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Resonance Raman scattering from defects in CdSe

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Resonance Raman scattering (RRS) in CdSe is investigated in the region of the A excitonic transition. Three new Raman lines at 182, 195, and 208 cm^{-1} are observed which become stronger than even the line due to the longitudinal optic (LO) phonon under appropriately resonant conditions. The modes at 182 and 195 cm^{-1} show resonant enhancement at 1.8206 eV whereas the mode at 208 cm^{-1} and the LO phonon exhibit maximum intensity at 1.8222 eV. The polarized luminescence spectra show that these energies correspond to the excitons bound to two different donors having different site symmetries. The peaks at 182 and 195 cm^{-1} are assigned to electronic Raman scattering from the levels of a donor complex which does not have the full symmetry of the lattice. Possible mechanisms for the mode at 208 cm^{-1} are discussed.

I. INTRODUCTION

There has been a considerable interest in the vibrational properties of a new class of compounds called diluted magnetic semiconductors (DMS) which exhibit unique semiconducting and magnetic behavior. The phonons in the zinc-blende-type DMS are well known by now,[1] whereas those in the wurtzite-type DMS like $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$ have been studied only to a very limited extent.[2] In this context, it is important to establish the behavior of phonons in CdSe, one of the end members of the system $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$, and their resonance enhancements. Although the zone-center optical phonons in wurtzite-type semiconductor CdS have been identified long ago,[3,4] the picture in the case of CdSe is still incomplete. In CdSe one of the phonons of E_2 symmetry was not observed in the most recent study.[5]

There have been a number of investigations of resonance Raman scattering (RRS) in many III-V and II-VI compound semiconductors. These studies have been mostly concentrated on phonons, especially the longitudinal optical (LO) phonons;[6] up to nine multiple peaks due to LO phonons have been seen under resonance.[7] It is well known that defects (including impurities) introduce new peaks in the Raman spectra.[8,9] Defects present in undoped single crystals even in concentrations as low as 10^{14} cm^{-3} can manifest themselves in the luminescence spectra and, under suitably resonant conditions, in the Raman spectra.[10] Defects can also trap excitons to form bound excitons whose electronic levels in turn can act as resonant intermediate states for the scattering process.[11,12] Elastic scattering of excitons by defects constitute one of the mechanisms of dipole-forbidden Raman scattering by LO phonons.[6,13] Inelastic scattering of excitons by a defect can excite the defect into an electronic or vibrational excited state.[8]

The Raman modes due to the defects are also expected to show the resonance enhancements similar to those of intrinsic phonons.[8] Berg and Yu[9] have reported the enhancement of the Raman scattering from the local mode of As vacancy in electron irradiated GaAs. Ulbrich *et al.*[10] have observed the enhancement of the Raman scattering from donor levels in CdTe and GaAs, both at the bound and the free exciton energies. Recently Yu and Hermann[14] have reported the first RRS investigation of impurities in the wurtzite-type semiconductor CdSe and also the forbidden Raman scattering (FRS) by LO phonons.[15] Two of the new Raman modes observed have been attributed by them to electronic Raman scattering (ERS) from the donor and acceptor levels, respectively; however, the resonance enhancement of the ERS was much weaker than that of the LO phonon. Their luminescence results and an unidentified Raman peak indicate the possible existence of a donor complex which needs further investigation.[14] In the present work, we report a complete polarized Raman spectrum of CdSe including the missing E_2 mode. In addition, we reinvestigate the resonance enhancement of the FRS by LO phonons in the vicinity of the A exciton bound to neutral donors and report new modes due to the defects which appear at positions different from those reported earlier.[14]

II. EXPERIMENT

Undoped bulk CdSe crystals grown by the Bridgman method were cut with the c axis lying parallel to the face and polished using the procedure described elsewhere.[16] CdSe crystals which are not intentionally doped are usually n type.[16] The samples used in the present investigations were also n type. Raman spectra of the samples were measured at 10 K in a glass optical cryostat and also at 5 K in a Super-Varitemp (Model 10DT, Janis Research Co.) by exciting the samples with a Kr^+ laser as well as by a Coherent Radiation, Inc. cw ring dye laser with DCM (4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran) as the dye. The laser power was kept below 1.5 mW to avoid sample heating. The scattered light was analyzed using a computer-controlled double monochromator and detected by a standard photon counting unit. The luminescence spectra was excited using the 6764 Å line of a Kr^+ laser.

III. RESULTS AND DISCUSSIONS

CdSe has the wurtzite structure and belongs to the C_{6v} point group with two formula units per primitive cell. Zone-center optical phonons predicted by group theory[3,4] are $A_1+2E_2+E_1$. Of these, the phonons of A_1 and E_1 symmetry are polar and, hence, split into phonons of transverse optical (TO) and LO character; i.e., A_1 becomes A_1(TO) or A_1(LO) and E_1 splits into E_1(TO) and E_1(LO) depending on the direction of the phonon propagation and its polarization. The anisotropy splitting—separation of A_1 and E_1 mode frequencies—is observed to be much less than the LO-TO splitting[5] indicating that the polar phonons not propagating along the crystallographic directions will have quasi-TO- and quasi-LO-like behavior. Similar behavior is seen in CdS also.[3]

Figures 1(a)—1(c) show polarized Raman spectra excited by the 7525 Å line of Kr$^+$ laser at 5 K in three different scattering configurations that are necessary to observe all the zone-center optical phonons. Scattering geometry (a) $y(xx)\bar{y}$ gives A_1(TO) and E_2, (b) $x(zx)y$ gives E_1(TO) and E_1(LO), and finally (c) $z(yy)\bar{z}$ gives E_2 and A_1(LO) phonons. We identify line 4 at 177.6 cm^{-1} in Figs. 1(a) and 1(c) to be the E_2 mode, consistent with the polarization selection rules; this line had not been observed by Plotnichenko *et al.*[5] If one draws a correspondence between the zone-center optical-phonon frequencies of CdS and CdSe,[3,4] one finds that one of the E_2 modes is at fairly low frequency, 43 cm^{-1} in CdS and 34 cm^{-1} in CdSe, while the frequency of the other E_2 mode is expected to lie in between those of E_1(TO) and A_1(LO) modes. The present assignment of the other E_2 mode in CdSe is consistent with the trend in CdS. The phonon frequencies observed in the present investigations and those reported earlier[5,15] are compared in Table I.

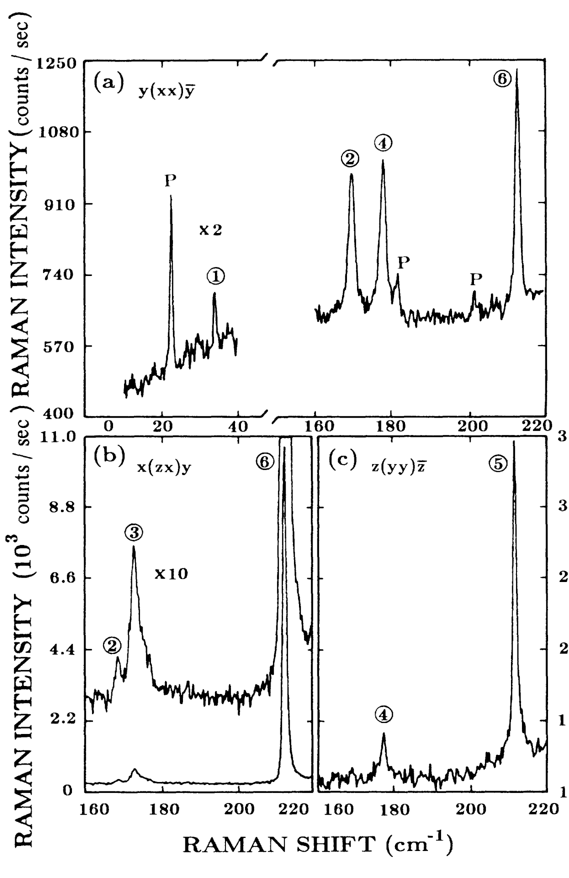

FIG. 1. Polarized Raman spectrum of CdSe at 5 K in three different scattering configurations using the 7525 Å line of Kr$^+$ laser. (a) $y(xx)\bar{y}$, (b) $x(zx)y$, and (c) $z(yy)\bar{z}$. Peaks marked P are plasma lines. Peaks marked 1—6 are identified as 1, E_2; 2, A_1(TO); 3, E_1(TO); 4, E_2; 5, A_1(LO); and 6, E_1(LO). Presence of E_1(LO) in $y(xx)\bar{y}$ and of A_1(TO) in $x(zx)y$ scattering configurations is a result of polarization leakage.

When a semiconductor crystal is excited with photons of energy close to the band gap, apart from the dipole-allowed Raman scattering by LO phonons,[17] one also observes dipole-forbidden Raman scattering by LO phonons[6] which does not obey the normal selection rules.[17] For the "forbidden" scattering a number of mechanisms have been proposed, e.g., electric field due to the band bending close to the surface[18] and the intraband matrix element of the Fröhlich electron-phonon interaction.[19] The Raman tensor in the latter case has the same symmetry as that of the dielectric tensor and leads to the scattered polarization parallel to the incident polarization; however, the Raman efficiency is proportional to q^2 where q is the magnitude of the wave-vector transfer. If the intermediate state happens to be a bound exciton, the Fröhlich interaction leads to a q-independent efficiency of the forbidden Raman scattering by LO phonons.[11] As stated earlier, the elastic scattering of excitons by defects (impurities) significantly contributes to the FRS by LO phonons.[13] Though it is a higher-order (fourth) perturbation theory, the large momentum transfer which takes place in the elastic exciton defect scattering enhances the scattering efficiency.[6]

Figure 2 shows a typical off-resonance Raman spec-

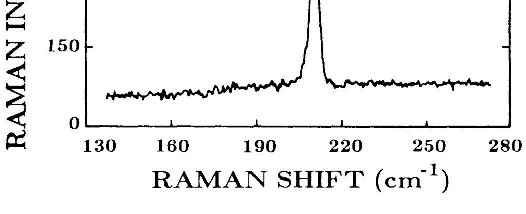

FIG. 2. Off-resonance Raman spectrum of CdSe in the $y(xx)\bar{y}$ configuration. Energy of the exciting radiation is 1.8857 eV which is much higher than the A and B exciton energies.

TABLE I. Zone-center optical-phonon frequencies (in cm^{-1}) in CdSe.

	Mode	Present investigation 5 K	Hermann and Yu[a] 2 K	Plotnichenko *et al.*[b] 300 K
1	E_2	34.0		34
2	A_1(TO)	169.1		166
3	E_1(TO)	174.0		169
4	E_2	177.6		
5	A_1(LO)	213.0	212.3	209
6	E_1(LO)	213.9	213.2	211

[a] Reference 15.
[b] Reference 5.

trum of CdSe at 10 K in the spectral range 130 to 280 cm^{-1} observed in the backscattering configuration $y(xx)\bar{y}$, using an exciting photon energy much higher than that of the A exciton. In this geometry one expects to see A_1(TO) and E_2 modes [see Fig. 1(a)]; however, since the incident photon energy is much higher than the band-gap energy, one observes only the FRS by LO phonons. When the scattered polarization is selected perpendicular to the incident polarization, $y(xz)y$, no Raman intensity is observed although E_1(TO) is allowed by selection rules. Thus the FRS by LO phonons has the same polarization as that of the incident photon, consistent with the diagonal Raman tensor attributed to the Fröhlich electron-phonon interaction.[19] As the separation of the LO phonons of A_1 and E_1 symmetry is rather small, the observed FRS intensity has contributions from the LO phonons of both the symmetries; however, the position of the FRS peak indicates that it has a dominant A_1 contribution.

As pointed out earlier, free and bound excitons provide resonant intermediate states for the Raman scattering process. They also give rise to luminescence peaks. In the wurtzite structure one has three free excitons—A, B, and C excitons, arising from the spin-orbit split and crystal-field split valence bands.[20] The luminescence peaks due to exciton bound to neutral donors and acceptors are usually called I_{2A} and I_{1A}, respectively;[15] subscript A denotes the A exciton. When the dye laser frequency is tuned across the A exciton bound to neutral donor, the Raman spectrum changes dramatically and a number of new Raman lines appear riding over broad luminescence peaks. Figure 3 shows a few typical spectra at different incident photon energies. Apart from the FRS by LO phonons at 213 cm^{-1}, the most dominant peak is at 182 cm^{-1}, with peaks at 195 and 208 cm^{-1} also unambiguously present. Similar to the FRS by LO phonons, all the new Raman peaks have a polarization identical to that of the incident photon.

In Fig. 4 the intensity of the new modes and that of the LO phonon are plotted as a function of incident laser energy. It can be seen that the mode at 208 cm^{-1} has the maximum intensity at 1.8222 eV along with that of the LO phonon, whereas the modes at 182 and 195 cm^{-1} have their maximum intensities at 1.8206 eV. It is worth emphasizing here that the resonance enhancement of the peak at 182 cm^{-1} is by a factor more than 2000 as compared to that of the LO phonon having a value of only around 30.

In order to understand the different resonant behavior of the two sets of Raman modes, polarized luminescence spectra were investigated with incident polarization perpendicular to the c axis and the emitted polarization analyzed parallel as well as perpendicular to the c axis. The 1.8328-eV (6764-Å) Kr^+ laser line was used to excite the luminescence. The results are shown in Fig. 5. It can be seen from Fig. 5(a) that the free exciton X at 1.8266 eV and the exciton bound to neutral donor, labeled as D_1^0X, at 1.8222 eV appear for the emitted polarization perpendicular to the c axis, consistent with selection rules for excitons.[20] The free and the bound exciton energies are in

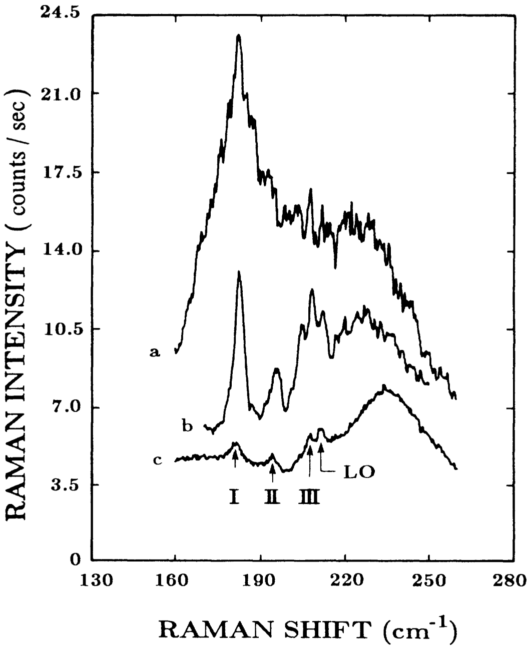

FIG. 3. Resonance Raman scattering from CdSe with the dye laser frequency tuned close to A exciton. New Raman peaks are seen at 182 (I), 195 (II), and 208 (III) cm^{-1}. Energies of the exciting radiation are (a) 1.8183, (b) 1.8211, and (c) 1.8246 eV.

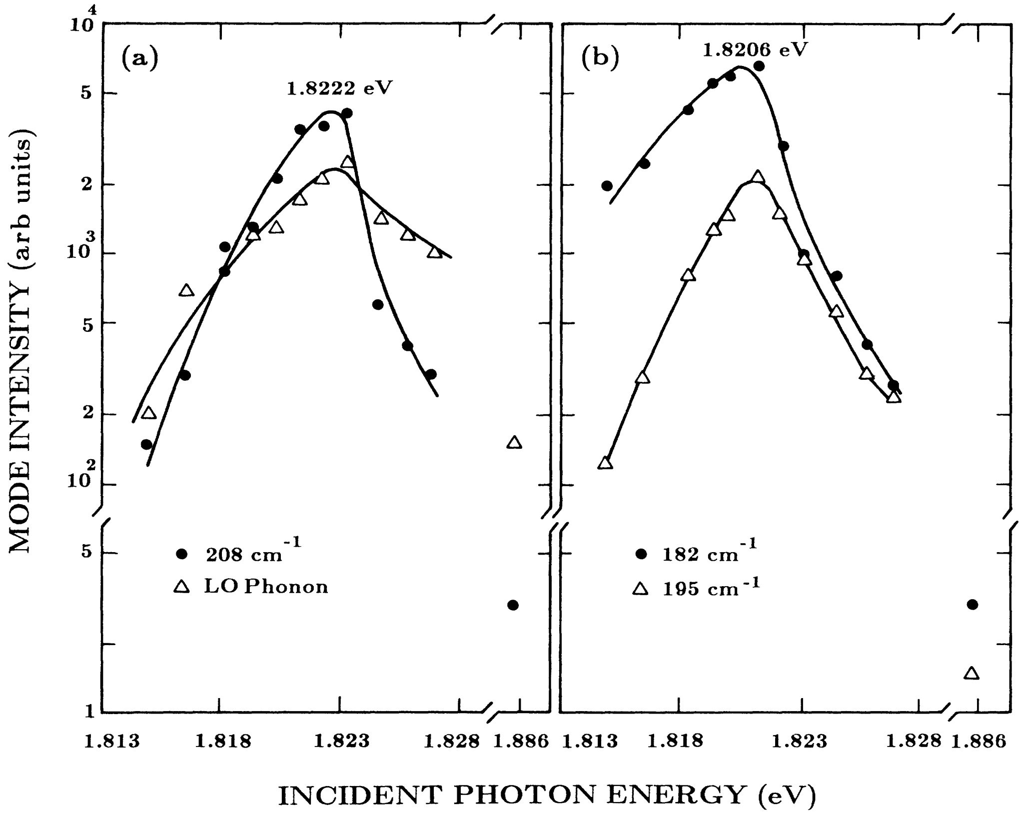

FIG. 4. Resonance enhancement of Raman intensities of the new Raman lines and that of the LO phonon in CdSe. Intensities of the modes away from resonance are also shown for the sake of comparison. The LO phonon and the mode at 208 cm^{-1} show a peak at 1.8222 eV, whereas modes at 182 and 195 cm^{-1} have maximum intensity at 1.8206 eV. Curves drawn through the points are only guides to the eye.

good agreement with those reported earlier.[21] The luminescence due to a bound exciton is known to have a polarization the same as that due to a free exciton if the defect has the full symmetry of the crystal point group;[22] for example, a substitutional impurity or a native defect like a vacancy. However, Fig. 5(b) shows that there is yet another bound exciton, labeled D_2^0X, at 1.8206 eV which has a polarization different from that of the free exciton. This indicates that the exciton D_2^0X is bound to a different donor which does not have the full symmetry of the point group. Recently Yu and Harmann[14] have suggested the possible existence of a donor complex on the basis of a weak shoulder in the I_{2A} peak in the luminescence spectra at 1.8227 eV. The present polarized luminescence spectra also suggest the presence of a donor complex; however, the position of the I_{2A} peak due to the exciton bound to the donor complex D_2 observed in the present study is different from the shoulder observed by them. We interpret the luminescence peaks at 1.8127 and 1.7947 eV as arising from the donors D_1 and D_2. The localization energy of the bound excitons[23] and the corresponding donor binding energies thus deduced are given in Table II. It may be noted from Table II that the ratio of the exciton localization energy and the defect binding energy is the same for both the defects which is expected from the Haynes rule.[25] This also supports the assumption that both the defects are donors.

From the luminescence spectra it is now clear that the modes at 182 and 195 cm^{-1} are resonantly enhanced at the bound exciton D_2^0X energy while the mode at 208 cm^{-1} and the LO phonon are enhanced at that of the D_1^0X bound exciton. As the resonance enhancement of the LO phonon and also that of the new modes appears at the bound exciton energies, the scattering mechanism responsible for the enhancement of the different modes seen in the present investigation is essentially the q independent Fröhlich interaction at the bound exciton.[11]

The Raman modes at 182 and 195 cm^{-1}, which show extremely high resonance enhancement at D_2^0X, are as-

TABLE II. Localization energy ($E_{\rm Bx}$) of bound excitons and the binding energy (E_D) of the corresponding donors. The band gap is taken as 1.8402 eV (Ref. 24); the binding energy of the A exciton obtained in the present work is 13.6 meV.

Donor	$E_{\rm Bx}$ (meV)	E_D (meV)	$E_{\rm Bx}/E_D$
D_1	4.3±0.1	27.5±0.2	0.156±0.05
D_2	6.0±0.1	37.6±0.2	0.160±0.05

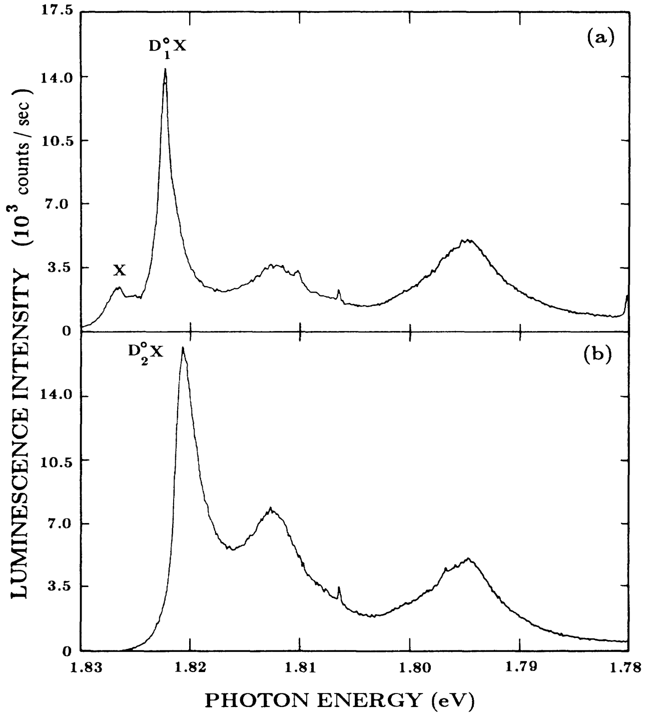

FIG. 5. Luminescence spectra of CdSe excited with the 6764 Å line of the Kr$^+$ laser. Incident polarization is perpendicular to the *c* axis. Emitted polarization is (a) perpendicular and (b) parallel to the *c* axis. The peak labeled *X* is due to free exciton. D_1^0X and D_2^0X are attributed to excitons bound to donors D_1 and D_2, respectively. The peaks at 1.8127 and 1.7947 eV are assigned to donor luminescences.

signed to the Raman scattering from the electronic excitations of the donor D_2. Although the energy levels of donors in cubic zinc-blende semiconductors are well known,[26] there has not been any theoretical estimate of those of the wurtzite-type semiconductor CdSe. Relative intensities of the modes at 182 and 195 cm^{-1} suggest that these modes could be due to the transitions $1s \rightarrow 2s$ and $1s \rightarrow 2p$, respectively. It may be noted that 182 cm^{-1} is approximately 0.6 of the binding energy of the donor D_2. In III-V semiconductors, electronic excitation of some donor complexes have been found to have energy $0.6E_D$ (Ref. 27) which supports the assignment of the peaks at 182 and 195 cm^{-1} to ERS from donor complex D_2. Recently in CdSe:Li Raman peaks at 109 and 189 cm^{-1} have been observed[14] which have been assigned to the ERS from the donor and acceptor levels, respectively. It is worth pointing out that the binding energy of a donor or an acceptor, and hence its electronic levels in any semiconductor, are determined by its chemical nature[28] which could be different in different systems. In CdSe an excited state of acceptor has been identified[14] at 195 cm^{-1} from the excitation of donor-acceptor pair bands; however, in the samples used in the present investigation no donor-acceptor pair bands are seen, and hence one can rule out the possibility of 195 cm^{-1} peak in the present investigation being due to acceptors.

As the resonance enhancement of the mode at 208 cm^{-1} occurs at an energy corresponding to the exciton bound to the donor D_1, it appears that this mode could be a local mode of vibration of the defect constituting the donor D_1. Resonance enhancement of the vibrational mode of a defect at the corresponding bound exciton energy has been observed earlier also.[8] Another possible explanation for the 208-cm^{-1} peak could be that it is due to the ERS from the levels of the donor D_1 which has the full symmetry of the point group. However, the ratio of the $1s \rightarrow 2s$ transition energy to the donor binding energy E_{D_1} turns out to be 0.94 which is much more than expected.

In order to have an insight into the structure and the composition of the donor complex D_2 responsible for the ERS observed in the present investigation one needs to consider various defects and impurities in this semiconductor. It is known that in CdSe, Se vacancy (V_{Se}) is a double donor while Cd vacancy (V_{Cd}) forms a deep acceptor.[29] Group I elements like Na,Li form shallow acceptors[30] while Li interstitial, group VII elements like Cl, or a complex of $\mathrm{Li}_{\mathrm{Cd}}$ with V_{Se} act as shallow donors. Thus, a number of possible defect complexes can be visualized, for example, a complex of a substitutional impurity with V_{Se}, which could constitute the donor complex D_2 having a symmetry lower than that of the lattice. Further experiments are needed to get a more precise information about the defect complex D_2.

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