Optical Studies of Shallow Acceptors in CdS and CdSe

C. H. Henry, K. Nassau, and J. W. Shiever

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 16 April 1970)

We show that Li and Na are the only soluble substitutional acceptors in CdS and CdSe with relatively small binding energies. A shallow acceptor is observed for P doping, but it arises from a complex. These results, and also the fact that the substitutional P is a deep acceptor in the sulfides and selenides, but not in the tellurides, are consistent with the trends in acceptor binding energy observed in other semiconductors. We present evidence that a native double donor exists in CdS, but that Li and Na acceptors are compensated by ordinary donors and not by isolated double donors. Analysis of thermodynamic data shows that isolated native donors should not be effective in compensating acceptors in ZnSe, CdSe, or CdTe. The compensating donors in CdS are found to be unusually shallow, indicating that they may be Li or Na interstitials. An attempt to drift out the Li-interstitial donors with an applied electric field is discussed.

I. INTRODUCTION

The II-VI compounds of Zn, Cd, S, and Se have direct band gaps ranging from 1.84 to 3.91 eV at low temperature. They readily form mixed crystals and thus have the capability of generating efficient luminescence throughout the visible spectrum. Unfortunately, these materials have never been made low-resistivity p type, despite studies in numerous industrial laboratories. As a result, the II-VI compounds have lost favor as materials for making visible electroluminescence devices. At present, effort in making electroluminescent junctions centers on the III-V compounds, particularly on GaP.

The understanding of why these II-VI compounds cannot be made to conduct p type is still rather uncertain. Papers by Mandel et al.[1] and Kroger[2] emphasize compensation of the acceptors by native donors. Aven[3] has speculated about other possibilities, such as that the solubility of suitably shallow acceptors may be lower than the minimum background of donor impurities; that acceptors' impurities may also act as donors on different sites; or that native defects may form electrically inactive complexes with the acceptor impurities.

In this paper, we report our optical studies of shallow acceptors in CdSe and CdS. We present in greater detail work reported earlier,[4] showing that Li and Na are the only shallow acceptors in CdS due to substitutional impurities. We show that this is also the case for CdSe, that it is consistent with the trends in the binding energies of acceptors in other semiconductors, and conclude that it is likely for the sulfides and selenides of Zn and Cd. Other shallow acceptors occur in CdS and CdSe, but they are most likely complexes. Evidence is presented that P doping forms a complex that acts like a shallow acceptor. The Li- and Na-doped samples are highly compensated with resistivities greater than $10^8 \, \Omega \, \text{cm}$. It is not clear whether these acceptors are compensated by Li- and Na-interstitial donors or by donors involving native defects. We are able to rule out the possibility that compensation is due to isolated native defects acting as double donors. Section II deals briefly with experimental details, Sec. III deals with chemical-doping experiments involving alkali metals in CdS and CdSe, Sec. IV with the Li isotope shift in CdS, Sec. V with shallow acceptors due to P doping, Sec. VI with trends in acceptor-binding energy, and Sec. VII with self-compensation and Li drifting experiments. Our conclusions are summarized in Sec. VIII.

II. EXPERIMENTAL

A. Crystal Growth

Crystals were grown by vapor-phase sublimation in rapid argon stream of 9-cm/sec velocity at the growth temperature. For CdS the sublimation temperature was 1120 °C and the growth temperature was about 920 °C with a gradient of 13 deg/cm. Temperatures for CdSe were about 50 °C lower. Alkali-metal dopants were added as sulfates or carbonates to the ultrahigh-purity Eagle Picher Co. CdS or CdSe. In the case of K, doping was also attempted with the metal, KF, KI, KCl, and KBr. In the case of phosphorus, this was added in the red form alone, with Ga (i.e., as GaP), or with I added to the gas stream as well (PI_3). Li diffusion was performed by sealing samples of CdS and Li_2S in quartz and by enclosing CdS or CdSe and metallic Li in a tantalum liner and then sealing the tantalum liner in a quartz capsule.

B. Spectroscopy

All data were taken photographically using a 2-m-focal-length Bausch and Lomb spectrograph. The highest dispersion used was about 0.33 meV/mm.
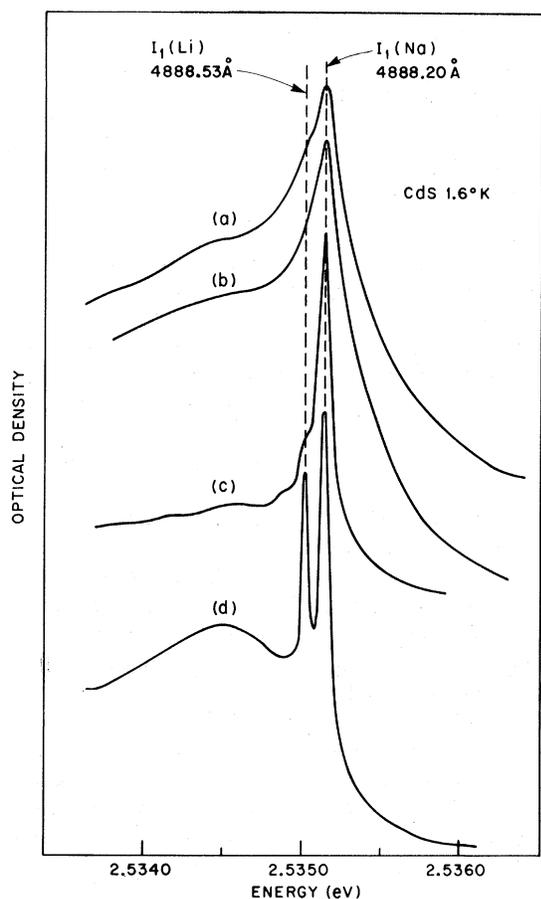
FIG. 1. I_1 lines arising from Li and Na. (a) CdS doped with Na_2SO_4 during growth; (b) no more Na_2SO_4 added; (c) after three successive growths with no more Na_2SO_4 added; (d) growth tube scraped clean and no more Na_2SO_4 added.

The linewidths of the bound excitons were limited by the samples and were about 0.04 meV wide in lightly doped unstrained crystals. The photoluminescence was excited using the 4880- and 4765-Å lines of an argon-ion laser. All data were taken with the samples at 1.6 °K.

III. DOPING WITH ALKALI METAL ATOMS

A. CdS

Thomas and Hopfield[5] showed that shallow acceptors in CdS give rise to the I_1 lines which are excitons bound to neutral acceptors. The I_1 lines correlate with the presence of the green-edge emission which has been established to be due to donor-acceptor recombination.[6,7] Only two I_1 lines are observed and in Ref. 4 we stated that the two I_1 lines correlate with the doping of Li and Na. The evidence for this is shown in Fig. 1. Undoped crystals, grown in a clean quartz apparatus, show

only the I_1(Li). Upon the addition of Na, I_1(Na) shows up as a broadened line, indicating the crystal is heavily doped [Fig. 1(a)]. Successive growths [Figs. 1(b) and 1(c)] in the Na-contaminated growth tube cause the lines to narrow somewhat, and the I_1(Li) can be seen partially resolved from I_1(Na). Finally, after scraping out the growth tube, the two I_1 lines sharpen and are well resolved [Fig. 1(d)].

Doping with Li produced a single broadened I_1(Li) line. Doping with K, Rb, or Cs gave only a sharp I_1(Li). The sharpness of the lines indicated that K, Rb, and Cs produced very little doping. The absence of new I_1 lines indicated that these elements were not incorporated as acceptors.

Similar conclusions are reached by observing the pair bands. Li or Na doping during growth results in intense pair-band luminescence. The pair luminescence is much stronger than the luminescence of excitons bound to neutral donors and acceptors as shown in Figs. 2(a) and 2(b). This is the usual situation in a heavily doped highly compensated crystal. The crystal contains high concentrations of donors and acceptors which are not readily neutralized by the light. In a lightly doped crys-
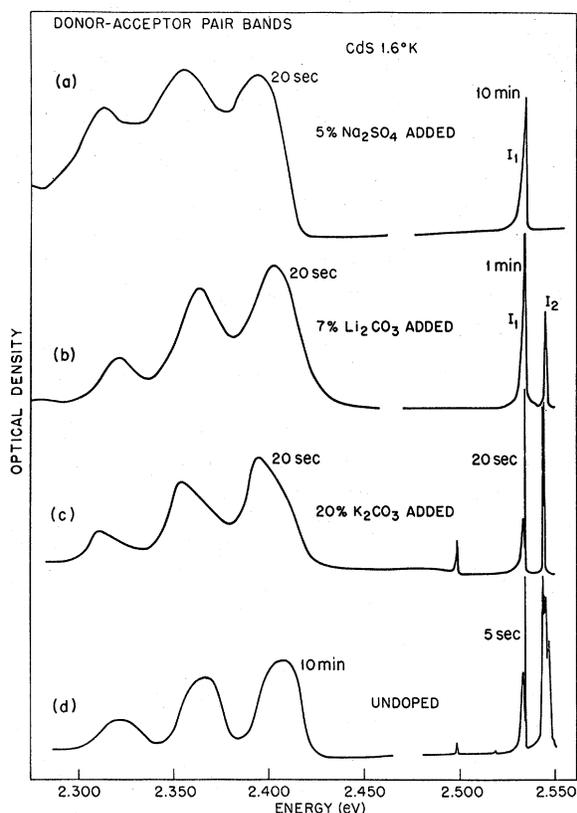
FIG. 2. Pair bands and bound excitons for CdS crystals doped with Li, Na, K, and undoped excited with 20-mW unfocused 4765-Å laser light.

tal, on the other hand, the concentrations of the donors and acceptors are low. They tend to be far apart and they are readily neutralized by focused laser light. In this case, the luminescence is dominated by excitons bound to neutral donors and acceptors. In Fig. 2(c) the bound excitons and pair bands are more equal in intensity and the bound exciton lines are sharp, indicating that this K-doped crystal is much more lightly doped. Figure 2(d) shows an undoped crystal. The pair bands are very weak compared to the bound excitons.

The I_1 lines have very similar energies: $E_{Ex}(Li)$ = 17.67 meV, $E_{Ex}(Na)$ = 17.50 meV.[8] It is expected that the exciton-binding energy is about one-tenth the acceptor-binding energies and that these are also very similar.[9] The acceptor-binding energy E_A may be estimated from the position of the distant pair peak, which we find to be 2.397 eV (5170 Å) for Li and 2.391 eV (5183 Å) for Na. Estimating $E_{Coulomb} \approx 10$ meV and estimating an average E_D from the strengths and energies of the I_2 lines (see Sec. VII B), we find $E_A(Li) = 165 \pm 6$ eV and $E_A(Na) = 169 \pm 6$ eV.

B. CdSe

Very similar results were found for CdSe. Addition of K during growth left the crystal undoped, whereas addition of Li or Na caused a strong-edge emission and broadened the bound exciton lines. The spectra due to Li and Na are shown in Fig. 3. The pair bands brought out by either Li or Na doping have the same position. Using $E_D = 19$ meV,[1] $E_{Coulomb} = 7$ meV, we estimate $E_A \approx 109 \pm 6$ meV for either Li or Na acceptors. In heavily doped crystals the I_1 line is broadened. Successive growths in a tube contaminated with Li or Na cause the

TABLE I. g values for bound excitons in CdSe.

Line	Electron g value	Hole g value
I_2	$g_e = 0.52 \pm 0.1$	$g_{H\parallel} = 1.35 \pm 0.02$
		$g_{H\perp} = 0.0$
I_1(Li)	$g_e = 0.52 \pm 0.01$	$g_{H\parallel} = 1.46 \pm 0.02$
		$g_{H\perp} = 0.0$
I_1 (P complex)	$g_e = 0.52$ (assumed)	$g_{H\parallel} = 1.43 \pm 0.03$
		$g_{H\perp} = 0.6 \pm 0.1$

lines to narrow until a single sharp I_1 line appears with $\lambda = 6822.69$ Å, corresponding to $E_{Ex} = 9.15$ meV. We conclude that either the I_1 lines due to Li or Na are unresolved or that for lightly doped crystals, showing sharp I_1 lines, one of two I_1 lines always dominated the luminescence.

The Zeeman splittings of the I_1 and I_2 lines in CdSe are similar to those in CdS. They can be fitted with isotropic electron g value and an anisotropic hole g value that goes to zero for $H \perp c$ axis. The g values are listed in Table I.

In Na-doped crystals an additional bound exciton appears between I_1 and I_2 of unknown origin.[11]

C. Size and Solubility

Spectrochemical analysis of the Li- and Na-doped crystals confirmed that both CdS and CdSe could be appreciably doped with either Li or Na. The results are shown in Table II. However, we were unable to dope CdS with K, Rb, or Cs. This can be understood when one considers the size of the alkali atoms. In Fig. 4, we plot the covalent radii[12] of the five alkali atoms and that of Cd. While Li and Na are roughly the same size as Cd, the size of K, Rb, or Cs is much larger. This means that incorporation of K, Rb, or Cs requires a considerable elastic strain energy.[13] Trumbore has reviewed

FIG. 3. Bound excitons and pair bands in Li- and Na-doped CdSe. The pair bands were excited with 10-mW unfocused 4880-Å laser light. The bound excitons were excited with 100 mW of focused 4880-Å laser light.

TABLE II. Alkali concentrations in CdS and CdSe (determined by x-ray emission and atomic absorption spectroscopy).

	Concentration (atoms/cc)		
	Li	Na	Ratio[a]
CdS			
With Li added[b]	1×10^{17}	3×10^{15}	33
With Na added[b]	1×10^{16}	4×10^{17}	40
Purest CdS grown	$\sim 2 \times 10^{15}$	$\sim 7 \times 10^{14}$	
Highest doping achieved	$\sim 4 \times 10^{17}$	$\sim 1 \times 10^{18}$	
CdSe			
With Li added[b]	7×10^{16}	7×10^{15}	10
With Na added[b]	$< 6 \times 10^{15}$	2×10^{17}	> 33
Purest CdSe grown	$< 6 \times 10^{15}$	$\sim 3 \times 10^{14}$	

[a] Ratio of concentration of added alkali (Li or Na) to concentration of other alkali (Na or Li).

[b] Amount to yield platelets showing a dominant, only slightly broadened, I_1 line.
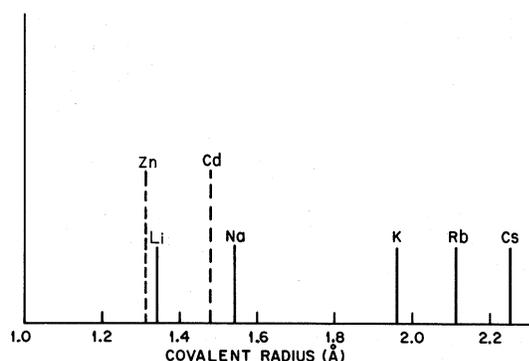
FIG. 4. Covalent radii of the alkali atoms
and of Cd and Zn.

the solubility data for impurities in Si and Ge.[14]
He finds that the solubility of any impurity (donor,
acceptor, or isoelectronic atom) is greatly de-
creased when its covalent radius is more than a
few tenths of an Å greater than that of the host
atom. This appears also to be true in our case.

The covalent radius of Zn is 1.31 Å compared to
1.48 Å for Cd. It is likely therefore that K, Rb,
and Cs will not be soluble in Zn II-VI compounds
and that the solubility of Na, which has a radius of
1.54 Å, may be low.

IV. Li ISOTOPE SHIFTS IN CdS

A. Double Donor-Acceptor Pairs

Our identification of Li as a shallow acceptor in
CdS was based not only on chemical-doping experi-
ments but on the observation of the Li^6-Li^7 isotope

shift of donor-acceptor pair lines. Figure 5 shows
the double donor-Li—acceptor spectrum described
previously in Ref. 4. Each of the pair lines con-
sists of two lines associated with the two isotopes
of Li. In Ref. 4, we argued that the Li acceptor
giving rise to this pair spectrum had the right g
value and binding energy to also be the acceptor
that gave rise to the I_1 line and to donor-acceptor
pairs in CdS. Unfortunately, the I_1 line did not
show a Li isotope shift, so that this assertion could
not be proved. We will now try to clarify why no
Li isotope shift was observed.

The isotope shift arises if the zero-point vibra-
tional energy of the Li atom changes as a result of
the optical transition.[15] Such changes are likely to
take place if the charge distributed on the Li-host
bonds is appreciably altered during the transition,
as it is for the more distant double donor-acceptor
pair lines shown in Fig. 5. For the distant pairs,
the hole in the initial state is bound to a Li acceptor
with a Bohr radius a_B of only about 7 Å. The charge
density on the Li neighbor bands should be propor-
tional to a_B^{-3}. In the final state, the hole has re-
combined and the hole charge density is zero. For
closer pairs the hole becomes delocalized due to
the repulsion of the double donor, the hole charge
density decreases, and so does the isotope shift.
Figure 6 shows a plot of the isotope shift versus
the energy of the pair lines. There is no detect-
able isotope shift for pairs with energies greater
than the I_1 line.

B. No Isotope Shift for the I_1 Line

In the case of the I_1 line, there are two electrons
and a hole in the initial state, and one hole in the
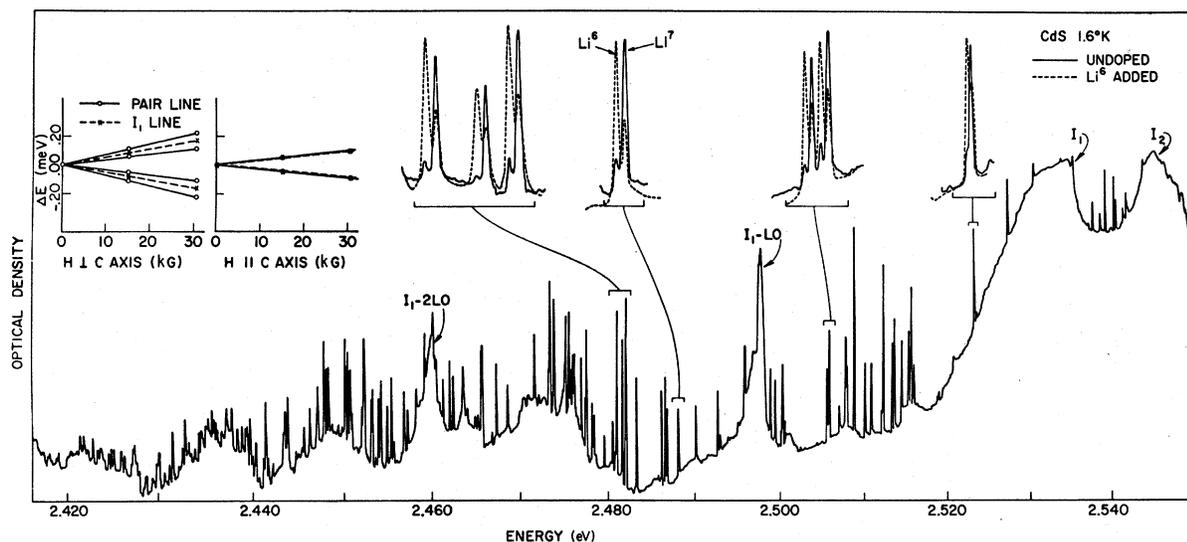
FIG. 5. Double donor-Li—acceptor pair lines in undoped (solid line) and Li^6-doped (dashed line) CdS. The Zeeman split-
tings of a typical pair line are shown in the insert and are compared with the Zeeman splitting of the I_1 line.
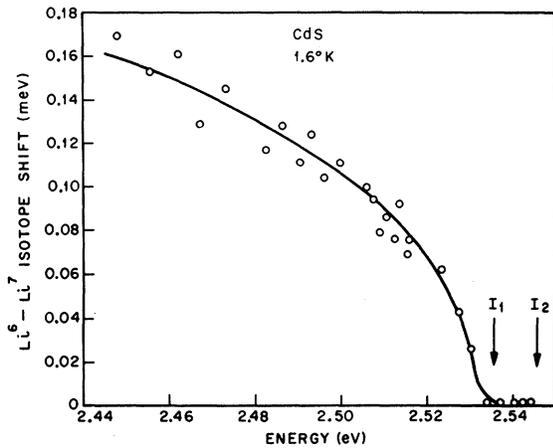
FIG. 6. Li^6-Li^7 isotope shifts of the double donor-acceptor pair lines vs energy. The arrows indicate the energies of the I_1 and I_2 lines.

TABLE III. Acceptor- and exciton-binding energies.

Acceptor		E_{Ex}(meV)	E_A (meV)	E_{Ex}/E_A
CdS	Li	17.67	165 ± 6	0.107
	Na	17.50	169 ± 6	0.103
	P complex	12.9 [a]	120 ± 6	0.107
CdSe	Li or Na	9.15	109 ± 6	0.084
	P complex	7.53	83 ± 6	0.091

[a]Energy corresponds to the stronger of the two lines observed in Fig. 8(a).

final state. The electron has a small mass, and a large orbital radius (>30 Å) and should contribute negligibly to the change in charge density. We must blame our lack of observation of an isotope shift of the I_1 line on the lack of an appreciable change in the hole charge density on the Li-host bonds during the transition. This has at least some theoretical justification. According to Halstead and Aven,[9] the exciton-binding energy E_{Ex} and the acceptor-binding energy E_A are related by $E_{Ex} \approx 0.10\ E_A$. Similarly, central cell corrections change both binding energies according to the relation $\Delta E_{Ex} \approx 0.10\ \Delta E_A$. This agrees roughly with the results of this paper (see Table III). Since central cell corrections are proportional to the hole charge density at the central cell, we interpret the latter relation to mean that the change in the hole charge density in the central cell, during the bound exciton transition, is only about 0.10 of

the hole charge density in the central cell of an isolated acceptor. Thus the isotope shift should be no more than about 10% the observed isotope shift of the distant pair lines, and thus too small to observe.

C. Single Donor-Acceptor Pairs

According to our interpretation, ordinary donor-acceptor pair lines[16,17] should also exhibit an isotope shift. These pair lines are very weak and hard to observe. It is not surprising, therefore, that isotope shifts due to the 7.42% abundant Li^6 were not observed. Such isotope shifts show up in donor-acceptor pair lines shown in Fig. 7. The samples were grown in a tube contaminated with Li^6. The pair lines were weak, but could be clearly observed on the photographic plate. The Zeeman splittings of a typical pair line are shown in the insert. This splitting is characteristic of ordinary (not double) donor-acceptor pair lines.[16] All of the pair lines showed up as doublets and the separation of the pair of lines decreased gradually as the energy of the pair lines decreased. The lowest-energy pair lines had a separation 0.18 $\pm$ 0.1 meV which was equal to the isotope shift observed for the low-energy double donor-acceptor pair lines. This was adequate evidence that we were observing an isotope shift due to ordinary
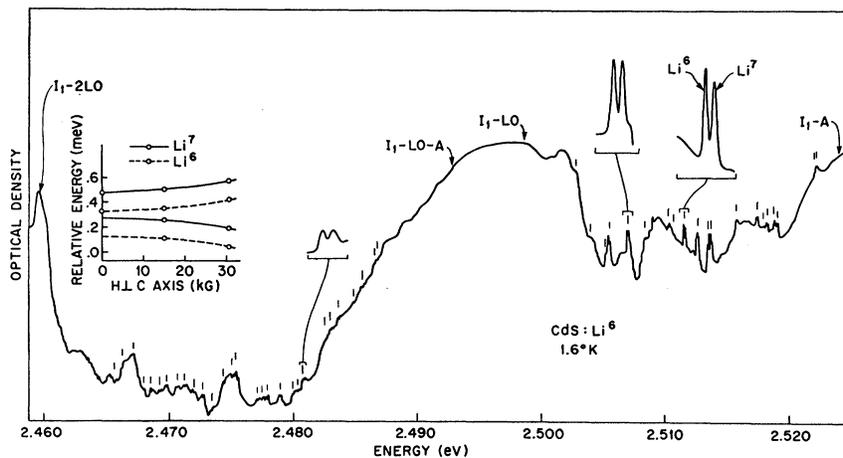
FIG. 7. Weak single donor-acceptor pair line spectrum observed in CdS doped with Li^6. The vertical lines indicate the lines clearly observable on the photographic plate. Inserts show magnetic splittings, revealing that these are normal donor-acceptor pairs. Other inserts show the isotope shift of the pair lines.

donor-acceptor lines.

V. SHALLOW COMPLEX ACCEPTORS DUE TO P

A. CdS

Besides the two I_1 lines arising from Li and Na, other weak I_1-like lines show up in CdS. They generally occur between the I_1 and I_2 lines in energy. Often two lines occur together, separated by about 1 meV. The lines are replicated by a strong sharp LO phonon replica. This is characteristic of I_1 lines, but not I_2 lines. The Zeeman splitting of the lines can be fitted with electron and hole g values. The hole g value is anisotropic, but does not go to zero for $H \perp c$. This indicates that the symmetry of the site is low. Such lines are probably due to a complex acting as a shallow acceptor.

Such "complex acceptor" lines show up for CdS crystals doped with P and I. The spectrum is shown in Fig. 8(a) for these crystals. The two I_1 lines correspond to exciton-binding energies of 13.65 and 12.9 meV. The pair is shifted to 45 meV higher in energy than the pair bands observed for Li and Na acceptors and corresponds to an acceptor with a binding energy of ≈ 120 meV.

Recently Hou and Marley[18] implanted CdS with P ions. They found two acceptor levels with depths of 0.13 eV and 0.75-0.80 eV. As discussed in Sec. VI, substitutional P is expected to be a deep acceptor in CdS. It may be that the shallow acceptor reported by Hou and Marley is the same as the complex acceptor we have just described. The deeper acceptor is probably substitutional P.

B. CdSe

Doping CdSe with P produces a pair band and an I_1 line shifted to higher energy than the corresponding pair band and I_1 line found by doping with Li or Na. The spectrum is shown in Fig. 8(b). The Zeeman splitting of the I_1 line can be fitted with an anisotropic hole g value which does not go to zero for $H \perp c$ axis, again indicating that the acceptor is a complex. The g values are listed in Table II. At present, we have no model for this complex. We have not observed any shallow acceptors when CdSe or CdS are doped with As.

In Table III we list the binding energies for the excitons and acceptors discussed in this paper. They roughly obey the rule of Halstead and Aven.[9]

VI. TRENDS IN ACCEPTOR BINDING ENERGY

We have found that the only shallow acceptors in CdS and CdSe are due to Li and Na. We attempted to dope CdS and CdSe with the group V elements N, P, and As, but found no new shallow acceptors except in the case of P, and this acceptor appeared to be a complex. Our results are in line with the results of others. Holton et al.[19] identified the P

acceptor in ZnSe by ESR and found that this acceptor is 0.6 to 0.7 eV deep. Tell[20] diffused P and As into CdS and found an acceptor level about 1 eV above the valence band. This is in sharp contrast with CdTe and ZnTe, where P as well as Li act as shallow acceptors.[21]

A. Trends in Hydrogenic Binding Energies

To understand these results it is appropriate to look at the systematic variation of acceptor-binding energies in other semiconductors. The acceptor-binding energy can be written as a hydrogenic value plus an additional energy due to central cell corrections. The hydrogenic value is

$$E_H = 13.6(m^*/\epsilon^2) \text{ eV} ,$$

where m^* is the appropriate effective mass and where ϵ is the static dielectric constant. The binding energy of the shallowest acceptors found in a semiconductor is approximately the hydrogenic-binding energy. These values are listed in Table IV together with exciton energy gaps of the semiconductors. Increasing the direct band gap tends to increase m^* and thus increases E_H. For atoms of the same two rows of the Periodic Table, increasing ionicity tends to decrease ϵ and to increase m^* and thereby to increase E_H. The variations of E_H shown in this table are explained reasonably well by the calculations of acceptor-binding energies of Lippari and Baldereschi[22] based on the band parameters of Lawaetz.[23]
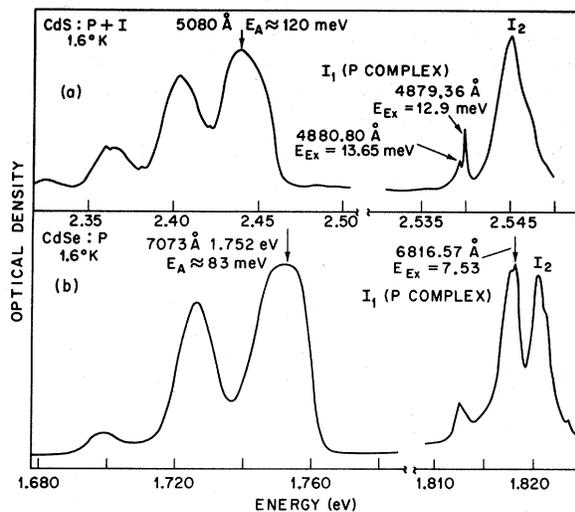
FIG. 8. Pair bands and bound excitons for CdS doped with P and CdSe doped with P. The bands were observed with 10 mW of unfocused argon laser light and the bound excitons were observed using 100 mW of focused argon laser light.

TABLE IV. Binding energies of shallow acceptors and exciton energy gap (in parentheses) of common semiconductors (in eV).

Group IV	Group III-V	Group II-VI	
C 0.27 (5.409)	GaN 0.20 (3.47)	ZnO ≈0.95 (3.45)	
SiC 0.179 (cubic) (2.390)	GaP 0.048 (2.329)	ZnS · · · (3.87)	CdS 0.165 (2.554)
Si 0.044 (1.151)	GaAs 0.028 (1.516)	ZnSe 0.10 (2.80)	CdSe 0.109 (1.826)
Ge 0.0105 (0.739)		ZnTe 0.04 (2.38)	CdTe 0.042 (1.596)

B. Trends in Central Cell Corrections

The binding energies of a wide variety of substitutional acceptors have been determined in Si and GaP. They are listed in Table V. There are two clear trends. First, the acceptor central cell corrections increase as one moves down a column of acceptor atoms in the Periodic Table. Second, the data on GaP indicates that the central cell corrections for substitution on a positive-ion (Ga) site tend to be small while the central cell corrections for negative ion (P) sites tend to be larger. Here it is relevant to compare atoms similar to the host atom. Zn, which is next to Ga in the Periodic Table, is a shallow acceptor, while Si, which is next to P in the Periodic Table, is a deep acceptor.

The conditions for an acceptor being shallow appear to be that the atom be small compared to the host atom, especially if the atom is substituting for a negative-ion site. Li, Na, and N are the only atoms that satisfy this requirement in CdS and CdSe. Unfortunately, N appears to be insoluble. P should be a deep acceptor, just as Si is a relatively deep

TABLE V. Binding energies (meV).

Si[a]	GaP[b,c]	
	Substitution on	
	Ga site	P site
B 44	Be 50	C 48
Al 69	Mg 53.5	Si 204
Ga 72	Zn 64	Ge ≈ 300
In 155	Cd 96.5	

[a]G. Pincus, E. Burstein, and B. Henvis, J. Phys. Chem. Solids 1, 65 (1956).

[b]P. J. Dean and M. Ilegems, Bull. Am. Phys. Soc. 15, 1342 (1970).

[c]P. J. Dean, E. G. Schönherr, and R. B. Zetterstrom, J. Appl. Phys. 41, 3474 (1970).

acceptor in GaP. Central cell corrections should be proportional to the charge density of the acceptor on the impurity host bonds. This charge density is proportional to $(\text{Bohr radius})^{-3} \sim E_H^{3/2} m^{*3/2}$ for small central cell corrections. Clearly, central cell corrections will tend to be large for crystals with large E_H and only a few elements will be able to give shallow acceptors in such crystals. For example, we would expect that only Be, Mg, and possibly Zn would be shallow substitutional acceptors in GaN. In CdTe and ZnTe, P is a shallow acceptor. This is not surprising considering that E_H and m^* are small and P is much smaller than the host.

We feel that this discussion adequately explains why Li and Na are the only shallow substitutional acceptors found in CdSe and CdS. It is likely that this result also holds for ZnSe and ZnS. Li has been established to be close to 1 eV deep in ZnO.[24] This does not contradict what we have been saying because according to Lawaetz,[23] E_H will be of order 1 eV in ZnO. There is no optical evidence for any shallow acceptors in this material.[25]

VII. SELF-COMPENSATION

A. Mechanisms

In order to make CdSe or CdS conduct p type, we must be able to incorporate a shallow acceptor (not more than 0.2 or 0.3 eV deep) that is not highly compensated. In Sec. VI B, we argued that only Li and Na are suitably shallow acceptors. However, when crystals are grown with up to 10^{18} Li or Na, they remain highly resistive. In this
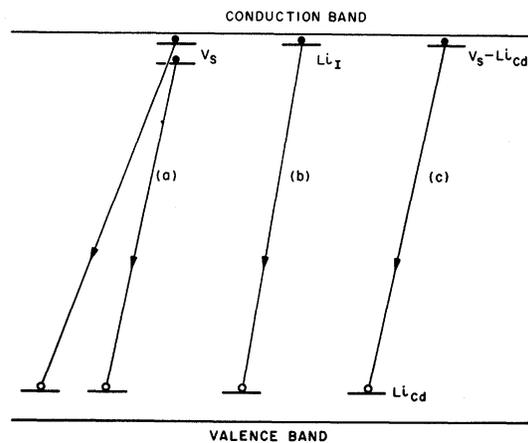
FIG. 9. Mechanisms of self-compensation. (a) Two Li acceptors compensated by a S vacancy acting as a native double donor; (b) a Li acceptor compensated by a Li interstitial donor; and (c) two Li acceptors are compensated by a S vacancy which make a nearest-neighbor complex with the first Li acceptor which then acts as a donor and compensates the second Li acceptor.

section we wish to examine the possible means of self-compensation. Three possibilities of self-compensation are shown in Fig. 9. The first mechanism is compensation by a native double donor, illustrated as a sulfur vacancy in the figure (Cd interstitials are also possible native double donors). Mandel[1] pointed out that double donors should be effective in compensation, since one such defect can compensate two acceptors, as illustrated in Fig. 9(a). The second is compensation by interstitial Li (or Na) acting as a donor, shown in Fig. 9(b). Li^+ and Na^+ have ionic radii of only 0.60 and 0.95 Å, respectively. They should be small enough to be incorporated interstitially and are known to act as interstitial donors in group IV and in III-V compounds.[26] Finally, a complex, consisting of a native double donor associated with an acceptor, is considered in Fig. 9(c).

B. Optical Evidence

Smith[27] has shown by high-temperature Hall measurements that native double donors exist in CdTe and CdSe, whereas he finds only native single donors in ZnSe. At present, no reliable measurements of this type have been made on CdS. These measurements do not distinguish between the possibility of a negative-ion vacancy and a positive-ion interstitial. Spin-resonance[28] measurements have revealed a native donor in ZnS due to a S vacancy. The pair spectrum in Fig. 5 involves a double donor and an acceptor. As stated in Ref. 5, this spectrum most
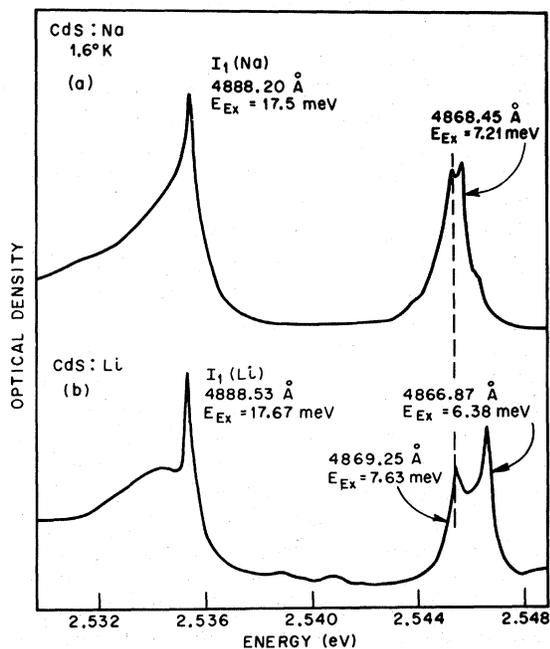
FIG. 10. Bound excitons due to acceptors and compensating donors in CdS doped with (a) Na and (b) Li.

likely involves a native double door, since it only appears in undoped crystals grown with excess Cd present. We have not been able to identify the pair-line spectrum and thereby determine the site of donor. However, the spectrum is definitely not type I, so that the Cd site can be ruled out and therefore double donors due to group IV elements substituted for Cd are excluded.

As soon as the slightest amount of Li and Na is added to CdS during growth, the double donor-acceptor spectrum disappears and a bright ordinary donor-acceptor recombination spectrum dominates the luminescence. We take this as evidence that compensation by isolated native defects is unimportant.

The I_2 lines associated with the compensating donors that occur when CdS is doped with Li or Na are shown in Fig. 10. The strong higher-energy I_2 line caused by Li doping is also the dominant I_2 line that occurs in doping by diffusion. The exciton-binding energy is only 6.38 meV. Using the linear relation between donor- and exciton-binding energy,[29] we find this corresponds to a donor-binding energy of 28.6 meV. Similarly the more intense I_2 line associated with Na doping corresponds to a donor-binding energy of 31.5 meV. A third line that is seen with either Na or Li doping and which also appears in many undoped crystals corresponds to a donor with $E_{Ex} = 7.63$ meV and $E_D = 32.9$ meV. This donor is unknown in origin. It was previously reported by us.[29] We will refer to the first two donors as the Li and Na donors. These donors have binding energies that are considerably less than we found associated with substitutional impurities. The latter ranged from 32.1 to 35.1 meV.[29] At present, we do not know the nature of the Li and Na donor, but the compensation is definitely not due to isolated double donors [mechanism (a) of Fig. 9]. The Li donor is the shallowest donor yet reported. The Li interstitial donor in Si is also very shallow[30] and it is tempting to use this as evidence that this donor is in fact interstitial Li.

C. Analysis of High-Temperature Hall Measurements

Mandel[1] pointed out that one could calculate the degree of compensation of acceptors as a function of temperature and metal-atom pressure. The calculation requires a knowledge of the enthalpy and entropy required to form an ionized native donor. We would like to point out that this is just the information provided by the high-temperature Hall measurements of Smith on CdTe, CdSe, and ZnSe[27] and by Hershman and Kroger[31] on CdS. Consider the case of CdSe and assume that the native donor is a selenium vacancy acting as a double donor that is completely ionized at the temperatures involved. The vacancy is formed through the reaction

$$\text{Se}_{\text{Se}} \rightleftarrows V_{\text{Se}}^{++} + 2e^- + \tfrac{1}{2}\text{Se}_2(g) - H_v \ , \tag{1}$$

$$\text{Cd}_{\text{Cd}} + \text{Se}_{\text{Se}} \rightleftarrows \text{Cd}(g) + \tfrac{1}{2}\text{Se}_2(g) - H_{\text{sub}} \ , \tag{2}$$
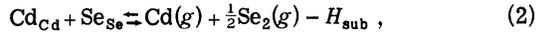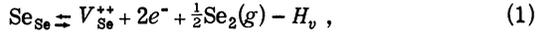
where H_{sub} is the enthalpy of sublimation and H_v is the enthalpy to form a Se vacancy. Subtracting Eq. (2) from Eq. (1) we obtain

$$\text{Cd}(g) \rightleftarrows V_{\text{Se}}^{++} + 2e^- + \text{Cd}_{\text{Cd}} - (H_v - H_{\text{sub}}) \ . \tag{3}$$
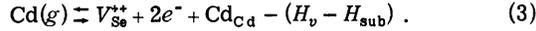
This gives via the law of mass action

$$[V_{\text{Se}}^{++}]n^2 = K \ P_{\text{Cd}} e^{-(H_v - H_{\text{sub}})/kT} \ . \tag{4}$$

From electrical neutrality, we find

$$2[V_{\text{Se}}^{++}] = n. \tag{5}$$

Therefore,

$$n = n_{PT} \equiv 2^{1/3} K^{1/3} P_{\text{Cd}}^{1/3} e^{-(H_v - H_{\text{sub}})/3kT} \ , \tag{6}$$

where n_{PT} is the carrier concentration measured as a function of T and P_{Cd}. Smith[27] finds $H_v - H_{\text{sub}} = 1.9$ eV, $H_{\text{sub}} = 3.3$ eV; therefore, $H_v = 5.2$ eV. From Eqs. (4) and (5) we have the general relation

$$2[V_{\text{Se}}^{++}]n^2 = n^3{}_{PT}. \tag{7}$$

Assume that the crystal is doped with an acceptor A and appreciably compensated by V_{Se}^{++}. The electrical neutrality condition is then approximately given by

$$[A^-] = 2[V_{\text{Se}}^{++}] \ , \tag{8}$$

where $[A^-]$ is the concentration of ionized acceptors and $[A]$ is the total acceptor concentration. Using the fact that the product of the electron concentration n and the hole concentration p is a constant

$$np = n_i^2 \tag{9}$$

we can write

$$p/[A^-] = n_i^2 / n_{PT}^{3/2} [A^-]^{1/2} \ . \tag{10}$$

If the degree of compensation is large, we have

$$[A^-] \approx [A] \ . \tag{11}$$

Assuming that the acceptors are sufficiently shallow to be completely ionized at high temperature, then p is equal to the concentration of neutral acceptors existing at low temperature which we will denote by $[A_0]$:

$$[A_0]/[A] \approx n_i^2 / n_{PT}^{3/2} [A]^{1/2} \ . \tag{12}$$

$[A_0]/[A]$ will be a maximum, when n_{PT} is a minimum. This occurs at maximum Se pressure (that is at the pressure over liquid Se). Evaluating this expression at 900 °C using the n_{PT} given by Smith's data and the n_i^2 appropriate for the high-temperature band gap, and the appropriate vapor pressure of Cd over CdSe in contact with liquid Se, and $[A] = 10^{18}$, we find

$$[A_0]/[A] \approx 0.24 \ .$$

Similarly, for CdTe we find

$$[A_0]/[A] \approx 0.18 \ .$$

Similar calculations for ZnSe, assuming a native single donor,[27] show that in this case the self-compensation by isolated native donors is negligible. We have evaluated Eq. (12) at 900 °C and P_{Cd} corresponding to a S_2 pressure of 10 atm., using the n_{PT} data of Hershman and Kroger.[31] We find $[A_0]/[A] \approx 0.06$. We conclude that, in all four cases where high-temperature Hall measurements have been carried out to determine dependence of native donors on temperature and pressure, *isolated* native donors do not yield a high degree of self-compensation. The same analysis can be carried through assuming that the native donor is a Cd interstitial and this yields exactly the same results for the degree of self-compensation. This result is in line with our optical results which indicated that Li and Na were not compensated by double donors.

We cannot rule out the possibility that compensation by native double donor-acceptor complexes is the dominant mechanism [Fig. 9(c)]. More microscopic measurements are still needed to determine the identity of the compensating donors.

D. Li Drifting Experiments

It is well known that Li interstitial donors will drift in an applied electric field.[32] If CdS doped with Li consists of Li acceptors compensated by Li donors, it may be possible to apply an electric field and drift out the compensating Li interstitial donors, leaving the sample p type. To test this idea we applied In-Ga contacts to a sample of CdS doped with Li. A typical result is shown in Fig. 11. Fields of order 8000 V/cm were applied across the sample. Initially, the samples were highly resistive and the current was much less than 1 μA. The current increased slowly in time and after about 50 min it rose quite rapidly and leveled off at about 0.5 mA. If the voltage was reversed, the reverse current was less than 1 μA, but slowly increased as shown in Fig. 11. When the voltage once more was reversed to the forward direction, the current rapidly (but not instantaneously) returned to its former value in the forward direction. For voltages of the order 0.5 mA or greater, green light was emitted from some of the CdS samples. By performing similar experiments in which contacts were placed on the ends of CdS needles, we established that the light emission comes from near the positive contact. For currents greater than 1 or 2 mA, the light emission and rectification suddenly stopped. The crystal then passed the same value of current, but in both
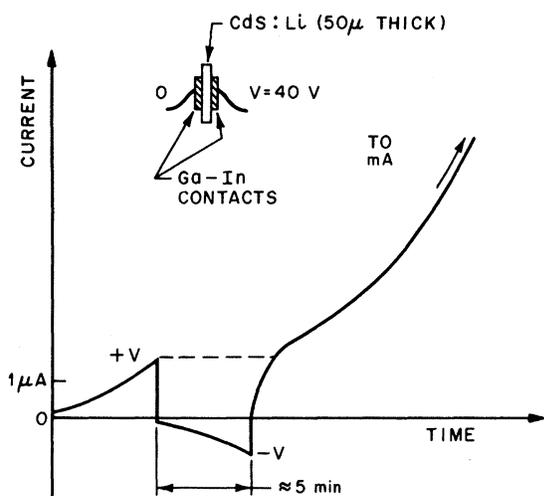
FIG. 11. Schematic diagram indicating the results of the Li drifting experiments.

directions that was previously passed in the forward direction. Thermoprobe measurements indicated that the sample was n type. The current conduction appeared to be in filaments. For example, when contacts were applied to the ends of a needle, after a time, current could be passed down the length of the needle, but the needle would not conduct in the perpendicular direction.

These effects were observed in Li- and Na-doped CdS and CdSe, but not in undoped crystals. They were most readily observed in Li-diffused samples. A possible explanation of these phenomena is that interstitial Li near the positive contact drifted down the crystal until the bulk of the crystal was high resistivity n type ($\delta \approx 10^4$ Ω cm). The region near the positive contact probably became p type. We believe that the light emission resulted from holes injected at the positive contact recombining with electrons injected at the negative contact; however, hole injection through electrical breakdown near the positive contact cannot be ruled out. The

"burn out" of the rectification and light emission at currents of 1 or 2 mA probably was due to heating at the positive contact, where there was a considerable voltage drop. Perhaps the heating caused the In or Ga to diffuse into the crystal.

VIII. SUMMARY AND CONCLUSIONS

We have presented optical data showing that Li and Na are the shallow substitutional acceptors in CdS and CdSe. We have also shown that the shallow acceptor that occurs during P doping is a complex and not a simple substitutional acceptor. These observations are in agreement with the work of others showing that P is a deep acceptor in the sulfides and selenides but not in the tellurides. We then argue that all of these results were consistent with the trends in acceptor-binding energy observed in Si and GaP. Our optical evidence supports the idea that a native double donor exists in CdS, but that Li and Na are compensated by ordinary donors and not double donors. Analysis of the results of Smith's high-temperature Hall measurements also confirms that compensation by isolated native donors is unimportant in CdTe, CdSe, and ZnSe. The observation of Li drifting and the fact that the compensating donors are quite shallow is evidence that the principal means of compensation is by Li and Na interstitial donors.

Regardless of the compensation mechanism, it is very unlikely that Zn or Cd sulfide or selenide can be made low-resistivity p type by doping with Li or Na. Since these are the only substitutional impurities which act as shallow soluble acceptors in the sulfides and selenides, the possibility that these materials will ever be doped low-resistivity p type is very remote.

ACKNOWLEDGMENTS

[1]G. Mandel, Phys. Rev. 134, A1073 (1964); G. Mandel, F. F. Morehead, and P. R. Wagner, ibid. 136, A826 (1964).

[2]F. A. Kroger, J. Chem. Phys. Solids 26, 1717 (1965).

[3]M. Aven, in II-VI Semiconducting Compounds, edited by D. G. Thomas (Benjamin, New York, 1967), p. 1232.

[4]C. H. Henry, K. Nassau, and J. W. Shiever, Phys. Rev. Letters 24, 820 (1970).

[5]D. G. Thomas and J. J. Hopfield, Phys. Rev. 128, 2135 (1962).

[6]D. G. Thomas, R. Dingle, and J. D. Cuthbert, in Ref. 3, p. 863.

[7]C. H. Henry, R. A. Faulkner, and K. Nassau, Phys. Rev. 183, 798 (1969).

[8]The binding energy E_{Ex} is the energy difference between the I_1 line energy and the $A(1S_T)$ exciton energy taken to

be 2.55304 eV.

[9]R. E. Halstead and M. Aven, Phys. Rev. Letters 14, 64 (1965).

[10]C. H. Henry, K. Nassau, and J. W. Shiever, Bull. Am. Phys. Soc. 16, 397 (1971).

[11]The photographic data for bound excitons in CdSe : Na in Fig. 3 are overexposed. As a result, the unidentified bound exciton between I_1 and I_2 appears stronger than it actually is.

[12]R. T. Anderson, Chemical Periodicity (Reinhold, New York, 1960).

[13]K. Weiser, J. Phys. Chem. Solids 7, 118 (1958).

[14]F. A. Trumbore, Bell System Tech. J. 39, 205 (1960).

[15]T. N. Morgan, B. Welber, and R. N. Bhargava, Phys. Rev. 166, 751 (1968).

[16]C. H. Henry, R. A. Faulkner, and K. Nassau, Phys.

Rev. 183, 798 (1969).

[17]D. C. Reynolds and T. C. Collins, Phys. Rev. 188, 1267 (1969).

[18]S. L. Hou and J. A. Marley, Jr., Appl. Phys. Letters 16, 467 (1970).

[19]W. C. Holton, A. R. Reinberg, R. K. Watts, and M. DeWit, J. Luminescence 1/2, 583 (1970).

[20]B. Tell, J. Appl. Phys. 41, 3789 (1970).

[21]B. L. Crowder and G. D. Petit, Phys. Rev. 178, 1235 (1969).

[22]N. O. Lippari and A. Baldereschi, Phys. Rev. Letters 25, 1660 (1970).

[23]P. Lawaetz (unpublished).

[24]O. F. Schirmer and D. Zwingel, Solid State Commun. 8, 1559 (1970).

[25]D. C. Reynolds and T. C. Collins, Phys. Rev. 185,

1099 (1969).

[26]G. D. Watkins, Phys. Rev. B 1, 4071 (1970).

[27]F. T. J. Smith, Met. Trans. 1, 617 (1970); Solid State Commun. 8, 263 (1970); 7, 1757 (1969); see also R. C. Wheelan and D. Shaw, Phys. Status Solidi 29, 145 (1968).

[28]J. Schneider and A. Räuber, Solid State Commun. 5, 779 (1967); K. Leutwein, A. Räuber, and J. Schneider, ibid. 5, 783 (1967).

[29]K. Nassau, C. H. Henry, and J. W. Shiever, Proceedings of the Tenth International Conference on Semiconductors (Cambridge U. P., New York, 1970), p. 629.

[30]R. A. Faulkner, Phys. Rev. 184, 713 (1969).

[31]G. H. Hershman and F. A. Kroger, J. Solid State Chem. 2, 483 (1970).

[32]E. M. Pell, J. Phys. Chem. Solids 3, 77 (1957).

Electrical Properties, Optical Properties, and Band Structure of CuGaS₂ and CuInS₂

B. Tell and J. L. Shay

Bell Telephone Laboratories, Holmdel, New Jersey 07733

and

H. M. Kasper

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 20 May 1971)

Various optical and electrical properties of the I-III-VI₂ compounds CuGaS₂ and CuInS₂ have been studied. From the results of low-temperature luminescence and reflectivity, both crystals are determined to have a direct band gap. The band gaps at 2 °K are 2.53 eV for CuGaS₂ and 1.55 eV for CuInS₂. CuInS₂ has been made conducting both n and p type, while CuGaS₂ has been made p type only. Electroreflectance measurements have been performed in an attempt to determine the band structure. The highest valence band appears to be a doublet with a large admixture of Cu 3d wave functions.

I. INTRODUCTION

The I-III-VI₂ sulphides are ternary analogs of the familiar II-VI compounds ZnS and CdS. Very little is known of either the electrical or optical properties of this class of materials. They are tetrahedrally coordinated semiconductors which crystallize in the uniaxial chalcopyrite structure. Since some of these compounds display large birefringence, they are potentially interesting as nonlinear optical materials[1,2] as well as semiconductors. In the present paper, we have studied optical and electrical properties of melt-grown single crystals of CuGaS₂ and CuInS₂. We have determined that they are direct-band-gap materials which are capable of controlled doping. In addition, we present electroreflectance and photoreflectance studies in an attempt to understand the band structure. The only previous work on the present compounds was performed on powders and polycrystals.[3,4] Single crystals of other I-III-VI₂'s have been briefly studied.[5,6]

Low-temperature optical studies show that in the wavelength vicinity of the absorption edge there are both sharp photoluminescence lines and reflectivity anomalies. The presence of reflectivity anomalies and luminescence at the same wavelength is unambiguous evidence that the crystals have direct energy gaps. These observations enable the determination of the band gaps at 2 °K to be 2.53 eV for CuGaS₂ and 1.55 eV for CuInS₂.

The band structure of these compounds is a complicated problem. As occurs in other copper compounds, the Cu 3d bands are expected to contribute appreciably to the highest valence band. The d-band mixing is probably responsible for the large downshift in the energy gap of the copper compounds (~1.5 eV) with respect to the II-VI analogs, and results in a valence-band structure unlike any previously observed in a "diamondlike" semiconductor.

Similar to the II-VI compounds, significant changes in electrical conductivity are achieved by