Resonant Raman Effect in Semiconductors

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Light scattering experiments on semiconductors are discussed in which the energy of the incident photon from the laser or that of the Raman-scattered photon is nearly coincident with that of an electronic transition in the scatterer. Experimental data on ZnTe, CdS, InAs, ZnSe, and GaP are analyzed, and a discussion of LO-overtone scattering mechanisms is presented. Some additional experiments are proposed and discussed.

INTRODUCTION: EARLY WORK ON CdS

LIGHT scattering experiments on semiconductors in which the laser energy was near that of an allowed electronic transition have been reported in six brief publications.[1–6] The results of these "resonant Raman scattering" experiments have been only partially anticipated by theories.[7–9]

The motivation for the early work[1,2] was that an increase in phonon scattering efficiencies was predicted for laser energy slightly less than the direct gap; CdS has a direct gap very near the high-power cw 4880 Å argon laser wavelength, which made it an obvious material to study.

The original study of CdS by Leite and Porto[1] confirmed the presence of enhanced cross sections near resonance, but was unable to determine the algebraic form of the expression for scattering efficiency. This was largely due to the difficulty and uncertainty involved in correcting the data for sample absorption, which is highly frequency-dependent near the direct gap. In addition to demonstrating enhanced cross sections, Ref. 1 also reported linelike features at approximately 2, 3, and 4 times the frequency of the LO(Γ) phonon.

An analysis of scattering data on CdS and ZnSe has been reported[2] which was essentially free of cross-section uncertainties due to sample absorption. The data were collected by means of a sandwich technique shown in Fig. 1. The intensities of the quartz lines relative to those of the calcite were measured simultaneously with the CdS or ZnSe spectrum. This gave a precise measure of absorption in the semiconductor at every wavelength and temperature employed. The principal result obtained from this study was the observation (i) that in both ZnSe and CdS, LO phonon cross sections for excitation energies less than the direct gap were accurately described by the theory of Ganguly and Birman,[9] which employs excitons as the intermediate states in the scattering process, and (ii) that the enhancement was incompatible with Loudon's Bloch-state model[8] in two respects—it evidenced a pole at or very near the free-exciton energy, rather than the gap energy, and the observed enhancement was more pronounced than predicted when Coulomb forces and discrete exciton states were ignored.

This work showed clearly that cross-section measurements could be used to assess the accuracy of alternative theoretical descriptions. All of the theories previously discussed[7–9] assume electron-hole pair states as the scattering intermediary. Our CdS results showed that the neglect of Coulomb terms in Loudon's Bloch-state description was important; however, the neglect of polariton coupling in the bare exciton model of Ganguly and Birman is apparently not important, at least for LO phonon scattering with excitation below the gap, since the frequency dependence of cross sections obtained with the bare free-exciton model accurately fit the data.

OVERTONE SCATTERING

Reference 2 revealed, in addition, overtone scattering in ZnSe, with $\omega \approx 2\times\omega_{LO}(\Gamma)$; it showed that cross-section enhancement of the 2 LO feature in CdS was

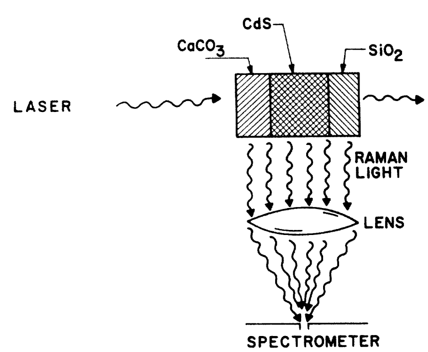

FIG. 1. Detection scheme for Raman scattering from thin samples and excitation below the band gap. The sample slices are glued together to form a sandwich.

[1] R. C. C. Leite and S. P. S. Porto, Phys. Rev. Letters **17**, 10 (1966).
[2] R. C. C. Leite, T. C. Damen, and J. F. Scott, in *Light Scattering in Solids*, edited by G. B. Wright (Springer-Verlag, Inc., New York, 1969), pp. 359–368.
[3] A. Pinczuk and E. Burstein, Phys. Rev. Letters **21**, 1073 (1968).
[4] R. C. C. Leite and J. F. Scott, Phys. Rev. Letters **22**, 130 (1969).
[5] R. C. C. Leite, J. F. Scott, and T. C. Damen, Phys. Rev. Letters **22**, 780 (1969); M. Klein and S. P. S. Porto, *ibid.* **22**, 782 (1969).
[6] J. F. Scott, T. C. Damen, R. C. C. Leite, and W. T. Silfvast, Solid State Commun. **7**, 953 (1969).
[7] L. N. Ovander, Fiz. Tverd. Tela **3**, 2394 (1961) [English transl.: Soviet Phys.—Solid State **3**, 1737 (1969)].
[8] R. Loudon, J. Phys. (Paris) **26**, 677 (1965); Advan. Phys. **13**, 423 (1964).
[9] A. K. Ganguly and J. L. Birman, Phys. Rev. **162**, 806 (1967).

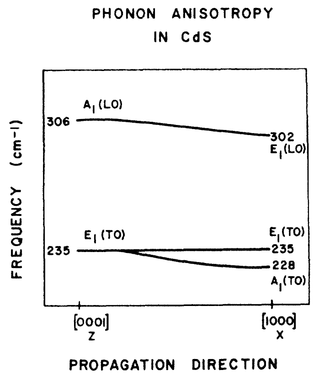

FIG. 2. Phonon frequencies for polar modes in CdS versus propagation direction, displaying the anisotropy due to noncubic lattice structure. The E_1(TO) branch is "ordinary," the other branches "extraordinary," phonons. ZnTe (see Fig. 3) is cubic and isotropic, and displays no such variation; hence, comparison of 1 LO and 2 LO frequencies is more significant for ZnTe than for CdS.

compatible with Ganguly and Birman's theory, and it showed that TO scattering cross sections saturate near resonance, in contrast to LO phonon behavior. A fairly complete analysis of polariton scattering near resonance in ZnSe was also given.[10]

One conclusion in our earlier paper[2] now appears to be unfounded. We inferred participation of large wave-vector phonons in the multiphonon scattering processes. This conclusion was based upon the fact that the frequency of the 2 LO feature was not exactly twice that of LO(Γ), and that an apparent enhancement of a feature at ~ 200 cm^{-1} we called 2 LA was observed. We have subsequently determined that the spectral feature near 200 cm^{-1} was primarily luminescence. The difference between ω(2 LO) and 2ω(LO) can be entirely attributed to anisotropy, as illustrated in Fig. 2, without invoking dispersion. The multiphonon processes involve an averaging of frequencies over all possible propagation directions for the individual participating phonons. Table I lists the frequencies of multiphonon lines in the materials studied and shows that in CdS, the discrepancy between $\omega(n\,\text{LO})$ and $n\omega$(LO) is within the 3-cm^{-1} spread in ω(LO) for different propagation directions.

The next phase of research was to examine Raman scattering near indirect gaps and direct but nonfundamental gaps, such as the E_1 saddle-point gap in the III-V's. Overtone scattering was observed in InAs near the E_1 direct interband gap.[4] The 2 LO feature[11] observed in InAs is at twice the frequency of LO(Γ), and it was concluded that zone-center phonons participate in resonant multiphonon scattering near direct gaps. In an attempt to verify this hypothesis, we have examined GaP using laser excitation energies near those of the indirect and direct gaps,[6] and ZnTe near the direct gap. The primary motivation for the study of ZnTe is that it is a cubic II-VI, and so we can support the contention that the slight deviation of overtone frequencies in CdS from multiples of LO(Γ) is due to anisotropy and not to anharmonicity. We have found in ZnTe that the overtones are, within experimental error, exact harmonics of $\omega_{\text{LO}}(\Gamma)$, as shown in Table I and Fig. 3. No overtones are observed near the GaP indirect gap, but 2 LO and 3 LO are seen near the direct gap.

The data contained in Table I are sufficient for us to conclude that multiphonon scattering near direct gaps involves only $k \approx 0$ phonons. The evidence is clearest in the case of GaP, for which inelastic neutron scattering data exist and show no critical-point phonon frequencies as high as LO(Γ)$=403$ cm^{-1}. Hence, 2 LO at ~ 805 cm^{-1} and 3 LO at ~ 1208 cm^{-1} are unambiguously assigned as scattering from two or three LO phonons at the Brillouin-zone center. Klein and Porto[5] have proposed that in CdS the LO branch is dispersionless, but that is not compatible with lattice dynamical calculations[12] and, of course, fails to explain the analogous data, especially on GaP.

MECHANISMS

We shall consider that multiphonon $k \approx 0$ processes are empirically established for direct-gap resonances, and will now consider mechanisms for their production. The three basic multiphonon scattering processes which we shall consider are shown in Fig. 4.

Process (a) involves a *virtual* photon recombination and was discussed by Loudon[8] and applied to the case of diamond. It satisfies the requirements of the data in two respects: First, it predicts that the two-phonon cross section should be approximately proportional to

TABLE I. Observed frequencies (in cm^{-1}) of multiphonon lines.

Line	CdS	GaP	ZnTe	ZnSe	InAs
1 LO	302–306	403[a]	210	253	241
2 LO	607[a]	805	421	506	483
3 LO	910	1208	632	759[b]	730[c]
4 LO	1214		843	1009[b]	
5 LO	1520		1055	1267[b]	
6 LO	1819				
7 LO	2118				
8 LO	2417				
9 LO	2716				

[a] All ± 3 cm^{-1} (*relative* frequencies accurate to about ± 1 cm^{-1}).
[b] Obtained with 4416 Å Cd II laser.
[c] Data of Ref. 11.

[10] An earlier attempt to observe scattering from polaritons in ZnSe was reported by S. Ushioda, A. Pinczuk, W. Taylor, and E. Burstein, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, 1967*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1968). [No polaritons were directly observed in this work, but a subsequent improvement in data is reported by S. Ushioda, Ph.D. thesis, University of Pennsylvania, 1969 (unpublished).]

[11] K. Nill and A. Mooradian have shown the presence of weak 3 LO scattering in InAs near resonance and do not observe the 2 TO reported in Ref. 4 [Bull. Am. Phys. Soc. 13, 1658 (1968)]. We conclude that the feature assigned earlier as 2 TO is spurious.

[12] M. A. Nusimovici, Ph.D. thesis, University of Paris, 1968 (unpublished); M. A. Nusimovici, M. Balkanski, and J. L. Birman (unpublished).

the square of the one-phonon line, which we observed[2] for LO phonons in CdS for laser excitation below the gap; second, it requires participation of only $k\approx 0$ phonons. Its defect, with respect to experimental verification, is that it has been thought to predict intermediate frequency poles,[9] i.e., enhancement of the 2 LO process when the incident photon is at ω(LO) above the exciton and the scattered photon is ω(LO) below the exciton, i.e., neither ω(incident) nor ω(scattered) near ω(exciton), but

$$\tfrac{1}{2}[\omega(\text{incident})+\omega(\text{scattered})]\approx\omega(\text{exciton}).$$

Such an intermediate pole has not been observed, although the reported work[5] has been of sufficient sensitivity to detect it.

Process (b) is that used to describe ordinary nonresonant second-order Raman scattering. A photon interacts with the electrons in the lattice, creating an exciton or free electron-hole pair; either the electron or hole is twice scattered before recombining. This process may be used to describe resonant multiphonon scattering, but to explain the experimental data, we must find some way of restricting the wave vector of the intermediate state to be nearly zero; this is done in a section which follows. Like (a), process (b) has been thought to yield poles or divergences in the 2 LO and other overtone cross sections at intermediate frequencies,[9] and like (a), (b) predicts that the frequency-dependent 2 LO cross section should be approximately proportional to the square of that for 1 LO scattering, as is observed.[2]

Hence the single "defect" of processes (a) and (b) as descriptions of second-order resonant Raman-scattering mechanisms is, as found by Ganguly and Birman[9] and Klein and Porto,[5] that these processes lead to unobserved poles in the two-phonon cross section at $\omega_L=\omega_{\text{ex}}+\omega_{\text{LO}}$. Ganguly and Birman's calculations involved dispersionless excitons. When the effects of exciton dispersion and finite-phonon wave vector are included, it is found[13] that the second-order pole at

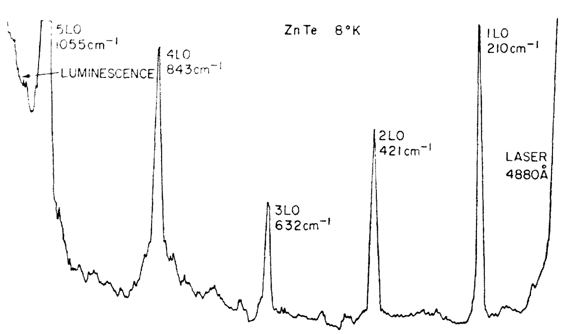

FIG. 3. Multiphonon resonant Raman spectrum of ZnTe. Scattering intensity is the ordinate; frequency shift from the laser frequency is the abscissa. Note the indicated resonance with the scattered photon near 5 LO.

[13] R. M. Martin (private communication).

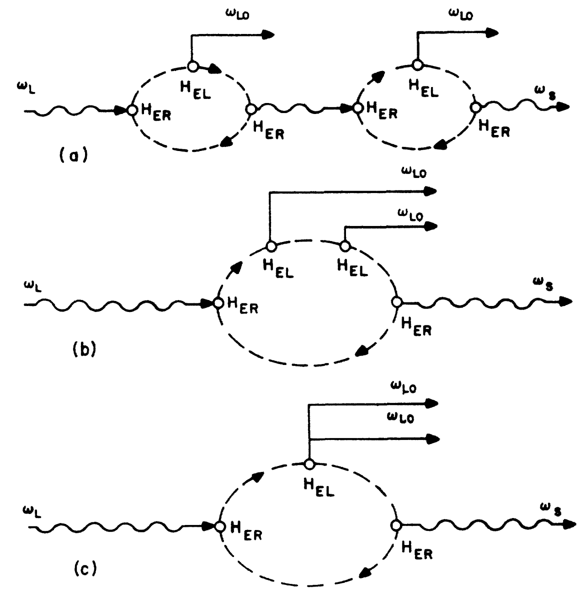

FIG. 4. Three possible scattering mechanisms for second-order Raman scattering, as discussed in the text.

the intermediate frequency in σ(2 LO) is removed and that only a square-root singularity remains. Hence the experimental data are actually compatible with the predictions of processes (a) and (b), since one would not expect to observe a square-root singularity in the vicinity of second-order poles, assuming damping constants are even roughly comparable.

Process (c) is that of simultaneous scattering of two (or more) phonons via a single electron-lattice interaction. This process requires higher-order anharmonic terms (of creation and annihilation operators) in the Hamiltonian and has, to our knowledge, not yet received theoretical treatment except in a purely formal way. The fatal defects of process (c) are, first, that it is not compatible with any restriction to $k\approx 0$ phonon constituents in the multiphonon processes, since the scattering events are not distinct, and, second, that the observed[2] proportionality between I(2 LO) and I^2(LO) would be completely coincidental and unexplained. On the basis of these two considerations, we believe that process (c) in Fig. 4 can be dismissed entirely. (We note that this was the process preferred by Klein and Porto.[5]) We show in the following sections that arguments exist for restriction of participation of phonons in process (b) to $k\approx 0$, and discuss the formal differences between (a) and (b).

Formally, process (a) involves two additional electron-radiation interactions, compared to (b). However, when polariton effects are included in the description, processes (a) and (b) are less distinct. In process (a) the intermediate state is a photon, in (b) it is an exciton. Neither pure state is a propagating mode in the medium; especially under the resonant conditions of the experiments summarized here, the intermediate

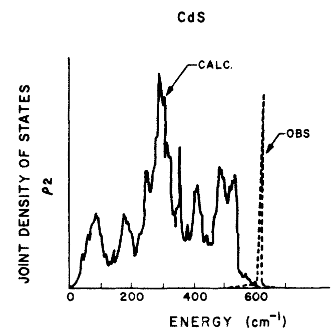

FIG. 5. Comparison of observed resonant second-order Raman spectrum of CdS with two-phonon density of states calculated by Nusimovici (Ref. 12, first citation).

state is an excitonic polariton, with both electromagnetic and displacive components. Farther from resonance it may be helpful, from a descriptive standpoint, to consider separately processes with excitons as intermediaries and those with photons. For present purposes, they are indistinguishable.

PARTICIPATION OF $k \approx 0$ PHONONS

Figures 5 and 6 show that the two-phonon spectra of CdS and GaP at resonance look like neither the two-phonon joint density of states nor the nonresonant second-order spectrum. It is clear that the coupling coefficient is very wave-vector–dependent, so that the intensity, which is the product $I=\xi\rho_2$ of coupling coefficient ξ and two-phonon joint density of states ρ_2, heavily weights small wave-vector phonons.

We suggested in an earlier paper[5] that this was due to the decrease in the Fröhlich interaction for large wave-vector phonons. In a very recent paper,[14] Hamilton has made an explicit calculation and shows that if Fröhlich terms dominate deformation-potential contributions, multiphonon processes in CdS at resonance will involve participation of phonons having wave vector $\leq 10^6$ cm^{-1}. Hamilton's calculations utilize parabolic bands and do not require purely exciton effects to predict the experimental observations. They predict multiphonon frequencies at essentially exact multiples of the one-phonon frequency, in accord with the experimental values given in Table I. The lowest-order perturbation theory used by Hamilton is insufficient for calculations of higher-order scattering cross sections, such as that of 5 LO, but it does indicate that they may be of comparable magnitude to first-order scattering.

In summary, Hamilton's arguments suffice to restrict phonons participating in process (b) to $k\approx 0$. They do not apply to process (c), since the phonon interactions in (c) are not distinct.

Although it is to a large degree made unnecessary by Hamilton's work, the simple physical argument sketched below yields a pleasant numerical agreement with his nonexcitonic calculation: Assume that phonons interact strongly only with excitons (free or bound) whose radii are of size comparable to the phonon wavelength. For CdS, the exciton radii are typically 100 Å. Hence, phonon wave vectors must be $\leq 1/100$ Å$=10^6$ cm^{-1} if the phonon is to effectively modulate the potential in which the exciton moves. This is exactly the same number ($<10^6$ cm^{-1}) deduced formally by Hamilton.

SURFACE PHONONS

We observe in passing that the observed multiphonon features cannot be due to surface modes. (The one-

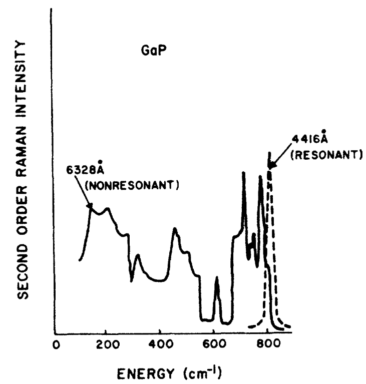

FIG. 6. Comparison of resonant second-order Raman spectrum of GaP with that observed by J. P. Russell, using excitation far below the direct gap [J. P. Russell, in *Phonons in Perfect Lattices and in Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Plenum Press, Inc., New York, 1966), p. 240].

phonon features are observed at accepted bulk frequencies.) While such an interpretation is altogether reasonable for features observed in reflection scattering and which show anomalous wave-vector constituents, the frequencies observed apparently preclude such an interpretation. A surface vibration having exponentially decaying e^{-kZ} dependence perpendicular to the surface and sinusoidal $e^{-ik_1X-ik_2Y}$ behavior along the surface can be shown to satisfy Maxwell's equations only for certain frequencies. The requirement is that the dielectric function equal -1 at the propagating frequency. Hence,

$$-1=\epsilon=\epsilon_\infty+\sum_{j=1}^{m}\frac{S_j\omega_j^2}{\omega_j^2-\omega^2+i\Gamma_j\omega}, \tag{1}$$

where ϵ_∞ is the high-frequency dielectric constant, and ω_j is the jth transverse phonon frequency with damping constant Γ_j and oscillator strength S_j.

When optical constants from GaP or ZnTe are inserted in Eq. (1), ω(surface) is found to be 6 and 4 cm^{-1} less, respectively, than ω_{LO}. From Fig. 3 and Table I we see that such an uncertainty does not appear to

[14] D. C. Hamilton, this issue, Phys. Rev. **188**, 1221 (1969).

be within experimental limits. We believe that the reason surface phonons are not seen is the difficulty in coupling light into a high-index medium in any way except propagation nearly normal to the surface. Further study of scattering at grazing incidence may reveal such surface phonons.

FREE AND BOUND EXCITONS AS INTERMEDIATE STATES

In a recent paper[15] it is shown that the contribution to LO phonon scattering cross sections in CdS is predominantly from continuum excitons, except for laser frequencies very near that of the $n=1$ discrete free-exciton level. Under such conditions in which the laser energy is very near the $n=1$ level, however, the contribution from discrete exciton intermediate states is dominant. In an earlier paper[5] we stated that the extent of participation of bound excitons was not clear. We believe that free excitons are the primary scattering intermediaries, since calculations using that assumption give such good agreement[15] with observed cross-section frequency dependence; however, we have new evidence which indicates that bound excitons do participate as intermediate states for phonon scattering in CdS. Figure 7 shows multiphonon scattering in CdS at different temperatures. The background luminescence is believed to be intrinsic; its maximum, therefore, marks (within $\sim 35\ \mathrm{cm}^{-1}$ self-absorption correction) the frequency of the $n=1$, A free exciton ($E\perp$hexagonal axis). Note that the greatest scattering cross section is observed when this luminescence maximum is at energies $\sim 100\ \mathrm{cm}^{-1}$ higher than that of the Stokes-scattered photon. Hence, scattering efficiency is greatest when the photon is at slightly lower energies than that of the free exciton, i.e., is near the frequencies of the bound excitons.

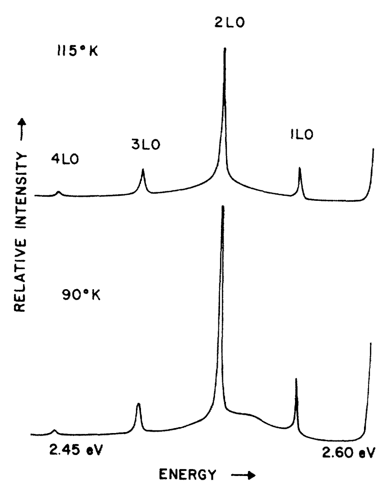

FIG. 7. Relative intensities of the 2 LO phonon scattering feature in CdS as a function of temperature and hence exciton energy. The 2 LO feature has maximum intensity when it is about a third of an LO phonon energy below the luminescence peak. If the luminescence maximum marks the position of the $n=1$, A free exciton, then the observed Raman-scattering maximum occurs for the scattered photon approximately coincident in frequency with the I_1 bound exciton, which is 0.0177 eV below the free exciton. In the upper trace, the luminescence is exactly coincident with the 2 LO line and forms a "skirt" on that feature.

Next we observe in Fig. 8 that the phonon sidebands on the I_1 luminescence feature (electron bound to a neutral acceptor) are at frequencies of LO(Γ). This indicates that for I_1 (I_2 and I_5 exhibit different sidebands), the phonon interaction is primarily through the macroscopic phonon electric field coupling to the bound Wannier exciton. We believe that the dynamical origin of multi-LO(Γ) phonon sidebands in Raman effect and in luminescence is the same, and suggest that I_1 in CdS is a principal intermediary. This interpretation is compatible with the giant oscillator strengths inferred by Rashba and Gurgenishvili[16] for bound excitons in CdS. The efficiency of any intermediate state in a scattering process is determined by the photon-exciton coupling coefficient (simply the oscillator strength in absorption) and the exciton-phonon or electron-lattice coupling. Hence, just as we found[6] direct excitons to be more efficient than indirect as intermediate states for Raman processes in GaP, as expected from their respective oscillator strengths, we believe that bound excitons with very large oscillator strengths are important contributors to measured cross sections near resonance. While I_2 in CdS has an even greater oscillator strength than I_1 and is more commonly present in CdS samples, it exhibits broad, weak phonon sidebands. I_2 exhibits, in our samples, an asymmetric sideband which peaks very near the TO frequency and resembles the one-phonon density of states in Nusimovici's calculation for that spectral region. This behavior is more suggestive of deformation potential interaction than Fröhlich interaction. We conclude that I_2 is an inefficient intermediary in LO phonon scattering. Our

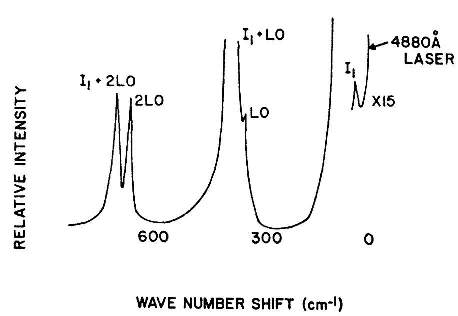

FIG. 8. Luminescence observed in our CdS samples with 4880 Å excitation, showing that the LO sidebands on I_1 have the same frequency shifts as the Raman LO(Γ) sidebands.

[15] B. Bendow, J. Birman, T. C. Damen, A. Ganguly, R. C. C. Leite, and J. F. Scott (unpublished).

[16] D. G. Thomas and J. J. Hopfield, Phys. Rev. 175, 1021 (1968); E. I. Rashba and G. E. Gurgenishvili, Fiz. Tverd. Tela 4, 1029 (1962) [English transl.: Soviet Phys.—Solid State 4, 759 (1962)].

cross-section enhancement near bound excitons is not as sharp or large as observed for spin-flip processes by Thomas and Hopfield. This is compatible with contribution from only I_2 in the latter case and contribution from discrete and continuum excitons for phonon scattering. Finally, we note that more and stronger multiphonon scattering is observed (see Table I) in the II-VI's than in the III-V's at resonance. This suggests that the electron-lattice interactions in the II-VI's are greater and is compatible with known polaron coupling coefficients.

TRANSVERSE-OPTICAL PHONONS

Thus far, little has been said about resonant scattering of transverse-optical (TO) phonons. We found earlier[2] that TO cross sections increase more rapidly with frequency than do LO for excitation far below the gap, but display less pronounced enhancement than LO just below the gap, and then disappear entirely for ω_L above $E_g/\hbar$. These observations are compatible with Loudon's Bloch-state model[8] in all respects, although the actual shape of the σ(TO)-versus-ω_L curve would require some phenomenological damping term to fit Loudon's predictions. While the existing TO cross-section data are too scanty to allow a detailed comparison with theory, we believe that while the LO-phonon cross sections can be explained by a Fröhlich interaction between free excitons and zone-center phonons, the TO cross sections describe a less pronounced resonance with continuum electron-hole states via a deformation potential.

SUMMARY

In summary, we believe that the experimental data for the several semiconductors considered favor a combination of processes (a) and (b) in Fig. 4 as the multiphonon scattering mechanisms, and that the principal intermediate states are free excitons, with a significant degree of participation by bound excitons, especially of I_1 in CdS.

The failure to observe "poles" in the scattering cross sections for multiphonon processes when ω(exciton) lies at intermediate frequencies between ω(incident) and ω(scattered) is compatible with calculations which do not ignore exciton dispersion.

FURTHER EXPERIMENTS

Clearly, additional study of CdS is warranted in order to determine which excitons are dominant as intermediate states. Some information has been obtained by continuously varying temperature[5] to vary ω(exciton), and some related information can be acquired by varying uniaxial pressure. Since both processes produce unwanted broadening of the luminescence features, a more desirable experiment is the measurement of cross sections at very low temperatures using a tunable source, such as a dye laser.[17] Not only will this allow identification of the intermediate-state excitons, it will permit examination of the situation in which scattered photon frequency is between two well-defined excitons, or between an exciton and the gap. Interference effects and small cross sections may exist under these conditions.

Another experiment worthy of attention is resonant scattering a nonpolar semiconductor. All overtone scattering observed thus far is LO in nature. It would be educational to excite silicon near the direct gap to look for two-phonon processes (in which only *local* electric field interaction with the excitons is possible). We note that the Cd II 3250 Å cw laser is ideally suited to this purpose, since its energy is near the direct gap in Si. Two-phonon scattering at resonance in Si should provide an interesting comparison with scattering in diamond.

While these experiments would help complete an empirical description of the resonance phenomena, there is a clear need for a microscopic theory of multiphonon scattering which includes damping mechanisms.[18]

ACKNOWLEDGMENTS

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[17] Such experiments have also been suggested by C. K. N. Patel (private communication).

[18] For recent polariton theories of resonant scattering see J. J. Hopfield, Phys. Rev. **182**, 945 (1969); E. Burstein, D. L. Mills, A. Pinczuk, and S. Ushioda, Phys. Rev. Letters **22**, 348 (1969); D. L. Mills and E. Burstein, Phys. Rev. (to be published).