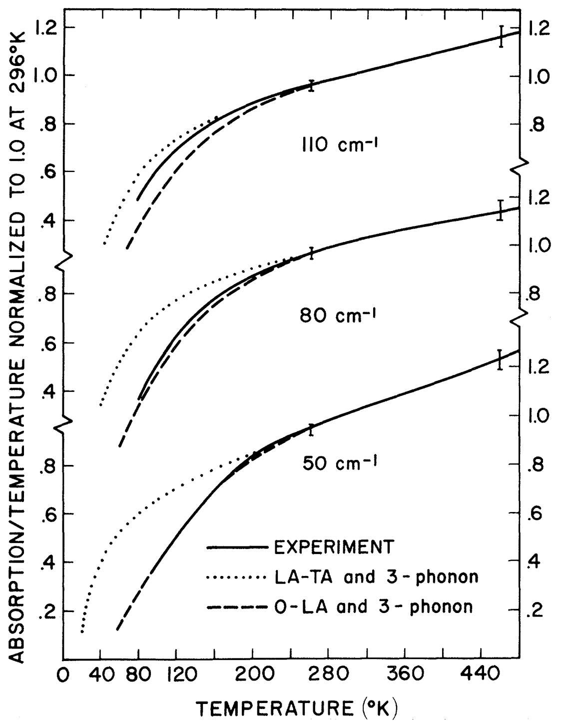

FIG. 1. Plots of absorption coefficient divided by temperature vs temperature; normalized to 1.0 at 296 °K. Solid lines are experimental data, dotted lines are calculated for the process LA–TA, dashed lines are calculated for O–LA. Both calculated curves include a three-phonon contribution which was determined from the absorption at 296 and 480 °K.

110.0 cm^{-1}. The samples were Monsanto high-resistivity GaAs ($\rho = 5.7 \times 10^7\ \Omega$ cm) ranging in thickness from 1 mm to 1.5 cm. Samples were mounted in an evacuated dewar, where the temperature could be lowered using liquid nitrogen or raised with a small heater mounted near the sample. The temperature was measured with a copper-constantan thermocouple and Hewlett-Packard temperature-input modules. Each curve is a composite of runs made on samples of different thickness. The uncertainty is due to the temperature measurement and is worse at high temperatures. The curves are all normalized to 1.0 at 296 °K. At room temperature the absorption coefficients at the frequencies 50, 80, and 110 cm^{-1} are 1.08, 4.51 and 5.74 cm^{-1}, respectively.

For all three cases the α/T is indeed a straight line at higher temperatures consistent with the interpretation of the absorption as a sum of two-phonon and three-phonon difference processes. Also at each frequency T_L is about 250 °K corresponding to an initial phonon frequency of about 175 cm^{-1}. This can be compared with phonon frequencies in GaAs. Figure 2 is a set of dispersion curves for GaAs which were taken from the neutron-diffraction results of Dolling and Waugh.[6] The figure is an average of the curves in the [100] and [111] directions; the error bars show the difference in frequency between the two directions. The vertical arrows represent difference processes at 50, 80, and 100 cm^{-1}. The optical branches are quite close together and have also been averaged to a single line. From these curves it appears that the measured absorption at all three frequencies is due to processes of the type O-LA rather than LA-TA since, for the latter processes, T_L should occur at considerably lower temperatures.

There are some obvious questions to ask. Does the O-TA process still appear to dominate the absorption after the temperature dependence is analyzed more carefully? Could the results be ascribed to differences in the density of states for different processes rather than to differences in the coupling coefficients?

III. ANALYSIS OF THE TEMPERATURE DEPENDENCE

The temperature dependence was calculated for each frequency by assuming the absorption was either LA-TA plus a three-phonon background or

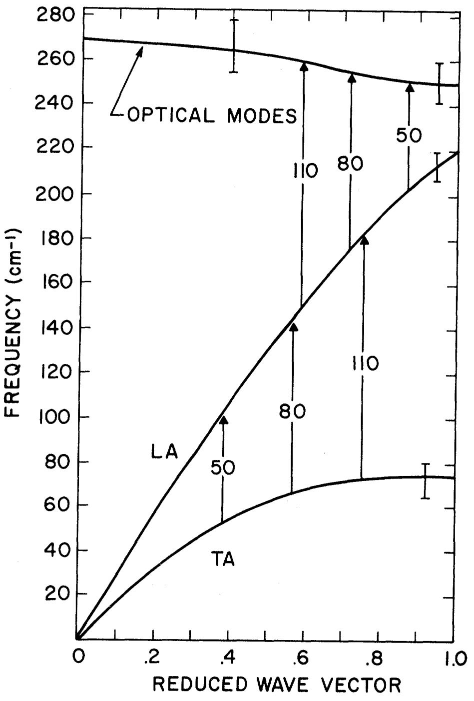

FIG. 2. Average over [100] and [111] directions of the phonon dispersion curves for GaAs. The vertical arrows represent possible two-phonon difference processes at 50, 80, and 110 cm^{-1}.

O-LA plus three-phonon. Equation (1) was used for the two-phonon part and the three-phonon background was assumed to vary as T^2 over the entire range. The relative contributions of two- and three-phonon absorption are determined from the measured absorption at 296 °K and 480 °K. The total absorption for LA-TA plus three-phonon normalized to 1.0 at 296 °K is plotted as the dotted line in Fig. 1. The process is repeated for the O-LA process and the sum of the two- and three-phonon contributions is plotted as the dashed line in Fig. 1.

The T^2 approximation for the three-phonon contribution was checked by using two extreme three-phonon processes. One is a process involving only acoustic phonons and the second is a process in which an optical phonon is destroyed and optical and acoustic phonons are emitted. For both these three-phonon processes the temperature-dependent term is of the form $(n_1n_3+n_2n_3-n_1n_2+n_3)$, where n_3 is the occupation number of the absorbed phonon.[1] The differences between the temperature dependence calculated using these three-phonon processes and the curves of Fig. 1, which were calculated using T^2, are negligible. At all three wavelengths the two-phonon contribution is about $\frac{2}{3}$ the total absorption at room temperature.

IV. DENSITIES OF STATES AND OCCUPATION NUMBERS

A comparison of the absorption from two different pairs of phonon branches must include the fact that the number of possible transitions per unit frequency can be quite different from the two combinations. If we include this combined density of states $\rho(\omega)$, Eq. (1) becomes

$$\alpha(\omega) \sim \omega\rho(\omega)D_1D_2C_{12}(n_1-n_2)/\omega_1\omega_2 \; . \tag{2}$$

For the simplified model of Fig. 2 in which the dispersion curves are independent of direction in the Brillouin zone,

$$\rho(\omega)=\frac{k^2}{|d(\omega_2-\omega_1)/dk|} \; , \tag{3}$$

where k is the absolute value of the phonon wave vector; $k=|k_1|=|k_2|$. D_1 and D_2 are the degeneracies of the phonon branches; $D=3$ for the O branch, 1 for LA, and 2 for TA.

Some conclusions can be drawn even without knowing the details of the combined densities of states. As the ir frequency increases $\rho_{\text{LA-TA}}$ will increase since the volume in k space is larger. By the same argument O-LA will decrease. For some ir frequency, ω', plots of $\rho(\omega)_{\text{LA-TA}}$ and $\rho(\omega)_{\text{O-LA}}$ vs ω will cross so that $\rho(\omega')_{\text{LA-TA}}=\rho(\omega')_{\text{O-LA}}$. For the model of Fig. 2, $\omega'=95$ cm^{-1}, since both processes involve phonons at the same wave vector and both processes include a fairly flat branch and have the LA branch in commom. The relative contributions to the absorption from LA-TA and O-LA will then be determined by the ratio of the factors $C_{12}(n_1-n_2)/\omega_1\omega_2$. At room temperature the ratio of the terms n_1-n_2 for LA-TA and O-LA is 3.8. The frequency factors in the denominator of Eq. 1 increase this ratio to 15. For LA-TA, $D_1D_2=2$ and for O-LA, $D_1D_2=3$. Thus, if the coupling constants C_{12}(LA-TA) and C_{12}(O-LA) were the same, one would expect the room-temperature absorption at 95 cm^{-1} from LA-TA to be a factor of 10 larger than from O-LA.

The actual dispersion curves will change somewhat for different directions in the zone. As a result the frequency where the densities of states are the same will differ slightly from 95 cm^{-1}. Measurements were made on each side of 95 cm^{-1}, at 80 cm^{-1} and 110 cm^{-1}. If C_{12}(LA-TA) = C_{12}(O-LA) one would expect that either at 80 cm^{-1} or 100 cm^{-1} the LA-TA absorption would be an order of magnitude larger than that from O-LA. From the data in Fig. 1, the absorption due to LA-TA is only between 20 and 50% of the two-phonon absorption in the 80 to 110 cm^{-1} region. This puts the ratio C_{12}(O-LA)/C_{12}(LA-TA) somewhere between 10 and 40. At higher frequencies $\rho_{\text{LA-TA}}$ increases and $\rho_{\text{O-LA}}$ decreases so the LA-TA contribution to the absorption should increase. This is in agreement with the observation in Fig. 1, where the LA-TA contribution is about 20% at 80 cm^{-1} and 50% at 110 cm^{-1}.

The LA-TA absorption at 50 cm^{-1} should be 95 times that from O-LA if only the occupation numbers and phonon frequencies in Eq. (1) are considered. From Fig. 2, $d(\omega_2-\omega_1)/dk$ is about the same for both processes at 50 cm^{-1} so that ratio of numbers of states is the ratio of the squares of the phonon wave vectors. Including this factor as well as the degeneracy factors, the LA-TA absorption would be 12 times larger than that from O-LA. Since the approximation of averaging the dispersion curves is worse near the zone boundary and for small frequency differences, it is, of course, difficult to place too much confidence in this number. Experimentally, no contribution from LA-TA is observed at 50 cm^{-1}.

The absorption plotted as extinction coefficient ($K=\alpha c/2\omega$) vs frequency[7] shows a sharp increase at about 150 cm^{-1} rising to a maximum at 175 cm^{-1}. This peak undoubtedly arises from an O-TA process near the zone boundary. At first sight this would appear to contradict the requirement that processes involving the TA branch are weak. Use of Eq. (2), however, shows that this is not the case. Neglecting for the moment differences in densities of states and considering only the term $(n_1-n_2)/(\omega_1\omega_2)$, which is proportional to the extinction coefficient, the absorption at 175 cm^{-1} from the process O-TA should be 14 times the absorption from the process O-LA at 80 cm^{-1}. The measured value at 175 cm^{-1} is only 3 times that at 80 cm^{-1}. If one considers the large density of states arising from the flat optical and TA branches which favors O-TA, the results are not at all inconsistent with the predictions of the nearest-neighbor selection rules.

An inspection of published data for the two-phonon sum process TA + TA provides additional qualitative evidence for the weakness of TA processes. Only a very weak contribution from the TA + TA band is observed at low temperature in InSb,[2] while the TA + TA band is not seen at all at low temperature in GaAs.[8]

V. CONCLUSION

There have been some discussion as to whether the high-temperature absorption is adequately explained by a simple mixture of T^{n-1} terms, particularly at high frequencies, where high-order ($n > 2$) sum processes are expected to dominate.[9] The present measurements at much lower frequencies show the absorption to be a mixture of T and T^2 contributions which is quite consistent with such an interpretation.

The observation that the two-phonon difference process where a longitudinal-acoustic phonon is destroyed and an optical phonon created (O-LA) is much larger than the process (LA-TA) is similar to a recently proposed quasiselection rule for NaCl-structure crystals.[10] Here, interactions involving optical and acoustic phonons are favored over those involving two optical or two acoustic phonons.

In conclusion, the measured temperature dependence of the far-infrared absorption in GaAs shows the behavior expected from a mixture of two- and three-phonon difference processes. Analysis of the temperature dependence shows there is an order of magnitude difference between the coupling coefficients for two different two-phonon processes.

ACKNOWLEDGMENTS

Discussions with J. F. Scott, J. M. Worlock, and A. Ashkin are gratefully acknowledged.

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