RESONANT CANCELATION OF RAMAN SCATTERING FROM CdS AND Si †

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A pronounced decrease in the TO Raman scattering efficiencies of CdS has been observed as the incident photon energy approaches the direct-energy gap. Previous resonant Raman measurements have shown only monotonically increasing efficiencies. A decrease of the F_{2g} mode in Si has also been observed as the resonance with the indirect-energy gap is approached. The observed decreases in CdS and Si can both be accounted for by extending Loudon's theory to include a destructive interference between the resonant and nonresonant contributions to the Raman scattering amplitudes.

Resonant enhancement of the Raman scattering efficiency from semiconductors has recently received much attention both theoretically[1-4] and experimentally.[5-8] We extended previous measurements on CdS[8] by starting with the incident photon energy ($\hbar\omega_1 = 1.17$ eV) far from the direct-energy gap ($E_c = 2.58$ eV). As the photon energy approaches the energy gap, pronounced decreases in the Raman scattering efficiencies of the TO modes (A_1 and E_1) are observed, prior to the onset of the previously reported resonant enhancements.[8] For silicon, a monotonic decrease in the F_{2g} mode scattering efficiency is also observed as the photon energy approaches and extends beyond the indirect-energy gap. Preliminary work on Si has been reported earlier.[9] At first, these observed decreases appear contrary to existing theories which all anticipate resonant enhancements. However, a simple extension of Loudon's theory[10] to include the nonresonant terms, neglected previously, along with the usual resonant term in the Raman scattering amplitude seems to account for the observed dispersion of the TO modes in CdS. In fact, the nonresonant and resonant terms must add destructively in order to fit our measurements. Similarly for Si, the observed decrease can also be qualitatively explained by postulating a partial destructive interference between the nonresonant terms and the weaker resonant terms in the Raman amplitude. The strengths of the resonant terms for Si can be shown to be weaker than that for a direct-gap material by using estimated phonon-assisted transition probabilities.

The experimental investigations in CdS were carried out with a Nd-doped yttrium aluminum garnet (Nd:YAlG) laser (1.064 μm) and a flowing-gas ion laser[11] whose wavelengths were 5017, 5145, 5287 (argon), 5208, 5682, 6471 (krypton), and 6271 (xenon) Å. The CdS was mounted in a cold-finger liquid-nitrogen Dewar with its c axis (here called z) parallel to the incident laser polarization and the xy plane of the crystal parallel to the scattering plane. The observed scattering efficiencies of the TO and LO modes are normalized with CS_2 for all the laser wavelengths and the data are shown in Fig. 1. To obtain absolute scattering efficiencies, one can use the reported scattering efficiency of CS_2 (2.69×10^{-7} cm^{-1} sr^{-1} at 4880 Å)[12] and suitable reintroduction of the ω_{Stokes}^4 dependence. Absorption corrections in CdS are unnecessary for all the wavelengths used. The enhancements of the TO Raman efficiencies for $\hbar\omega_1 > 2.38$ eV have been reported by Leite, Damen, and Scott[8] and their points are shown in Fig. 1. The most striking new feature in Fig. 1 is the pronounced dips in the Raman scattering efficiencies for the TO modes of A_1 and E_1 symmetry, prior to the onset of resonant enhancements. By contrast, the LO scattering increased monotonically as resonance condition was approached.

The starting point of our calculation for theoretical TO curves shown in Fig. 1 is Eq. (14) of Ref. 10, which expresses the Raman scattering amplitude in terms of momentum and deformation-potential matrix elements. In order to segregate the resonant terms from nonresonant terms in Eq. (14) of Ref. 10, one can isolate terms involving virtual transitions from the highest valence band of Γ_7 symmetry to the first conduction band. Only one of the isolated terms will possess a double-order divergence as the laser photon energy approaches this energy gap. This term will be called the resonant term and is given by

$$(\text{resonant term})_{\text{direct}} = \frac{P_{0\alpha}{}^2 \Xi_{\alpha\alpha} P_{\alpha 0}{}^1}{(\omega_c - \omega_2)(\omega_c - \omega_1)}, \qquad (1)$$

where state $|0\rangle$ is the electronic ground state before each scattering event, and state $|\alpha\rangle$ is the single electron-hole pair state. ω_c is the energy of the first Γ_7 conduction band with the highest Γ_7 valence band considered as zero energy. The superscripts 1 and 2 on the momentum matrix

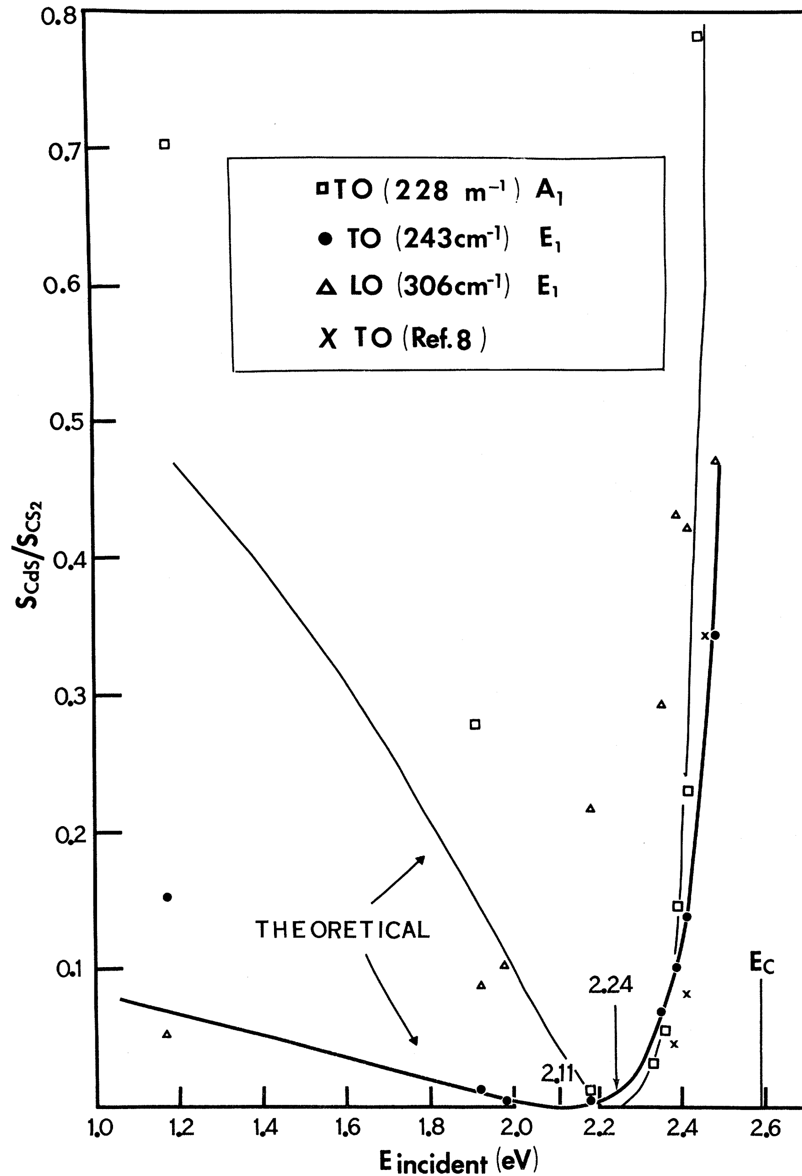

FIG. 1. The Raman scattering efficiencies of CdS (80°K) normalized to CS_2 as a function of incident photon energy. E_c is the electron-energy gap of CdS. The solid curves are computed from Eq. (3) (see text). The data points of Ref. 8, normalized to the present work at 2.47 eV, are shown for comparison purposes.

elements $P_{\alpha 0}{}^1$ and $P_{0\alpha}{}^2$ indicate that only components parallel to the polarizations of the incident and Stokes radiations, ω_1 and ω_2, respectively, are to be taken. $\Xi_{\alpha\alpha}$ is the deformation-potential matrix element, which in the absence of the electron-hole coupling will be an algebraic sum of the electron-lattice interaction in the conduction band and the hole-lattice interaction in the valence band. All other Raman amplitude terms having virtual transitions between the highest Γ_7 valence band and the first conduction band do not have double-order poles and are lumped with terms which involve other valence and higher conduction bands as intermediate states. The summation of all such terms will henceforth be referred to as nonresonant terms in the Raman amplitude. If one assumes the Γ_7 energy bands to be parabolic as well as the P-matrix and Ξ-matrix element to be constant in the Brillouin zone, the denominator of Eq. (1) summed over all $\vec{k}$ space is given by

$$f(\omega_c-\omega_1)=(\omega_c-\omega_2)^{1/2}-(\omega_c-\omega_1)^{1/2}, \qquad (2)$$

which is identical to Eq. (24) of Ref. 8. Using all

the above-stated approximations, the Raman scattering efficiencies of the TO modes in CdS, $S_{\mathrm{CdS}}^{\mathrm{TO}}$, normalized by the CS_2 scattering S_{CS_2}, are expressible as

$$\frac{S_{\mathrm{CdS}}^{\mathrm{TO}}}{S_{\mathrm{CS}_2}} = \pm A f(\omega_c - \omega_1) + B. \tag{3}$$

B represents all the nonresonant terms in the Raman amplitude, and A represents appropriate constants, P-matrix, and Ξ-matrix elements. The uncertainty of the sign in Eq. (3) stems from the uncertainty of the sign in the deformation-potential matrix element $\Xi_{\alpha\alpha}$. To account for our experimental results on the TO modes, we choose the minus sign. Using two adjustable parameters for the A_1 data and another two adjustable parameters for the E_1 data, the fits of Eq. (3) to our measurements are shown by the solid curves in Fig. 1. The photon energy at which complete vanishing of the Raman efficiency occurs depends on the ratio of the resonant to the nonresonant terms. Our data (2.11 eV for E_1 and 2.24 eV for A_1) imply that this ratio can be different for the different TO modes. The inclusion of the nonresonant terms along with the resonant term in the Raman scattering amplitude appears to be important for future theoretical discussions of resonance Raman effect.

No cancelation effects are evident from our LO data shown in Fig. 1. The enhancement of the LO phonon in CdS near resonance is well substantiated in Ref. 5. Unlike the TO Raman scattering, the LO has both contributions from the deformation potential and the electric field associated with the longitudinal optic mode in a polar medium.[13] Interference between these two contributions along with the interference between the nonresonant and resonant terms must also exist, although this has yet to be measured.

For Si, the experimental investigations made use of Nd:YAlG laser at 1.06 μm (1.17 eV), 1.12 μm (1.10 eV), and 1.32 μm (0.94 eV) and the temperature dependence of the indirect band gap[14] E_c' to vary the effect of resonance between incident laser photon energy and the indirect-energy gap. Our experimental results are summarized in Fig. 2. A decrease in the F_{2g} scattering efficiency is observed for the following two experimental conditions: (1) at a fixed temperature, with the incident photon energy increasing (see dashed curve); (2) at a fixed incident photon energy, with the sample temperature increasing (see solid curve).

The Raman efficiency of Si never vanishes completely, implying that the complete cancelation between the resonant and nonresonant terms in the Raman amplitude is not reached as was the case for CdS. This is because of the weaker nature of the resonance between the incident photon energy and the indirect-energy gap. In fact, the resonant terms must be described by a fifth-order time-dependent perturbation theory, i.e., two perturbation orders higher than for the nonresonant terms in Si and the resonant term in CdS. Resonant terms involving E_c' have the following form:

$$(\text{resonant term})_{\text{indirect}} = \frac{P_{0\alpha}{}^{2}\Xi_{\alpha\beta}{}^{\Delta}\Xi_{\beta\beta}\Xi_{\beta\alpha}{}^{\Delta}P_{\alpha0}{}^{1}}{(\omega_c-\omega_2)(\omega_c-\omega_1)(\omega_c'+\omega_A-\omega_2)(\omega_c'+\omega_A-\omega_1)}, \tag{4}$$

where $\hbar\omega_c$ is the energy of the conduction band at $\vec{k}=0$, $\hbar\omega_c'$ is the indirect-energy gap at $\vec{k}=\vec{\Delta}$, and $\hbar\omega_A$ is the phonon energy emitted for the phonon-assisted transition between $\vec{k}=0$ and $\vec{k}=\vec{\Delta}$. The two Ξ^{Δ}-matrix elements embody the deformation potentials associated with the phonon-assisted transitions, and they involve the LA, TA, LO, and TO phonons with momentum vector $\vec{\Delta}$.[14] $|\alpha\rangle$ represents the electron-hole pair states with the electron in the first conduction band at $\vec{k}=0$ and $|\beta\rangle$ is with the electron in the $\vec{k}=\vec{\Delta}$ conduction band minima. There will be other resonant terms like that shown in Eq. (4) involving permutations of the three Ξ-matrix elements, each with slightly different energy denominators. Furthermore, at high temperatures, additional resonant terms in the Raman amplitude will become significant, e.g., those involving the absorption of phonons with $\vec{k}=\vec{\Delta}$ to accomplish the phonon-assisted transition. The indirect nature of the resonant process reduces the strength of the resonant terms by a factor of $[\Xi^{\Delta}/(\omega_c-\omega_1)]^2$. Cf. Eq. (1) with Eq. (4). For silicon, $\hbar\omega_c = 3$ eV and $\Xi^{\Delta} = 1$ eV[15] at 300°K deduced from the temperature dependence of E_c'. This factor is 0.25 for $\hbar\omega_1 = 1$ eV.

The solid lines shown in Fig. 2 connect the data points measured at a fixed laser wavelength (indicated in the figure) at various crystal temperatures. The transformation from the crystal temperature to E_c' made use of the data by MacFarlane et al.[14] In an indirect-gap material, the resonant parameter $(\hbar\omega_1 - E_c')/E_0$ is not sufficient to

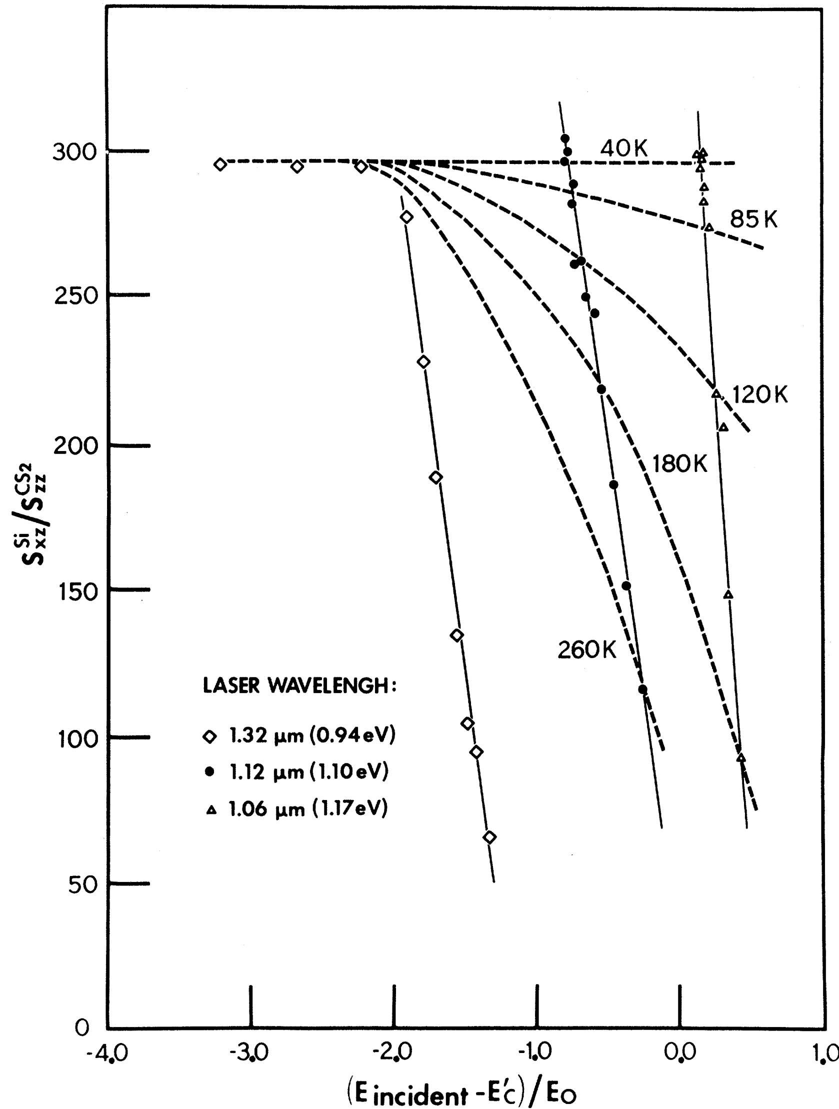

FIG. 2. The Raman scattering efficiency of F_{2g} mode in Si normalized to CS_2 as a function of the difference between the incident photon energy and the indirect-energy gap, E_c' (in units of the Raman phonon energy E_0). The dashed lines connect data points measured at a fixed temperature (as indicated) while the laser wavelengths are changed. The solid lines connect data points measured at a fixed laser wavelength (as indicated), while changing the crystal temperature, thereby E_c'. The effect of absorption has been eliminated using our data and that of Ref. 14.

describe the dispersion of the Raman scattering. There is a significant difference whether $\hbar\omega_1$ is varied while E_c' is held fixed (at fixed temperature) or vice versa. Changing E_c' by varying the crystal temperature will effect the strength of the matrix elements in the resonant terms, as we have discussed in terms of phonon-assisted transitions. Consequently, the F_{2g} Raman scattering for the three wavelengths shown (solid curves in Fig. 2) need not fall on the same curve, which might have been expected since it is a reduced variable on the abscissa.

At a low temperature, the observed Si Raman efficiency normalized by CS_2 remains constant as $\hbar\omega_1$ approaches E_c' (see Fig. 2, dashed curves). At a higher temperature, a decrease in the Raman efficiency is observed. Such temperature dependence can be qualitatively explained by noting that the strength of the resonant terms involves the presence of two Ξ^Δ-matrix elements [see Eq. (4)]. Consequently, the strength of the resonant terms will increase faster with temperature than that of the nonresonant terms. The latter only involve virtual transitions to higher

conduction bands at $\vec{k}=0$. Our data (dashed curves) imply that at low temperature, the resonant terms must be too weak to significantly cancel the nonresonant terms. However, at high temperatures partial resonant cancelation becomes observable.

Detailed calculation on the dispersion of the resonant terms for the indirect-gap semiconductors requires exact knowledge of $\vec{k}$-space dependence of the highest valence band and lowest conduction band. A recent calculation by Loudon,[16] assuming an idealized two parabolic energy-band model indicates that the strength of the resonant terms increases linearly and smoothly as $\hbar\omega_1$ passes through E_c' and continues to increase beyond E_c'. This result is supported by the solid lines shown in Fig. 2, which show the same effect on the Raman scattering amplitude whether the resonant parameter $(\omega_1-\omega_c')/\omega_0$ is increasing below or above zero.

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OPTICAL DISPERSION AND IONICITY

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The theories of $A^N B^{8-N}$ semiconductors and salts due to Phillips and Van Vechten and to Wemple and DiDomenico are compared and their similarities discussed. The dispersion energy is found to be proportional to ionicity. A simple operational definition of ionicity, based on experimentally determined moments of $\epsilon_2(\mathcal{E})$, is proposed. This definition can potentially be extended to provide a useful scaling parameter for other classes of materials such as metals and intermetallic compounds.

It is a remarkable and provocative fact that the physics of binary semiconductors and salts can be described in terms of a very simple dielectric model proposed by Phillips and Van Vechten (PV).[1-3] Recently, Wemple and DiDomenico (WD)[4] suggested another simple model for describing the same materials and a large group of oxides as well. In this Letter we begin by comparing the PV and WD theories and emphasizing their equivalent features. Then we show that the "dispersion energy" introduced by WD is not uniquely defined in terms of moments of $\epsilon_2(\mathcal{E})$ for a single oscillator model. We have consequently suggested a model-independent definition of the dispersion energy, $\mathcal{E}_d$, which we find can be related directly to the ionicity, f_i, defined by PV. The details of this relation suggest a slight revision in the PV prescription for scaling homopolar energy gaps. We furthermore find that the new definition of $\mathcal{E}_d$ when applied to the WD model predicts that the optical conductivity decreases with increasing f_i, a result which is