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# Excitation spectroscopies of impurities in CdSe

Peter Y. Yu
*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*
*and Physics Department, University of California, Berkeley, California 94720*

Claudine Hermann*
*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*

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Two kinds of excitation spectroscopies, namely, resonant Raman scattering and photoluminescence excitation spectroscopy, have been used to study impurities in CdSe. At excitons bound to neutral donors we observe enhancement of a Raman mode at 109 $\mathrm{cm}^{-1}$ which we identify as due to electronic Raman scattering in which the donor is excited from the 1*S* to the 2*S* state. At excitons bound to neutral acceptors in CdSe we observe enhancement of two new Raman peaks at 189 and 257 $\mathrm{cm}^{-1}$, respectively. The former is identified as an electronic Raman mode of the acceptor in CdSe in which the hole is excited from the ground state (derived from the $\Gamma_9$ valence band of CdSe) to an excited state (derived from the $\Gamma_7$ valence band). The peak at 257 $\mathrm{cm}^{-1}$ is tentatively identified as a local vibrational mode associated with substitutional Na. We also observe enhancement of four donor-acceptor pair transitions in CdSe when they are resonantly excited (other authors have labeled such pair transitions as selectively excited). Two such resonantly excited pair transitions involve excited states of the donor and acceptor in CdSe. The remaining two are assigned to phonons. A qualitative theory is also proposed to explain the dependence of the enhancement on excitation frequencies.

## I. INTRODUCTION

Optical techniques such as Raman scattering (RS) and photoluminescence (PL) have been applied extensively in the past to study impurities in semiconductors.[1] In these techniques the wavelength of the excitation radiation is usually not critical and fixed frequency lasers are used as the light source. With the appearance of tunable dye lasers it becomes possible to add a new dimension to these techniques by varying the wavelength of the excitation. These excitation spectroscopies are known as resonant Raman scattering (RRS) and luminescence excitation spectroscopy (LES). While extensive literature exists on RRS in intrinsic semiconductors,[2] both RRS and LES are not widely used to study defects in semiconductors. Only recently has LES been applied to measure excited-state energies of impurities in zinc-blende-type semiconductors[3-5] and RRS used to study vibrational and electronic levels of donors and acceptors in CdS.[6] In this paper we report the first RRS and LES study on impurities in the wurtzite-type semiconductor CdSe. We measure the energies of an excited state and of a localized phonon mode of an acceptor in CdSe. We also discuss the distinction between RRS and LES in terms of their emission mechanisms and the kind of information they provide.

## II. BACKGROUND THEORIES

Theories on electronic and vibrational properties of impurities and on their interaction with radiation have been treated extensively in the literature so they will not be elaborated here.[7] The purpose of this section is to outline these theories and to define the symbols we will use.

We will denote donors and acceptors as D and A, respectively. Bound states of donors and acceptors will be denoted by $\mathrm{D}_{1S}$, $\mathrm{A}_{2P}$, etc. The notation $\mathrm{D}_{1S} \rightarrow \mathrm{D}_{2S}$ stands for the transition of an electron from the donor 1*S* level to the donor 2*S* level. A bound exciton is an electron-hole pair localized near an impurity. Depending on whether the impurity involved is a donor or an acceptor, bound excitons will be denoted by $\mathrm{D}^0X$ and $\mathrm{A}^0X$, respectively. The superscript zero denotes the charge state of the impurity.

External radiation can excite impurities via three types of transitions: (a) creation of a bound exciton, (b) excitation of an electron from an impurity level to the continuum (bound-to-free transition), and (c) $\mathrm{A}^- + \mathrm{D}^+ \rightarrow \mathrm{A}^0 + \mathrm{D}^0$ (donor-acceptor pair transition). In this article we will be mainly concerned with bound excitons (BE) and donor-acceptor pair (DAP) transitions. Since a BE consists of three mobile particles (e.g., two electrons and one hole in $\mathrm{D}^0X$) it is rather difficult to calculate its energy levels. Binding energies of BE's have been calculated by various authors with quite different results.[7] A DAP on the other hand has only two mobile particles so its energy levels can be calculated readily. The energy required to make a DAP transition is[8]

$$E_{\mathrm{DA}}(R) = E_g - E_{\mathrm{A}}^0 - E_{\mathrm{D}}^0 + \frac{e^2}{\epsilon R} + J_{\mathrm{DA}}(R)\ , \qquad (1)$$

where $E_g$ is the band-gap energy and $E_A^0$ and $E_D^0$ are, respectively, the ionization energies of *isolated* acceptors and donors; $e^2/\epsilon R$ is the Coulomb energy of the two ionized impurity centers separated by distance $R$, while $J_{DA}(R)$ is a small correction term due to the interaction between the neutral donor and acceptor. $J_{DA}(R)$ vanishes when $R$ approached infinity. A pair transition can also occur so that in the final state the donor or the acceptor is in an excited state (denoted by D* and A*, respectively). In these cases the energy of the transition will become

$$E_{DA^*}(R) = E_g - E_A^* - E_D^0 + (e^2/\epsilon R) + J_{DA^*}(R) \qquad (2)$$

or

$$E_{D^*A}(R) = E_g - E_A^0 - E_D^* + (e^2/\epsilon R) + J_{D^*A}(R) \ . \qquad (3)$$

There are in general two processes in which a medium excited by photons with energy $\hbar\omega_i$ will emit photons with energy $\hbar\omega_s$. These two processes are RS and PL. Raman scattering is due to inelastic scattering of light by elementary excitations in the medium. It is a one-step process in which the outgoing photon is coherent with the incoming photon. Photoluminescence is a two-step process consisting of absorption of the incoming photon by electrons and emission of the outgoing photon by the thermalized electrons. As a result of the thermalization, the outgoing photon is not coherent with the incoming photon. Usually the two processes are distinguished by the different dependence of $\omega_s$ on $\omega_i$, namely, in RS $\omega_s$ follows $\omega_i$ while in PL $\omega_s$ is independent of $\omega_i$.

The information one obtains with RS and PL is also different. In RS one is interested in the Raman frequency, $\omega_i - \omega_s$, which is equal to the frequency of the elementary excitation in the medium. In PL, $\omega_i - \omega_s$ is usually equal to the frequency of a large number of acoustic phonons so nothing can be learned from $\omega_i - \omega_s$. The information one obtains from RRS and LES is, however, not as different. In RRS one follows the Raman cross section as a function of $\omega_i$, and in general this cross section shows enhancement when $\omega_i$ or $\omega_s$ resonates with electronic transitions of the medium.$^2$ In LES the luminescence intensity is monitored as a function of $\omega_i$ and this intensity often shows enhancement also when $\omega_i$ is resonant with an excited state which has a large probability of relaxing into the luminescing lower-energy state. Thus both RRS and LES will give excited-state energies although the excited states observed in the two techniques can be different. We will now consider the two techniques in more detail when the resonant states involved are BE's and DAP bands.

Recently it has been shown that LES of DAP bands can give excited-state energies of impurities.$^{4,5}$ It was found that when $\omega_i$ is tuned to the pair-band energies $E_{DA^*}(R)$ or $E_{D^*A}(R)$, the emission intensity of the pair band with energy $E_{DA}(R)$ becomes enhanced. The mechanism responsible for this enhancement as proposed by Tews *et al.*$^5$ is the following. Assume a monochromatic photon flux excites donors and acceptors in their respective 1$S$ state at distances $R'$ apart. When these donors and acceptors recombine, most of the emission will come from pairs at distance $R'$ apart as may be expected and the resultant photons have the same frequency as the incident photons. In addition, there will be a broad background due to pairs whose separations are different from $R'$. Such pairs can arise from electrons and holes not excited by the same photon originally. We will refer to this background as nonresonantly excited DAP band luminescence. If the incident photon frequency $\omega_i$ is resonant with the pair-band energy $E_{DA^*}(R)$, then pairs at distance $R$ will be excited also. For such pairs the acceptors are in an excited state A*. If these acceptors relax to the ground state before they recombine with donors, an additional number of DA pairs at separation $R$ are now created on top of the number of pairs which are non-resonantly excited by $\omega_i$. As a result a relatively sharp peak with energy $E_{DA}(R)$ is superimposed on the broad, nonresonantly excited pair-band spectrum. From Eqs. (1)–(3) we can easily show that the difference between the excitation frequency, $\omega_i$, and the frequency of the sharp peak, $\omega_s$, is equal to

$$(E_A - E_A^*) + J_{DA^*}(R) - J_{DA}(R)$$

or

$$(E_D - E_D^*) + J_{D^*A}(R) - J_{DA}(R) \ .$$

Since the $J$ terms are usually small, we obtain the interesting result that $\omega_i - \omega_s = E_A - E_A^*$ or $E_D - E_D^*$ and is constant as $\omega_i$ is varied. In other words, the enhanced DAP peak behaves like a Raman mode in that $\omega_i - \omega_s$ is not dependent on $\omega_i$. But this is not a Raman mode because as $\omega_i$ is changed, pairs with different separations $R$ are excited in each case and relaxation occurs between absorption and emission. Usually $J_{DA}(R)$ is slightly different from $J_{DA^*}(R)$ or $J_{D^*A}(R)$, and this difference depends on $R$. As a result, $\omega_i - \omega_s$ for the enhanced DAP band will vary slowly with $R$ until becoming constant for large $R$.$^5$ This peculiar feature of resonantly enhanced DAP bands can be used to distinguish them from RS.

Enhancements of both electronic and vibrational RS have been reported when $\omega_i$ or $\omega_s$ are resonant with the lowest-energy state of BE's.[6] So far there seems to be no confusion between scattering and luminescence at bound excitons. However, it is worthwhile to point out a special case where RS and PL can be confused with one another. This arises when the bound-exciton levels are strongly broadened by inhomogeneity in the sample. Let us denote the inhomogeneous and homogeneous width of a bound exciton level by $\Delta E_I$ and $\Delta E_H$. Let us assume that $\Delta E_I \gg \Delta E_H$. When the sample is excited by high enough energy photons so that the photoexcited electron-hole pairs are inside the continuum, bound excitons can be formed by impurities at different sites. As a result the emission will have the full inhomogeneous width $\Delta E_I$. Now, however, if we excite the sample with a laser tuned to a BE excited level $|E_2\rangle$ and the laser width $\Delta E_L$ is such that $\Delta E_H < \Delta E_L < \Delta E_I$ (see Fig. 1) only a small group of impurity atoms will be excited. When these BE's relax to the lowest state $|E_1\rangle$ and radiatively recombine the emission will have a width $\sim\Delta E_L$, smaller than $\Delta E_I$. As the excitation frequency is changed, different groups of impurity atoms will be excited and the emission frequency will also change so that $\omega_i - \omega_s$ is constant. Thus, this reasonantly excited BE behaves in the same way as Raman scattering. However, in this case $\omega_i - \omega_s$ is equal to the separation between the excited state and ground state of the bound exciton while in electronic RS $\omega_i - \omega_s$ is equal to the separation between the excited and ground state of the impurities. Such resonantly excited BE luminescence has been reported in GaAsP alloys doped with nitrogen.[9]

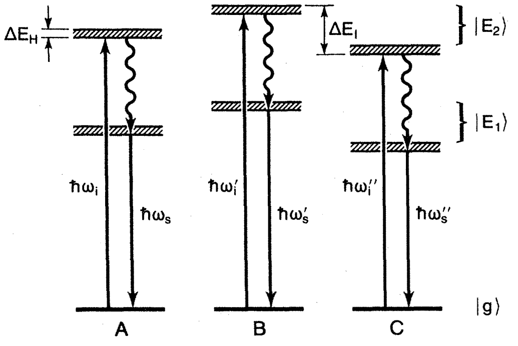

FIG. 1. Schematic diagram of emission processes in an inhomogeneously broadened system. $|g\rangle$ represents the ground state. $|E_1\rangle$ and $|E_2\rangle$ are excited states with homogeneous widths $\Delta E_H$ and inhomogeneous widths $\Delta E_I$. $A$, $B$, and $C$ represent the energy levels of the impurity under three different environments. The straight arrows represent optical transitions while the wavy arrows represent relaxation processes. Notice that as the excitation frequency $\omega_i$ is varied the emission frequency $\omega_s$ also changes.

In summary one classifies peaks in the emission spectra into PL and RS by the dependence of their emission frequency on the excitation frequency. For the PL peaks the LES spectra can be obtained simply by setting the spectrometer at $\omega_s$ and scanning the excitation laser frequency. For the Raman peaks it is necessary to obtain a separate emission spectrum for each $\omega_i$. However, when studying impurities by RRS it is important to distinguish cases when PL peaks behave like RS peaks.

## III. PROPERTIES OF CdSe AND EXPERIMENTAL DETAILS

The lowest conduction-band minimum in CdSe occurs at $k=0$ and has symmetry $\Gamma_7$. The top valence bands have symmetries $\Gamma_9$, $\Gamma_7$, and $\Gamma_7$ in order of decreasing energy.[10] The lower $\Gamma_7$ valence band is separated from the two upper valence bands by a large spin-orbit coupling and will not be important to this work. The two upper valence bands are separated by $\sim$200 cm$^{-1}$ and form the $A$ and $B$ excitons. Bound excitons have been identified in CdSe by several authors using PL.[11-14] The frequencies of the $A$ exciton bound to neutral donors and acceptors are found to be 14 694.8 and 14 657 cm$^{-1}$, respectively. From PL Henry *et al.*[12] determined the ionization energy of an unidentified donor in CdSe to be 19.5 meV (157 cm$^{-1}$). From the DAP bands they estimated the ionization energy of shallow acceptors in CdSe to be $\sim$109 meV. The nature of the donors in these previous studies is in general not known. The acceptors are identified by Henry *et al.* to be substitutional Li and Na.

The zone-center optical phonon energies in CdSe have been determined by Plotnichenko *et al.*[15] Phonon dispersion in CdSe has not yet been investigated experimentally or theoretically, although calculations of phonon dispersion and local-mode frequencies in the related material CdS have been reported by Nusimovici *et al.*[16-18] When necessary we shall draw on the results in CdS to aid the interpretation of our CdSe results.

The experimental setup we use consists of a cw dye laser pumped by an Ar$^+$ laser, a liquid He immersion Dewar ($T \lesssim 2$ K), a Spex double monochromator (spectral slit width $\lesssim 1$ cm$^{-1}$), and a photon counting system.

Most of the results presented here have been obtained on two CdSe samples. Both are bulk samples grown from the melt. One sample to be denoted by CdSe-L has been heavily doped with Li. The other sample is labeled CdSe-EP. Both samples were found to be insulating and it was not possible to determine their carrier concentration by Hall measurements. Spark-source mass spectrometry was used to determine the dominant impurity concentrations. The results are listed in Table I. We note that in spite of the high concentration of Li in CdSe-L the sample was not conducting. This indicates that there is segregation of Li in the sample so that most of the Li atoms are not electrically active. The concentration of Na was not determined because it is a contaminant of the mass spectrometer.

## IV. RESULTS AND DISCUSSIONS

In Figs. 2 and 3 we show the luminescence spectra of the two CdSe samples when excited at photon energies well above the band gap. In both figures the emission is polarized perpendicular to the *c* axis. Unless otherwise specified, in all the spectra shown in this paper the emission is polarized perpendicular to the *c* axis. The spectrum for the CdSe-L sample is dominated by the BE peaks denoted by $I_{1A}$ and $I_{2A}$ (at 14 659 and 14 699 cm$^{-1}$, respectively). The donor and acceptors involved are presumably $\mathrm{Li_{Cd}}$ (Li replacing Cd) and $\mathrm{Li}_I$ (interstitial Li). The two higher-energy peaks are associated with free excitons. On the high-energy side of the $I_{2A}$ peak, a shoulder is visible around 14 702 cm$^{-1}$. The shoulder develops into a distinct peak when the excitation frequency is lowered. The identification of this structure is not definite. It may be due to excitons bound either to a different donor or to impurity complexes. The identifications of the structures in the CdSe-EP spectrum are listed in Table II.

Resonant Raman scattering of the intrinsic phonon modes in both CdSe samples has been published elsewhere and will not be reported here.[19] In this article we are interested in the extrinsic modes and in both samples these extrinsic modes are not observed in off-resonant Raman spectra. They become observable due to resonance with either BE's or with DAP bands. We will consider these cases separately.

TABLE I. Concentration of impurities in CdSe samples as determined by spark source mass spectrometry. The units are in atomic parts per million (equivalent to ~$3.6\times10^{16}$ cm$^{-3}$).

| | CdSe-L | CdSe-EP |
|---|---|---|
| Li | 400 | <0.5 |
| F | <0.1 | <0.1 |
| B | <0.05 | <0.1 |
| Al | <0.2 | <0.2 |
| P | <0.2 | <0.2 |
| Cl | 3 | <0.1 |
| Ga | <0.1 | <0.1 |
| Br | <0.05 | <0.2 |
| As | ≲1 | <0.2 |
| Br | <0.2 | <0.1 |
| I | <0.1 | <0.1 |

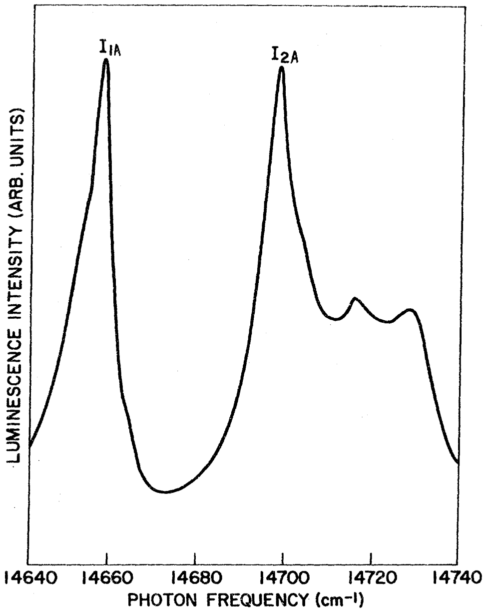

FIG. 2. Photoluminescence spectrum of CdSe-L showing the $I_{1A}$ and $I_{2A}$ bound exciton peaks. The radiation is polarized perpendicular to the *c* axis. The sample temperature is 2 K.

### A. Bound exciton–$D^0X$

When the incident laser frequency is resonant with the $I_{2A}$ bound exciton peak in CdSe, one Raman mode at about 110 cm$^{-1}$ usually becomes enhanced. This mode is observed in nearly all CdSe samples which show a well defined $I_2$ peak in the luminescence spectra. Depending on the sample the frequency of this mode varies from 109 to *112*

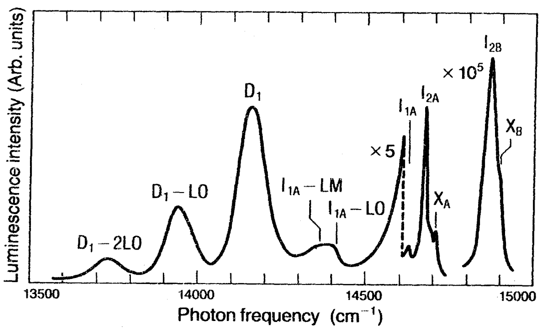

FIG. 3. Photoluminescence spectrum of CdSe-EP excited at incident photon energies above the *B* exciton. The notations used to identify the different peaks are listed in Table II. The sample temperature is 2 K.

TABLE II. Identification of the luminescence peaks of CdSe-EP (see Fig. 3).

| Notation | $\omega$ ($cm^{-1}$) | Identification |
|---|---|---|
| $X_B$ | 14900 | Free *B* exciton |
| $I_{2B}$ | 14870 | *B* exciton bound to $D^0$ |
| $X_A$ | 14707 | Free *A* exciton |
| $I_{2A}$ | 14674 | *A* exciton bound to $D^0$ |
| $I_{1A}$ | 14628 | *A* exciton bound to $A^0$ |
| $I_{1A}$-LO | ~14400 | LO phonon replica of $I_{1A}$ |
| $I_{1A}$-LM | ~14354 | Local-mode replica of $I_{1A}$ |
| $D_1$ | 14155 | Donor-acceptor pair band |
| $D_1$-LO | 13942 | LO phonon replica of $D_1$ |
| $D_1$-2LO | 13735 | 2LO phonon replica of $D_1$ |

$cm^{-1}$. In case of the CdSe-EP sample this mode resonates also with the $I_{2B}$ bound exciton. We have identified this mode as an electronic Raman mode associated with the transition $D_{1S} \rightarrow D_{2S}$ because this mode resonates with excitons bound to neutral donors and because Henry *et al.*[12] have determined the $D_{1S}$ to $D_{2S}$ separation to be 114 $cm^{-1}$ from the "two-electron" peak in luminescence. This two-electron PL peak is also present in our spectra and forms part of the changing luminscence background on which the Raman peak is superimposed in Fig. 4.

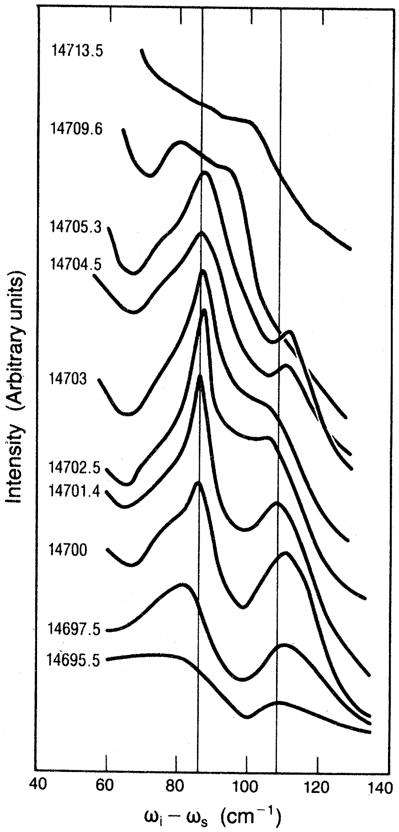

FIG. 4. Emission spectra of CdSe-L when excited by photons at or near resonance with the $I_{2A}$ bound exciton (14 697 $cm^{-1}$). The excitation frequencies are given adjacent to the curves which have been displaced vertically for clarity. The light vertical lines identify the Raman peaks at 109 and 86 $cm^{-1}$ discussed in the text. The analysis of these lines is complicated by the changing background due to photoluminescence.

In CdSe-L we observed another Raman peak at ~86 $cm^{-1}$ when the incident photon was in the vicinity of the $I_{2A}$ bound exciton. Figure 4 shows a series of Raman spectra obtained with $\omega_i$ varying between 14 695.5 and 14 713.5 $cm^{-1}$. All the spectra have been displaced vertically for clarity. The peak at 86 $cm^{-1}$ is sharper than the $D_{1S} \rightarrow D_{2S}$ electronic Raman mode at 110 $cm^{-1}$ and is strongest at $\omega_i \sim 14\,702$ $cm^{-1}$. The spectra are complicated by the fact that the 86-$cm^{-1}$ peak seems to be superimposed on a broader background which also becomes enhanced. For $\omega_i = 14\,709.6$ and 14 713.6 $cm^{-1}$ most of the Raman structures have disappeared and the remaining features can all be identified as due to luminescence. At present we have no positive identification of this 86-$cm^{-1}$ Raman peak. Its resonance enhancement suggests that it may be associated with donors. However, since its resonance occurs at a slightly lower frequency compared to the $D_{1S} \rightarrow D_{2S}$ Raman transition, it may not be associated with isolated donors. We note that 86 $cm^{-1}$ is ~ 60% of the donor binding energy in CdSe. In moderately heavily doped III-V semiconductors peaks have been observed in infrared absorption spectra at frequencies ~60% of the donor binding energy.[20] The identification of these peaks in the III-V compounds is still uncertain although it is generally agreed that they are associated with donor complexes. If the 86-$cm^{-1}$ Raman line has the same origin as those donor complex peaks in the III-V compounds, this would suggest that the shoulder of the $I_{2A}$ line at ~14 703 $cm^{-1}$ may be due to excitons bound to such donor complexes. This would be an interesting point worth further investigation. However, the possibility that the 86-$cm^{-1}$ peak and the underlying broad structures are due to two-phonon Raman scattering cannot be ruled out. The room-temperature two-phonon Raman spectrum of CdSe shows broad structures between 70 and 100 $cm^{-1}$ with peaks at 75 and 85 $cm^{-1}$.[15] These two-phonon modes can also be enhanced at bound excitons if their electron-phonon interaction has a long-range component similar to that of the Fröhlich interaction. This identification is, however, considered less likely because the two-phonon mode resonance should occur at the $I_{2A}$ peak and also because we found the strength of the 86-cm$^{-1}$ peak to be sample dependent.

### B. Bound exciton—$A^0X$

When the laser frequency is tuned to resonant with the $I_{1A}$ bound exciton we observe two new Raman peaks in CdSe-L at 189 and 399 cm$^{-1}$. A Raman spectrum of CdSe-L obtained at $\omega_i = 14\,657.5$ cm$^{-1}$ is shown in Fig. 5 where the new Raman peaks have been labeled $E$ and $E$+ LO. In Fig. 6 the intensity of the 189-cm$^{-1}$ peak is plotted as a function of $\omega_i$ showing its enhancement at the $I_{1A}$ bound exciton. The solid line in Fig. 6 is a plot of the absorption profile of the $I_{1A}$ bound exciton assuming it ot be a Lorentzian with a full width at half maximum of 3.5 cm$^{-1}$. Based on this resonance and on the fact that the separation between the $\Gamma_9$ and $\Gamma_7$ valence bands in CdSe is ~200 cm$^{-1}$, we have identified the 189-cm$^{-1}$ peak as an electronic Raman mode due to the transition $A^0_{1S}(\Gamma_9) \rightarrow A^0_{1S}(\Gamma_7)$. This electronic Raman transition is similar to the $A^0_{1S}(\Gamma_8) \rightarrow A^0_{1S}(\Gamma_7)$ electronic Raman mode observed in $p$-type GaP (denoted as $B$ line in Ref. 21). This identification of the 189-cm$^{-1}$ peak as due to electronic Raman scattering is supported by the excitation spectra of DAP bands in CdSe-EP. In the DAP excitation results to be presented later it will be shown that acceptors in CdSe have excited states around 195 cm$^{-1}$ above the ground state. The fact that the 189-cm$^{-1}$ mode shows a rather strong LO phonon replica at 399 cm$^{-1}$ is also consistent with its identification with the acceptor. Being more localized than the donors in CdSe, acceptors are expected to have stronger coupling to LO phonons.

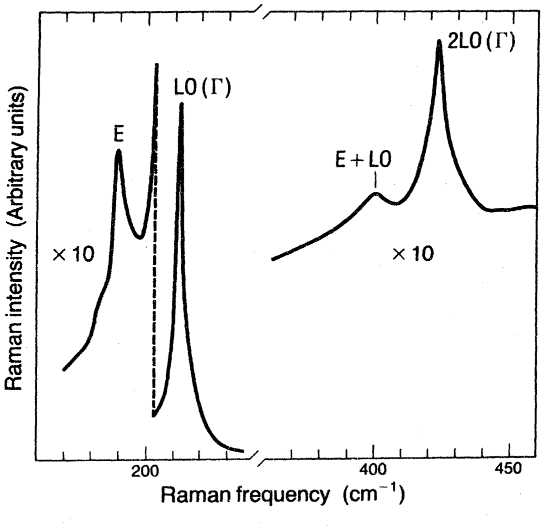

FIG. 5. Raman spectrum of CdSe-L showing the peak $E$ and its LO phonon replica. The excitation frequency of 14 657.5 cm$^{-1}$ is chosen to resonate with the $I_{1A}$ bound exciton (14 657 cm$^{-1}$) in this sample. The peak labeled LO(Γ) is the zone-center longitudinal optical phonon which is also resonantly enhanced at the bound exciton.

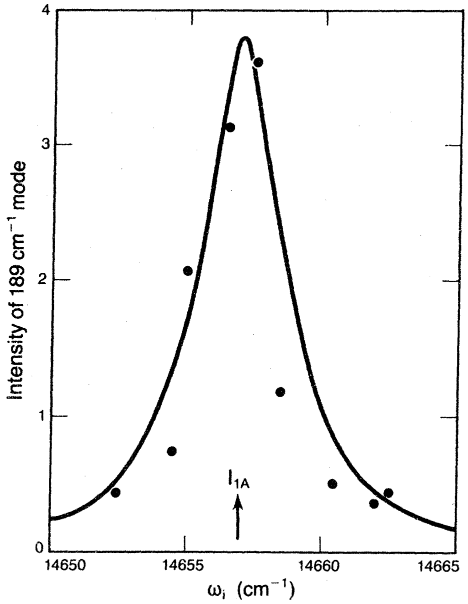

FIG. 6. Intensity of the 189-cm$^{-1}$ peak (labeled $E$ in Fig. 5) in CdSe-L plotted as a function of the incident photon frequency. The solid curve represents the absorption profile of the $I_{1A}$ bound exciton which is assumed to be a Lorentzian with peak position and half width equal to 14 657 and 3.5 cm$^{-1}$, respectively.

In CdSe-EP, besides observing the two electronic Raman peaks discussed above, a new peak appears at 257 cm$^{-1}$ when $\omega_i$ resonates with the $I_{1A}$ BE. This peak is relatively broad and is always superimposed on a luminescence background (due to $A^0X$-LO) so it is difficult to map out its resonance enhancement. Since the 257-cm$^{-1}$ mode is not observed in CdSe-L and is apparently associated with acceptors in CdSe, we have identified it as a local mode due to a light substitutional impurity. Henry *et al.*[11] have found that only $Li_{Cd}$ and $Na_{Cd}$ form shallow acceptors in CdS and CdSe. Their explanation for this is that only Li and Na have ionic radii small enough to allow them to replace the Cd ions. To calculate the local mode frequencies of $Li_{Cd}$ and $Na_{Cd}$ in CdSe we resort to the calculation of Nusimovici *et al.*[18] for CdS. By assuming that the dependence of the local mode frequencies on the mass defect is the same in CdS and CdSe, we deduce the frequencies of $Li_{Cd}$ as 376 and 409 cm$^{-1}$ and of $Na_{Cd}$ as 263 cm$^{-1}$ in CdSe. Since the frequency of $Na_{Cd}$ is quite close to the observed value of 257 cm$^{-1}$

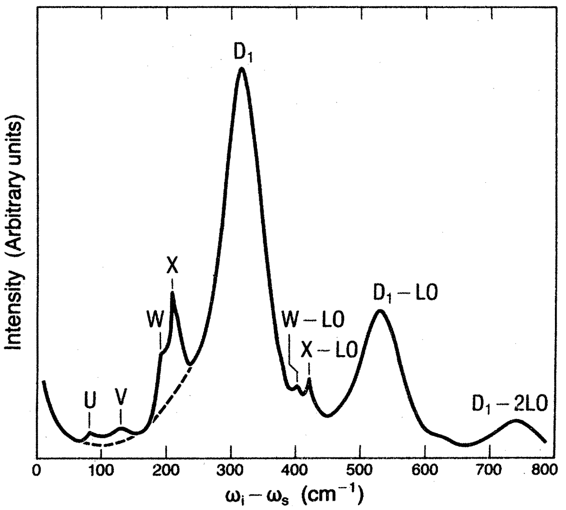

FIG. 7. Emission spectrum of CdSe-EP excited by photon at 14 438 cm$^{-1}$ showing the nonresonantly excited DAP band $D_1$ and its LO phonon replicas and the resonantly excited pair bands $U$, $V$, $W$, and $X$. The peaks labeled $W$-LO and $X$-LO are identified as LO phonon replicas of the peaks $W$ and $X$, respectively.

we have tentatively identified this peak as due to $\mathrm{Na}_{\mathrm{Cd}}$ in CdSe. This can also account for the fact that this peak is not observed in CdSe-L which is doped with Li. We have also attempted to observe the $\mathrm{Li}_{\mathrm{Cd}}$ local modes in CdSe-L and in spite of the high Li concentration we failed to detect these modes. The only explanation we can find is that the coupling between the Li local modes and the BE is probably very small.

### C. Donor-acceptor pair bands

Figure 7 shows the DAP bands in CdSe-EP when excited at 14 438 cm$^{-1}$. By comparing this spectrum with the DAP bands of the same sample excited at a higher frequency and shown in Fig. 3, we found several additional peaks. These peaks have been labeled in Fig. 8 as $U$, $V$, $W$, $X$, and their LO phonon replicas. In order to determine whether these new peaks are due to RS or to PL we plot in Fig. 9 their frequencies $\omega_i - \omega_s$ as a function of $\omega_s$. The peaks $V$ and $W$ show a slow increase in frequency with decrease in $\omega_s$. As pointed out in Sec. II this behavior can be explained by DAP bands which are selectively excited into excited states of the donor or of the acceptor.[4,5] The frequencies of these peaks are equal to the frequencies of the excited states of the impurities involved. These frequencies change with $\omega_s$ because of the dependence of $J_{\mathrm{DA}^*}(R)$ or $J_{\mathrm{D}^*\mathrm{A}}(R)$ on the pair separation $R$. For a particular $\omega_s$ the value of $R$ can be calculated from Eq. (1). When $\hbar\omega_s$ approaches $E_g - E_A^0 - E_D^0$, $R$ becomes

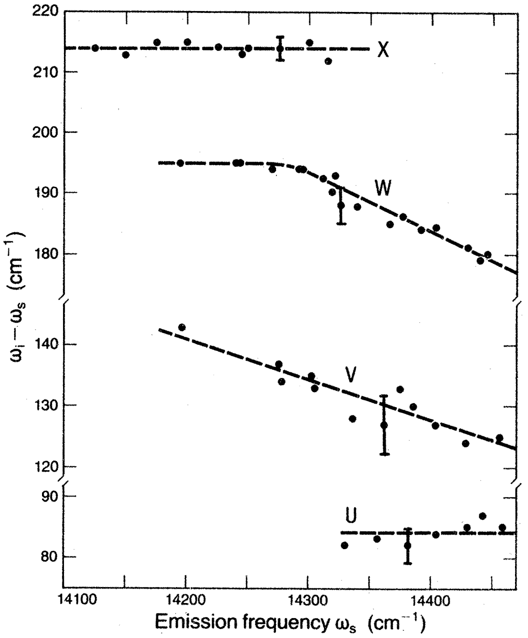

FIG. 8. Frequency shift $\omega_i - \omega_s$ of the resonantly excited pair bands $U$, $V$, $W$, and $X$ plotted as a function of the emission frequency $\omega_s$. The broken curves are guides to the eye only.

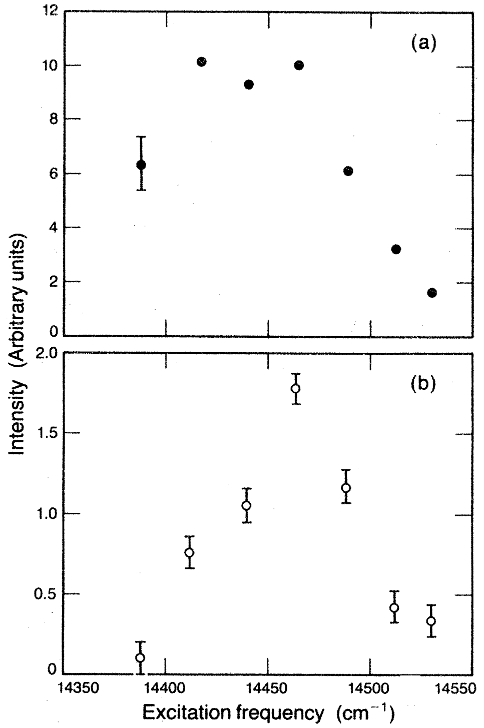

FIG. 9. Intensity of the resonantly excited DAP bands $X$ (a) and $U$ (b) plotted against the excitation frequency. The vertical bars represent typical errors in determining the intensities.

infinite and the enhanced pair-band frequency approaches a constant value equal to the excited-state frequency of an isolated impurity. This is essentially what happens in case of the peak $W$ whose frequency approaches 195 $\mathrm{cm}^{-1}$ for small $\omega_s$. We identify, therefore, peak $W$ with an excited state of the acceptor in CdSe since its frequency is too high for excited states of donors in CdSe. This is consistent with our identification of the 189-$\mathrm{cm}^{-1}$ Raman peak as an electronic Raman mode due to the acceptor transition $A_{1S}^0(\Gamma_9) \rightarrow A_{1S}^0(\Gamma_7)$. We note that the energy separation between $A_{1S}^0(\Gamma_9)$ and $A_{1S}^0(\Gamma_7)$ measured in the two cases is slightly different. This slight difference can probably be explained by the different initial states involved in the two emission processes. Although the frequency of the peak $V$ does not approach a constant as in the case of the peak $W$, its values are not far below the ionization frequency (157 $\mathrm{cm}^{-1}$) of the 1$S$ donor in CdSe. We therefore identify it as due to excited states of the donor in CdSe.

The peaks $V$ and $X$ do not show a dependence in their frequencies on $\omega_s$ so they are tentatively identified as due to phonons. Since their frequencies do not agree with the known zone-center phonon frequencies in CdSe, they are either due to phonons away from zone center or due to two phonons. The two-phonon Raman spectra of CdSe (Ref. 15) show strong peaks near the frequencies of $V$ and $X$ so it is quite likely that these are two-phonon peaks. We therefore tentatively identify the peaks $V$ and $X$ as due to resonantly enhanced DA pairs which recombine radiatively with the simultaneous emission of two phonons. Similar phonon structures have been observed in the DAP excitation spectra in ZnTe and ZnSe.[4,5]

To understand the excitation mechanism of these peaks $U$, $V$, $W$, and $X$ we plot their intensities as a function of the excitation frequency. The results are shown in Figs. 9 and 10. We find that the behavior of the peaks $U$ and $X$, associated with phonons, is quite different from those of $V$ and $W$ which are associated with impurity excited states. For the peaks $U$ and $X$ their intensities show a single maximum occuring at $\omega_i$ equal to ~ 14 440 $\mathrm{cm}^{-1}$. We explain this maximum by assuming that the peaks $U$ and $X$ result from a "hot luminescence" process in which the incident photon is absorbed by a DA pair at distance $R$ apart. This pair radiatively decays with simultaneous emission of two phonons. The excitation spectrum of these hot luminescence peaks should therefore resemble the absorption spectrum. From Fig. 3 the DAP emission spectrum of CdSe-EP shows a broad maximum ($D_1$) whose position is determined by the pair distribution function in the wurtzite lattice and the probability for an electron to tunnel from a donor to an acceptor. As pointed out by Williams[8] the absorption spectrum of DAP's can be calculated similarly to the emission spectrum. However, the peak of the absorption spectrum could be blue shifted from the peak of the emission spectrum in ionic crystals. This shift is caused by the screening of the impurity binding energy by the LO phonons. In case of emission the initial state consists of an electron and hole pair residing on a DAP. These charges are screened by the LO phonons so their binding energies are lowered. In absorption the DAP initially carries no charges so this screening is absent. As a result of this screening the emission peak occurs at a lower frequency. Williams has shown that the energy difference between the DAP absorption and emission peak is given by[8]

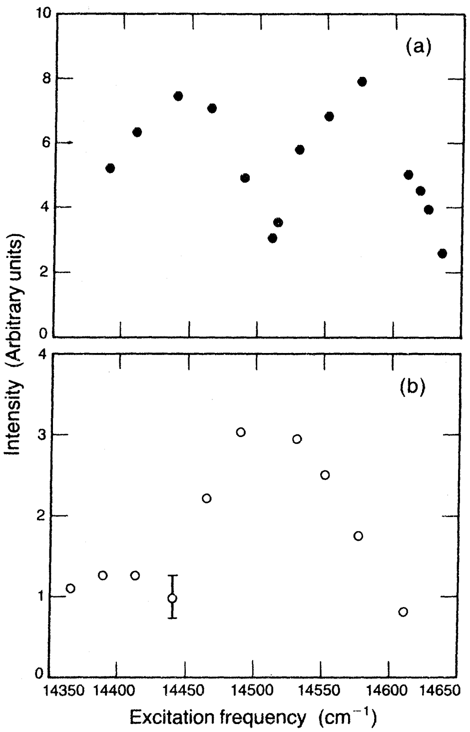

FIG. 10. Intensity of the resonantly excited DAP bands $W$ (a) and $V$ (b) plotted against the excitation frequency.

$$\Delta E \lesssim \left(\frac{\epsilon_0}{\epsilon_\infty} - 1\right)(E_A^0 - E_D^0)\,, \qquad (4)$$

where $E_A^0$ and $E_D^0$ are the "unscreened" binding energies of isolated impurities, and $\epsilon_0$ and $\epsilon_\infty$ are, respectively, the low-frequency and optical-frequency dielectric constants of CdSe. Taking spherically averaged values of $\epsilon_0 = 9.1$ and $\epsilon_\infty = 6.2$, $E_A^0 = 109$ meV and $E_D^0 = 19.5$ meV, we obtain

$\Delta E \lesssim 41.9$ meV (338 $\mathrm{cm}^{-1}$). Since the DAP emission peak in the CdSe-EP smaple occurs at ~14 150 $\mathrm{cm}^{-1}$ the predicted DAP absorption peak should occur $\lesssim$ 14 490 $\mathrm{cm}^{-1}$ which is consistent with the maximum in the excitation spectra (Fig. 9) at ~14 440 $\mathrm{cm}^{-1}$.

For the peaks *V* and *W* we find two maxima in their excitation spectra. Furthermore these maxima occur at different frequencies for the two peaks, We again interpret the high-frequency maxima in both Figs. 10(a) and 10(b) as associated with the DA absorption maximum. Since in case of the peaks *V* and *W* the final states in the absorption processes are excited states rather than ground states of the impurity, the absorption peaks will be upshifted by the energies of the excited states involved. For example, for the peak *W* the final state in the absorption process is an acceptor excited state 195 $\mathrm{cm}^{-1}$ above the ground states. The DAP absorption maximum should therefore be shifted by ~195 $\mathrm{cm}^{-1}$ toward higher frequency. This explains qualitatively why the high-frequency maxima in Figs. 10(a) and 10(b) occur at higher frequencies than the maxima in Figs. 9(a) and 9(b). It also accounts for the fact that the maximum for peak *W* is at a higher frequency than that of peak *V* because of the larger acceptor excited-state energy. This simple theory does not, however, explain quantitatively the frequencies of the observed excitation maxima nor does it explain the presence of a lower-frequency maximum in the excitation spectra of peaks *V* and *W*. This suggests that additional effects have to be considered. One such possible effect is that the enhanced DAP band involves the relaxation of one of the impurities, say, an acceptor, from an excited state to the ground state before recombining with a donor. The enhancement of the DAP band depends on the rate of relaxation relative to the rate of recombination. Although the relaxation rate should be independent of the pair separation, the recombination rate is strongly dependent on the pair separation.[22] Hence, for small pair separations it is possible that the rate of recombination becomes comparable to the rate of relaxation. This will decrease the number of resonantly excited pairs and hence their intensity. The result of this competition between relaxation and recombination is to shift the excitation maximum toward lower frequency (corresponding to larger pair separation). This is consistent with the experimental results in Fig. 10.

## V. CONCLUSION

We have examined in detail the excitation spectra of Raman scattering and photoluminescence in doped CdSe crystals. From the enhancement of the Raman spectra at bound excitons in CdSe we obtained the frequencies of the lowest excited states of donors and acceptors in CdSe. We also observed a localized phonon mode due to acceptors in CdSe which we attributed tentatively to substitutional Na. The RRS results are confirmed by the excitation spectra of donor-acceptor pair emission bands in CdSe. We also explained qualitatively the dependence of the resonantly enhanced DAP peak intensities on the excitation frequency.

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*Present address: Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau, France.

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