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Shallow-donor ionization energies in the II-VI compounds

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Hall data on ZnSe, CdS, CdSe, and CdTe have been analyzed to determine the shallow-donor ionization energies E_d and the total donor and acceptor impurity concentrations N_d and N_a, respectively. Lowering of the E_d values owing to impurity concentration effects are noted even in the purest samples. When the data are analyzed using linear plots of E_d vs $(N_{d^+})^{1/3}$, the resulting values of the ionization energy for infinite dilution are in good agreement with optical data and with the hydrogenic model.

I. INTRODUCTION

Of the six Zn and Cd chalcogenides, all but ZnTe can be made to exhibit moderate to high n-type conductivity. In these systems, electrical-transport measurements have yielded a variety of values for the shallow-donor ionization energies.[1] Because of apparent conflicting results between different workers and between these values and those determined by optical measurements, we have reviewed our electrical data taken over a ten-year period and some data of others. In four systems, ZnSe, CdS, CdSe, and CdTe, sufficient purity of the material has been obtained to permit an approximate measure of the "hydrogenic"-donor-level depth from Hall-coefficient data. Even in these systems, however, appreciable concentration effects are observed. Taking such effects into account, level depths of 31.3 ± 1.0, 28.1 ± 1.4, and 14.3 ± 0.5 meV are obtained for the shallow donors in CdS, ZnSe, and CdTe, respectively, in good agreement with the values determined from optical measurements. The more limited data for CdSe are consistent with the estimates from optical measurements of 19.5 ± 0.3 meV. All of these level depths are in agreement with the hydrogenic model.

The analysis of the data also indicates that the residual electrically active acceptor concentrations in the "best" samples of ZnSe, CdS, and CdSe are of the order of 1×10^{15} cm^{-3} and approaches 2×10^{14} cm^{-3} for CdTe. In CdS and CdTe an anomalous behavior has been observed in samples which show a high degree of donor compensation. These samples give E_d values lower than expected and low-temperature-mobility values much higher than expected for the calculated acceptor concentrations.[2] Such anomalously high mobility values have led to erroneous conclusions concerning the degree of purity of some of these samples.[3]

II. ANALYSIS OF DATA

A. Hall-coefficient measurements

The use of Hall data to obtain ionization level depths usually depends on several assumptions. The first is the relation between the Hall coefficient R_H and the free-carrier concentration, n. (We will only consider n-type conductivity to simplify the discussion.) In general,

$$n = r/(eR_H) = 6.24 \times 10^{18} r/R_H, \tag{1}$$

where R_H is in units of cm^3/C, n is in units of cm^{-3}, and r is a dimensionless parameter equal to the ratio of the Hall mobility to the drift mobility.

According to Devlin,[1] optical-mode scattering produces a variation of r between 1.0 and 1.2 in the approximate temperature range of 20–120°K. In this temperature range a typical freeze-out traverses more than 3 factors of 10 in R_H for CdS and the assumption of a constant r would introduce an error of less than 2% in E_d. Hence the assumption of $r = 1$ is quite valid for our present purposes. (See also Segall *et al.*[4])

The relation between the donor ionization energy E_d, the absolute temperature T, and the carrier concentration n, is given by

$$n(N_a + n)/(N_d - N_a - n) = gN_c e^{-E_d/kT}, \tag{2}$$

where N_d and N_a are the total number of donors and compensating acceptors, respectively, g is a degeneracy factor, and (in cm^{-3})

$$N_c = 2(2\pi m^* kT/h^2)^{3/2} = 1.527 \times 10^{20} \left(\frac{m^*}{m} \frac{T}{1000}\right)^{3/2}.$$

The applicability of Eq. (2) assumes a single donor level, nondegenerate carrier densities, and an isotropic band minimum. Any impurity banding or

degeneracy effects will dominate the conductivity at low enough temperatures giving a lower measured E_d (Fritzsche's ϵ_2 and ϵ_3).[5] For samples of interest to us, the concentrations of the defects are low enough that appreciable freeze-out of the free carriers is usually seen. Under these conditions, at low temperatures, $n \ll N_a, N_a - N_d$, and

$$n \cong gN_c[(N_d - N_a)/N_a]e^{-E_d/kT}, \quad (3a)$$

or

$$n \propto 1/R_H \propto T^{3/2} e^{-E_d/kT}. \quad (3b)$$

A fit to Eq. (3b) over many decades ensures that the assumptions are met and provides the most accurate measure of E_d. Under these conditions, $N_{d^+} = N_a + n \cong N_a$. In practice, the temperature range over which such freeze-outs are measured in the II-VI compounds is between 70 and 10°K. Hence, the E_d value would correspond to the low-temperature (below 77°K) crystalline state. Inasmuch as the various crystalline parameters do not show significant variations in this temperature range, little intrinsic change in E_d is expected to occur. Also, any linear dependence of E_d on temperature does not affect the measured slope using Eq. (3b) and thus, to first order, such a measure of E_d actually represents the 0°K value. Such a linear temperature dependence would appear as a multiplying constant to the right-hand side of Eq. (2) and could be considered as part of the coefficient $g(m^*)^{3/2}$.

The above standard analysis assumes no more than a linear temperature dependence of E_d. It has been suggested by Neumark[6] that the influence of the free carriers on E_d through screening may be important in Hall-curve analysis. Our analysis indicates that her conclusions are not valid and that neglecting the effect of screening on the *temperature* dependence of E_d for our samples introduces no greater error than the usual assumption that r and the materials parameters are temperature independent.[7] Such variations can, in part, be "compensated for" by varying the effective mass to obtain optimum fits.

In order to obtain the total concentrations of the donors and compensating acceptors, it is necessary to fit the data to Eq. (2) up to temperatures where the donors are mostly ionized. Here, the actual value and variations in r and the temperature dependence of the pertinent materials parameters introduce uncertainties, particularly since the high-temperature or saturation value of n (equal to $N_d - N_a$) is quite critical. Somewhat deeper lying levels, such as those resulting from the well-documented double-acceptor-type defects,[8] pose additional problems. Because of these difficulties, fits of Eq. (2) to the data are generally made with data points only below 100–150°K, which, at least in the more lightly doped samples, is close to saturation, although good fits to all of the data (usually up to 400°K) are often obtained.

Two computer programs were used for fitting the Hall data to Eq. (2). The majority of the data were fitted for a fixed density-of-states effective mass

TABLE I. Parameters relating to the hydrogenic donor levels and their calculated and measured values.

	$\bar{m}^*/m$	$\bar{k}$	E_h meV	E_{op} meV	E_0 meV	α 10^{-5} cm meV
CdS	0.208 ± 0.005 [a]	9.13 ± 0.2 [b]	33.9 ± 2	32.7 ± 0.4 [c]	31.3 ± 1.0	4.0 ± 0.4
ZnSe	0.16 ± 0.01 [d]	8.66 ± 0.1 [e]	29 ± 2	26.6 ± 0.9 [f]	28.1 ± 1.4	4.1 ± 0.6
CdSe	0.13 ± 0.005 [g]	9.44 ± 0.2 [h]	20 ± 2	19.5 ± 0.3 [i]	···	4.5 ± 0.6
CdTe	0.0963 ± 0.0008 [j]	9.65 ± 0.1 [b,e]	14.1 ± 4	14.3 ± 0.1 [k]	14.3 ± 0.5	3.8 ± 0.4

[a] G. P. Vella-Coleiro, Phys. Rev. Lett. 23, 697 (1969).
[b] D. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. 129, 1009 (1963).
[c] C. H. Henry and K. Nassau, Phys. Rev. B 2, 997 (1970). (Value for Cl doping.)
[d] Reference 14.
[e] S. Roberts and D. T. F. Marple (unpublished data).
[f] Average of values for Al and Cl dopants. See Ref. 14.
[g] C. H. Henry *et al.*, Phys. Rev. B 5, 458 (1972).
[h] An extrapolated value using room-temperature values from Ref. b and the 77°K value for $k_{\parallel}$ from S. S. Devlin, Appendix to L. R. Shiozawa and J. M. Jost, Final Technical Report, Contract No. AF33(657)-7399, U.S.A.F.-A.R.L., Wright-Patterson Air Force Base, Ohio, 1965, p. 184 (unpublished). $k_{\perp}$ is assumed to show the same temperature dependence as $k_{\parallel}$.
[i] Unidentified donor. See Ref. g.
[j] A. L. Mears and R. A. Stradling, Solid State Commun. 7, 1267 (1969).
[k] Calculated from optical absorption data of D. R. Cohn *et al.*, Solid State Commun. 8, 1707 (1970) by multiplying the (2*P*-1*S*) energy difference by $\frac{4}{3}$ and doubling the error.

and for $r=1$. The other parameters in Eq. (2), N_a, N_d, and E_d, were optimized to give the least absolute value error. Later, a least-squares criterion was used and the density-of-states effective mass was also optimized. No significant difference in the final analysis resulted from these or other minor changes in the handling of the data. During the analysis of each sample, a printout of each datum point vs the computer value would be obtained to check anomalous data or sample behavior. Where indications of banding or degeneracy were evident, the lowest temperature points would be successively eliminated until the last point fell within the typical error of the remaining points (<3%). This would give the highest E_d and lowest N_a values compatible with the data.

B. Ionization-energy dependence on impurity concentration

The ionization energy E_d is dependent on the total impurity content of the semiconductor through Coulombic interactions. Different mechanisms for the lowering of E_d have been suggested involving free carriers (Coulombic and screening effects), neutral impurities (polarization effects), and charged defects of the same species.[9] Also, interactions between charged defects of the opposite sign ("distant" pairing) will lower the ionization energy.[10] We will adopt here, in a phenomenological spirit, the following relation used by Debye and Conwell[9]:

$$E_d = E_0 - \alpha (N_{d^+})^{1/3} \tag{4}$$

where E_0 is the E_d value for infinite dilution, N_{d^+} is the concentration of the positively charged atomic defects, and α is a proportionality constant.

The cube-root dependence of N_{d^+} in Eq. (4) minimizes the problem of determining highly accurate values of N_a and N_d from Eq. (2). Also, it was found that varying the effective mass (m^*) changed the best-fit values of both E_d and N_a such that α in Eq. (4) was little affected. This removed from the final results much of the arbitrariness inherent in Hall curve fitting.

III. RESULTS

A. CdS

The electrical-transport properties of CdS have been studied more extensively than in any of the other II-VI compounds. In the course of our work, 48 samples of CdS have been measured to 20°K or below and computer fitted to Eq. (2) using $r=1$, $g=0.5$, and $m^*/m = 0.208$ (see Table I). The data include measurements made on a variety of doped and undoped samples as-grown and/or annealed at various temperatures and Cd partial pressures. Sources of the crystals included those grown previously in this laboratory by Piper and coworkers,[11,12] and crystals obtained from Harshaw

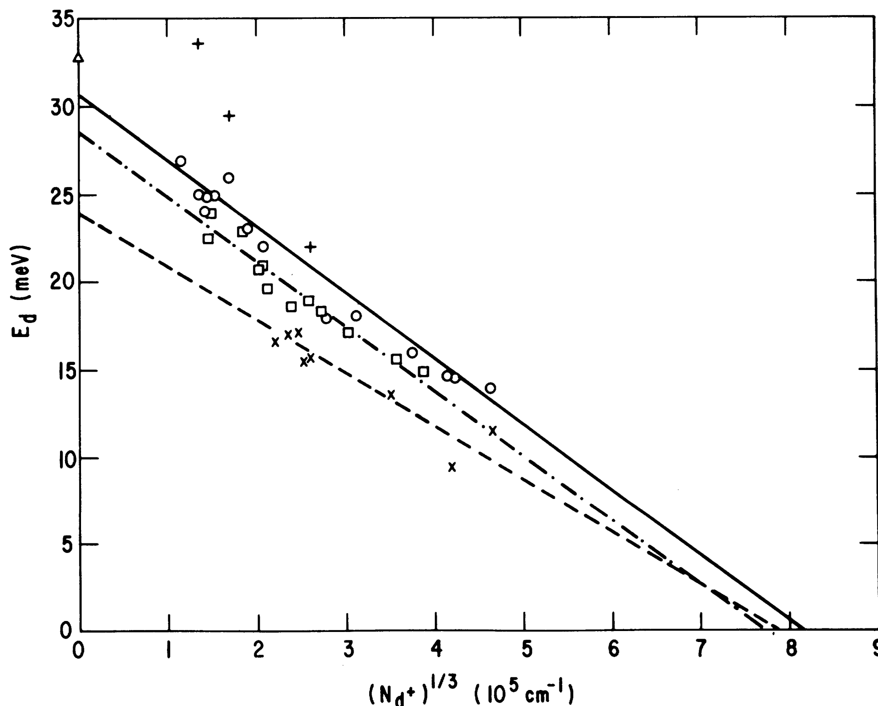

FIG. 1. E_d as a function of $(N_{d^+})^{1/3}$ for the CdS samples shown in Fig. 5 of Ref. 2. The triangle point is from optical measurements. See the text for an explanation of the various data points.

Chemical Co. and Clevite Corp. The majority of the samples, however, came from boules of UHP-grade CdS obtained from Eagle-Pitcher Co. over an eight-year period. No systematic differences were noted between samples from different sources or between samples containing different dopants.

Of the 48 samples analyzed, 12 were rejected because of too few data points, poor fit, or too great an interference with deeper levels. The 36 remaining samples were tested against a phenomenological-theoretical mobility expression discussed in the preceding paper.[2]

Figure 1 shows the measured E_d values vs $(N_{d+})^{1/3}$ for samples selected as follows: The circle data points correspond to the group-I data points in Fig. 5 of Ref. 2 (14 samples); the square data points correspond to the group-II data points in Fig. 5 of Ref. 2 (12 samples); while the data points indicated by ×'s correspond to the group-III points. The three points indicated by crosses in Fig. 1 are calculated from the data curves published by Piper and Halsted.[11] These will be discussed later. The point at $(N_{d+})^{1/3}=0$ indicated by the triangle is from optical experiments (see Table I and below).

The lowering of E_d with deviation of the mobility maximum from the theoretical value is apparent comparing Fig. 1 to Fig. 5 of Ref. 2. A statistical analysis was carried out as follows: For each group of data points, a least-squares linear regression of E_d on $(N_{d+})^{1/3}$ was carried out and then the regression of $(N_{d+})^{1/3}$ on E_d was calculated. The resulting parameters were averaged and an error calculated by taking $\frac{1}{2}$ the difference between the two regression values plus the 50% confidence limits. The resulting regression lines are plotted in Fig. 1 for the three groups of data points. Numerically, the resulting values are the following: 30.6 ± 0.7 meV, $(3.8\pm0.5)\times10^{-5}$ cm meV; 28.5 ± 1.0 meV, $(3.7\pm0.4)\times10^{-5}$ cm meV; and 23.8 ± 2.1 meV, $(3.0\pm0.7)\times10^{-5}$ cm meV for E_0 and α, respectively. The difference in slope in the lines is not statistically significant as noted by the errors. Also, the last group of data points represents heavily compensated samples and showed considerable arbitrariness in fitting.

Taking the variation of E_d vs the deviation from the calculated mobility as a physically significant relationship and assuming that the correct value of E_0 for the "isolated" donors is given by those samples where the measured and calculated mobility maximums agree, an extrapolation can be carried out to correct for the anomalous mobility behavior. Several *ad hoc* relationships were tried which all resulted in small increases in the E_0 and α values over that for the group-I data. These adjusted values are listed in Table I.

B. ZnSe

The ZnSe crystals studied were all grown in this laboratory.[13] The majority of the samples were not intentionally doped. The major residual donor

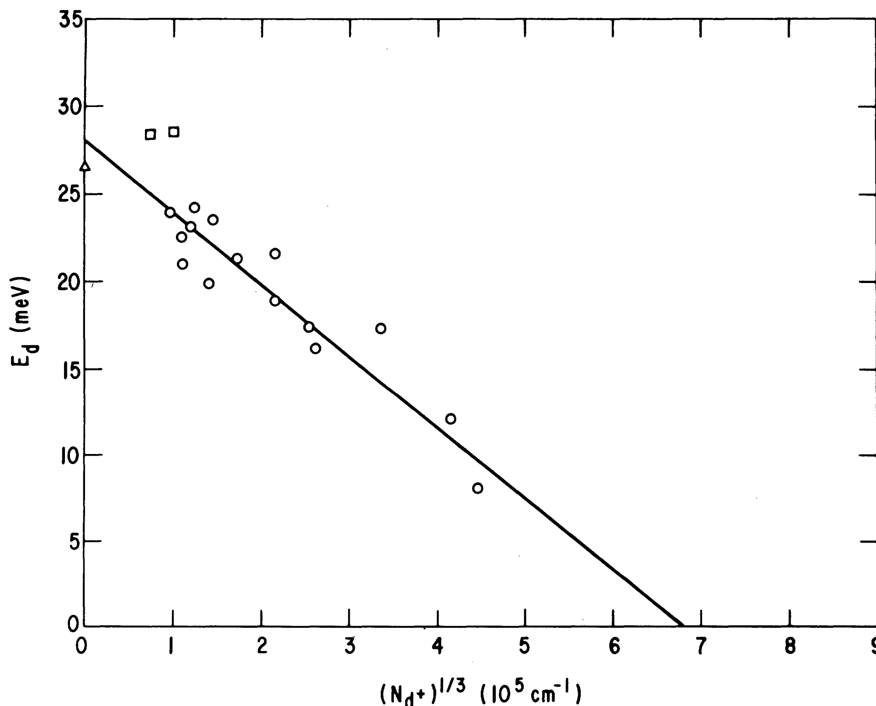

FIG. 2. E_d as a function of $(N_{d+})^{1/3}$ for a variety of ZnSe samples. The triangle point is from optical measurements. The line is the least-squares fit to the circle data points.

impurities were the halogens and Al. Except for the three samples (see Fig. 2) exhibiting the highest concentrations, the analytically determined total donor impurity concentration was generally *higher* than the electrically active donor concentration, indicating that not all donor impurities were electrically active. Hall data of 17 samples were computer fitted to Eq. (2) using $r=1$, $g=0.5$, and $m^*/m=0.16$ (see Table I). The resulting values of E_d and $(N_{d^+})^{1/3}$ are shown in Fig. 2 by the circles and squares. The samples giving the two square data points showed high compensation and a significant double-acceptor concentration; however, some of the other samples were similar in these respects. It is believed that these samples could represent a deeper "hydrogenic" defect,[14] although experimental problems cannot be ruled out. These two samples were discarded in the least-squares fit of E_d vs $(N_{d^+})^{1/3}$ shown by the line in Fig. 2. It is noted that these two data points lie outside the 95% confidence limits of the remaining data points which all lie well within these limits. The triangle datum point is again the E_0 value from optical experiments (see Table I). A fit to the circle points similar to that for CdS gives values of 28.1 ± 1.4 meV and $(4.1\pm0.6)\times10^{-5}$ meV cm for E_0 and α, respectively. The mobilities in the samples analyzed were well behaved[13] and no systematic trend of the data with compensation was observed as in the case of CdS.

C. CdSe

Good low-temperature data for CdSe are more sparse than for the other systems. In order to more meaningfully analyze the available data, the value of E_0 from optical studies has been included as a datum point at $(N_{d^+})^{1/3}=0$ (see Table I and is indicated in Fig. 3 as the upper triangle point. The circle point in this figure is taken from the work of Burmeister and Stevenson,[15] while the three square points are from measurements made on "undoped" CdSe crystals obtained from Harshaw Chemical Co. In the analysis of these samples, the following values were used: $r=1, g=0.5$, and $m^*/m=0.13$ (see Table I). The least-squares linear-regression fit carried out as described above (including the triangle point) is indicated by the upper line in Fig. 3. The parameters obtained are 19.5 ± 0.9 meV and $(4.5\pm0.6)\times10^{-5}$ meV cm for E_0 and α, respectively. Leaving out the $(N_{d^+})^{1/3}=0$ point makes little difference in the E_0 and α values. This is fortuitous, however, since in doing so the statistical errors in the values for reasonable confidence limits are excessive.

D. CdTe

The lower part of Fig. 3 shows data on CdTe taken from two sources. The crosses are from the group-I samples of Agrinskaya *et al.*[16] which include one Al-doped sample and three undoped

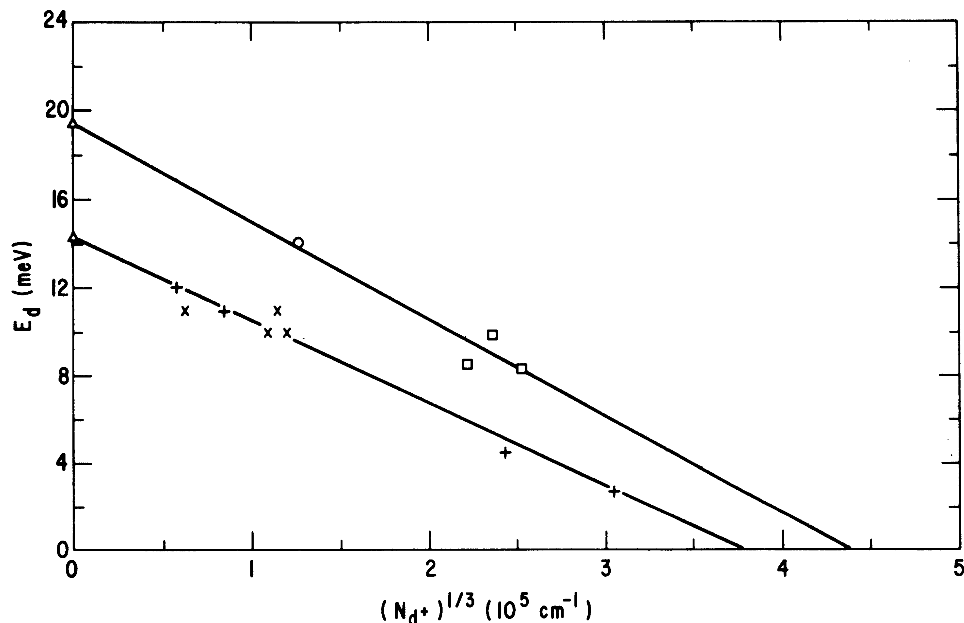

FIG. 3. E_d as a function of $(N_{d^+})^{1/3}$ for CdSe (circles and squares, upper line) and for CdTe (x's and crosses, lower line). The triangle points are from optical measurements.

samples. In the analysis of their data, g was set equal to 1. Since throughout our paper we have assumed we are dealing with a simple, single donor defect, we have used $g=0.5$. Thus, the acceptor concentrations calculated by Agrinskaya *et al.* have been exactly halved before inclusion in in Fig. 3. This is probably an overcorrection, but the exact correction would depend on the type of curve fitting they carried out as well as the particulars for each sample. Their group-II samples, which show a 20% deeper level, are hard to understand. They suggest that they arise from the column-VII donors whereas the group-I samples are dominated by the column-III donors. However, optical studies[14] indicate less difference (and this is only 0.2%) between Al- and Cl-doped ZnSe than between Al- and In-doped ZnSe. (CdTe is not expected to behave differently.) It is noted that these group-II samples are very highly compensated. Also, no samples showing these deeper levels have been measured in our laboratory. The possibility that they represent different dopants or different native defects cannot be ruled out as, for example, the difference between F- and Cl-doped ZnSe is of the same order of magnitude.[14] All in all, we do not consider their group-II samples typical and we have not included them in our analysis.

The second source of data is from the work of Segall *et al.*[4] and is indicated in Fig. 3 by the ×'s. These are all from undoped samples. One of their samples (B) has not been included in Fig. 3. This sample shows an anomalously low E_d value and a high mobility maximum for the calculated acceptor concentration, similar to that noted above for many of the CdS samples.[2]

Carrying out the statistical analysis, as described above, on these eight selected CdTe data points yields the following: $E_0 = 14.3 \pm 0.5$ meV and $\alpha = (3.8 \pm .4) \times 10^{-5}$ cm meV. The triangle datum point is again the value obtained from optical studies (see Table I).

IV. DISCUSSION

A. Hydrogenic model

The only simple theory for "shallow" donor (or acceptor) defects in a semiconductor is the hydrogenic model. The criterion for the use of this model is largely a self-consistent one. It is based on the idea that the wave function describing the bound electron is spread out over many lattice atoms and hence can be described in terms of the single-electron effective-mass theory. Thus, only the long-range Coulombic interaction is effective as in the case of the hydrogen atom. Because of the relatively large dielectric constant of most semiconductors, the Coulombic field and the corresponding binding energy between the donor atom and the bound electron are reduced over that of the hydrogen atom. This, in turn, ensures that the electron is indeed in a large orbit and justifies the use of the macroscopic crystalline dielectric constant and the conduction-band effective mass. In particular semiconducting systems, however, the actual chemical character of the defect can make a significant difference since the 1s ground-state orbit does spend considerable time on the donor atom and its immediate environs (central core corrections). For example, the ratio of the ionization energy of the interstitial Li donor to that of the substitutional As donor in both Ge and in Si is 0.7 while the same ratio between Li and Bi in Si is less than 0.5.

Numerically, the hydrogenic binding energy E_H is given by

$$E_H = 13\,600\;(m^*/m)/k^2, \quad (5)$$

where E_H is given in meV, m^*/m is the electron-effective-mass ratio, and k the relative dielectric constant. There are choices as to which effective mass and dielectric constant values should be used. Most simply stated, the choice for the effective mass revolves around whether the lattice atoms can follow the motion of the hydrogenic bound electron. Three general frequency or energy ranges have been discussed. These are, first, piezoelectric frequencies and lower frequencies, important in CdS and to a lesser extent in CdSe; second, the range between the piezoelectric resonance and the reststrahlen resonance; and third, the range above the reststrahlen frequency. The hydrogenic model in the systems of interest to us involves energies corresponding to the middle range. Hence, the proper mass values to use are the polaron effective mass values excluding any piezoelectric effects. The use of the polaron effective mass for electrons bound to donors has been investigated by Larson who concluded that the simple hydrogenic model is valid even for a polar coupling constant of 1.[17] The choice of the proper dielectric constant is simpler since the potential around the fixed donor atoms is determined by the true static (dc) dielectric constant taken at constant stress.

For CdS and CdSe, a further complication is introduced relating to the fact that these systems have the hexagonal wurtzite structure and exhibit a degree of crystalline anisotropy. Where anisotropies have been measured, the geometric averages have been taken, i.e., $\bar{k} = (k_\perp^2 k_\parallel)^{1/3}$ and $\bar{m}^* = (m_\perp^{*2} m_\parallel^*)^{1/3}$. The use of an averaged dielectric constant in standard effective-mass theory has been reexamined by Schechter for the II-VI compounds.[18] The simple geometric average em-

ployed here is numerically equivalent to Schechter's Eq. (5) for the anisotropies and accuracies involved. It is noted that Schechter uses room-temperature values for the dielectric constant whereas we use estimated 77°K values.

Table I lists the various parameters discussed and the calculated and measured values of the hydrogenic donor ionization energies. To summarize, $\overline{m}^*/m$ is the polar effective-mass ratio (averaged for CdS and CdSe), $\overline{k}$ is the low-temperature dc dielectric constant taken at constant stress (averaged for CdS and CdSe), E_H the calculated hydrogenic donor ionization energy using Eq. (5), E_{op} the donor ionization energy determined from optical measurements, and E_0 and α as given by Eq. (2). Considering the known[14] and potential differences that can exist between different defects and the many uncertainties involved, the various values for E are in excellent agreement.

B. CdS

An often quoted value of E_0 for CdS is that of Piper and Halsted[11] of 32 ± 2 meV. This value was obtained as an average value of two samples, the data of which are shown as the top two curves in their Fig. 1. Inasmuch as this value is considerably higher than any we had measured, a reanalysis of their data was undertaken. Since neither the original data nor the samples were available, data were reconstructed from the original drawings. This was carried out for the top three curves of their Fig. 1 represented by the filled circles, open circles, and open diamonds, and designated here as samples PH1, PH2, and PH3, respectively. The data were then computer fitted to Eq. (2) resulting in N_a and E_d values of 2.4×10^{15} cm^{-3} and 34 meV, 5.0×10^{15} cm^{-3} and 30 meV, and 1.8×10^{16} cm^{-3} and 22 meV for PH1, PH2, and PH3, respectively. These results are shown in our Fig. 1 as crosses. As indicated above, other samples of CdS grown by Piper and co-workers,[11,12] were included in the present study. They, like PH3, fit in well with the present data. Also, the measured mobility maximum for PH2 and PH3 agree well with the calculated mobility while the mobility maximum for PH1 is actually lower than for PH2. It is concluded from the mobility maximum and N_a values that these samples are not purer than typical "undoped" CdS and that the measured E_d values for PH1 and PH2 are anomalously high. Whether they represent an experimental problem or a nontypical defect center cannot be ascertained.

C. Models

Formulations other than Eq. (4) for analyzing the lowering of E_d have been suggested and used by others.[9] These involve, for the most part, the substitution of n, N_d, N_a, or combinations of these for N_{d^+} in Eq. (4). Replacing N_{d^+} by N_a makes little difference in our data since the two are equal except for our heaviest doped samples where there is only a slight difference. Since most of our samples show normal freeze-out, substitution of n makes little sense. The substitution of N_d for N_{d^+} does not give satisfactory fits to our data. It is noted that we are interested in the lowering of E_d for the purest samples available rather than in the actual onset of degeneracy or metallic conduction and, as has been pointed out,[5] no one model or interaction is expected to explain the lowering of E_d from the infinitely dilute situation to degeneracy.

No attempt will be made to critique various theoretical ideas. However, we would like to point out that "distant" or "random" pairing, involving simple Coulombic interactions and which has been successful in explaining exciton line spectra and luminescent emission spectra,[10] can be qualitatively invoked here. For example, the lowering of the potential energy at a donor atom by a distant compensated acceptor (a singly, negatively charged defect) is q^2/kr or, numerically for CdS, 1.58×10^{-5} meV$/r$, where r is in cm. Taking the average distance between donors and acceptors to be $\frac{1}{2}$ the average distance between the acceptors, then,

$$E_d = E_0 - 3.2\times 10^{-5} N_a^{1/3} . \qquad (6)$$

The numerical coefficient is in reasonable agreement with α (see Table I). The more detailed calculations of Wallis *et al.*[19] indicate that when the binding energy is about half the unperturbed value, deviations from Eq. (6) become noticeable and, in fact, give a convex downward curve such as exhibited by the circle and square data points of Fig. 1. A quantitative fit, however, is beyond the accuracy of the data. Also, there is the problem of averaging the potential over the many neighboring ions and as pointed out above, other mechanisms for lowering E_d may become important at the higher doping levels. Any tendency for clustering or nonrandom association of donor acceptors will drastically change this simple Coulombic model. Such pairing may, in fact, be part of the problems noted above for highly compensated CdS, not only in the observed lowering of E_0, but in the substitution of dipole scattering for isolated charged impurity scattering, raising the extrinsic mobility.[2] A more detailed quantitative examination will be required to judge the significance of these ideas.

V. CONCLUSIONS

This study has been concerned with the shallow donor defects in the II-VI compound semiconductors ZnSe, CdS, CdSe, and CdTe which dominate

the electrical conductivity. It has been shown from electrical measurements that the defects are hydrogeniclike and, when defect interactions are considered, their level depths are given by the simple hydrogenic formula to within the experimental accuracies of the measurements involved. The primary defect interaction lowering the level depth for these dilute samples (undoped or lightly doped samples only were studied) is described by a $(N_{d^+})^{1/3}$ dependence. Highly compensated samples show an additional shift which, it is suggested, may be related to nonrandom pairing of donors and acceptors.

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[1]See, e.g., S. S. Devlin, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967), Chap. 11.

[2]H. H. Woodbury, preceding paper, Phys. Rev. B 9, 5188 (1974).

[3]H. H. Woodbury, in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 244.

[4]B. Segall, M. R. Lorenz, and R. E. Halsted, Phys. Rev. 129, 2471 (1963).

[5]H. Fritzsche, Phys. Rev. 99, 406 (1955). See also N. F. Mott and E. A. Davis, Philos. Mag. 17, 1269 (1968).

[6]G. F. Neumark, Phys. Rev. B 5, 408 (1972).

[7]Also included would be the effects of excited states which have been neglected in Eq. (2). See J. S. Blakemore, *Semiconductor Statistics* (Pergamon, New York, 1962), Chap. 3.

[8]H. H. Woodbury and M. Aven, in *Radiation Damage in Semiconductors, Proceedings of the Seventh International Conference on Physics of Semiconductors, Paris, 1964* (Dunod, Paris, 1965), p. 179.

[9]See, e.g., Ref. 6 and P. P. Debye and E. M. Conwell, Phys. Rev. 93, 693 (1954), and references quoted therein.

[10]See, e.g., F. Williams, Phys. Status Solidi 25, 493 (1968) and references therein. Also, R. E. Halsted, in Ref. 1, Sec. 8.4.

[11]W. W. Piper and R. E. Halsted, in *Proceedings of the International Conference on Semiconductor Physics* (Czechoslovak Academy of Sciences, Prague, 1961), p. 1046.

[12]W. W. Piper and S. J. Polich, J. Appl. Phys. 32, 1278 (1961).

[13]See, e.g., M. Aven, J. Appl. Phys. 42, 1204 (1971).

[14]J. L. Merz, H. Kukimoto, K. Nassau, and J. W. Schiever, Phys. Rev. B 6, 545 (1972).

[15]R. A. Burmeister and D. A. Stevenson, Phys. Status Solidi 24, 683 (1967).

[16]H. V. Agrinskaya, E. N. Arkadeva, and D. A. Matreev, Sov. Phys.-Semicond. 5, 762 (1971).

[17]D. M. Larsen, Phys. Rev. 187, 1147 (1969).

[18]D. Schechter, Phys. Lett. A 26, 622 (1968).

[19]R. F. Wallis, R. Herman, and H. W. Milnes, J. Molec. Spectros. 4, 51 (1960).