PHYSICAL REVIEW B VOLUME 9, NUMBER 12 15 JUNE 1974

Anomalous mobility behavior in CdS and CdTe: Electrical evidence for impurity pairs

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(Received 5 November 1973)

An anomalous mobility behavior in certain n-type CdS and CdTe samples has been observed. This behavior is characterized by low-temperature-Hall-mobility maximums which are much higher than can be understood on the basis of simple impurity-charge scattering. The anomaly correlates with the level depth of the hydrogenic-donor defects controlling the conductivity, the degree of compensation, and with the thermal annealing history of the sample. It is suggested that the effect is due to defect pairing.

I. INTRODUCTION

In the course of a reexamination of electrical-transport data on CdS,[1] a correlation was noted between the shallow-donor level depth, the low-temperature-mobility maximum, and the degree of compensation which in turn correlated with the thermal annealing treatment of the sample. This correlation is described in this paper and is tentatively explained by the interaction of donor and acceptor defects as "distant" or randomly distributed pairs. Such distant pairs have been predicted in semiconductor systems and have been extensively studied through optical experiments.[2] Close or preferential pairing occurs when the attractive interaction between the defects forming the pair are greater than the randomizing effects of kT and a significant fraction of the paired defects occupy neighboring and/or nearby ("close") lattice sites. Close pairing results essentially in the annihilation of the levels and has been observed electrically.[3] This paper, however, is believed to be the first report of "small" perturbations of the electrical-transport properties by distant donor-acceptor pairs.

In Sec. II an analytical expression for the mobility in CdS is derived. This is used in the analysis of Hall-mobility data in Sec. III. Also included in Sec. III are some results on CdTe and a description of the correlations that exist among different samples. Section IV discusses these results and some qualitative considerations of defect pairing.

II. ANALYSIS OF THE MOBILITY

For convenience in the interpretation and analysis of the mobility data, an analytical expression for the Hall mobility of CdS was developed. To keep the expression as simple as possible, it was assumed that the mobilities determined by the various scattering mechanisms added reciprocally. Also, no attempt was made to include the temperature dependence of the various materials parameters involved nor the variations in the Hall factor with scattering mechanisms, temperature, etc. In the numerical expressions below, the mobility is given in units of $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{sec}^{-1}$ and the temperature T is in °K.

The intrinsic mobility in CdS is determined by longitudinal-optical-phonon scattering (μ_0)[4] and by piezoelectric scattering (μ_p).[5] The form of these mobilities was taken to be

$$\mu_0 = A\,T^{1/2}[e^{\theta/T} - B]\,,$$

$$\mu_p = C\,T^{-1/2}\,,$$

where, theoretically, $B=1$ and A and C depend on the various materials parameters. Using the low-temperature values of the materials parameters, Devlin[6] finds, with no adjustable parameters, that $C=81\,000$. Attempts to adjust the value of $C \pm 10\%$ from this value (along with adjustments in A and θ) resulted in worse fits to our data. The experimental values of Fujita *et al.*[7] are too low to fit our data. Because of the onset of impurity scattering, the intrinsic mobility in the dominantly piezoelectric temperature range (below 50 °K) has not been measured in conducting samples under normally dark conditions and thus the anisotropy in the piezoelectric scattering are largely masked.[6,7] In the present measurements, no attempts were made to measure anisotropies. Most samples, in fact, were cut avoiding simple crystallographic directions to minimize chipping.

The parameter θ in μ_0 (equal to $\hbar\omega_l$) was taken to be 0.038 eV or 440 °K.[8] Again, attempts to adjust this parameter to obtain a better fit to the data were unsuccessful. Because of the approximations noted at the beginning of this section, it was impossible to get a good fit to the data over the whole temperature range (up to 367 °K) taking $B=1$. A reasonable fit to the data below 200 °K could be obtained, however, with $A=8.1$ and $B=1$. This value of A is in good agreement with theoretical estimates. To obtain a better empirical fit, values of A and B of 8.6 and 1.8, respectively, were adopted. This gave a fit to the data of better than 5% in the intrinsic range up to 298 °K using the expression

$$\mu(\text{intrinsic}) = 1/(1/\mu_0 + 1/\mu_p).$$

Above room temperature this empirical relationship deviates rapidly from the correct value but below it agrees well with Devlin's calculations and data[6] as well as our own.

The Hall mobility determined by charged-impurity scattering (μ_I) was calculated using the formulation of Blatt.[9] This expression involves the use of the Born approximation and is valid for the parameter $b \gg 1$ (see below). Our interest is principally the determination of the low-temperature-mobility maximum which, in our CdS samples, occurs with values of $b > 10$ for the highest dopings considered. No adjustments in the parameters of μ_I were attempted, the various coefficients being calculated using the appropriate effective mass and the averaged low-temperature dielectric constant.

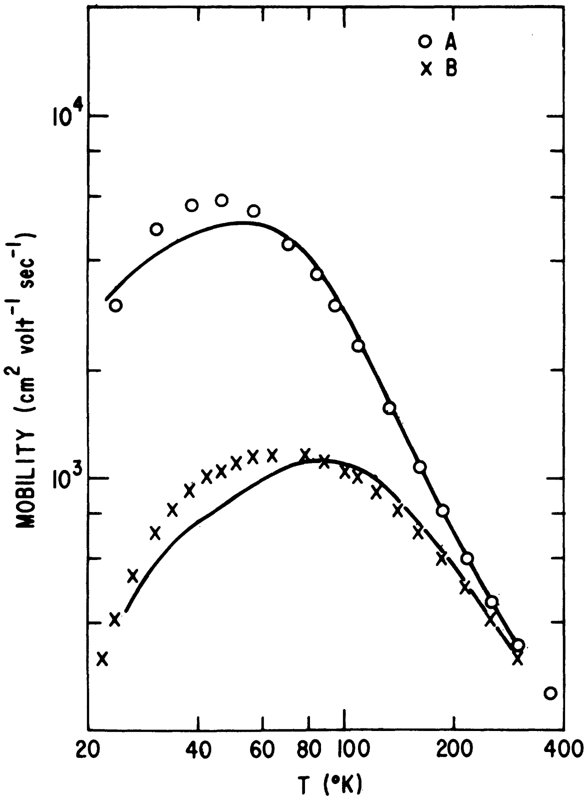

FIG. 1. Data points are the Hall mobilities vs temperature for two CdS samples described in Table I. The two curves are the corresponding mobilities using Eq. (1) and the values given in Table I.

In practical units, this semiempirically derived expression for the Hall mobility is

$$\mu = 1/(1/\mu_0 + 1/\mu_p + 1/\mu_I), \tag{1}$$

where

$$\mu_0 = 8.6T^{1/2}(e^{440/T} - 1.8), \tag{2}$$

$$\mu_p = 81\,000T^{-1/2}, \tag{3}$$

and

$$\mu_I = 1.16\times10^{18}T^{3/2}N_I^{-1}(\ln b - 1)\,[\ln(3b/2) - 1]^{-2}, \tag{4}$$

where

$$b = 2.45\times10^{14}T^2N^{-1},$$

$$N_I = 2N_a + n,$$

$$N = n + (N_a + n)\,(N_d - N_a - n)/N_d,$$

and N_d, N_a, and n are the total donor, compensating acceptor, and free-carrier concentrations, respectively, all in units of cm^{-3}.

When the compensating acceptors are not randomly distributed in the lattice (actually, a "random" distribution is interpreted above as a uniform distribution) but are preferentially paired

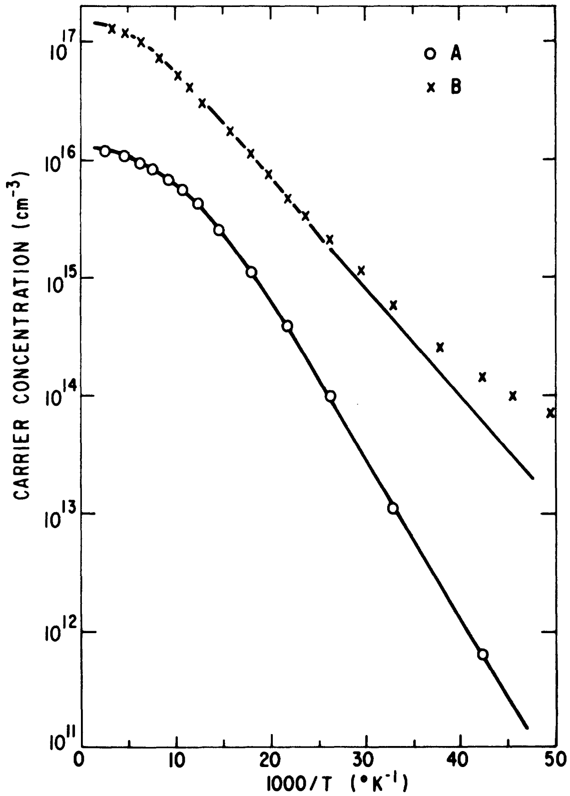

FIG. 2. Carrier concentration $[1/(eR_H)]$ vs 1000/T for the samples shown in Fig. 1.

with donors, the impurity scattering will become dipole scattering with a resultant increase in the mobility under extrinsic conditions. For a complete association of donors and acceptors on neighboring sites, the scattering is negligible, particularly in CdS where the piezoelectric scattering dominates the low-temperature intrinsic mobility. The same is true of neutral-impurity scattering[10] for the doping levels considered here.

III. RESULTS

A. CdS

The data reported here were taken, for the most part, on "Hall bars" typically 10×3×2 mm although some "van der Pauw plates" were also measured. Rather large In contacts were also typical and no attempt was made to calculate corrections for geometry or contact size. Instead, the mobility was normalized to the room-temperature (298 °K) value of 350 $\mathrm{cm^2\,V^{-1}\,sec^{-1}}$ or the calculated lower value in cases where impurity scattering affects the room-temperature value. To the extent that the geometric corrections are mobility independent, this normalization provides a first-order correction to the data. It was seldom more than 10%. A magnetic field strength up to 7.5 kG was used and no significant field dependence down to 1 kG was observed. The mobility was always calculated from the ratio of the Hall coefficient and resistivity with the Hall factor taken to be 1. The Hall factor was also always taken to be 1 in determining carrier concentrations, etc.[11]

Figures 1–4 give typical results of Hall measurements taken on CdS. Table I lists the sample characteristics for the four samples shown in these figures. Figure 1 shows "normal" behavior with the solid curves being the calculated mobilities using Eq. (1). Figure 3 shows typical "anomalous" behavior of two samples. The top solid curve is the "intrinsic" mobility calculated using Eq. (1) with $1/\mu_I = 0$, while the two lower curves are the calculated mobilities for the two samples including μ_I using the concentrations given in Table I. It is clear that the defect concentrations determined from a fit of the Hall-coefficient data do not correspond to isolated charged defects as far as the mobility is concerned. In particular,

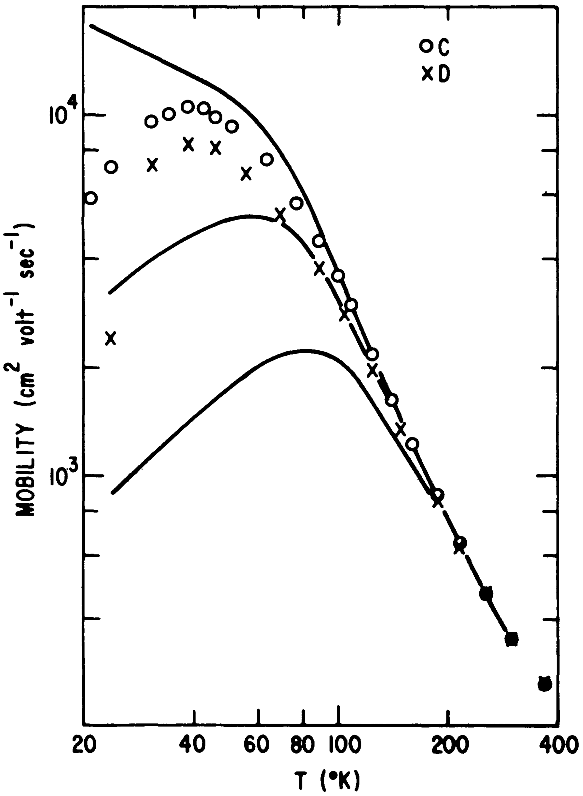

FIG. 3. Data points are the Hall mobilities vs temperature for two CdS samples described in Table I. The top curve is a plot of Eq. (1) with $1/\mu_I = 0$. The two lower curves are the calculated mobilities for the two samples using the values given in Table I.

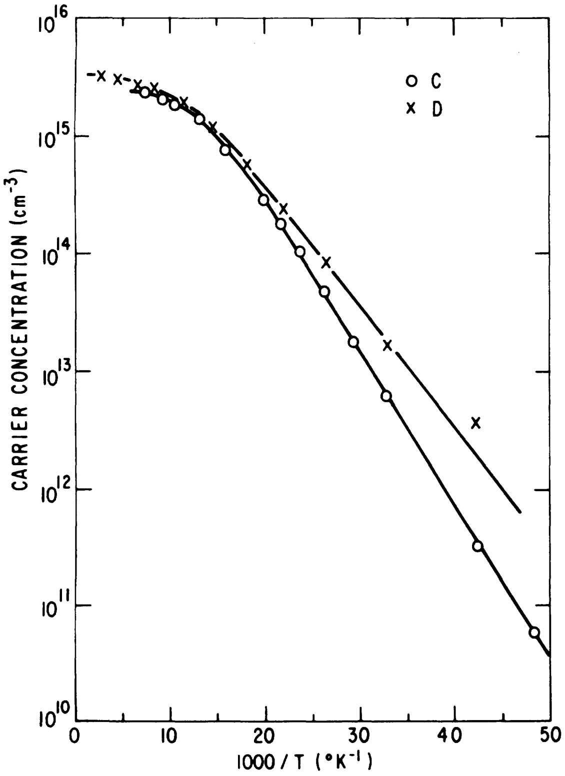

FIG. 4. Carrier concentration $[1/(eR_H)]$ vs 1000/T for the samples shown in Fig. 3.

the acceptor concentration required in Eq. (4) to fit the data of sample *D* is $\frac{1}{10}$ of that measured.

Rather poor fits were obtained in all cases in the extrinsic region (note Fig. 1) although the absolute value of the mobility maximums were consistently given in a large number of cases. The success of this type of analysis for the other II-VI compounds[6,12] leads us to believe that such a calculation of the mobility maximums (which is only a limited test for the impurity-scattering formulation) is a valid test of the sample defect structure. Further analysis on this problem is being pursued.[13]

A plot of the measured mobility maximums (normalized against the 298 °K values) versus N_a is shown in Fig. 5 for the 36 samples referred to in Ref. 1. The calculated mobility maximum is shown by the solid line. This curve was calculated using Eqs. (1)–(4) assuming 50% compensation and typical measured values of n as a function of temperature. For the range of compensations actually measured (15%–85%) no significant differences occur. The two data points lying to the left of the solid line are unique. These samples were taken from "as-grown" ingots. Such samples are often found to be inhomogeneous although the data of these particular two showed a well-behaved pattern, and they did not show any measurable double-acceptor-type defects.

For purposes of exposition, the data in Fig. 5 are divided into three groups, labeled I, II, and III, as delineated by the dotted and dashed lines. These two lines correspond to mobility maximums lying 1.6 and 2.6 times the expected values, respectively. There are some interesting correlations in these samples with respect to E_d, compensation, annealing, and the deviations from the calculated mobility maximums. These are discussed in Ref. 1 and in Sec. III B. It is emphasized that the anomaly presented here consists in a discrepancy between the acceptor concentrations as determined from Hall curve fitting and the acceptor concentrations required to give the observed extrinsic mobility. The observed intrinsic mobility for all samples fits the theoretical temperature dependence very well and no geometrical artifacts or strange behavior in the transport properties are involved.

TABLE I. Characteristics of samples shown in Figs. 1–4.

Curve	A	B	C	D
Annealing[a]				
time (h)	3	none	110	282
temp. (°C)	800		800	700
N_a (10^{15} cm^{-3})	2.8	65	3.0	17.5
N_d (10^{15} cm^{-3})	12.3	270	5.5	21
E_d (meV)	24.8	14.7	22.5	15.7
Mobility maximum				
temp. (°K)	46	70	40	40
n^b (10^{15} cm^{-3})	4	25	0.07	0.10
μ (cm^2 V^{-1} sec^{-1})	5900	1180	10500	8300

[a] In liquid Cd or under Cd vapor.

[b] Free carrier concentration at temperature indicated.

B. Correlations between different samples

The CdS samples which show the anomalously high-mobility maximums (Fig. 5) exhibit several interesting features. All the samples corresponding to the data points in region III of Fig. 5, for example, show greater than 70% compensation and none showing this degree of compensation lie elsewhere. All samples, except two, lying in region II show compensation of 44%–70% and all the remaining samples show less compensation. In general, the samples which have been annealed at the lowest temperature (700 °C) and the longest times (100 h or more) show the greatest compensation and deviations from the calculated mobility maximums. The majority of the samples corresponding to region II were annealed at 800 °C for very long times while the samples in region I were either not annealed after growth, annealed at 900 °C or

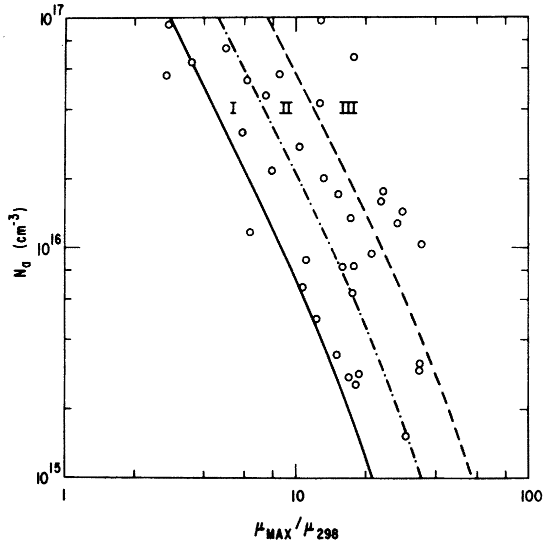

FIG. 5. Plot of the ratio of the mobility maximum to the mobility at 298 °K vs the acceptor concentration as determined from Hall curve fitting for a variety of CdS samples. The solid curve is the calculated value. The dotted and dashed curves divide the data into three convenient regions marked I, II, and III. (See text.)

above, or received only a short (less than 16 h, usually less than 4 h) anneal at 800 °C.

In the following paper,[1] a correlation between the donor level depth and the mobility anomaly is pointed out. Specifically, the shift in level depth (the level depth varies primarily as a function of N_a) for the samples with data points in region II of Fig. 5 is 2 meV less than the samples with data points in region I. The shift between the region-I and -III samples is about 5 meV.

C. CdTe

Sample B of Segall *et al.*[14] appears to exhibit the same anomaly as the anomalous CdS samples described above. This sample shows a factor of 2.1 higher mobility at 25 °K than calculated, whereas the other samples show 0–25% *lower* mobility than calculated. (See Table II of Ref. 14.) The 7-meV ionization energy level of this sample is about 2 meV less than predicted from Fig. 3 of the following paper.[1]

Data taken on "high-purity" multizoned CdTe[15] have also shown this anomaly. For example, an analysis on a recently measured sample gave the following results: $E_d = 9.0$ meV, $N_d = 1.8\times10^{14}$ cm^{-3}, $N_a = 1.4\times10^{14}$ cm^{-3}, and a mobility maximum of 130 000 cm^2 V^{-1}sec^{-1} at 20 °K. This sample was kept at room temperature for 34 months following growth. A companion sample was stored in liquid nitrogen for the same period. Measurement and analysis of this latter sample gave the following: $E_d = 9.1$ meV, $N_d = 3.0\times10^{14}$ cm^{-3}, $N_a = 2.1\times10^{14}$ cm^{-3}, and a mobility maximum of 140 000 cm^2 V^{-1} sec^{-1} at 20 °K. These mobility maximums are the highest seen for CdTe as determined from Hall-transport data.[16] However, they are about a factor of 2 higher than expected from the calculated acceptor concentrations, similar to the anomalous CdS samples. Likewise, the E_d values appear low (compare against the plot on Fig. 3 of following paper[1]).

Annealing these samples at 900 °C in saturated-Cd pressure increased the room-temperature carrier concentrations to over 10^{16} cm^{-3} with the electrical properties dominated by the double-acceptor defect. Annealing at lower temperatures and/or lower Cd pressure results in complete compensation or *p*-type conductivity. These effects are essentially identical to those previously reported,[17] except the starting material exhibits the lower carrier concentrations and higher mobilities noted above. It is concluded that the electrical properties of high-purity CdTe is entirely dependent on deviations from stoichiometry during growth[16] and the specific annealing conditions the ingot sees immediately following growth. In particular, it is suspected that the electrical properties of the multizoned CdTe depend more on the fact that the crystals are grown very slowly under highly controlled conditions rather than reflecting a high degree of chemical purity, which it is believed these crystals also possess. Attempts to reproduce the electrical characteristics of such crystals by carrying out programmed anneals have not been successful; the particular chemical and thermal environment the growing ingot sees apparently is not simple to reproduce. Thus we have the situation where the as-grown ingots, although exhibiting an apparent low defect concentration, also exhibit anomalous mobility behavior while attempts to anneal these samples results in the introduction of higher defect concentrations typical of samples described in the literature.

IV. DISCUSSION

The above facts strongly suggest some type of pairing or clustering of defects although a quantitative correlation has not yet been worked out. Such defect clustering may also explain the deviations in the temperature dependence of the extrinsic mobility from Eq. (4).[13] If a quantitative correlation could be established, this would be the first direct evidence from electrical transport measurements of "distant" pairing effects. Such "pairs" might also be the source of the very low activation energies occasionally reported in CdS.[6]

As noted above, CdTe shows similar behavior to this behavior of CdS. It would be expected that CdSe would be no different. The fact that ZnSe, on the other hand, does not show such effects[1, 12] for similar annealing conditions is taken as an indication that the character of the native defect structure plays an important role in this "pairing-compensation" behavior. The ease with which the Cd chalcogenides can be made *n*-type conducting (attributed to the ability to suppress Cd vacancies) as compared to ZnS and ZnSe (where Zn vacancies and Zn vacancy-donor complexes are always present compensating, to some degree, the donor impurities) is noted as one possibly important difference.

In a more quantitative vein, several items are pertinent. First consider the question of the nature of the defects involved. The CdS samples used in these experiments were either undoped or doped only with donors, in particular, indium or chlorine. The ubiquitous donor impurities, Al and Cl, are in sufficient concentrations in "undoped" material to explain the observed conductivity seen in these crystals.[18, 19] These impurities are not only in the original grown crystals in the range $(1-10)\times10^{15}$ cm^{-3}, but they can be easily introduced in greater concentrations through the handling of the samples and subsequent diffusion on thermal treatment. Acceptor impurities are not the problem in the Cd chalcogenides that they are in the Zn chalcogenides and are more easily controlled, especially under Cd firing conditions.[20] The isolated native defects are very rapid diffusing entities and are not seen electrically at room temperature no matter how fast the samples are quenched. Thus, although the compensation of our samples is probably through *complexes* involving native defects, it is difficult to formulate a defect model that is consistent with all the data.

In the description of donor-acceptor pair formation arising from electrostatic interactions, the ratio of the Coulombic energy to the thermal energy, properly weighed by available site densities and distances, determines the pairing distribution. For our lowest annealing temperatures of 700 °C and highest impurity concentration of 3×10^{17} cm^{-3}, the calculations of Prener[21] indicate that close-pair formation would not occur in any significant degree between singly charged defects. If one of the species were doubly charged, however, then pairing would take place under these conditions. However, the extrinsic mobility would be expected to show more normal values or be even lower. Another factor is that a high concentration (10^{17} cm^{-3} and greater) of native donors is created under the conditions employed (usually excess Cd) which keeps the samples intrinsic and washes out the electrostatic interactions between charged species. Thus close pairing must take place during the cooling of the samples[22] or result from other energy considerations such as lattice strains arising from the dissimilar physical nature of the various defects.

Without a definitive defect model, much that can be said is speculative. However, a quantitative approach to the problem could be made using simple models. For example, is it possible, assuming singly charged defects uniformly distributed in the lattice, to explain the Hall curve analysis (i.e., the determination of N_a and N_d), the increase in the extrinsic mobility due to dipole formation,[23] and the decrease in the ionization energy of the electrically controlling species due to Coulombic interactions[1]? A preliminary calculation on dipole scattering indicated that the defects would have to be so close that the ionization energy would be reduced much lower than what is measured. However, the total Coulombic interaction of all of the defects is very complicated and further analysis is needed.

In conclusion, it is emphasized that the anomalies described in this paper are amply described, qualitatively, by "distant" defect pairing. However, a more detailed quantitative analysis needs to be carried out to verify such a model. In particular, it is well to keep in mind that the defect structure of these compound semiconductors is proving to be quite complicated and the nature and properties of many types of complexes are yet to be unraveled.

ACKNOWLEDGMENTS

Many individuals have contributed to this work, either in assistance in preparing samples and taking of data and/or in the aiding in its interpretation. The author in particular thanks R. S. Lewandowski for the recent work on CdTe and M. Aven and G. Mahan for valuable help and comments.

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