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Phonon Coupling in Edge Emission and Photoconductivity of CdSe, CdS, and Cd(Se_xS_{1-x})

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In mixtures of Cd(Se_xS_{1-x}) two longitudinal optical (LO) phonons (and their additive combinations) couple to the edge-emission centers and to the conduction electrons. The phonon frequencies as a function of the CdSe/CdS ratio—which are observed in the edge emission spectra—agree well with the eigenfrequencies calculated for a linear chain of Cd-Se-Cd-S-Cd-⋯atoms. The spectral response of the photoconductivity of pure CdS and CdSe shows oscillations at the high-energy side of the absorption edge. The energy separation between successive photocurrent maxima or minima corresponds approximately to the LO phonon energy of each crystal lattice. The minima are explained by a shortened electron lifetime at the respective energies, because electrons having such energies may easily drop to a recombination center (exciton or impurity near band edge) by the emission of one or several LO phonons. It is shown that in mixed crystals the two LO phonons (and their combinations) shorten the lifetime of the conduction electrons. Thus, when excitation occurs via the conduction band, the recombination center will be populated faster in mixed crystals than in pure crystals. Hurwitz's observation, namely, that the lasing threshold in Cd(SeS) mixtures is lower than that of either CdSe or CdS, might therefore be accounted for.

I. INTRODUCTION

MANY studies have been devoted to the origin of the light emission which occurs in II–VI compounds near the fundamental absorption edge, the so-called edge emission. Early investigators[1] pointed out that this spectral emission in CdS, ZnS, and ZnO showed a characteristic periodic structure, the period of which, as Kröger and Meyer[2] have shown, corresponds to the energy of the longitudinal optical (LO) phonon in the respective lattices.

In more recent studies at lower temperatures further structure was observed. In CdS for instance, two types are observed, (a) within the broad green emission band, and (b) sharp emission lines closer to the band edge (often referred to as "blue edge emission").[3] Again it was observed that many of these lines can be grouped into several series having separations between lines which correspond to the longutidinal optic (LO) lattice vibration of CdS. Additionally, Thomas and Hopfield[4] and Klein[5] reported for CdS and ZnS, respectively, the coupling of transverse optical (TO) and acoustical (TA) modes of the lattice vibration to the annihilation of excitons bound to an impurity. In addition to multiphonon coupling (LO, 2LO, 3LO, ⋯) they also found coupling of the combinations of different phonons (LO+TA), LO+TO, etc.). In all cases, however, the emission of the LO phonon-coupled lines was stronger by at least one order of magnitude than that of lines involving TO or TA coupling. This is in accordance with the results of Fröhlich and Mott[6] who showed that electrons moving in a crystal interact mainly with the longitudinal-optic vibrations as long as the polar forces are sufficiently large.

There is no doubt that the observed phonon frequencies are the ones of the unperturbed host lattice and are not due to some localized vibrational modes at the emission center. There exists good agreement between the phonon energy values measured by infrared (ir) absorption and reflection techniques and with those values derived from energy differences between phonon-coupled and zero-phonon emission lines. Besides, it is improbable that bound excitons or donor-acceptor recombinations—which are mostly the origin of the zero-phonon emission lines—couple exclusively to the

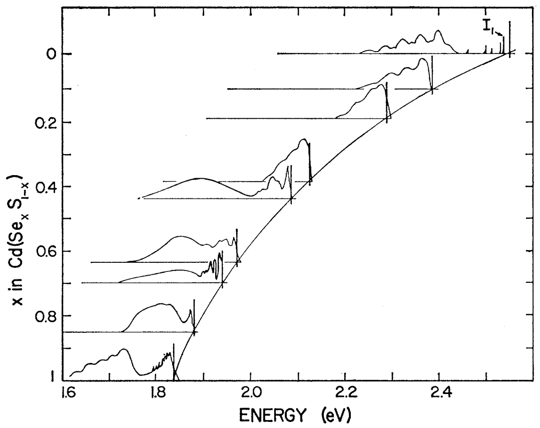

FIG. 1. The edge emission of Cd(Se_xS_{1-x}) is shown schematically for different values of x. The vertical bars indicate the position of the absorption edge for each composition. The broad-band donor-acceptor recombination observed in pure CdS and CdSe does not follow uniformly the trend of the edge. The sharper line structure in compositions with higher Se content is probably due to free or bound excitons.

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particular lattice cell which contains the impurity because the wave functions in both cases extend well over several hundred unit cells.[7]

In the next section, we analyze the edge emission of mixed CdSe-CdS crystals in terms of the exhibited phonon structure; we also derive the values of the LO phonons as a function of the composition. Using the linear chain of Cd-Se-Cd-S-Cd-··· as an approximation to the actual Cd (Se S) crystal, we calculate its vibrational eigenvalues and eigenvectors. A comparison with the observed LO phonon energies shows that this model represents the observed values well.

In Sec. III we point out the effects of phonon coupling to the free electrons in the conduction band. In the intrinsic region of InSb, GaSb[8–11], and CdS,[12] oscillations in the spectral response of the photoconductivity have been reported and these oscillations have a period corresponding to the energy of a LO phonon. It has been observed that the conductivity is lower whenever the energy of the exciting light is equal to the energy of either an impurity (in InSb or GaSb) or an exciton (in CdS) plus an integral number m of LO phonons of the respective lattice. This observation can be explained by the assumption that the exciton acts as a center of fast recombination (fast in comparison to band-to-band recombinations). Hence, electrons possessing the corresponding amount of energy plus a multiple of the LO phonon energy may recombine faster through this center after losing their excess phonon energy; consequently, they contribute less to the conductivity than those excited with light of slightly different energy.

In a detailed study on CdS and CdSe we show that free excitons as well as excitons bound to various impurities act like centers of fast recombination. The observed oscillations have the energy difference corresponding to the LO phonon energies of CdS and CdSe. In Cd(SeS) mixed crystals, minima are observed which are interpretable in terms of a coupling (and shortening of lifetime) via two different LO phonons and their combinations, similar to those observed in the edge emission spectra.

II. EDGE EMISSION OF Cd(Se_xS_{1-x})

The edge emission of CdS below 4.2°K consists of a number of sharp lines due to the annihilation of free excitons or excitons bound to impurities,[13] as well as broad bands and lines due to donor-acceptor recombinations.[7] Most of these lines and bands also show phonon side bands. The value of the most strongly coupled phonon, the LO phonon, is usually quoted as 38 meV.[4] By precisely measuring the separation of the I_1 line (4888.5 Å) and its first phonon satellite, we determined that a more accurate value of the LO phonon in CdS is 37.7±0.1 meV. This determination should be even more reliable than those based on reststrahl reflection as the latter involve the values of dielectric constants which have not been determined very accurately at low temperatures. The LO values obtained by this method usually lie between 38 and 39 meV.[14]

Similarly, from the measurement of four broad peaks, we determined the LO phonon energy of CdSe to be 26.6±0.3 meV. The first of these peaks, which should correspond to the broad green emission in CdS and therefore originate in donor-acceptor recombination, was located at 7154.3 Å. Also, from such measurements, Gross and Sobolev[15] obtained the value of 26 meV, which was measured similarly by Pedrotti.[16] Likewise, Wardzynski and Wojtowica-Natanson[17] had measured the LO value to be 27 meV. From ir measurements, Geik *et al.*[18] calculated the LO values of 212 cm^{-1} and 210 cm^{-1} for $\mathbf{E}\perp C$ and $\mathbf{E}\| C$ at 100°K which corresponds to 26.3 and 26.0 meV, respectively.

The edge emission in solid solutions of Cd(SeS) has been studied by Gross and Sobolev,[19] by Pedrotti,[16] and most recently, by Balkanski, Beserman, and Besson.[20] The aim of Pedrotti's work was to present the shift of the absorption edge and to investigate the spin-orbit and crystal-field splitting in these solid solutions.[21] He did not make an attempt to interpret the results of his uv stimulated edge emission. He pointed out, however, one particular feature which we also observed in our present studies and we have illustrated this feature in Fig. 1. Shown schematically is the edge emission for different compositions. The absorption edge in each composition, as it appears in reflection or absorption for the same crystals, is indicated by a solid bar. It

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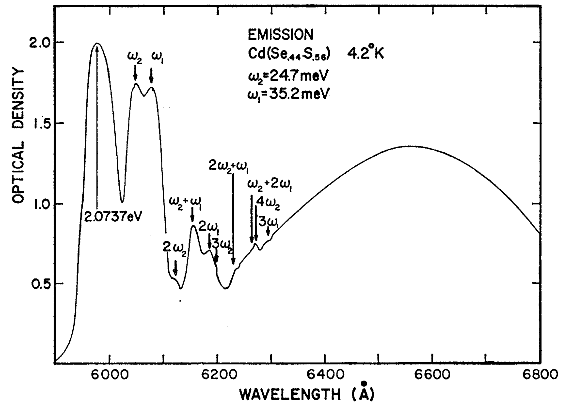

FIG. 2. Densitometer trace of the polarized emission of a $Cd(Se_{0,44}S_{0,56})$ platelet at 4.2°K ($E\perp C$). With reference to the line at 2.0737 eV the arows mark the computed spectral positions of the two LO phonons ($\omega_1=35.2$ and $\omega_2=24.75$ meV) and their additive combinations. These particular values were chosen because they gave the best over-all fit.

appears that, while the edge itself moves uniformly, the broad-band emission does not follow the same trend. Broad emission bands shift closer to the edge in the mixed crystals of less than 40% CdSe, and in crystals of higher CdSe concentrations the emission near the edge becomes sharper. Higher order multiple-phonon coupling is observed on either end of the mixture range. Using polycrystalline films, Gross and Sobolev[19] found that the phonon energy in these mixtures varies linearly between the value of the CdSe LO phonon and that of the CdS in proportion to the composition of these mixtures. Similar results were obtained for single crystals of mixed compositions by Balkanski *et al.*[20] with electron beam stimulation at temperatures somewhat above liquid-helium temperature; however, in reststrahl reflection and thin-film ir absorption measurements on these mixed crystals they observed two different phonon modes, one characteristic for the pure CdSe and one characteristic for the pure CdS.

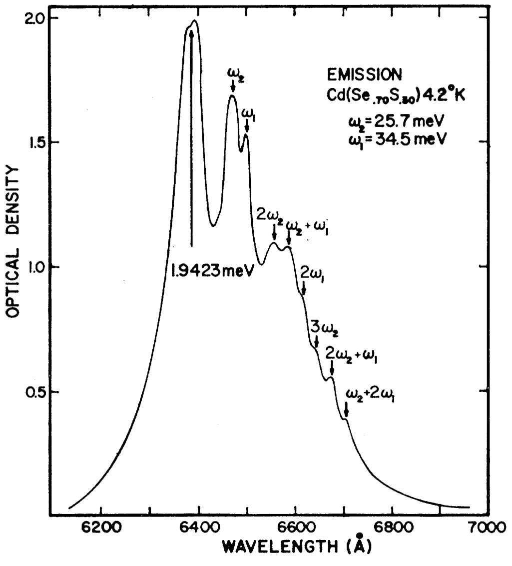

FIG. 3. Densitometer trace of the emission of a $Cd(Se_{0,70}S_{0,30})$ platelet at 4.2°K ($E\perp C$). With reference to the line at 1.9423 eV the arrows mark the computed spectral positions of the two LO phonons ($\omega_1=34.5$ and $\omega_2=25.7$ meV) and their additive combinations. These values were chosen because they gave the best over-all fit.

In our experiments we used Cd(SeS) mixed crystals which were grown as platelets from the vapor phase and which showed no visible inhomogeneity. They were uv stimulated and submerged in liquid helium. Figures 2 and 3 show densitometer traces of the edge emission of $Cd(Se_{0,44}S_{0,56})$ and $Cd(Se_{0,70}S_{0,30})$. The structure can be analyzed by the assumption that two phonons of energy ω_1 and ω_2 couple to the parent transition. With respect to the zero-phonon lines (2.0737 eV and 1.9423 eV in Figs. 2 and 3 respectively) the arrows show the computed position of various combinations of ω_1 and ω_2 using their indicated values. In these and other measurements the energy values of ω_1 are always smaller (and increasingly smaller for higher Se concentration) than the LO phonon energy in pure CdS ($\omega_0'=37.7$ meV). Similarly ω_2 is also smaller (and increasingly smaller with higher S concentration) than the LO phonon energy in pure CdSe ($\omega_0=26.6$ meV). Their values as a function of concentration are compared with a simple model in Fig. 5.

The data presented make it evident that, in solid solutions, two different LO phonons couple to the recombination radiation.

One might like to think of the solid solutions as mixtures of microcrystalline regions of the pure CdSe and CdS, where each microregion might consist of up to 1000 unit cells of each material, with the lattice constant of CdS stressed by the surrounding CdSe and that of CdSe compressed by its CdS neighbors. Such a model could explain the uniform shift of the absorption edge with composition because the extent of the electron wave functions in conduction and valence bands is large with respect to the size of the microregion; it also would explain the linear change of the lattice constant. Of course, this model can also explain the existence of the two LO phonons seen in ir reflectivity, absorption, edge emission, and, as we will show, in photoconductivity as well. Difficulties might arise with this model if one wants to explain the coupling of the sum of the two phonons. Difficulties expecially arise when one wants to explain the shift of the phonon energies, ω_1 and ω_2, with composition. The expanded CdS lattice would have a lower force constant and consequently a lower phonon energy, which is what we observe. The compressed CdSe, however, should have a larger force constant and therefore a higher LO phonon energy, which is contrary to what we observe.

A simpler model would be that the solid solutions consist of a statistical distribution of CdSe and CdS with respect to their over-all concentration. Unfortunately, the computation of vibrational frequencies in a three- or even in a two-dimensional lattice of Cd(SeS) in a wurtzite structure is very difficult; moreover, such calculations are usually so restrictive that they do not lend meaningful support to a physical model of the measured frequencies. Under such circumstances it is likely that the interpretation of the observed modes in the mixed crystals would remain questionable.

We therefore calculated the eigenfrequencies and the respective oscillator strengths (dipole moments squared times the frequency to the fourth power) of a linear chain model of CdSeCdSCdSe···. For each composition we chose a "perfect ordering," i.e., the most probable arrangement of CdSe and CdS molecules within a 12-molecule cell, and we assumed that the total chain was composed of repetitions of this cell. We used the force constant f_0 between Cd and Se and f_0' between Cd and S atoms, taking only nearest-neighbor interactions into account. The constants f_0 and f_0' are derived from the observed phonon energies of the pure CdSe and CdS crystals according to

$$f_0=\omega_0^2 mM/2(m+M) \quad \text{and} \quad f_0'=(\omega_0')^2 m'M/2(m'+M),$$

where M, m, and m' are the masses of cadmium, selenium, and sulfur atoms, respectively.[22]

It is clear, however, that because of the change of the lattice parameter the force constants acting, e.g., between Cd and Se should differ increasingly from the value in a CdSe lattice as the lattice becomes more and more diluted by CdS. Therefore, as a second approximation we computed the eigenfrequencies and the respective oscillator strengths for these chains, with the force constant of Cd-Se increasing linearly with increasing concentration of CdS up to the force constant of CdS (zero CdSe concentration) and the force constant of CdS decreasing linearly in a similar way. In other words, we used a common force constant F for both Cd-Se and Cd-S, which was a function of the composition. It is given by $F=f_0'-(f_0'-f_0)x$, where x is the fraction of CdSe in $\mathrm{Cd(Se}_x\mathrm{S}_{1-x})$.

These results are presented in Fig. 4. Each chain, of course, has 24 eigenfrequencies. The oscillator strengths of most of them are, however, many orders of magnitude lower than those depicted. The heights of the peaks in Fig. 4 correspond to the logarithm of the calculated oscillator strengths. Clearly, one distinguishes two branches ω_1 and ω_2, and in Fig. 5 we show the center of gravity of these ω_1 and ω_2 branches as solid lines and corresponding branches from the results of the calculation, with f_0, $f_0'=$constant, as dashed lines.

When comparing these results of the linear chain model to the actually observed values one should keep in mind that the model is mainly idealized: (1) by using a "perfect order" rather than a statistical distribution in forming the different compositions, and (2) by the assumption of either the two constant force constants (f_0 and f_0'), or the one common force constant.

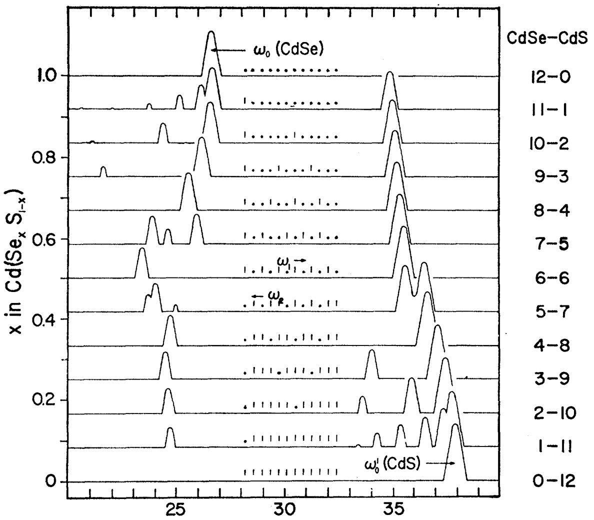

FIG. 4. The computed eigenfrequencies of a linear chain of 12 CdSe and CdS molecules (their sequence is indicated by dots and bars, respectively) as a function of crystal composition, using a common force constant F between all atoms of a given composition. The logarithm of the calculated oscillator strength is represented by the actual peak heights as drawn at each eigenfrequency. The left-hand ordinate reflects the crystal composition and the right-hand ordinate gives the molecular composition of the model.

A consequence of the first idealization is, e.g., the singularity at the (50-50)% composition. In actual crystals the composition varies statistically near its average, the nominal composition. The actual ω value, then should be a weighted average of the ω values of a concentration distribution. In particular, this will have its effect on the singularity in that it will be smoothed out. The second idealization also affects the computed results. The first approximation, with f_0 and f_0' inde-

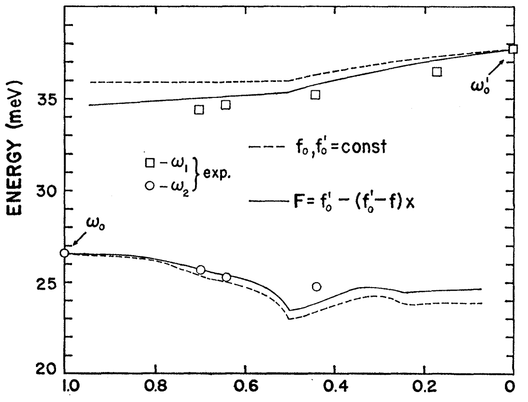

FIG. 5. The centers of gravity of the ω_1 and ω_2 branches of Fig. 4 are connected by solids lines. The dashed lines represent a similar calculation with constant force "constants" (f_0 between Cd and Se, and f_0' between Cd and S). The observed LO values, ω_1 and ω_2 are plotted for comparison.

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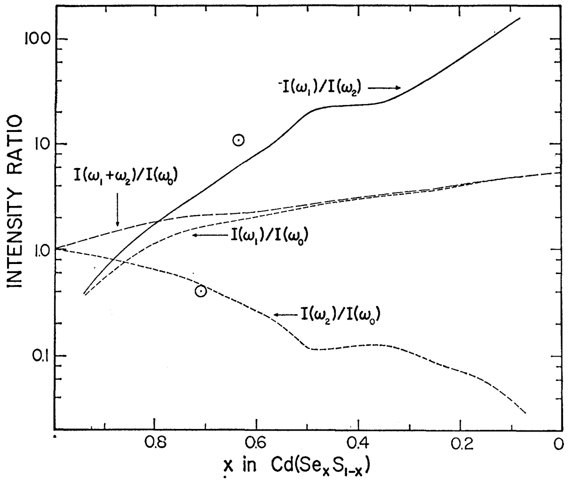

FIG. 6. The dashed curves are the computed oscillator strengths of the ω_1 branch, $I(\omega_1)$; of the ω_2 branch, $I(\omega_2)$; and of the sum of the vibrational modes, $I(\omega_1+\omega_2)$. All curves are normalized with respect to the oscillator strength of pure CdSe, $I(\omega_0)$. The solid line shows the intensity ratio of the ω_1 branch with respect to the ω_2 branch, $I(\omega_1)/I(\omega_2)$. The two circled points are experimental values for the comparison with the latter curve.

pendent of the composition, accounts already, importantly enough, for the fact that the observed phonon frequencies in the mixed crystals ω_1 and ω_2 are both lower (and increasingly lower with higher concentration of Se or S, respectively) than those of similar frequencies, ω_0 and ω_0', in the pure CdS and CdSe crystals. The second approximation, with f_0 linearly increasing and f_0' linearly decreasing as functions of the admixed CdS and CdSe, respectively (both by the same amount, in order to form the common force constant F) should represent, at least in part, the effect of the change of the intermolecular separation. It also represents better the experimental results. Further approximations to the actual case should involve a stronger concentration dependence of f_0 than of f_0', and finally even linearity of this dependence might be questionable.

Figure 6 shows the computed oscillator strengths of different branches, (normalized to that of the LO mode in pure CdSe): $I(\omega_1)$, $I(\omega_2)$, and $I(\omega_1+\omega_2)$. It is interesting to note that equal oscillator strengths of ω_1 and ω_2 should be found at a composition of $Cd(Se_{0.87}S_{0.13})$. [Experimental results, though not very reliable as far as the intensity measurements are concerned, show this point to be closer to the $Cd(Se_{0.7}S_{0.3})$ composition.] The agreement of the computed and the observed intensity ratios of $I(\omega_1)/I(\omega_2)$ is not too good. It is to be expected, however, that the linear chain as a model is weakest in the prediction of intensities.

The over-all agreement of the observations with the predictions of this model leads on the other hand to the conclusion that the mixed Cd(SeS) crystals actually form a solid solution in that the CdS and CdSe molecules are arranged statistically according to their relative concentrations.

III. OSCILLATORY PHOTOCONDUCTIVITY

Periodic structure in the spectral dependence of photoconductivity (PC) with a period corresponding to the LO phonon energy has been observed in the intrinsic region of InSb and GaSb by Habegger and Fan[8]; by Stoker *et al.*,[9] and, more recently, by Nasledov *et al.*,[10] and Mazurczyk *et al.*[11] We also had reported similar observations for CdS.[12] The phenomenon is illustrated in Fig. 7, which shows the photocurrent of a CdS platelet at 4.2°K with the **E** vector of the incident light polarized (a) perpendicular and (b) parallel with respect to the crystalline *c* axis. The structure below the absorption edge (2.582 eV for $\mathbf{E}\perp C$) is due to a contribution of current carriers from dissociated excitons.[23,24] The initial absorption of light at the exciton energy leads to the formation of direct excitons, which in part may decay radiatively; but such excitons may also dissociate, in part, into current carriers and thus appear as maxima in the spectral response curves of the photoconductivity. The dissociation might occur either by the interaction with impurity centers, or other excitons, or by the absorption of a phonon.

Toward higher energy, the structure marked by arrows is separated by equal energy differences which correspond approximately to the energy of the LO phonon in CdS. There are two series of minima indicated by long and short arrows. The first, let us call then the I-series, is displaced by a LO phonon from the $A_1(n=1)$ exciton peak ($\Gamma_5=4854$ Å for $\mathbf{E}\perp C$), the second, the II series, is displaced by the same amount from the $B_1(n=1)$ exciton peak at 4826 Å. In other words, the two sets of minima are displaced by an amount equal to the separation of the two upper valence bands. The position of the II-minima is less conspicuous because of the composite nature of the two series; their positions become clearer when the composite spectral response curve of the intrinsic region is decomposed as shown by the dashed curves. The spectral response curve can be considered, in principle, as a superposition of an intrinsic unmodulated response (long dashes) and the energy-dependent oscillations indicated by short dashes with respect to a displaced baseline.

An explanation for the above observation has been put forward by several other investigators[9–11]; they propose that the oscillatory behavior of the photoconductivity is due to an oscillatory value of the electron lifetime in the conduction band as function of its energy. The lifetime of the conduction electron at a certain energy value is smaller than that at adjacent energy values whenever this energy coincides with the sum of the energies of a shallow impurity[9] (or bandgap[8]) plus integral multiple *m* of the longitudinal optical phonon

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[23] E. F. Gross, K. F. Linder, and B. V. Novikov, Fiz. Tverd. Tela 4, 1135 (1962) [English transl.: Soviet Phys.—Solid State 4, 836 (1962)].

[24] Y. S. Park and D. C. Reynolds, Phys. Rev. 132, 2450 (1963).

energy. The explanation of our data in Fig. 7 requires that the ground state of excitons play the role of the "shallow impurity."

Figure 8 shows a simplified model of the band structure applicable to CdS, CdSe, or Cd(SeS) crystals with wurtzite structure. The symmetries of the top valence band at $k=0$ and in the Δ direction are Γ_9 and Δ_9, respectively. The lower valence band and the conduction band have Γ_7 or Δ_7 symmetry. In the Σ and T directions, away from $k=0$, both the Γ_9 and Γ_7 valence bands and the Γ_7 conduction band split into bands with Σ_3, Σ_4, and T_3, T_4 symmetries. The minimum of the conduction band in these directions is actually not exactly at $k=0$ and its slope at $k=0$ was estimated by Hopfield and Thomas[25] to be less than 5×10^{-10} eV cm. The curvature of the valence bands in CdS is at least three times smaller than the curvature of the conduction band. The splitting of the upper valence bands S and therefore the energy difference between A_1 and B_1 is 16 meV in CdS. The ground state of the A exciton is actually split into a state of Γ_6 symmetry (spins of electron and hole are parallel) and a state of Γ_5 symmetry (with antiparallel spins).

The binding energy of exciton A is taken equal to that of exciton B and has the value 28 meV in CdS.[26] The selection rules allow electronic transitions to occur between levels $\Gamma_9 \leftrightarrow \Gamma_7$ (or $\Delta_9 \leftrightarrow \Delta_7$, $\Sigma_3 \leftrightarrow \Sigma_4$ and $T_3 \leftrightarrow T_4$) for excitation with the **E** vector perpendicular to the crystal c axis, and between $\Gamma_7 \leftrightarrow \Gamma_7$ (or $\Delta_7 \leftrightarrow \Delta_7$, $\Sigma_3 \leftrightarrow \Sigma_3$, $\Sigma_4 \leftrightarrow \Sigma_4$, $T_3 \leftrightarrow T_3$ and $T_4 \leftrightarrow T_4$) levels for both modes of polarization. The creation of the Γ_5 exciton is allowed for $E \perp C$. For direct band-to-band transitions in arbitrary directions of $k[k\neq(0.0.0)$ and $k\neq(0.0.k_z)]$ there exist no selection rules because of the breakdown of all the symmetry to a mere translational one.

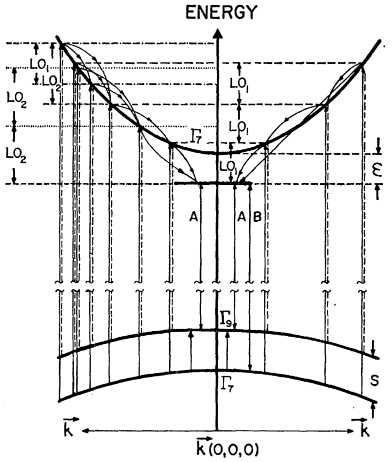

FIG. 8. Energy-band model, showing upper valence bands, conduction band, and recombination level in CdS-like crystals. The right-hand side illustrates the observations in pure crystals. Conduction electrons cascade to the recombination center via LO phonon emission. The left-hand side shows a similar situation for a mixed crystal, where conduction electrons cascade via energy increments LO_1 and LO_2.

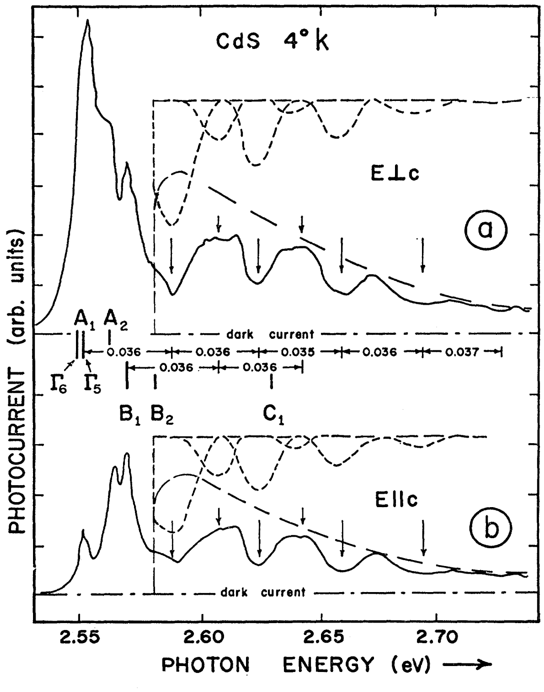

FIG. 7. The solid curves show the spectral response of the photoconductivity (a) for the E vector perpendicular and (b) parallel to the c axis of a CdS platelet at 4.2°K. Long arrows indicate I-minima, short arrows II-minima. The positions of A, B, and C excitons are indicated by bars. Dashed curves are the separate contributions of the processes causing I and II minima.

The right-hand side of Fig. 8 shows what might be a model of the observation in Fig. 7. In an arbitrary direction of k space, excitation may occur from the top and the lower valence bands; this is indicated by dashed and solid vertical arrows, respectively. The positions of the transitions along k are chosen such that their corresponding energies are equal to the sum of an A or B exciton, respectively, plus a multiple of LO phonons, i.e., they are equal to the energies at which minima were observed. The dashed vertical transitions correspond to the I minima, indicated by long arrows in Fig. 7; the solid vertical transitions correspond to the II minima, indicated by short arrows. From these points in the conduction band, transitions via LO phonon emission might easily occur to the exciton level. The exciton in turn may be an A or B exciton depending on the valence band from which the hole has been captured. In both cases the formation of an A exciton will probably be favored because of the thermalization which will favor a higher concentration of holes in the upper valence band; but these details of the recombination process are not observable in the above experiments. They have been observed, however, in the emission, where A excitons with $\mathbf{E}\perp C(\Gamma_5)$ are favored with respect to Γ_6 and B excitons with $\mathbf{E}\|C$[27]; the laser emission in CdS is also polarized completely with its **E** vector perpendicular to the c axis.[28]

Two inportant conditions for the observability of PC oscillations which have the period of a LO phonon

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[25] J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).
[26] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).
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[28] C. E. Hurwitz, Appl. Physics Letters **8**, 121 (1966).

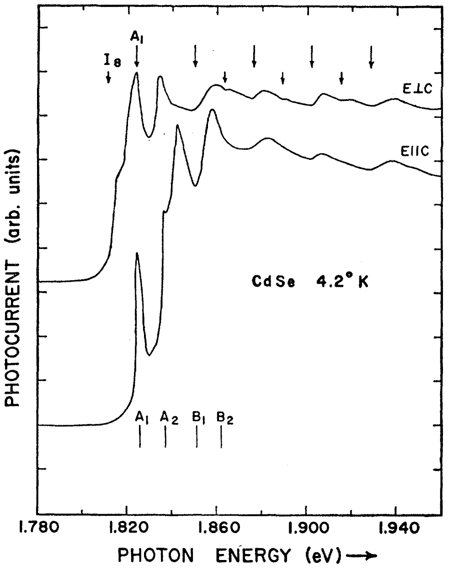

FIG. 9. Spectral response of the photoconductivity of a CdSe platelet at 4.2°K. Long arrows indicate I-, II minima, short arrows represent minima due to recombination via the I_8 center. Positions of excitons A and B ($n=1$ and $n=2$) are indicated by the vertical bars marked A_1, A_2, $\cdots$.

energy are: (1) That the mean time in which the conduction electron will cascade (by the emission of m LO phonons only) to the exciton level ($\tau_{\rm op}$) is smaller than its mean lifetime, as limited by band-to-band recombination ($\tau_{\rm bb}$). (2) That $\tau_{\rm bb}$ is smaller than the mean time ($\tau_{\rm ac}$) in which it may lose an energy equal to the energy of one LO phonon, by the emission of several other phonons, i.e., $\tau_{\rm op} < \tau_{\rm bb} < \tau_{\rm ac}$. The observations of the minima displaced by LO phonons from the exciton energies mean that the exciton lifetime ($\tau_{\rm e}$) has to be smaller than the band-to-band recombination time, i.e., $\tau_{\rm e} < \tau_{\rm bb}$. In other words the exciton level acts as a fast recombination center.

The above stated conditions for oscillations in terms of lifetimes may easily be rephrased in terms of transition probabilities, requiring, namely, that the probability for the annihilation or creation of an exciton–plus–m-LO-phonon comples is larger than that of a complex consisting of an exciton plus other phonons. The assumption is supported by the fact that the radiative decay of an exciton with simultaneous emission of an LO phonon is observed to be more frequent than the exciton decay with the emission of other phonons.

In the spectral response curves, photons with the exciton energy gave rise to a maximum in the photocurrent; on the other hand, photons with an energy equal to that of an exciton plus m LO phonons appear to cause minima in the photocurrent. This occurs because only a fraction of the excitons formed in the latter case will again dissociate, which is the process responsible for the current maxima at the exciton energies. The other fraction, however, which annihilates without dissociation, effectively decreases the number of current carriers in the conduction band.

In CdSe,[29] we observe essentially the same phenomena as in CdS. Figure 9 shows the photoconductivity (PC) response curve of a CdSe platelet at 4.2°K. In CdSe the exciton binding energy is 15 meV; S and the LO phonon accidentally have very similar values (S = 25 meV, LO = 26.6 meV from edge emission, and LO = 26 to 26.3 meV from ir measurements[18]). Thus, minima corresponding to the I and II series in CdS coincide in CdSe. They are indicated by the long arrows in Fig. 9. Various other series of minima are also observed in different crystals as, e.g., the one indicated by short arrows in Fig. 9. It shows the same spacing between minima as does the I, II series. Its origin, however, can not be connected with an energy level of a free exciton. Plotting the positions of these minima versus their order number, (curve d in Fig. 10) we find an intercept with the order number zero at 1.811 eV; this indicates that the recombination responsible for this series originates at a center having this energy level. In the edge emission of CdSe, Reynolds, Litton, and Collins[30] observe a line doublet, called I_8, at 6847 Å (1.811 eV) which has been associated with the annihilation of an exciton bound to an impurity complex. We think that the same complex might also act as the recombination center responsible for the second series of minima, although the center itself was not observable in the PC response curve.

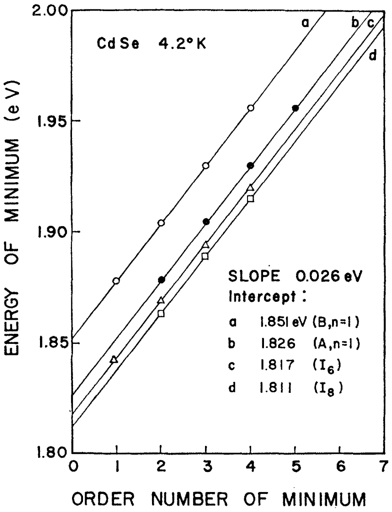

FIG. 10. The photon energy of photocurrent minima plotted as a function of their-order number for several series in various CdSe crystals. The intercept indicates the recombination center energies and identifies the ground states of the A and B excitons, well as the I_6 and I_8 exciton complexes, as such center. The slope ot the lines (26 meV) corresponds to the energy of the LO phonon in CdSe.

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[30] D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. (to be published).

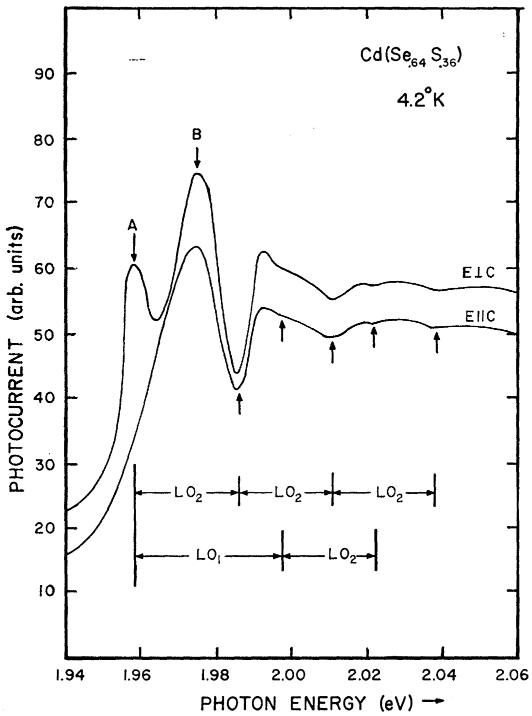

FIG. 11. Spectral response of the photoconductivity of a Cd($Se_{0.64}S_{0.36}$) platelet at 4.2°K. Minima on the high-energy side of the exciton peaks are due to the fast recombination via simultaneous or consecutive emission of LO_1 and LO_2 phonons.

Curve c in Fig. 10 shows the position of PC minima in another CdSe crystal. In this case, the origin can be extrapolated to the energy 1.817 eV which is identical with that of the I_6 line (6822 Å), a well-investigated emission line due to the annihilation of a bound exciton.[30] In the present case, a maximum in the photoconductive response curve appeared at the energy associated with radiative recombination at the center itself. It was, however, much weaker than the maxima due to the dissociation of free excitons; also observable is the energy difference of the A exciton maximum in perpendicular and parallel polarization, corresponding to the positions of the Γ_5 and Γ_6 excitons. The slopes of all curves in Fig. 10 give us the value of 26 ± 1 meV for the separation of successive minima. This is, as we have seen, the energy of the LO phonon in CdSe.

In mixtures of Cd(SeS) the spectral response of the photocurrent also exhibits structure, which is shown in Fig. 11. The maxima due to the dissociation of free excitons are easily observable, as Park and Reynolds have shown earlier.[24] Structure also occurs on the high-energy side of the exciton peaks; hence, minima can be identified which are separated from the A exciton peak by energies which correspond roughly to the energies of the LO_1 phonons in CdS and the LO_2 phonons in CdSe. These energies correspond to the three additive values obtainable from the two phonon energies: $2LO_1$, LO_1+LO_2, and $2LO_2$. (The frequency deviation of the LO model in mixed crystals from that in pure crystals, which we observed in the edge emission, is not well observable in the analysis of the photocurrent minima because of the large width of the structure and the resulting experimental uncertainty.) Furthermore, in comparison with the spectral response curves of pure CdS or CdSe crystals, the mixed crystals do not show a long series due to multiple phonon emission. The highest order number is very seldom larger than two. Also, in contrast to the pure crystals, the photocurrent drops to the dark current value more rapidly when scanning toward higher energies.

The observations lead to the conclusion that, in Cd(Se_xS_{1-x}) mixtures, coupling to two different optical phonons, LO_1 and LO_2, and also to their additive combinations, give rise to energy levels which are distinguished by a high transition probability. As in pure crystals, the emission of LO phonons to the lattice permits the electrons to cascade faster to the energy level of the exciton than would be possible by the emission of acoustical phonons only. In comparison with the pure crystals, however, it is evident that with the possibility of cascading via the emission of the two different LO phonons, electrons from a larger number of energy levels will have ways of fast cascading toward the exciton level. The left-hand side of Fig. 8 shows this process schematically in contrast to the case of the pure crystal, as shown on the right-hand side. At energies between 0.1 and 0.2 eV above the bottom of the conduction band, e.g., there exist three levels in CdS—four in CdSe—from which electrons may cascade fast to the recombination level. In the mixed crystal, however, 23 such levels should exist in the same energy interval. Thus, the electron lifetime may be effectively decreased, especially at higher energies, and this might be the explanation for the more rapid decline of the PC spectral response curves toward higher energies.

At the same time an observation made by Hurwitz[31] might also be explained. The Cd(SeS) mixed crystals show laser action with electron-beam stimulation of lower threshold currents than that required for either pure CdS, or pure CdSe. The fact that electrons in a given energy region of the conduction band cascade to a recombination center from an increased number of levels in the mixed crystals means that, after a polychromatic excitation, more electrons will cascade in a given time τ_{op}; hence, the population density of the recombination center will be increased, provided the lifetime in this state τ_c is not shorter than τ_{op}.

IV. CONCLUSIONS

We observed the coupling of the two discrete branches of the LO vibrational modes in homogeneous mixtures of Cd(SeS). The dependence of the frequency of these branches on the composition is well represented by a linear chain model. The calculated oscillator strengths of

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[31] C. E. Hurwitz, Appl. Phys. Letters 8, 243 (1966).

the different LO branches do not agree closely with the observations. However, both the model and the experiments indicate that equal coupling of both branches in $Cd(Se_xS_{1-x})$ mixtures occurs for a composition where x is well above its 0.5 value.

Both of the LO phonon branches also couple to the free electrons in the conduction band; this has the effect of shortening the free-electron lifetime since more ways are provided for a fast cascade to the level of the free or bound exciton from which recombination will occur. This interpretation leads to the conclusion that, after excitation into the conduction band has occurred, the cooperation of two different phonons (and their combinations) will populate such recombination levels faster in mixed crystals than in pure crystals, since in the latter the electrons in the conduction band are depleted only by one LO phonon (and its multiples). This higher rate will lead to an increased population density of the recombination center. (The condition that τ_{op} be less than τ_c must obtain.) Thus, we might account for Hurwitz's observation that the threshold for lasing action in some Cd(SeS) mixtures is lower than that of either CdSe or CdS.[31]

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Low-Temperature Specific Heat and Density of States of Boronated Graphite*

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The increase in the low-temperature specific heat upon boronation of natural Madagascar flake graphite has been measured. For the pure material below 1.2°K, $C=13.8T+27.7T^3$ μJ/mole deg; for the same graphite boronated to 0.23 at.%, $C=34.5T+29.3T^3$ μJ/mole deg. The change in electronic density of states at the Fermi surface is found to agree well with theoretical expectation. These results allow one to predict the Fermi-level shifts that would be necessary to account for the increased linear specific heat of disordered graphites. However, the Fermi-level shifts so predicted would require much larger changes in other electronic properties than are actually observed. Thus, the excess specific heats cannot be explained as being due to Fermi-level shifts.

INTRODUCTION

CONSIDERABLE experimental[1-3] and theoretical[4,5] work has been done in recent years on the low-temperature heat capacity of graphite. In particular, it is now established that the peculiar temperature dependence of the heat capacity is due to the unusual phonon dispersion relations. Quantitative agreement[5] now exists between theory and experiment for the lattice heat capacity of perfect graphite and for graphites of various degrees of imperfections (especially stacking faults).

The agreement is also good between the theoretical[6] electronic heat capacity of pure single-crystal graphite and the most recent and most accurate experimental

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