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Multiphonon absorption in highly transparent semiconducting crystals

Bernard Bendow and Herbert G. Lipson
Solid State Sciences Division, Rome Air Development Center, Deputy for Electronic Technology, Hanscom AFB, Massachusetts 01731

Stanford P. Yukon*
Parke Mathematical Laboratories, Carlisle, Massachusetts 01741

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We perform experimental and theoretical investigations of multiphonon infrared spectra in the three- and four-phonon regimes of semiconducting crystals, including GaAs, ZnSe, ZnS, and Si, over a range of frequencies and temperatures. The most striking aspect of these spectra is the persistence of structure at higher frequencies and elevated temperatures. A simple theoretical model which we develop and apply to interpret the data suggests that nonlinear moments and selection rules have a relatively weak effect on the observed spectra. Rather, the principal characteristics of the observed spectra appear to be consistent with highly simplified calculations emphasizing phonon density-of-states effects and multiphonon interactions induced by the anharmonic crystal potential.

I. INTRODUCTION

Considerable attention has been given in recent years to the theoretical interpretation of the multiphonon infrared absorption spectrum of solids.[1-20] However, although overall trends in frequency (ω) and temperature (T) dependence manifested by observed spectra have been accounted for reasonably well, very few calculations aimed at reproducing the detailed structural features of such spectra have been reported. Boyer *et al.*[18] predicted detectable structure in the absorption coefficient $\alpha(\omega)$ of certain ionic crystals in various temperature ranges; they utilized a hybrid calculation which combined single-particle theory[5,14] with a realistic density of phonon states for the crystal. Harrington *et al.*[21] and Duthler[22] later refined the calculations for alkali halides by incorporating approximate selection rules in a more explicit fashion. In essence, the contributions to the higher-order densities of states in the latter treatment become tagged according to the type of phonon contributing, and these contributions would interfere constructively or destructively, as dictated by appropriate approximate selection rules. The predicted behavior, which indicates suppression of even-phonon regions of the spectrum, has been confirmed experimentally in the two- to four-phonon regime of selected alkali halides.[21] We note that both of the above-mentioned theoretical treatments incorporate only linear contributions to the electric moment when calculating the absorption.

In the case of semiconductors, both previously available data[23] as well as the present measurements manifest a dominance of structure in the spectrum, as contrasted with the relatively smooth variation manifested in ionic spectra. We will see that there does not appear to be a strong influence of selection rules (which would favor various processes in different orders, say) on higher-order spectra. This suggests that to the first approximation it might be reasonable to ignore selection rules entirely when calculating the multiphonon ($n \geq 3$) absorption spectra of semiconductors. A rather general approach to calculations of this type, which accounts for both anharmonicity as well as nonlinear moments, had been given previously by Bendow *et al.*[11,12] However, computations were not performed utilizing models which were capable of accounting for detailed structure in spectra. In the present paper, we combine various elements in the latter approach to obtain an approximate expression for the absorption coefficient α which is aimed primarily at incorporating effects due to structure in the phonon density of states, yet is reasonably compact and well suited for numerical computations. This expression for α is a functional of the anharmonic displacement-displacement correlator σ of the lattice.[7] We choose to calculate σ utilizing a highly simplified but exactly soluble model for the anharmonic interactions in the lattice, whence we obtain a final expression for $\alpha(\omega)$ in the form of a double convolution series involving functions which are quite similar to the lattice density of states. For the linear-moment case, the double series collapses to the single one familiar from other treatments of multiphonon absorption.[2,7,18,19] We find that the formulation developed here is especially convenient for theoretically investigating the effects of variations in anharmonicity and nonlinearity in the electric moment on the multiphonon absorption spectrum.

The present measurements are aimed at extending the available data on multiphonon absorption for various semiconductors (see Refs. 24 and 25 for Si, Refs. 26 and 27 for GaAs, Refs. 28 and 29 for ZnS, and Ref. 27 for ZnSe) into the three- and four-phonon regimes (and over an expanded range of higher temperatures); and providing appropriate data for a detailed comparison between theory and experiment in the many-phonon regime. The measurements were performed utilizing a Digilab FTS-14 Fourier-transform spectrophotometer in the double-beam mode, and absorption values deduced from transmission in the usual fashion. A small furnace was placed close to the focal point of the spectrophotometer compartment for the elevated-temperature measurements. The sample temperature was monitored by a Cu-Constantan thermocouple in contact with the edge of the sample. Corrections were incorporated for variations of the 100% line, and variations in the reflectivity, as functions of both frequency and temperature in the ranges investigated. The spectrophotometer values were verified at selected frequencies using emittance spectroscopy,[30] standard thermocouple calorimetry,[31,32] and/or photoacoustic calorimetry.[33] The samples utilized for the present study consisted of Texas Instruments Lopex (111) single-crystal silicon, Raytheon chemical-vapor deposition-grown ZnS and ZnSe, and high-resistivity horizontal Bridgman-grown GaAs obtained from Laser Diode Labs, Inc. (The ZnS samples displayed either strong impurity bands or considerable scattering above 1000 cm^{-1}, limiting their usefulness somewhat for the present study.)

In Sec. II the formal theory is developed, and expressions for $\alpha(\omega)$ are obtained. In Sec. III, we perform calculations for a variety of cases, present the experimental results, and compare them with theoretical predictions. We also discuss certain implications of the present study and indicate the significance of our results with respect to the field of multiphonon absorption in general.

II. SIMPLIFIED MODEL FOR MULTIPHONON ABSORPTION

A. Expression for $\alpha(\omega)$ as a functional of the lattice correlator

The formal expression for the absorption coefficient in terms of the susceptibility χ is[7,11]

$$\alpha(\omega) = (4\pi\omega/n_1 c)\,\mathrm{Im}\,\chi(\omega)\,, \tag{2.1}$$

where n_1 is the refractive index, and $\chi(\omega)$ is the Fourier transform of the susceptibility

$$\chi(t) = (1/\hbar V)\langle\langle M(t); M(0)\rangle\rangle\,, \tag{2.2}$$

where V is the crystal volume, M is the dipole moment of the lattice, and $\langle\langle\ \rangle\rangle$ indicates a Green's function. We adopt an independent-cell approximation[11] for M, in which the crystal moment is replaced by $M = Nm$, where m is the moment of a single cell.[34] Such an approximation for the moment is appropriate for the many-phonon response sought here, in which we suppress all selection rules, thereby allowing phonons from all branches and points in the zone to be excited. This choice does not restrict the distribution; indeed, we will utilize the *full* distribution of phonon modes throughout the calculations, although the moments are restricted to a single cell. This "hybrid" approach follows closely the spirit of Refs. 11, 18, and 19, for example. One then has

$$\alpha(\omega) = \frac{4\pi\omega}{v_a \hbar n_1 c}\,\frac{1}{2[n(\omega)+1]}F(\omega)\,, \tag{2.3}$$

where v_a is the volume per particle, $F(\omega) \equiv \langle m(t)m(0)\rangle_\omega$ is the Fourier transform of the correlation function $F(t)$ for the moment m, and $n(\omega)$ is the Bose-Einstein function, $n(\omega) = [\exp(\beta\omega) - 1]^{-1}$, $\beta^{-1} = k_B T$. The well-known relationship[35] between the imaginary part of the Green's function and the corresponding correlator has been utilized in obtaining (2.3). If we further define a dimensionless moment $f(x)$ through

$$m(x) = m_0 e r_0 f(x)\,,$$

where r_0 is the equilibrium atomic separation; and constants $\gamma_{1,2}$ through

$$v_a \equiv \gamma_1 a_0^3\,,\quad r_0 \equiv \gamma_2 a_0\,;$$

then

$$\alpha(\omega) = \frac{2\pi m_0^2}{n_1}\,\frac{\gamma_2^2}{\gamma_1}\,\frac{e^2}{\hbar c}\,\frac{1}{a_0}\,\frac{\omega}{\omega_0}\,\frac{F(\omega/\omega_0)}{n(\omega)+1}\,, \tag{2.4}$$

where F is now the correlator for the dimensionless moment $f(x)$, and an arbitrary scaling frequency ω_0 has been introduced for convenience. The present model will assume one "bond" moment[34] per unit cell, depending on just the relative atomic displacement u. These restrictions are introduced solely for reasons of convenience; the present development may be straightforwardly generalized to account for multiple bonds, and for the vector character of the moments. Nevertheless, we believe that the single-bond, scalar model to be employed here does incorporate the essential physics of the multiphonon absorption process.

In what follows, we will utilize moments of the form

$$f(u) = e^{-2\xi_1 u}\,. \tag{2.5}$$

For this case, one can express F in terms of a cumulant expansion[11] in the form

$$F(t) = \exp[-W + 4\xi_1^2\sigma_1(t) + \cdots]\,, \tag{2.6}$$

where the omitted terms involve higher-order correlators (containing more than two displacements) and where W is a Debye-Waller factor. Thus, neglecting the time-independent factor W and the higher-order correlations,

$$F(\omega)=\sum_{n=1}^{\infty}\frac{(2\xi_1)^2}{n!}\sigma_n(\omega)\,, \tag{2.7}$$

where the $n=0$ term has been omitted since it contributes only at $\omega=0$. (We note that as long as M is a sum of bond moments, $M=\sum m_{ij}$, then a cumulant expansion similar to that in Eq. (2.6) can be carried out for more general forms of M, as described in detail in Refs. 11 and 36. The results indicate that if the series similar to the one in the exponent in Eq. (2.6) is cut off at quadratic (two-displacement) terms as done above, and if correlations between moments in different cells are neglected, then one essentially obtains

$$F(\omega)=\sum_{n=1}^{\infty}\frac{(f^{(n)})^2}{n!}\sigma_n(\omega)\,,$$

where $f^{(n)}$ is the nth derivative of $f(x)$, and σ_n is the nth convolution of the anharmonic displacement-displacement correlator $\sigma_1(\omega)\equiv\langle u(t)u(0)\rangle_\omega$. This expression is equivalent to Eq. (2.7) for the particular $f(x)$ chosen in Eq. (2.5).) Thus, within the present approximations, $\alpha(\omega)$ becomes a functional of $\sigma_1(\omega)$, $\alpha=\alpha(\sigma_1(\omega))$, and is therefore determined essentially by just the single correlator $\sigma_1(t)$. Since σ_1 is an anharmonic correlator, F and therefore α will contain contributions from couplings of all orders in the nonlinear moments and the anharmonicity. For the linear moment case one obtains the familiar result $\alpha\sim\langle u(t)u(0)\rangle_\omega$.

B. Evaluation of $\sigma_1(\omega)$

The evaluation of an anharmonic correlator of the type $\sigma_1(\omega)$ for a real crystal is a formidable task, even in the few-phonon regime, let alone the multiphonon regime of interest in the present treatment. Rather than starting from general formulas applicable to real crystals and then invoking a series of approximations to make the calculations tractable, we choose instead to start from an exactly soluble model to begin with. We believe that this model, although admittedly somewhat oversimplified, nevertheless contains the principal physics of the many-phonon response in crystals. The Hamiltonian we adopt for this purpose is essentially the one utilized for studying electronic impurity sidebands[37] (Huang-Rhys model and its variations),

$$H=\omega_0\begin{pmatrix}0&0\\0&1\end{pmatrix}+\sum_i\omega_i a_i^\dagger a_i+\sum_i V_i\begin{pmatrix}1&0\\0&-1\end{pmatrix}(a_i^\dagger+a_i)\,, \tag{2.8}$$

where ω_0 is an arbitrary phonon and the ω_i's (creation-annihilation operators $a_i^\dagger, a_i$) are the remaining phonon modes; V_i is a measure of the coupling between the mode ω_0 and the mode ω_i. Note that although the interaction term in H is linear in V_i, the coupling between the excited and unexcited states of ω_0 will, in general, lead to response functions containing contributions from all orders in V_i (all orders of phonons). In effect, in the present model one truncates the space of ω_0 from $\infty\times\infty$ to 2×2, to allow exact calculation of the response of the mode ω_0 interacting with the rest of the lattice. The two levels represent the absence of the phonon ω_0 (zero energy) and its presence, i.e., its excitation (energy ω_0). For this system the many-phonon response will consist of the virtual excitation of the state ω_0, followed by its decay through interactions (V_i's) with phonons ω_i. This situation is quite similar to the usual picture of (damped) anharmonic absorption where a single TO mode is excited (virtually) and subsequently damps through interactions with other phonons. A principal limitation of the present model is the neglect of higher-order terms involving multiple excitations of ω_0 in a single transition. Although such an approximation cannot be rigorously justified, it does nevertheless appear reasonable for calculating the *many*-phonon response, since multiple transitions involving all of the remaining ω_i's except for ω_0 are indeed properly included. There is one other important consequence of the use of the present model which requires consideration. Since the mode ω_0 here takes on a fermion rather than boson character, it will be necessary at finite temperatures to alter the results so that in fact a boson temperature dependence will be obtained for ω_0. The T dependence of the remaining modes will, of course, be correct to begin with, and will not require modification.

In the truncated representation we require the response function for the displacement

$$u_0(t)=\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}\begin{pmatrix}0&e^{i\omega_0 t}\\e^{-i\omega_0 t}&0\end{pmatrix}. \tag{2.9}$$

We define the dimensionless correlator σ_0

$$\sigma_0(t)=\langle u_0(t)u_0(0)\rangle\frac{2m\omega_0 a_0^2}{\hbar}=\sigma_1(t)\frac{2m\omega_0 a_0^2}{\hbar}\,, \tag{2.10}$$

where u_0 is now measured in units of a_0. The evaluation of σ_0 is given in Appendix A, with the result

$$\begin{gathered}\sigma_0(\omega)=\tilde\sigma(\omega-\omega_0)D_1(T)+\tilde\sigma(\omega+\omega_0)D_2(T)\,,\\ D_1^{-1}=z_0=1+e^{-\beta\omega_0}\,,\quad D_2=e^{-\beta\omega_0}D_1\,,\end{gathered} \tag{2.11}$$

where z_0 is the (fermion) partition function for the mode ω_0. $\tilde\sigma$ is the usual response function obtained for a generalized Huang-Rhys model[37] (T dependence of ω_0 ignored),

$$\tilde\sigma(\omega)=\sum_n\frac{1}{n!}\rho_n(\omega)\,, \tag{2.12}$$

where ρ_n is the nth convolution of

$$\begin{aligned} &\rho_1(\omega) = \sum_i a_i^2\,\delta(\omega - \omega_i)\,[n(\omega)+1] \quad \text{for } \omega > 0\,, \\ &\rho_1(\omega) = e^{-\beta|\omega|}\rho_1(|\omega|) \quad \text{for } \omega < 0\,, \\ &F_i \equiv 2V_i/\omega_i\,. \end{aligned} \tag{2.13}$$

If the F_i's are assumed constant then the ρ_n's become simply the n-phonon densities of state for the lattice.[35] We will return to the question of choosing the values of the a_i's later on.

As remarked previously, the appearance of the fermion T dependences D_1 and D_2 is a result of the truncated representation for the mode ω_0 in the model Hamiltonian H. There are various physically reasonable ways to patch up this deficiency although strictly speaking none of them can be justified rigorously. One way is to simply utilize the results obtained by ignoring the T dependence associated with ω_0, i.e., by setting $D_1, D_2 = 1$, but then it would be necessary to remove the $n(\omega)+1$ factor in the denominator of Eq. (2.4) so as to obtain the T-independent one-phonon absorption which follows from a rigorous theory. However, the T dependence for j-phonon absorption would then vary as $[n(\omega_i)+1]^{j-1}$, as opposed to the correct variation $[n(\omega_i)+1]^j/[n(\omega)+1]$ (although this difference is not really substantial unless $\beta\omega \gtrsim 1$). We therefore elect here to take a somewhat different approach, by replacing the Fermi factors D_1 and D_2 by the boson factors $n(\omega_0)+1$ and $n(\omega_0)$, respectively. This replacement is motivated by the $V_i = 0$ results, for which

$$\tilde{\sigma}(\omega) \sim \delta(\omega - \omega_0)\,[n(\omega_0)+1] + \delta(\omega + \omega_0)\,n(\omega_0)\,. \tag{2.14}$$

Such a replacement may be alternatively postulated as the result of assuming a boson thermal dependence for the fermion operators representing the mode ω_0, when performing the thermal average in σ_0. This choice automatically provides correct results for $V_i = 0$, and leads to the correct form for the multiphonon T dependence as well. We thus retain an exact treatment of multiphonon dynamics, i.e., the interaction of the mode ω_0 with the modes $\{\omega_i\}$, but alter the thermodynamics (T dependence of ω_0) to conform to the physically correct behavior. The expression for σ_0 takes the form

$$\sigma_0(\omega) = \tilde{\sigma}(\omega - \omega_0)\,[n(\omega_0)+1] + \tilde{\sigma}(\omega + \omega_0)\,n(\omega_0)\,. \tag{2.15}$$

The above development provides an expression for the response function of a single mode ω_0. To obtain $\alpha(\omega)$, we may either choose the ω_0 in σ_1 as some suitably averaged phonon mode and utilize σ_1 directly or else we may take an appropriately weighted average of σ_1 over all the modes of the lattice, and employ the resulting averaged quantity $\bar{\sigma}_1$ in the calculation. We will here employ the latter procedure in which $\sigma_1 \to \bar{\sigma}_1$, with

$$\bar{\sigma}_1(\omega) = B\int_0^\infty d\omega_0\, g(\omega_0)\frac{1}{\omega_0}\sigma_0(\omega, \omega_0)\,, \tag{2.16}$$

where $B \equiv \hbar/2ma_0^2$, and $g(\omega_0)$ is the normalized density of phonon states $\int g\, d\omega / \int d\omega = 1$. Then

$$\bar{\sigma}_1(\omega) = \int_{-\infty}^{\infty} dx\, \varphi(x)\tilde{\sigma}(\omega - x)\,,$$

where

$$\varphi(x) = \begin{cases} B\dfrac{\varphi(x)}{x}[n(x)+1]\,, & x > 0 \\ B\dfrac{\varphi(|x|)}{|x|}n(x)\,, & x < 0\,. \end{cases} \tag{2.17}$$

$\varphi(x)$ is simply the harmonic response function for the lattice,[35]

$$\varphi(\omega) = \langle u(t,0)\,u(0,0)\rangle_\omega\,. \tag{2.18}$$

Thus, $\bar{\sigma}_1$ is obtained by convolving $\tilde{\sigma}$ with φ; the resulting quantity may be then utilized to calculate $F(\omega)$ [Eq. (2.7)] and consequently $\alpha(\omega)$ [Eq. (2.4)].

In order to calculate $\tilde{\sigma}$ or $\bar{\sigma}_1$, one must first obtain the function $\rho_1(\omega)$ given by Eq. (2.13), which in turn requires the choice of the parameters $F_i = 2V_i/\omega_i$. Because of the highly simplified nature of the present model, it is not possible to postulate a single unique and unambiguous relationship between the parameter F_i and the anharmonic coupling of a realistic crystal lattice. Instead, it appears more reasonable to adopt the simplest possible choice for the value of F_i, namely, F_i = constant for all i. In Appendix B, we indicate a possible prescription from which one may obtain a rough estimate for the magnitude of F_i, and infer its dependence on lattice parameters as well. The results of the latter analysis indicate that

$$F_i^2 \cong \lambda_i^2\omega_0/8m_i\omega_i^2\,, \tag{2.19}$$

where m_i is an appropriate mass, and λ_i is the range parameter associated with mode i; a Morse interaction potential[11] has been assumed. Because of the crudeness of the model as well as the prescription, it seems reasonable to simplify matters further by replacing ω_0^2/ω_i in Eq. (2.19) with an average optical mode frequency $\bar{\omega}$, λ_i^2 by the usual thermodynamically determined λ, and m_i by the reduced mass in the bond, so that $F_i^2 = a^2 = \lambda^2(8m\bar{\omega})^{-1}$. With this replacement, $\rho_1(\omega)$ becomes

$$\rho_1(\omega) = 3\,ra^2\varphi(\omega)\,[n(\omega)+1]\,, \tag{2.20}$$

where r is the number of atoms per unit cell. Thus, apart from the constants involved, each $\bar{\sigma}_j$ is obtained from j convolutions of $\varphi(\omega)\,[n(\omega)+1]$, followed by a single final convolution with

$\omega^{-1}\varphi(\omega)[n(\omega)+1]$. If we had chosen V_i constant rather than $F_i = \text{const}$, then $j+1$ convolutions of $\omega^{-1}\varphi(\omega)[n(\omega)+1]$ would have been required. As stated previously, a rigorous basis for choosing between such alternative prescriptions is not available because of the simplified model utilized here. As we will see in Sec. III, the details of the calculated spectra may depend sensitively on the particular density of states utilized as input, so that certain of the distinctions under discussion here pertain to a level of accuracy beyond that achievable in the computations in the first place. For calculations in this paper we will utilize the prescription $F_i^2 = a^2$ for all i, but we will consider a^2 as a variable which may, in general, differ somewhat from its estimated value of $\lambda^2(8m\bar{\omega})^{-1}$. Such variations are not unreasonable due to the uncertainty in the values of the range parameters characteristic of interatomic interactions in semiconducting solids.[38]

III. RESULTS AND DISCUSSION

We first examine some general characteristics of spectra calculated via the procedure described in Sec. II. Let us employ a density of states appropriate to ZnSe,[39] along with the moment function given by Eq. (2.6). If we vary both the parameter ξ_1 in the moment and the potential parameter a^2, then we obtain the behavior indicated in Fig. 1 (the curves have been adjusted to make the peak near 600 cm^{-1} coincide for all). Inspection of the values for the range parameters given in Ref. 11 suggests that the potential will have a relatively larger effect than the moment in determining the rate of decrease of α vs ω, and this is indeed borne out by the curves presented in Fig. 1. One can show[11, 16] that the relative insensitivity to changes in the moment occurs only when the linear and nonlinear portions possess differing signs, as is the case for the semiconductors considered here. As expected, the shape of the curves is determined primarily by the input density of states rather than the parameters characterizing the potential or moment. Also, although the moment is more effective in changing the shape of structural features than the potential, such changes are in any case relatively small compared to those associated with variations in the phonon density of states. The substantial differences in the latter function obtained by various workers is perhaps the primary difficulty one faces when attempting comparison between theory and experiment. For example, typical differences in spectra predicted for different inputs for GaAs are indicated in Fig. 2. The uncertainties which arise in this fashion suggest that a comparison of overall trends over a range of frequencies, temperatures, and different materials should be more significant than detailed comparisons for particular cases.

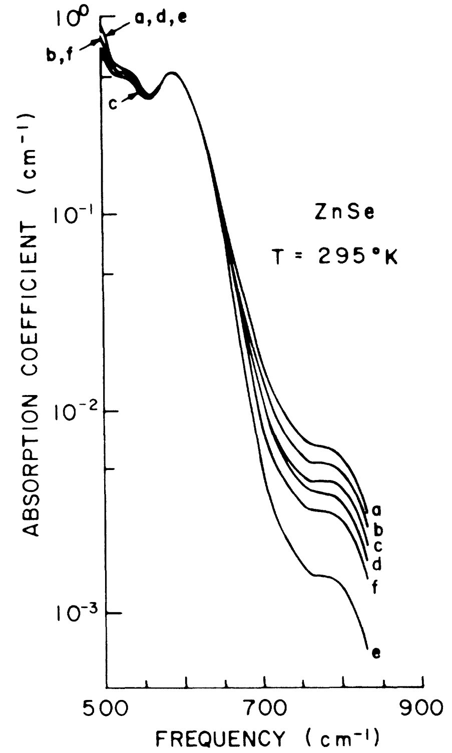

FIG. 1. Calculated absorption coefficient vs frequency in the three- to four-phonon frequency regime of ZnSe, for different values of potential (a^2) and moment (ξ_1^2) parameters. Curve (a) is calculated using parameter values from Ref. 11; for (b), $\xi_1^2 \rightarrow 0.5\xi_1^2$; (c), $\xi_1^2 \rightarrow 0.1\xi_1^2$; (d), $a^2 \rightarrow 0.5a^2$; (e), $a^2 \rightarrow 0.1a^2$; (f), $\xi_1^2 \rightarrow 0.5\xi_1^2$ and $a^2 \rightarrow 0.5a^2$.

Thus, rather than focusing our efforts at obtaining more accurate densities of states, we instead utilize those which are readily available in the literature, and concentrate on deducing the overall trends which emerge from the calculations.

The results of both our measurements and calculations are indicated in Figs. 3–6, for the case of GaAs, ZnSe, ZnS, and Si, respectively. In all of the calculations, the moment parameters obtained in Ref. 11 were utilized. The potential parameter λ [see Eq. (2.18)] from Ref. 11 was utilized for ZnSe and ZnS. A value of twice the listed λ was utilized for GaAs to obtain a best fit, and λ was varied to obtain a best fit for Si, where a starting value was not available (the λ chosen was about one and a half times the typical values for III-V and II-VI's listed in Ref. 11). λ was not varied for ZnSe because the fit was relatively good without it, and it was not varied for ZnS because of the uncertainties in the absorption background induced by impurities in the samples. For each crystal the absolute magnitude of α was adjusted to obtain a best fit, and to facilitate comparison with experiment.

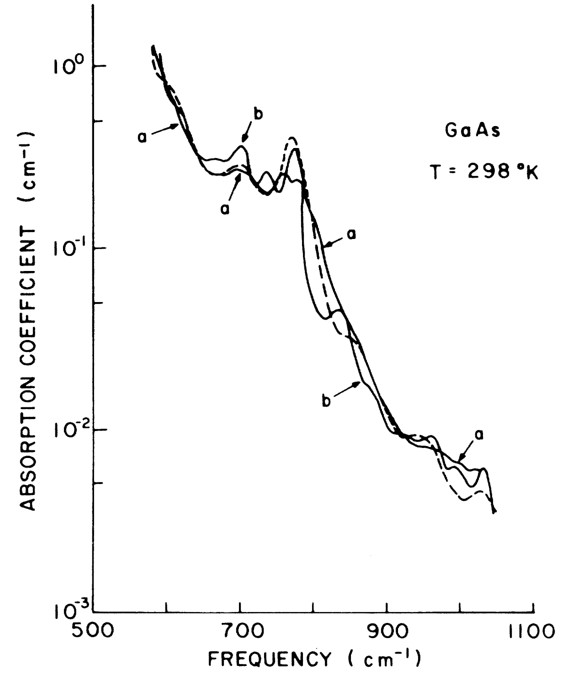

FIG. 2. Absorption coefficient vs frequency for GaAs. Broken curves were calculated using density of states from (a) K. Kunc *et al.*, Phys. Status Solidi 72, 229 (1975) and (b) G. Dolling and R. A. Cowley, Proc. Phys. Soc. Lond. 88, 463 (1966). Solid curve is experimental measurements (this work).

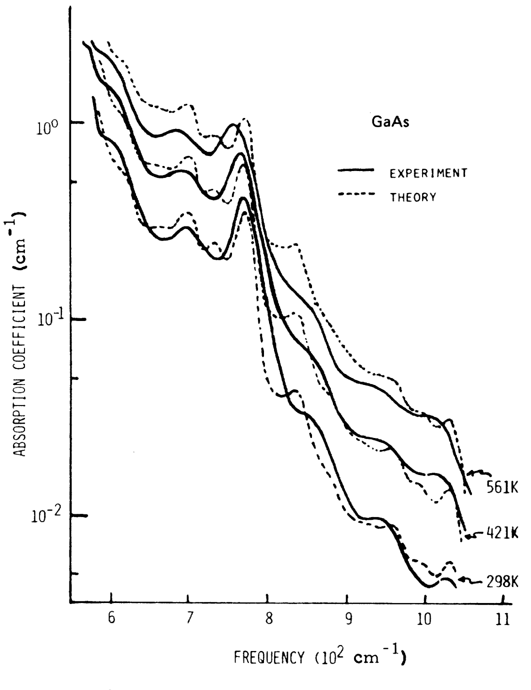

FIG. 3. Absorption coefficient vs frequency at selected temperature for GaAs. Density of phonon states taken from Dolling and Cowley (see Fig. 2).

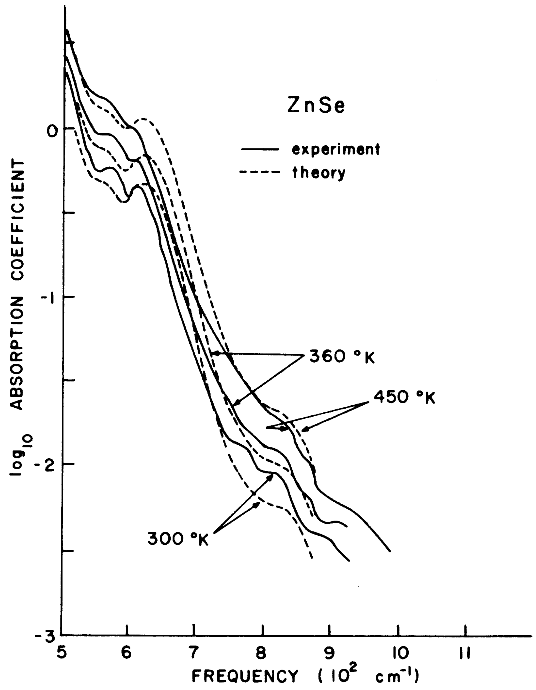

FIG. 4. Log$_{10}$ of absorption coefficient (cm^{-1}) vs frequency at selected temperatures for ZnSe. Density of phonon states taken from Kunc *et al.* (see Fig. 2).

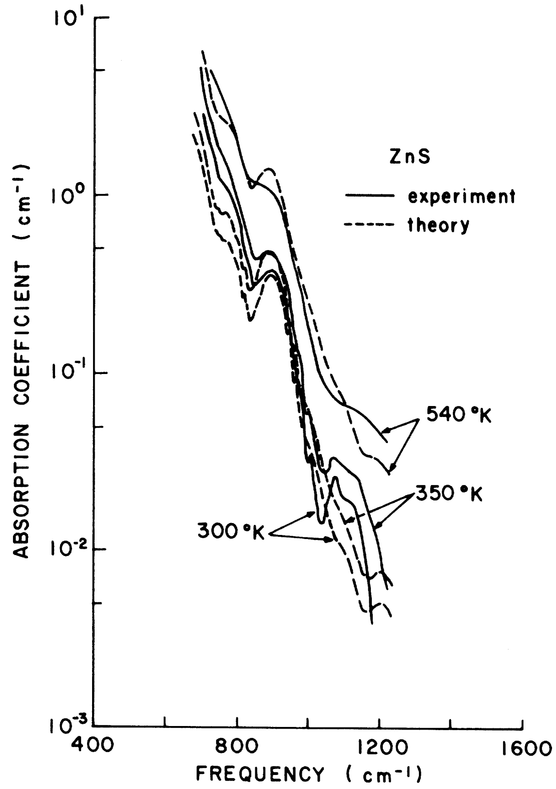

FIG. 5. Absorption coefficient vs frequency at selected temperatures for ZnS. Density of phonon states taken from Kunc *et al.* (see Fig. 2).

The single most striking characteristic of both the experimental and theoretical spectra is the persistence and dominance of structure well into the three- and four-phonon regimes, and up into elevated temperatures. This behavior contrasts sharply with that for ionic solids such as alkali halides[27] and alkaline earth fluorides,[40] where even the room-temperature (and for some cases the low-temperature) spectra are nearly structureless, and close to exponential-like as a function of frequency. As can be seen from the figures, the overall agreement between theory and experiment with respect to both frequency and temperature variations is reasonably good, which suggests that the presently observed structure at lower levels of absorption is due indeed to intrinsic multiphonon processes. In general, peak and shoulder positions in the experimental and calculated spectra agree quite well, suggesting that the observed structure is associated with phonon density-of-states effects. It is reasonable to infer that selection rules have at best a weak influence on the observed spectra. Although it is possible that various extra predicted peaks which are absent or weak in the experimental data (in the 700–800 cm^{-1} and approximately 1000 cm^{-1} regimes in GaAs and approximately 1400 cm^{-1} in Si, for example) are suppressed as a result of selection rules, uncertainties in the accuracy of the input density of states prevents one from drawing more definite conclusions. Although the detailed selection rules for the present crystals have not been worked out theoretically for three- and four-phonon processes, their weak effects in the many-phonon regime as manifested in the present study is in agreement with the preliminary work of Duthler,[41] who finds that strong effects of selection rules do not obtain for tetrahedral semiconductors as they do for rocksalt crystals,[22] for example.

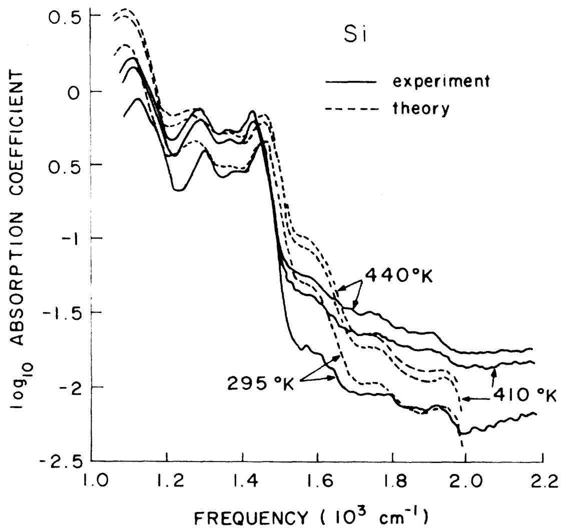

FIG. 6. Log_{10} of absorption coefficient (cm^{-1}) vs frequency at selected temperatures for Si. Density of phonon states taken from C. S. Wang *et al.*, Phys. Lett. 44A, 517 (1973).

One additional factor of importance which must be considered in comparing theory with experiment is the effect of anharmonic broadening and shifting of peaks in the spectrum.[38,42] In a real crystal, the anharmonicity potential induces a complex self-energy for all phonon modes,[42] a phenomenon which is not accounted for by the highly simplified Hamiltonian of Eq. (2.8). Nonetheless, the general characteristics of the anharmonic broadening are well known and ought to be involved to interpret aspects of the present data: specifically, the linewidth increases and the line position shifts to lower frequency[43] with increasing temperature. These phenomena are clearly manifested by the peaks in the ZnSe data near 600 cm^{-1}, in GaAs near 700, 750, 950, and 1000 cm^{-1}, and in ZnS near 900 cm^{-1}, for example. One observes that the suppression is more striking for the more ionic semiconductors (least evident for IV-IV's, most evident for II-VI's). This pattern fits in well with the absence of structure in the spectra of the more highly ionic solids[27,35,44] such as alkali halides, crystals which presumably are characterized by a greater degree of anharmonicity (large anharmonic potential). Correspondingly, as one progresses through a series of increasingly ionic solids, the spectrum tends toward the exponential-like frequency dependence which is predicted[2,5,7,14] when structural features are absent in the density of states, behavior which is clearly manifested by the present data.

It is interesting to compare the absolute magnitude of α_{cal} predicted by theory with experimental values α_{exp}. In the case of ZnSe, where no parameters were varied, $\alpha_{cal}/\alpha_{exp} \approx 25$; the greatest departure was for ZnS, where $\alpha_{cal}/\alpha_{exp} \approx 70$. This disagreement probably arises from a combination of factors: the oversimplified form for the potential which lumps the anharmonicity into a single parameter a^2, and the uncertainty in the form of the moment and the value of m_0 characteristic of semiconductors. For example, certain authors assign zero static charges to the atoms in zinc-blende semiconductors, while others assign charges in excess of unity.[38] Moreover, returning to the potential, note that an uncertainty in λ of a factor of 2 leads to an uncertainty in the calculated four-phonon absorption by a factor of 256. These simple observations point to the necessity for highly accurate input values for moments and potentials if quantitatively accurate predictions are really anticipated.

In conclusion, we have measured the many-phonon absorption in typical semiconducting crystals, and find persistent structure in the spectrum over a range of frequencies and elevated temperatures. We have performed simplified calculations which account well for the principal trends in the frequency and temperature dependence of the observed spectra. Comparison of theory with experiment suggests that the principal factor determining the spectral shape is the density of phonon states, and that selection rules play a relatively minor role in the many-phonon regime. The present study has hopefully contributed towards a more comprehensive and unified picture of the nature and origins of the spectral characteristics of multiphonon absorption in the highly transparent regime of crystals.

APPENDIX A

The impurity Hamiltonian (2.8) may be diagonalized exactly by a linear shift of the phonon creation and annihilation operators. The unitary transformation that diagonalizes the full Hamiltonian may be written as $U=e^S$ with

$$S=\sum_i \begin{pmatrix} f_{0i} & 0 \\ 0 & f_{1i} \end{pmatrix} (a_i - a_i^\dagger) \text{ and } f_{0i} = -f_{1i} = \frac{V_i}{\omega_i}, \tag{A1}$$

where the linear shifts $f_{\alpha,i}$ have been determined by minimizing the ground-state energy. The transformed phonon operators are then given by

$$U \begin{pmatrix} a_i & 0 \\ 0 & a_i \end{pmatrix} U^{-1} = \begin{pmatrix} A_{0i} & 0 \\ 0 & A_{1i} \end{pmatrix} = \begin{pmatrix} a_i + f_{0i} & 0 \\ 0 & a_i + f_{1i} \end{pmatrix}, \tag{A2}$$

and the diagonalized Hamiltonian may be written as

$$H = \begin{pmatrix} \Delta_0 & 0 \\ 0 & \omega_0 + \Delta_1 \end{pmatrix} + \sum_i \begin{pmatrix} \omega_i A_{0i}^\dagger A_{0i} & 0 \\ 0 & \omega_i A_{1i}^\dagger A_{1i} \end{pmatrix}, \tag{A3}$$

where $\Delta_0 = -\sum_i \omega_i f_{0i}^2$ and $\Delta_1 = \Delta_0$ are the energy shifts for the $\chi_0 = \binom{1}{0}$ and $\chi_1 = \binom{0}{1}$ states, respectively. The original and transformed phonon states are related by

$$|\psi_{n_i}\rangle = U|n_i\rangle, \quad \text{where } |n_i\rangle = \frac{(a_i^\dagger)^{n_i}}{(n_i!)^{1/2}}|0\rangle. \tag{A4}$$

Thus, we have

$$|\psi_{n_i}\rangle = \begin{pmatrix} \frac{(A_{0i}^\dagger)^{n_i}}{(n_i!)^{1/2}} & 0 \\ 0 & \frac{(A_{1i}^\dagger)^{n_i}}{(n_i!)^{1/2}} \end{pmatrix} |\phi\rangle, \tag{A5}$$

where $|\phi\rangle = U|0\rangle$ denotes the ground state of the full Hamiltonian.

We may now calculate the correlation function $\langle u(t)u(0)\rangle_T$ where the subscript T indicates that a thermal average with respect to both phonon and fermion states is to be taken. The matrix elements appearing in $\langle u(t)u(0)\rangle_T$ for a given ith phonon mode may be reexpressed as

$$\langle\psi_{n_i}|u(t)u(0)|\psi_{n_i}\rangle = \langle n_i|U^{-1}u(t)u(0)U|n_i\rangle = \langle n_i|e^{iU^{-1}HUt}[U^{-1}u(0)U]e^{-iU^{-1}HUt}[U^{-1}u(0)U]|n_i\rangle. \tag{A6}$$

Considering first the zero-temperature limit, we evaluate the Fourier transform of the correlation function $\sigma_0(t)$ in the χ_0 sector

$$\begin{aligned} \sigma_0(t)_{T=0} &= \frac{2m\omega_0 a_0^2}{\hbar}\langle\phi;\chi_0|u(t)u(0)|\phi;\chi_0\rangle \\ &= \langle 0|e^{-i\omega_0 t}\exp\Big(\sum_i (a_i e^{-i\omega_i t} - a_i^\dagger e^{i\omega_i t})(f_{0i}-f_{1i}) - (a_i - a_i^\dagger)(f_{0i}-f_{1i})\Big)|0\rangle. \end{aligned} \tag{A7}$$

Defining the Fourier transform as

$$\sigma_0(\omega)_{T=0} = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\sigma_0(t)_{T=0}\,dt, \tag{A8}$$

we then have

$$\sigma_0(\omega)_{T=0} = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(\omega-\omega_0)t}\left\langle 0\left|\exp\Big(\sum_i (i\gamma_i a_i + i\gamma_i^* a_i^\dagger)\Big)\right|0\right\rangle \exp\Big(-\sum_i iF_i^2\sin(\omega_i t)\Big)\,dt, \tag{A9}$$

where

$$i\gamma_i = (e^{-i\omega_i t} - 1)F_i \quad \text{and} \quad F_i = f_{0i} - f_{1i} = \frac{2V_i}{\omega_i}.$$

Replacing the ground-state expectation value with a thermal average over phonon states yields

$$\tilde{\sigma}(\omega-\omega_0)=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(\omega-\omega_0)t}\exp\left(-\frac{1}{2}\sum_i \gamma_i\gamma_i^* \coth(\theta_i)\right)\exp\left(-\sum_i iF_i^2\sin(\omega_i t)\right)dt$$
$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left(-\sum_i F_i^2\coth(\theta_i)\right)\exp[i(\omega-\omega_0)t]\exp\left(\sum_i F_i^2[\coth(\theta_i)\cos(\omega_i t)-i\sin(\omega_i t)]\right)dt\,, \tag{A10}$$

where $\theta_i=\hbar\omega_i/2kT$.

A similar result holds in the χ_1 sector

$$\langle\chi_1|u(t)u(0)|\chi_1\rangle_T=\tilde{\sigma}(\omega+\omega_0)$$
$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\left(-\sum_i F_i^2\coth(\theta_i)\right)\exp[i(\omega+\omega_0)]t\exp\left(\sum_i F_i^2[\coth(\theta_i)\cos(\omega_i t)-i\sin(\omega_i t)]\right)dt\,. \tag{A11}$$

Taking a thermal average over the two fermion states χ_0 and χ_1 with energies Δ_0 and $\omega_0+\Delta_1$ yields

$$\sigma_0(\omega)=\{\tilde{\sigma}(\omega-\omega_0)\exp(-\beta\Delta_0)+\tilde{\sigma}(\omega+\omega_0)\times\exp[-\beta(\omega_0+\Delta_1)]\}Z^{-1}\,, \tag{A12}$$

where $Z=\exp(-\beta\Delta_0)+\exp[-\beta(\omega_0+\Delta_1)]$. The full temperature-dependent correlation function can thus be written as

$$\sigma_0(\omega)=\frac{\tilde{\sigma}(\omega-\omega_0)+\tilde{\sigma}(\omega+\omega_0)\exp(-\beta\omega_0)}{1+\exp(-\beta\omega_0)}\,. \tag{A13}$$

APPENDIX B: ESTIMATION OF THE INTERACTION PARAMETER V_i

Assume that the dynamics in a single crystal cell or bond to be determined by an interionic potential $v(u)$. Then the cubic anharmonicity is given by

$$V_A=(1/3!)v'''u^3\,. \tag{B1}$$

We can manipulate this term into a form similar to the interaction term in H of Eq. (2.8) if we replace one of the u's by the prescription

$$p\leftarrow im\omega_0 u \tag{B2}$$

in order to write

$$V_A=(1/3!)v'''(p/im\omega_0)u^2\,. \tag{B3}$$

Then, replacing p and one of the u's by the truncated representations

$$p=\frac{1}{i}\left(\frac{\hbar m\omega_0}{2}\right)^{1/2}\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}\,,$$
$$u=\left(\frac{\hbar}{2m\omega_0}\right)^{1/2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\,, \tag{B4}$$

and the remaining u by $(\hbar/2m_i\omega_i)^{1/2}(a_i^\dagger+a_i)$, one obtains

$$V_A=-\frac{1}{3!}v''C_0C_i^{1/2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}(a_i^\dagger+a_i)\,,$$
$$C_0\equiv\hbar/2m\omega_0\,,\quad C_i=\hbar/2m_i\omega_i\,. \tag{B5}$$

Then,

$$-(1/3!)v'''C_0C_i^{1/2}\leftarrow V_i\,. \tag{B6}$$

For a Morse potential, utilizing dimensionless displacements $u\leftarrow u/a_0$,

$$v(u)=v_0(e^{-2\lambda_i u}-2e^{-\lambda_i u})\,, \tag{B7}$$

we find

$$v_i\leftarrow v_0\lambda_i^3C_0C_i^{1/2}\,. \tag{B8}$$

If we identify the quadratic term in $v(u)$ with the harmonic energy $\frac{1}{2}m_i\omega_i u^2$, then

$$\tfrac{1}{2}m\omega_i^2\leftarrow v_0\lambda_i^2\,. \tag{B9}$$

If we use the above correspondences then

$$a_i^2=\lambda_i^2C_0^2/4C_i=\lambda_i^2\omega_0/8m_i\omega_i^2\,. \tag{B10}$$

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