

## Transformation from Raman Scattering to Photoluminescence at the *C* Exciton of CdSe

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In studying resonant Raman scattering around the *C* exciton of the wurtzite semiconductor CdSe we have observed a Raman mode with an unusual dependence on the incident photon frequency. As the incident photon is tuned across the *C* exciton, this Raman mode gradually broadens and shifts in frequency until it becomes a photoluminescence peak centered at the *C* exciton frequency. A phenomenological theory is proposed to explain the behavior of this mode by the presence of a "bottleneck" in the decay of resonant intermediate states involved in the scattering of this mode.

Raman scattering (RS) and photoluminescence (PL) are two well-known optical processes in solids. In both processes a solid is excited by an incident photon of energy  $h\nu_i$  and a photon with energy  $h\nu_s$  is emitted. RS is generally regarded as a "one-step" process with  $\nu_s$  always related to  $\nu_i$  by the equation  $\nu_i - \nu_s = \pm \nu_0$ , where  $\nu_0$  is the frequency of the Raman-scattered elementary excitation. On the other hand PL consists of three separate steps: (1) absorption of the incident photon in creating an electron-hole pair; (2) relaxation of the electron-hole pair by scattering with a large number of phonons; and (3) radiative recombination of the relaxed electron-hole pair. Because of the relaxation of the intermediate electron-hole pair  $\nu_i - \nu_s$  is no longer a constant in PL. Thus in general RS and PL can be distinguished from each other by plotting  $\nu_i - \nu_s$  as a function of  $\nu_i$ .<sup>1</sup> For RS the result would be a horizontal line while for PL it would be a line with slope equal to unity.

When the incident photon frequency is tuned to the vicinity of strong absorption bands in solids, the RS becomes enhanced (resonant Raman scattering or RRS). Recently both theory<sup>2</sup> and experiment<sup>3</sup> have indicated that under certain circumstances RRS can be regarded as a two-step process of absorption followed by emission (AE) during which the correlation between  $\nu_i$  and  $\nu_s$  is preserved. Now if this correlation is gradually lost through relaxation of the intermediate electron-hole pair, one may expect this AE process to develop into PL. We report here the first experimental observation of this phenomenon in CdSe.<sup>4</sup> A phenomenological theory is also proposed to explain our results by the presence of a "bottleneck" in the decay of the intermediate electron-hole pair in CdSe.

Our experiment was performed with a Raman scattering set up which has been described elsewhere.<sup>3</sup> The CdSe sample was excited by a Co-

herent Radiation cw dye laser using coumarin 6 as the lasing dye (tuning range 5600–5200 Å). Both bulk single crystals and thin platelets of CdSe have been studied. The phenomenon presented in this paper is observed in both kinds of crystals. The bulk single crystals are cleaved while the platelets are used as grown. In both cases the experiment was performed in a back-scattering configuration with the incident and emitted photons propagating perpendicular to the crystal *c* axis. The samples were cooled to ~2 K.

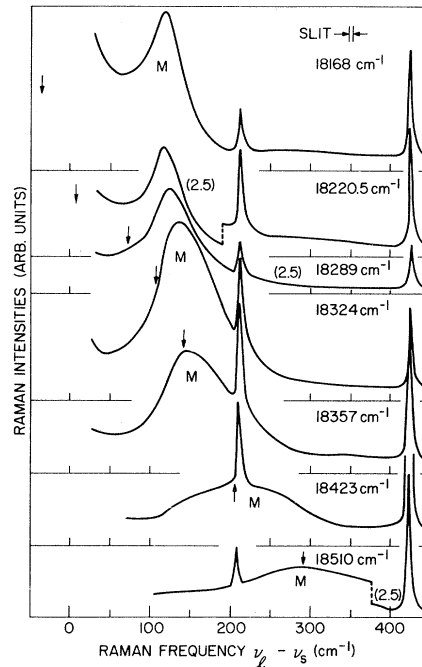


FIG. 1. Raman spectra of CdSe at ~2°K when the incident photon frequencies, given with each spectrum, are in the vicinity of the *C* exciton. The *C*-exciton frequency is indicated by an arrow in each spectrum. Numbers in parentheses adjacent to some parts of the spectra give the reduction in gain of the detector at these parts relative to the rest of the spectra. The peak labeled *M* is the subject of this paper.

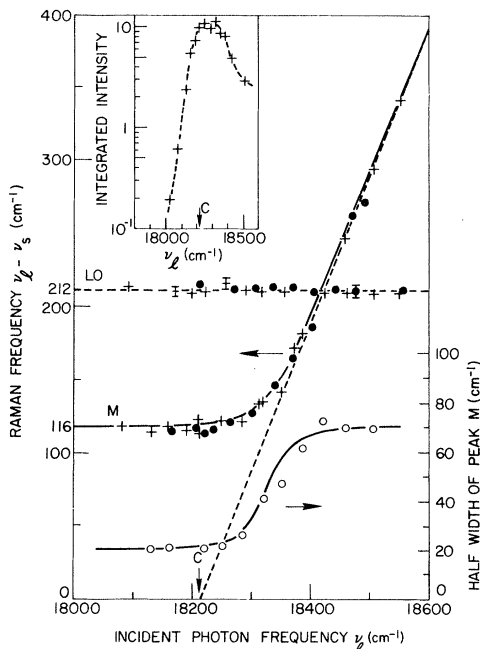


FIG. 2. The Raman frequencies  $\nu_i - \nu_s$  of peaks  $E_1(\text{LO})$  and  $M$  and the half-width of peak  $M$  plotted as a function of the incident photon frequency. The closed circles and the crosses correspond, respectively, to two different scattering configurations: incident photon polarized parallel to the  $c$  axis but perpendicular to the scattered photon, and both photons polarized perpendicular to the  $c$  axis. The slanted broken line gives the plot of  $\nu_i - \nu_s$  for the  $C$ -exciton photoluminescence peak whose frequency is indicated by  $C$ . The solid lines are results of theoretical calculations based on the model discussed in the text. The inset shows the dependence of the integrated intensity of  $M$  on the incident photon frequency.

The absorption spectrum of CdSe, like that of CdS, exhibits three strong excitonic peaks known as the  $A$ ,  $B$ , and  $C$  excitons.<sup>5</sup> These arise from transitions from the three top valence bands to the bottom conduction band of CdSe at the zone center. But unlike in CdS the  $C$  exciton in CdSe is well separated (by  $\sim 3400 \text{ cm}^{-1}$ ) from the  $A$  and  $B$  excitons.

Figure 1 shows a series of Raman spectra of CdSe with  $\nu_i$  tuned to the vicinity of the  $1s$   $C$ -exciton frequency ( $\nu_C = 18212 \text{ cm}^{-1}$ ) whose position in each spectrum is indicated by an arrow. The sharp peaks at 212 and  $424 \text{ cm}^{-1}$  are, respectively, the  $E_1(\text{LO})$  and  $2E_1(\text{LO})$  Raman modes. The structure of interest is the broad peak labeled  $M$ . For  $\nu_i \lesssim \nu_C$ ,  $M$  has a Raman frequency of  $116 \text{ cm}^{-1}$ . When  $\nu_i$  is about  $100 \text{ cm}^{-1}$  larger than  $\nu_C$  both its Raman frequency and linewidth begin to increase. When  $\nu_i$  is more than  $200 \text{ cm}^{-1}$  above

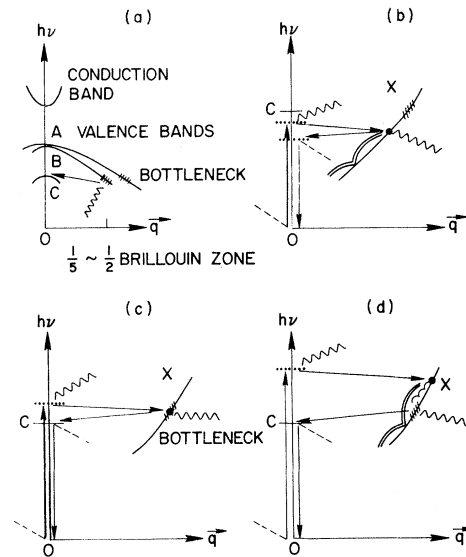


FIG. 3. (a) Schematic diagram of the relevant one-electron energy bands in CdSe. In (b), (c), and (d) these bands are redrawn as exciton bands. Also shown in these figures are the optical processes responsible for the peak  $M$  for incident photon frequency in three different regions: (b)  $\nu_i \lesssim \nu_C$ ; (c)  $\nu_i \approx \nu_C + 2\nu_\Sigma$ ; and (d)  $\nu_i \gg \nu_C + 2\nu_\Sigma$ . The notations are the following: dots, virtual intermediate states; dashed line, photons; wavy lines,  $\Sigma$  phonon; double trochoidal line, relaxation by emission of LO phonons; single trochoidal line, relaxation by scattering with acoustic phonons; the hatched area, the bottleneck region.

$\nu_C$ , the scattered photon frequency,  $\nu_s$ , of  $M$  is constant and it behaves like the  $C$ -exciton peak.

These results are more clearly displayed in Fig. 2 where the Raman frequencies of the  $M$  and  $\text{LO}$  peaks are plotted against  $\nu_i$ . We note that the data points for a Raman mode like the  $\text{LO}$  phonon fall on a horizontal line as expected. On the other hand the plot of  $\nu_i - \nu_s$  versus  $\nu_i$  for the  $C$ -exciton PL peak will fall on the slanted broken line. The striking feature of the peak  $M$  is that for  $\nu_i \lesssim \nu_C$  it behaves like a Raman mode while for  $\nu_i \gg \nu_C$  it behaves like the  $C$ -exciton PL peak. In the intermediate crossover region its behavior can be classified neither as RS nor as PL. The inset of Fig. 2 shows how the total integrated intensity of  $M$  depends on  $\nu_i$ . Note that the enhancement peak is much broader than the  $C$  exciton whose full width in absorption is  $\sim 140 \text{ cm}^{-1}$ .

There are two unusual features about the behavior of this peak  $M$  which cannot be explained by a model involving the  $C$  exciton alone. Firstly, instead of changing abruptly from RS to PL as was recently observed in x-ray resonant Raman scat-

tering,<sup>6</sup> the peak  $M$  changes gradually from RS to PL. Secondly, this change does not occur exactly around  $\nu_C$  but rather about  $100 \text{ cm}^{-1}$  above  $\nu_C$ .

In the rest of this paper we present an outline of our explanation of the unusual behavior of  $M$ . The novel idea in this theory is that the continuous transformation from RS to PL of peak  $M$  is due to the presence of a "bottleneck" in the decay of large-momentum  $A$  and  $B$  hole states in CdSe [see Fig. 3(a)]; the bottleneck is a result of the strong mixing of these holes with the  $C$  hole state via the phonons involved in the  $M$  peak.

For convenience we shall describe our theory in terms of excitons rather than electrons and holes. The relevant exciton states in our theory are drawn schematically in Figs. 3(b), 3(c) and 3(d). We have denoted by  $\times$  the large-momentum regions of the  $A$  and  $B$  exciton bands which overlap in energy with the bottom of the  $1s$   $C$ -exciton band at zone center. We postulate that these excitons ( $X$  and  $C$ ) are coupled together sufficiently strongly via a large-momentum phonon  $\Sigma$  that a mixed state  $\Psi$  is formed.<sup>7</sup> Normally the decay rate of large-momentum excitons in polar semiconductors such as CdSe is very fast as a result of intraband scattering by LO phonons via the Fröhlich interaction ( $\approx 10^{13} \text{ sec}^{-1}$ ).<sup>8</sup> On the other hand the zone-center  $C$  exciton can decay only to the  $A$  and  $B$  excitons by emitting either a number of phonons or one phonon with large momentum. Since these are less efficient processes, the  $C$  exciton has a longer lifetime than the  $X$  exciton.<sup>9</sup> The lifetime of the mixed state  $\Psi$  is now determined by the admixture of  $X$  and  $C$  in  $\Psi$ . When the difference between the frequencies of the  $X$  and  $C$  excitons is large,  $\Psi$  consists mainly of the short-lived  $X$  excitons. But at the point where the energy of the  $X$  exciton is approximately equal to that of the  $C$  exciton plus the  $\Sigma$  phonon,  $\Psi$  has a longer lifetime because of a large admixture of the longer-lived  $C$  exciton. The result is a bottleneck in the decay of the  $X$  exciton at this point. We note that a similar bottleneck formed by a different mechanism has been predicted theoretically<sup>10</sup> and recently observed experimentally<sup>11</sup> in the decay of the exciton-polariton in CdS.

The presence of this bottleneck in CdS is the basis of our explanation of the behavior of the  $M$  peak. For  $\nu_i \lesssim \nu_C$ ,  $M$  is due to absorption and emission processes shown schematically in Fig. 3(b). Since the lifetime of the  $X$  exciton below the bottleneck is too short for relaxation to occur between absorption and emission, the entire process is an AE type of resonant Raman scattering,

and  $M$  is a  $2\Sigma$  Raman mode. This two-phonon process is normally very weak because of the short lifetime of the  $X$  exciton and becomes observable mainly because of resonance of the incident photon with the  $C$  exciton. This is shown by the sharp rise in the intensity of  $M$  at  $\nu_C$  in the inset of Fig. 2. The larger width of  $M$  as compared to the LO-phonon modes is presumably due to dispersion of the  $\Sigma$  phonon. For  $\nu_i \sim \nu_C + 2\nu_\Sigma$  ( $\nu_\Sigma$  being the frequency of the  $\Sigma$  phonon), the incident photon starts to excite  $X$  excitons which are coupled to the  $C$  exciton (i.e., in the bottleneck region) as shown in Fig. 3(c). The lifetime of these excitons is probably long enough to allow them to be relaxed by scattering with acoustic phonons but not long enough to be completely thermalized. As a result the peak frequency and line shape of  $M$  are now determined by the distribution of excitons in the bottleneck and can vary with  $\nu_i$  within the width of the bottleneck.<sup>12</sup> This accounts for the gradual change in the frequency of  $M$  in the cross-over region. For  $\nu_i \gg \nu_C + 2\nu_\Sigma$  the photoexcited  $X$  excitons will lie above the bottleneck. During their decay down the exciton band these excitons will tend to accumulate in the bottleneck region as shown in Fig. 3(d).  $M$  is now simply the PL peak due to recombination of these excitons. The  $2\Sigma$  Raman mode is now too weak to be observed since it is no longer resonantly enhanced by the  $C$  exciton while the slow decrease in the intensity of  $M$  above  $\nu_C$  now reflects the gradual decrease in the probability of photoexcited  $X$  excitons to relax down to the bottleneck.

The above picture qualitatively explains the observed dependence of the intensity and frequency of  $M$  on  $\nu_i$ . However, to calculate the variation of the lifetime of the  $X$  exciton around the bottleneck region is more difficult. For illustration purpose the wave function and energy of  $\Psi$  were calculated using degenerate perturbation theory by first neglecting damping.<sup>13</sup> From the energy of  $\Psi$  the  $\nu_i - \nu_s$  dependence of  $M$  on  $\nu_i$  is obtained. Dampings of the uncoupled  $X$  and  $C$  excitons are then surmised and used together with the wave function of  $\Psi$  to calculate the half-width of  $M$ . These theoretical results are shown as the solid lines in Fig. 2. In fitting the data points the exciton-phonon coupling constant between the  $X$  and  $C$  excitons was adjusted to be  $\sim 2.7 \text{ meV}$ . Although the agreement between theory and experiment is satisfactory, a more conclusive proof of the presence of a bottleneck in CdSe would be a time-resolved measurement of the peak  $M$  as a function of the exciting photon frequency. Unfortunately

such an experiment is very difficult at present because of the short time scales involved ( $\sim 10^{-13}$  sec $^{-1}$ ).

Finally we should also point out that the LO-phonon Raman modes in CdSe do not show the same behavior as the peak  $M$  and this is consistent with our theory. The LO phonon is not expected to couple strongly the  $A$  and  $B$  excitons with the  $C$  exciton because of the wave-vector dependence of the Fröhlich interaction.<sup>10</sup> The momentum of the LO phonon involved will be too large compared with the reciprocal of the exciton radii which are  $\approx 50$  Å in CdSe. However, we did observe enhancement of the LO-phonon Raman scatterings in the vicinity of the  $C$  exciton in CdSe and these results can be interpreted in terms of the  $C$  exciton alone.

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<sup>1</sup>Another way to distinguish RS from PL is by the

presence of an anti-Stokes component in RS. However at the low temperatures used in this experiment the anti-Stokes component is too weak to be observed.

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<sup>7</sup>At present we cannot identify the  $\Sigma$  phonon because the phonon dispersion curve of CdSe is not known. It is probably associated with the low-energy  $\Gamma_6$  optical branch.

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## Far-Infrared Absorption in Ultrafine Al Particles\*

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The first far-infrared measurements on metallic particles with diameters  $< 10$  nm are reported. The absorptivity is well approximated by  $\alpha_{\text{exp}} \approx C_{\text{exp}} \tilde{\nu}^2$ , where  $3 < \tilde{\nu} < 150$  cm $^{-1}$ . The results are compared with the Gor'kov-Eliashberg (GE) theory of particles with quantized electronic levels as well as with the classical Drude theory. When a size distribution is included,  $\alpha_{\text{GE}} = C_{\text{GE}} \tilde{\nu}^2$  irrespective of level statistics. However,  $C_{\text{exp}} \gg C_{\text{GE}}$  and the observed dependence on the diameter is directly contrary to predictions of the GE theory. Neither can the data be reconciled with the classical theory.

About a decade ago Gor'kov and Eliashberg (GE) published a theory of the electromagnetic properties of minute metallic particles due to a quantized conduction band.<sup>1</sup> One conspicuous re-

sult was the prediction of a periodic frequency dependence of the electronic susceptibility for a set of particles of equal size. If observed unambiguously this would uncover a unique test of ba-