spins—is clearly impossible.) It appears that just as long-range ferromagnetic interactions are good for classical methods, long-range oscillatory interactions lead to these fluctuations and are bad for classical or semiclassical methods applied for small spins.

We have examined the Anderson spin-wave theory of antiferromagnetism[14,15] which is patently correct in case (a) (although it is not mathematically exact). However, in spin-wave stable systems the approximate antiferromagnetic eigenstate has in general a complex energy and is, therefore, unstable, even in such a favorable model as we have considered, where nearest neighbor bonds are antiferromagnetic, and the lattice is three-dimensional simple cubic.

This suggests that in those spin-wave stable systems which are not actually ferromagnetic because small spins ($\frac{1}{2}$ or 1) and antiferromagnetic bonds favor quantum fluctuations, the long-range ground-state correlations might either vanish, or exhibit a more complicated structure than has heretofore been thought likely on theoretical grounds without introducing anisotropy.

Carrier Mobility and Shallow Impurity States in ZnSe and ZnTe†

M. Aven and B. Segall

General Electric Research Laboratory, Schenectady, New York

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Electrical transport measurements have been made on p-type ZnTe and n-type ZnSe. In ZnTe crystals, doping with Cu, Ag, and Au produces acceptor levels at 0.15, 0.11, and 0.22 eV, respectively. An acceptor with an ionization energy of 0.048 eV was found in the undoped crystals and is identified as the first charge state of the Zn vacancy. A shallow donor state, at approximately 0.01 eV below the conduction band, was found in n-type ZnSe. It also proved possible to prepare degenerate ZnSe. The scattering mechanisms limiting the lattice mobilities of both materials were considered. It was found that the polar interaction with the longitudinal optical phonons dominates the scattering of electrons in ZnSe. This mechanism probably also predominates in the scattering of the holes in ZnTe. However, the nonpolar interaction with the optical modes could also contribute significantly if the appropriate coupling parameter is larger than we presently believe.

I. INTRODUCTION

SEVERAL of the II–VI compounds have been under investigation by luminescence and photoconductive techniques for a great many years. Much of this work was directed toward the goal of understanding the role of the impurities and of identifying the states associated with them. Despite this work, however, the identification of the specific impurity states is still a matter of considerable debate and uncertainty. At present there is still little conclusive evidence about the identity of any shallow impurity states, which, for example, play an important role in the optical properties of these crystals.

The primary aim of the present work was to obtain additional information about the shallow donor and acceptor levels in some of the II–VI compounds by means of electrical transport studies. In the past, extensive electrical measurements have not generally been possible due to the unavailability of suitable material. However, considerable advances have recently

been made in the preparation of some of these materials, including the compounds that are the subject of the present study, ZnSe and ZnTe.[1-3] It is, of course, well known that in addition to yielding information about the energy levels of the defects, the electrical transport measurements provide a valuable means for studying the mechanism by which the carriers are scattered. This question was considered in some detail for the two compounds studied.

In an earlier work, the results of optical and preliminary electrical measurements on ZnSe were reported.[4,5] The electrical measurements of the n-type

[1] L. R. Shiozawa, J. L. Barrett, G. P. Chotkevys, S. S. Devlin, and J. M. Jost, Aeronautical Research Laboratory Contract No. AF 33(616)-6865, Final Report, Period January 1960–December 1961 (unpublished).

[2] A. G. Fisher and A. S. Mason, Air Force Cambridge Research Laboratories Contract No. AF 19(604)-8018, Scientific Reports Nos. 1, 2, and 3, 1961 (unpublished).

[3] M. Aven and W. W. Piper, Air Force Cambridge Research Laboratories Contract No. 19(604)-8512, Scientific Report No. 1, 1961 (unpublished).

[4] M. Aven, D. T. F. Marple, and B. Segall, J. Appl. Phys. 32, 2261 (1961).

[5] M. Aven, Extended Abstracts, Meeting of the Electrochemical Society, Los Angeles, 1962, p. 46.

material have been considerably extended in the present work. A moderately deep level, apparently similar to one reported by Bube and Lind,[6] was observed to have a depth of 0.19 eV. In more strongly n-type material a shallow level with an ionization energy $\sim$0.01 eV was observed for the first time. It has also proved possible to prepare crystals of this compound which exhibit degenerate conduction characteristics.

We have also investigated some of the transport properties of p-type ZnTe. The study of this compound is of considerable interest since the knowledge gained about the transport of holes in the valence bands and of the acceptor states would be expected to be helpful in understanding the corresponding properties and states of the other II-VI semiconductors. In regard to the study of acceptor levels, significant progress was made possible as a result of the successful purification by the zinc extraction technique recently described by Aven and Woodbury.[7] By impurity diffusion and extraction cycles, in conjunction with radioactive tracer studies, it was possible to identify the acceptor levels associated with the most prominent acceptor impurities —Cu, Ag, and Au. Concomitantly, the acceptor state of the native defect, which we believe to be the zinc vacancy, could be identified. It is to be emphasized that analogous states are believed to be associated with the other crystals of this family of semiconductors, but until this time the identification of these states has not been conclusively established.

From the study of the Hall mobility, the intrinsic (or lattice) mobility for the two materials could be determined for temperatures above about 100°K. The various possible lattice scattering mechanisms were considered with the aim of determining which of them play the major role in limiting the intrinsic mobility. For n-type ZnSe it is found that the electrons are scattered much more strongly by the polar scattering of optical phonons than by other mechanisms. A similar conclusion is probably also true for ZnTe, unless the parameter characterizing the strength of the nonpolar coupling to the optical mode phonons is much larger than presently believed.

II. EXPERIMENTAL

The ZnSe and ZnTe crystals were grown by the vapor growth technique first described by Greene *et al.*[8] and modified by Piper and Polich.[9] The starting material for ZnSe was General Electric Chemical Products Plant ZnSe powder which was first sintered in the presence of excess Se in hyprogen atmosphere. ZnTe was synthesized by heating together high-purity Zn obtained from the Consolidated Mining & Smelting Com-

pany and high-purity Te obtained from the American Smelting & Refining Company. The single crystals were grown by passing the sintered charge at the rate of approximately 0.2 mm/h through a furnace heated to 1350°C for ZnSe and to 1050°C for ZnTe. The product was usually a boule of several cm^3 containing single-crystal regions of a tenth to one cm^3.

The majority of the crystals were subjected to the purification technique in which the crystals are heated in contact with molten Zn at 900–1000°C for one or two days. This treatment has been shown[7] (by using radioactive tracer techniques) to reduce the concentration of the acceptor impurities Cu and Ag in II–VI compounds to the 10^{14} to 10^{15} cm^{-3} range. With the exception of Cl-doped ZnSe, all the doped crystals were obtained by diffusing impurities into crystal purified by the solvent extraction method. Chlorine-doped ZnSe was prepared by adding SrCl$_2$ to the starting material prior to the crystal growth.

The Hall measurements were performed with sample bars 8–10 mm long and 1–4 mm^2 in cross-sectional area, cut from the boules described above. Prior to electroding, the bars were chemically polished in hot concentrated NaOH. The electrodes to ZnSe were In dots fused-in under hydrogen atmosphere at 300°C. The electrodes to ZnTe were chemically formed Au patches, to which Pt wires were soldered with In-Ag alloy.

The Hall effect apparatus used for electrical measurements covered the range from liquid-hydrogen temperature to approximately 150°C. The measurements were performed by the standard six electrode technique widely used on semiconductor materials. The voltage drop across the crystal was usually of the order of 0.1 V. The magnetic fields used were between 7 and 8 kG. To assure that no irreversible changes had occurred in the bulk of the crystals or the electrodes during the thermal cycling, several of the crystals were remeasured over the entire covered temperature range. A few crystals were removed from the apparatus, re-electroded and remeasured. In no cases were any irreversible effects observed. However, with all crystals a minimum temperature was always encountered below which the measurements became unreliable because of the onset of non-Ohmic behavior of the electrical contacts. Thus, for any given crystal, the temperature range for which the measurements are given was determined by the lowest temperature at which the Hall voltage and the potential drop across the crystal were linear functions of the current through the crystal.

III. RESULTS AND DISCUSSION

Before discussing and analyzing the experimental results, it is useful to state the assumptions about the band structure of ZnSe and ZnTe that are to be used. It appears that both of these compounds are direct transition semiconductors, presumably having the absolute extrema of their conduction and valence

[6] R. H. Bube and E. L. Lind, Phys. Rev. **110**, 1040 (1958).
[7] M. Aven and H. H. Woodbury, J. Appl. Phys. Letters **1**, 53 (1962).
[8] L. C. Greene, D. C. Reynolds, S. J. Czyzak, and W. M. Baker, J. Chem. Phys. **29**, 1375 (1958).
[9] W. W. Piper and S. Polich, J. Appl. Phys. **32**, 1278 (1961).

Fig. 1. Temperature dependence of the Hall coefficient for ZnTe crystals doped with Au (squares), Cu (triangles), and Ag (circles) and for an undoped ZnTe crystal fired in liquid Zn at 900°C (diamonds).
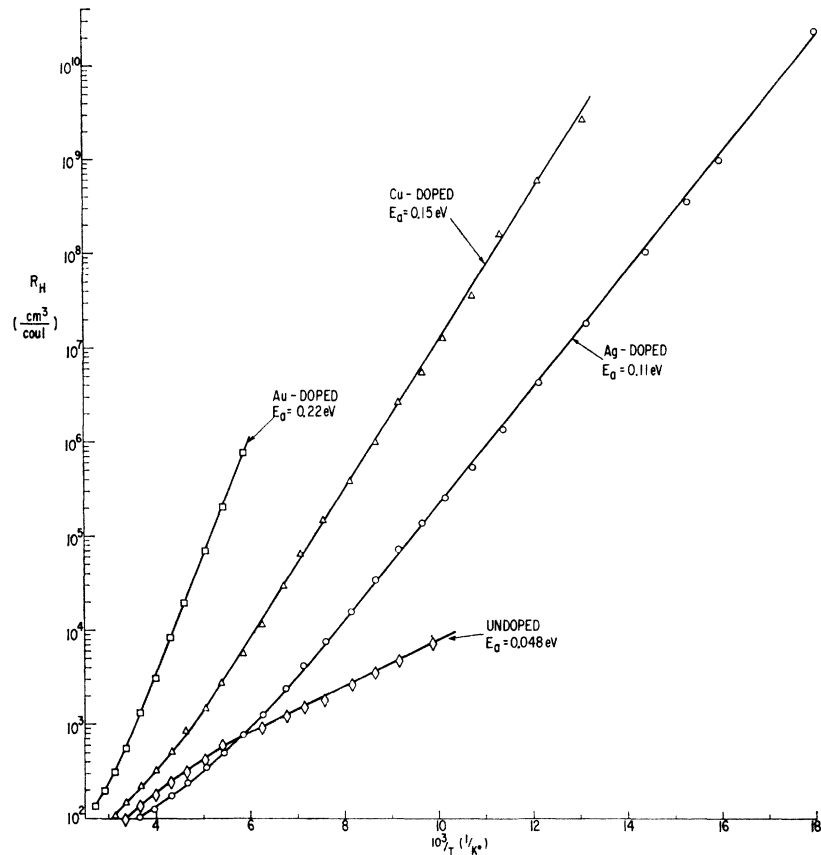
bands at $k=0$. These conclusions are based primarily on the absorption spectra[4,10] (particularly on the sharp exciton lines which are not appreciably broadened by autoionization) and on the emission spectra[11,12] which exhibit sharp lines very close to the band edges.[13] Since we are only to be concerned with n-type ZnSe and p-type ZnTe, only the assumptions about the location of the conduction band minimum of the former and the valence band maximum of the latter have a bearing on the following discussion. The chief effect of this assumption is to exclude the possibility of intervalley scattering.

In addition, it will be necessary to assume values for the effective masses for the carriers. On the basis of a

reduced exciton mass of $(0.10\pm0.03)m$ as deduced in the optical studies of ZnSe,[4] we take $m^*=0.15m$ as a reasonable estimate of the electron mass. Since information relating to the hole mass in ZnTe is unavailable, we are forced to make a more arbitrary choice in this case based on the known hole masses in CdS[14] and CdSe.[15] We take the value of $0.6m$ for the density-of-states mass. Inasmuch as we are not seeking to fit the data precisely this estimate of the hole mass should be adequate for our purpose.

In analyzing the carrier concentration data from a single level, we will use the well-known formula[16] for nondegenerate statistics, e.g.,

$$p(p+N_d)/(N_a-N_d-p) = (N_v/g) \exp(-E_a/kT), \quad (1)$$

for the hole concentration p. Here $N_v = 2(2\pi m_v kTh^{-2})^{3/2}$, m_v being the density-of-states mass and g the degeneracy factor which depends on the nature of the impurity state and the band edge involved. Later when considering the carrier concentration associated with an imperfection which we believe to be a double acceptor,

[10] E. Loh and R. Newman, J. Phys. Chem. Solids, 21, 324 (1961).

[11] R. E. Halsted and M. Aven, Bull. Am. Phys. Soc. 6, 312 (1961).

[12] D. C. Reynolds, L. S. Pedrotti, and O. W. Larson, J. Appl. Phys. 32, 2250 (1961).

[13] On the basis of their optical absorption measurements at absorption constants in the range 5 to 100 cm⁻¹, Aten et al. [A. C. Aten, C. Z. van Doorn, and A. T. Vink, Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962 (unpublished)], have concluded that the lowest energy optical transition in ZnTe is indirect. However, at such low values of α the effects of impurities and of phonon assisted direct exciton transition can be important; and it does not appear that these have been adequately studied. In addition, it would be very difficult to understand the occurrence of the sharp emission lines at energies appreciably larger (~0.1 eV) than the energy of the ndirect gap.

[14] J. J. Hopfield and D. G. Thomas, Phys. Rev. 122, 35(1961).

[15] J. O. Dimmock and R. G. Wheeler, J. Appl. Phys. 32, 2271 (1961).

[16] See, for example, T. H. Geballe, Semiconductors, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), p. 313.
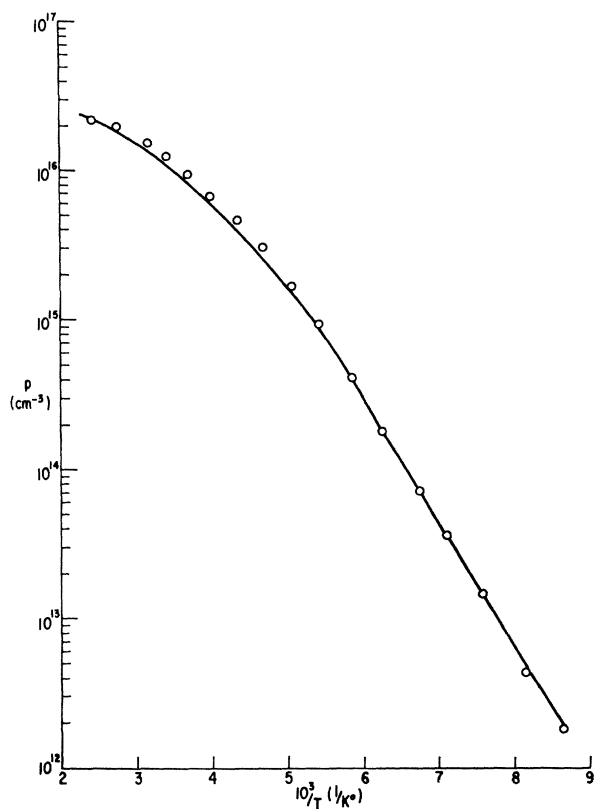
FIG. 2. Temperature dependence of the free-hole concentration for a ZnTe crystal found (by chemical analysis) to contain $(2\pm1)\times10^{16}$ cm^{-3} Cu. The data are indicated by circles. The solid line represents the hole concentration calculated from Eq. (1) with $N_a=3.5\times10^{16}$ cm^{-3}, $N_d=3.1\times10^{15}$ cm^{-3}, and $E_a=0.149$ eV.

curve for the undoped sample, the p-type nature of which we believe to be due to a Zn vacancy, an ionization energy of 0.048 eV is found. The acceptor ionization energies for the Cu-, Ag-, and Au-doped samples are found to be 0.15, 0.11, and 0.22 eV, respectively.

Figure 2 shows more detailed data for a crystal which was found by chemical analysis to contain Cu at a concentration of $(2\pm1)\times10^{16}$ cm^{-3}. The behavior at low T corresponds to the freeze-out of the holes into an acceptor level at 0.15 eV as in the Cu curve of Fig. 1. Using the value of $g=4$ which is appropriate for a simple acceptor associated with the fourfold degenerate valence band maximum,[18] it is possible to fit the data satisfactorily with $N_A=3.4\times10^{16}$ cm^{-3} and $N_D=3.1\times10^{15}$ cm^{-3}. In Fig. 2 the experimental points are indicated by circles, and the theoretical values by the solid curve. It should be noted that the above value of N_A agrees reasonably well with the result of the chemical analysis.

Figure 3 shows the free-hole concentration vs T^{-1} for four undoped ZnTe crystals fired under different Te pressures. The shapes of these curves are sufficiently similar to indicate that the same level is involved in all the crystals. The energy value that corresponds to the low-temperature end of the curves is 0.048 eV (the temperature range for the two lower curves being admittedly very small). The vertical displacement of these curves

we set up the generalization of (1) appropriate to that case. In the following, we take the carrier concentrations p and n to be given by $|R_H e|^{-1}$ for simplicity, where R_H is the Hall constant and e is the electronic charge. The factor $r=\mu_H/\mu_d$,[16] the ratio of Hall to drift mobilities is, thus, taken to be unity. This is, in fact, a fairly good approximation since r is reasonably close to unity for polar scattering[17] which we show below to be the principal scattering mechanism in the temperature range of primary interest here.

ZnTe—Impurity and Native Defect Levels

In the following we discuss the results of Hall measurements on several ZnTe crystals prepared in such a way as to produce a dominance of one type of impurity (including native defect) over all others. With such crystals it is a straightforward matter to identify the various defects giving rise to the energy levels found by the electrical measurements.

A survey of the behavior of the Hall constant R_H vs T^{-1} for typical undoped crystals and crystals doped with the noble metals is provided by Fig. 1. From the
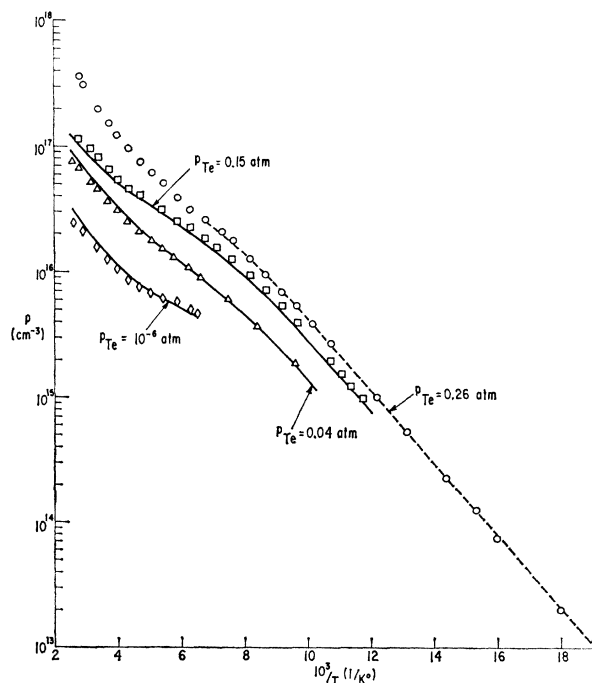

FIG. 3. Temperature dependence of the hole concentrations for undoped ZnTe crystals fired under various partial pressures of Te. Theoretical curves, calculated from Eq. (3), are indicated by solid lines. The dashed curve represents the low-temperature range for the $p_{Te}=0.26$-atm crystal fitted using Eq. (1) (see text).

[17] R. T. Delves, Proc. Phys. Soc. (London) 73, 572 (1959).

[18] S. Teitler and R. F. Wallis, J. Phys. Chem. Solids 16, 71 (1960).

from one another indicates that the free-hole concentration at any temperature increases with increasing partial pressure of Te. The increasing partial pressure of Te increases the concentration of Zn vacancies, which in turn increases the free-hole concentration. These results are consistent with our belief that the native acceptor center is the Zn vacancy.

The above evidence *per se* does not preclude the possibility that the acceptor is interstitial Te. However, this possibility can probably be ruled out on the basis of the very large size of the Te atom and also because it appears unlikely that interstitial Te could bind extra electrons. The tendency of ZnTe to form an excess of Zn over Te vacancies, on the other hand, is consistent with the greater volatility of Zn.

The Zn vacancy is expected to be a double acceptor. In contrast to the curves for the Cu, Ag, and Au-doped samples, the curves for the undoped samples have a shape above about 200°K which suggests the ionization of holes from a deeper level. In order to check the identification and determine the ionization energy of the deeper level, it would be desirable to have hole concentration data available over a wide high-temperature range, and to fit these data with the expression for p appropriate to the case of a double acceptor associated with the fourfold degenerate valence band. Although the present data are perhaps not as extensive as would be desired, it still is useful for a preliminary investigation of this point. To obtain the equation for p we use for the probabilities that the double acceptor is in the neutral, single, or doubly ionized state the expressions derived by Teitler and Wallis,[18] which are

$$N_a^0/N_a = 6R_0^{-1} \exp[2\alpha + \beta(E_1 + E_2)],$$
$$N_a^-/N_a = 4R_0^{-1} \exp(\alpha + \beta E_2), \qquad (2)$$
$$N_a^{2-}/N_a = R_0^{-1},$$

with $N_a^0 + N_a^- + N_a^{2-} = N_a$, $\alpha = -E_F/kT$, and $\beta = 1/kT$. For nondegenerate statistics, the charge neutrality condition $p + N_d = N_a^- + 2N_a^{2-}$ leads to the following cubic equation for p:

$$6p^3 + p^2[4N_v^{(1)} + 6N_d]$$
$$+ p[N_v^{(1)}N_v^{(2)} + 4N_v^{(1)}(N_d - N_a)]$$
$$+ N_v^{(1)}N_v^{(2)}(N_d - 2N_a) = 0, \qquad (3)$$

where $N_v^{(i)} = N_v \exp(-E_i/KT)$ for $i = 1$ and 2. At temperatures low enough so that $N_v^{(2)}$ is negligible Eq. (3) reduces to Eq. (1) with $g = 3/2$ which is the correct statistical factor[19] for this case, while at high temperatures it leads to the proper saturation value of $2N_a - N_d$.

The solid curves in Fig. 3 represent the fit of the data for the three lower Te pressures using Eq. (3). The sample fired at the highest Te pressure was only fitted at low temperatures, using Eq. (1), as this sample was not purified by the Zn extraction method and was known to contain some Cu.[20] In Eq. (3) we used the previously determined value of 0.048 eV for E_1, and 0.13 eV for E_2, although a range of values (roughly 0.12 to 0.16 eV) for E_2 provided reasonably good agreement. The acceptor concentrations, N_a, determined from the fitting of the data for the samples fired under the Te pressures of 10^{-6}, 0.04, and 0.15 atm, were approximately 0.35×10^{17}, 1.2×10^{17}, and 1.7×10^{17} cm^{-3}, respectively. The value of 0.14 ± 0.02 eV for E_2 is admittedly rather close to the ionization energy for Cu acceptors. The high-temperature portion of the curves cannot, however, be due to Cu in the purified samples for, as is shown below, its concentration in these samples is much too low. It is, of course, possible that the ZnTe crystals contain an unidentified acceptor, unextractable by the liquid Zn treatment, in concentrations comparable to that of the Zn vacancies, and that the observed level is due to it. We believe this possibility to be unlikely.[21] However, before the deeper level can be definitely established as the second charged state of the Zn vacancy, more extensive investigations on additional purified and analyzed samples over a more extended high-temperature range would be required.

Three experiments were performed to assure that the thermal treatment to which the crystals were subjected during the diffusion process was not producing other significant changes besides the incorporation of the desired impurities. First, Cu was diffused into two ZnTe crystals which were previously fired under 2-atm Zn pressure and 0.5-atm Te pressure,[22] respectively, and which exhibited the 0.048-eV acceptor levels. In each case the incorporation of Cu resulted in the disappearance of the 0.048-eV level and the appearance of the 0.15-eV level.

In a complementary experiment two crystals, previously doped with Cu and exhibiting the 0.15-eV level, were fired in liquid Zn and liquid Te, respectively. In each case the crystals lost their 0.15-levels and acquired

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[19] This value can be understood by noting that g is the ratio of the number of ways a hole can occupy a singly ionized acceptor to the number of ways a hole can be ionized from a neutral acceptor. Since there are three occupied electronic orbitals in each singly ionized double acceptor (see reference 18) while there are two holes in the neutral state, the ratio is 3/2.

[20] In order to get a precise estimate of the ionization energy of the lower level, it was necessary to extend the measurements for at least one crystal to as low a temperature as possible. This was accomplished by intentionally leaving a small amount of Cu in this crystal, which technique helped to maintain Ohmic behavior of the electrical contacts to lower temperatures.

[21] Of the possible acceptor elements in ZnTe, the alkali metals, the 3d transition elements, and Sb can be ruled out since their concentrations in our samples (as determined by spectroscopic analysis) was too low. P and As, on the other hand, cannot be ruled out on this basis because of their very high limits of detectability. Judging by the available (but admittedly limited) information about these elements in other II-VI compounds (reference 6), the levels introduced by P and As would probably be much deeper than 0.15 eV.

[22] Firing under higher Te pressures led to disintegration of the crystals.
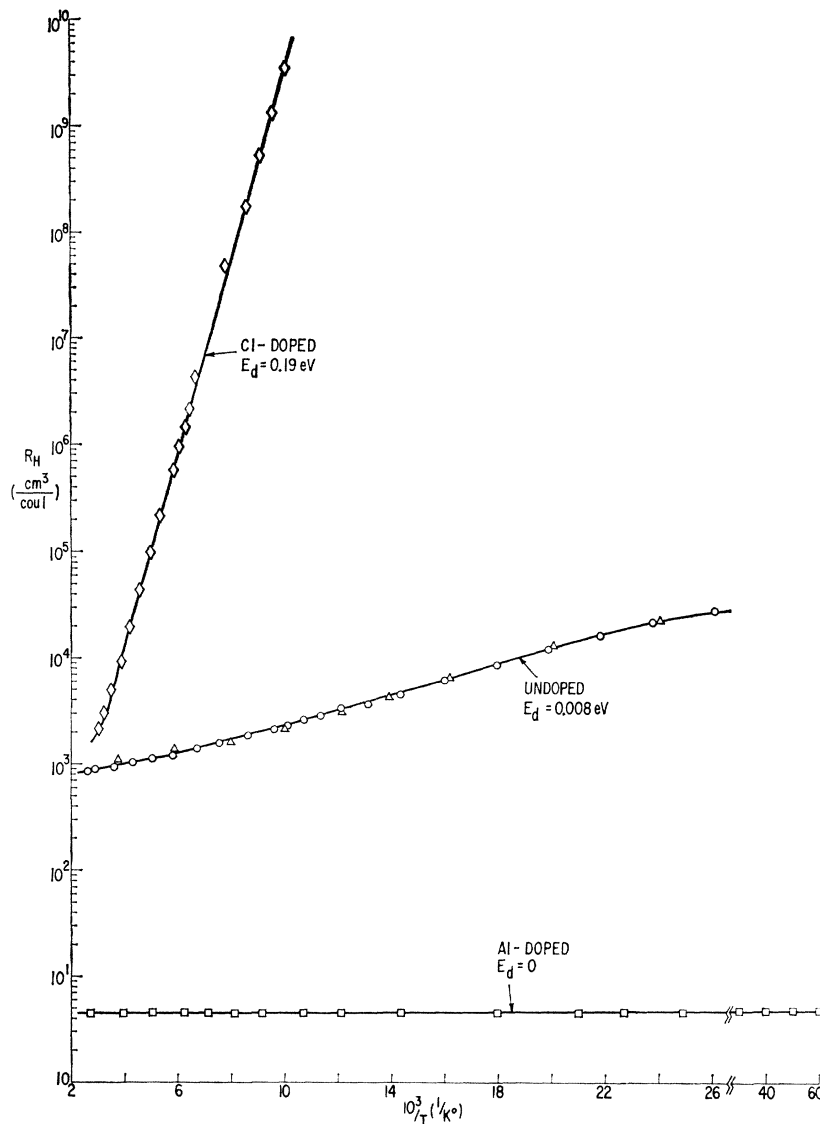
FIG. 4. Temperature dependence of the Hall coefficient for ZnSe crystals doped with Cl (diamonds) and Al (squares) and for an undoped ZnSe crystal (circles). The points calculated from Eq. (1) for the undoped crystal, with $N_d = 9.5 \times 10^{16}$ cm^{-3}, $N_a = 8.7 \times 10^{16}$ cm^{-3}, and $E_d = 0.008$ eV, are indicated by triangles.

the 0.048-eV levels. One crystal was subjected to several Cu diffusion-Zn extraction cycles and was found always to come back to the 0.15-eV level after Cu diffusion and to the 0.048-eV level after the Zn extraction. An analogous behavior was observed with an Ag diffusion–Zn extraction cycle and an Au diffusion–Zn extraction cycle.

In the third experiment the radioactive isotopes Cu[64] and Ag[110] were separately diffused into two undoped ZnTe crystals. The incorporation of the radioactive dopants was carried out by exactly the same technique as that used with the crystal on which the Hall measurements were performed. The Cu and Ag concentration after the diffusion, as determined by an appropriate counting technique, was approximately 10^{17} cm^{-3}. By several successive etchings and countings it was found that the dopants were uniformly distributed throughout the body of the crystal. After extracting both crystals

with liquid Zn, the residual concentration of Cu and Ag in them was found to be approximately 10^{14} cm^{-3}.

These experiments show that the introduction of the employed acceptor impurities is independent of whether the crystal was previously fired under Zn or Te atmosphere. Because of the reversibility of the impurity diffusion–Zn extraction cycles, it is also certain that electrically active uncontrolled impurities were not entering the crystals in significant amounts during the various firing techniques to which the crystals were subjected. It is significant to note that the analysis of the carrier concentration of the Cu-doped sample discussed above leads to an acceptor concentration in fair agreement with the Cu concentration determined by chemical analysis. The experiment with the radioactive Cu and Ag demonstrates that the employed diffusion technique leads to a uniform distribution of the dopant in the crystal in concentrations where it exists in the

crystal as the dominant impurity. The complementary study of the removal of the Cu and Ag radioisotopes by Zn extraction shows that the residual concentration of these impurities in the crystals subjected to this purification technique is several orders of magnitude below the concentration of any of the intentionally introduced acceptors which have determined the electrical properties of the crystals.

Thus, we see there are acceptor states in ZnTe having ionization energies of 0.15, 0.11, and 0.22 eV definitely associated with the presence of Cu, Ag, and Au, respectively. The simplest interpretation of these results is that these metal impurities go into ZnTe substitutionally replacing the Zn. The acceptor states are then directly attributable to the impurities. One feature of this picture which is perhaps disturbing is the closeness of E_a for Cu and for the second level of the Zn vacancy. This circumstance might suggest the possibility of more complex models for the acceptors. For example, it might be assumed that Cu acts as a donor but that it is paired with the vacancy. The 0.048-eV vacancy level is thereby compensated. While complex models like this cannot be completely excluded at present, their complexity alone makes them less attractive. Unless further evidence is adduced to indicate that complexes are involved, we tend to favor the simpler model of the acceptor. The near equality of the two ionization energies is believed to be fortuitous.

ZnSe—Donor Levels

The information to be reported below about donor levels in ZnSe is much less detailed than the above study of acceptor levels in ZnTe. Although the Zn extraction method was found to remove acceptor impurities from ZnSe as effectively as from ZnTe, as yet little is known of its effect on donor impurities. Therefore, in the experiments with n-type ZnSe to be described below, it was not possible to identify the donor levels with particular impurities or native defects.

Figure 4 shows the results of Hall measurements for a ZnSe crystal grown with 10^{19} cm^{-3} Cl (as determined by chemical analysis) and subjected to one extraction with liquid Zn. From the behavior of R_H between 100°K and room temperature, a donor level at 0.19 eV is determined. This value is very close to the 0.21-eV level found by Bube and Lind[6] in Br-doped ZnSe. It is possible that these levels are due to the halogen dopants used, although the identification has yet to be conclusively established.

The previously reported donor ionization energies in ZnS and ZnSe are in the range of 0.2 to 0.3 eV while those for CdTe, CdSe, and CdS are much smaller[6] and are approximately equal to those expected on the basis of the hydrogenic model (i.e., 0.01 to 0.03 eV). The donor depth of ZnSe predicted by the hydrogenic model, $E_d = 13.6(m^*/m)\epsilon_s^{-2}$ eV, for the estimated m^*/m of 0.15 and for the static dielectric constant ϵ_s of 8.1, is

0.03 eV. This is almost a factor of 10 less than the value of about 0.2 eV noted above.

The question arises as to why a shallow level is not found in ZnSe (and also in the other zinc compounds) while shallow levels are found in the cadmium compound semiconductors. A simple explanation of this could be obtained from the fact that the previous observations have been made in insulating or weakly n-type crystals. This suggests that the shallow levels were completely compensated, and therefore, did not contribute to the free-carrier concentration.

This explanation was tested by preparing a more strongly n-type sample by subjecting an undoped[23] crystal to two successive Zn extractions in an attempt to reduce the concentration of the compensating acceptors. From the data for this sample, shown as the intermediate curve in Fig. 4, it can be seen that the carrier concentration is higher and the slope much lower than for the previous sample. Using Eq. (1) with $g = 2$, which is appropriate to the case of a simple donor, the data are fitted using $N_d = 9.5 \times 10^{16}$ cm^{-3}, $N_a = 8.7 \times 10^{16}$ cm^{-3} and $E_d = 0.008$ eV. The calculated points are shown as triangles in Fig. 4. This level is indeed shallow. In fact, it is considerably shallower than the hydrogenic value. At these moderately large values of N_d and N_a, the latter fact undoubtedly reflects the dependence of the ionization energy on impurity concentration as has been observed, for example, in Ge.[24] The relatively large degree of compensation, found to be present in this sample in spite of the extraction of acceptor impurities and the suppression of the concentration of native acceptors (Zn vacancies) by the liquid-Zn treatment, demonstrates the strong tendency of ZnSe toward self-compensation.

Finally, a sample with a still higher carrier concentration was prepared by diffusing 1.5×10^{20} cm^{-3} Al into a previously purified ZnSe crystal. The Hall constant for this crystal is given as the lowest curve in Fig. 4. It is evident from the fact that R_H is constant from about 16° to 370°K that the ionization energy has vanished. Evidently the impurity concentration is greater than the critical value at which $E_d = 0$, and the Fermi level either coincides with the conduction band edge or lies within the conduction band. The sample thus represents the first case of degenerate conduction in the zinc II–VI compounds.

Mobilities of ZnTe and ZnSe

The mobility data for ZnSe and ZnTe are presented in Figs. 5 and 6, respectively. While more extensive

[23] It should be noted that crystals grown from undoped ZnSe powder are likely to contain less acceptor impurities than those grown from Cl-doped powders. It has been observed that the presence of halogens during crystal growth tends to favor the incorporation of acceptor impurities by vapor transfer from the original powder charge to the growing crystal boule. (P. Kovács and J. Szabó, paper presented at the International Conference on Luminescence, Balatonvilágos, Hungary, 1961).

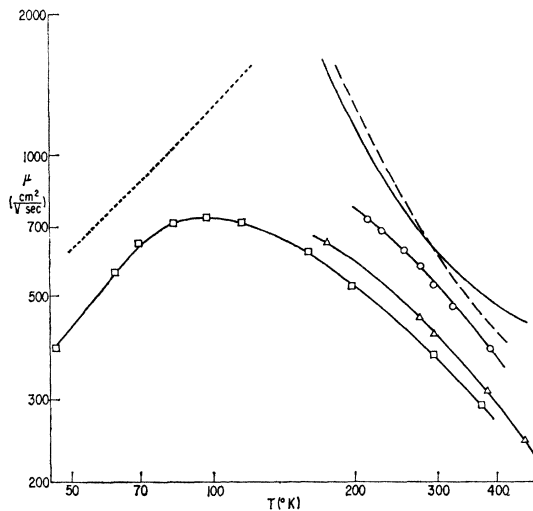[24] P. P. Debye and E. M. Conwell, Phys. Rev. 93, 693 (1954).

FIG. 5. Temperature dependence of the Hall mobility for an undoped ZnSe crystal with $n_{300°K} = 6.9 \times 10^{16}$ cm^{-3} (squares), a Cl-doped crystal with $n_{300°K} = 8.6 \times 10^{16}$ cm^{-3} (triangles), a Cl-doped crystal with $n_{300°K} = 6.8 \times 10^{16}$ cm^{-3} (circles) and an Al-doped crystal with $n_{300°K} = 1.1 \times 10^{16}$ cm^{-3} (diamonds). The solid curve represents the calculated mobility for polar scattering of optical phonons. The dashed curve includes an approximate correction for the temperature variation of ϵ_s. The dotted curve is the mobility calculated for charged impurity scattering for the undoped sample.

data might be desirable for a detailed analysis of the mobilities, the present results are quite adequate to permit a study of the dominant scattering mechanisms. From the near equality of the mobilities (μ) for $T \gtrsim 100°K$ for samples with significantly different defect concentrations and from their fairly rapid increase with decreasing temperature, it appears that the μ for $T \gtrsim 100°K$ are determined by the intrinsic properties of the two materials and not by the crystal defects. In addition, it is shown below that the magnitude and temperature dependence can in fact be accounted for by a lattice-scattering mechanism. Below about 100°K on the other hand, charged impurity scattering is indicated by the increase in μ with temperature. This is supported by the study of μ for the one sample for which low-temperature data are available (lower experimental curve in Fig. 5). Using the donor and compensating acceptor concentrations obtained from the analysis of the carrier concentration and the Brooks-Herring formula, we obtain the dotted curve in Fig. 5. The agreement is satisfactory considering the uncertainties in the data and in the simple application of the theory.

It should be noted that a study of the mobilities of ZnTe and ZnSe will, in a general way, parallel the corresponding studies of the more thoroughly investigated semiconductors in the III–V compound family. For as Ehrenreich[25] has shown, at least for the n-type materials, the polar character of these semiconductors plays a

[25] H. Ehrenreich, J. Phys. Chem. Solids 9, 129 (1959); Phys. Rev. 120, 1951 (1960); J. Appl. Phys. 32, 2155 (1961); see also C. Hilsum and A. C. Rose-Innes, Semiconducting III–V Compounds (Pergamon Press, New York, 1961).

major role in their transport properties. This would also be expected to be true for the II–VI compounds because of their strongly polar nature. To provide a reasonably complete study of the intrinsic (or lattice) mobility of these materials, four scattering mechanisms should be considered. These are scattering by the piezoelectric activity of the acoustic modes, the deformation potential, and the nonpolar and polar interactions with the optical modes. For all four, μ drops off with increasing T. As we will attempt to determine which of these mechanisms contribute appreciably to the observed μ, we will in the following consider each of them separately and in some detail. Unless otherwise indicated, we avoided the complications arising from the degenerate valence bands (for p-type ZnTe) by the relatively rough approximation of treating them as a simple band. With a suitable m^* this should provide us with results which are at least semiquantitatively correct; and this is all that will be required for our purposes.

The scattering by piezoelectrically active acoustic modes, first treated by Meijer and Polder[26] and Harrison,[27] results from the small component of polarization present in the long-wavelength acoustic modes. The mobility of carriers in a simple band with this interaction is

$$\mu_{piezo} = 1.05\rho\langle u_l^2 \rangle \epsilon_s^2 e_{14}^{-2}(m^*/m)^{-3/2}T^{-1/2} \text{ cm}^2/\text{V sec}, \quad (4)$$
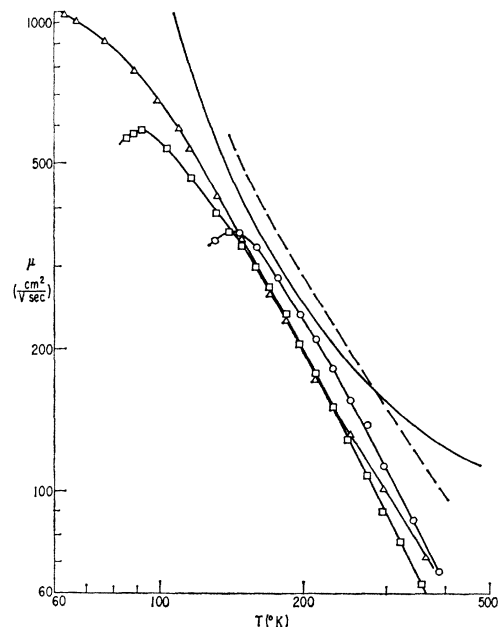

FIG. 6. Temperature dependence of the Hall mobility for two undoped (circles and squares) and a Ag-doped (triangles) ZnTe crystal. The solid curve represents the calculated mobility for polar scattering of optical phonons. The dashed curve includes an approximate correction for the temperature variation of ϵ_s.

[26] H. J. G. Meijer and D. Polder, Physica 19, 255 (1953).
[27] W. A. Harrison, Phys. Rev. 101, 903 (1956), thesis University of Illinois, 1956 (unpublished).

TABLE I. Parameters used in calculating mobilities for
ZnSe and ZnTe.

	ZnSe	ZnTe
$\epsilon_s(T=300°K)$	8.1[a]	10.1[d]
ϵ_∞	5.75[a]	8.26[d]
$\hbar\omega_l(eV)$	0.0314[a]	0.0259[e]
$e_{14}\left(\dfrac{stat.\ coul.}{cm^2}\right)$	1.5×10^4 [b]	8.5×10^3 [b]
$\rho\langle u_l^2\rangle\left(\dfrac{dynes}{cm^2}\right)$	1.06×10^{12} [c]	8.5×10^{11} [c]

[a] See reference 4.
[b] D. Berlincourt, H. Jaffe and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).
[c] Derived from the elastic constants in d.
[d] See reference 1.
[e] See reference 11.

where ϵ_s is the static dielectric constant, e_{14} is the piezo-electric constant (in esu/cm^2), ρ is the density, and $\langle u_l^2\rangle$ is the square of longitudinal sound velocity averaged over direction. Aside from m^*/m, for which we use the values stated above, the values of the various parameters used in Eq. (4) are given in Table I. The resulting mobilities are

$$\mu_{piezo}(ZnTe)\approx1.6\times10^5(300/T)^{1/2}\ cm^2/V\ sec.$$

$$\mu_{piezo}(ZnSe)\approx3.5\times10^5(300/T)^{1/2}\ cm^2/V\ sec.$$

These values exceed the measured ones by well over a factor of 100 and, thus, indicate that this mechanism does not play an important role in determining the μ for either of the two materials.

The theory of deformation potential (or acoustic mode) scattering is well known. The mobility for this case can be expressed as

$$\mu_{dp}=3.0\times10^{-5}(m^*/m)^{5/2}\rho\langle u_l^2\rangle T^{-3/2}E_b^{-2}\ cm^2/V\ sec,\quad(5)$$

where E_b denotes the deformation potential (in eV) for the relevant band edge.[28]

Unfortunately, there is no direct information about these quantities for ZnSe and ZnTe. However, information about the pressure coefficients of a fairly large number of semiconductors is available. From the regularity of the pertinent data it appears that estimates of the required quantities can be made which are sufficiently accurate for our purpose. We take the values of 4 eV and 2 eV as the deformation potentials for the conduction band edge of ZnSe and the valence band edge of ZnTe, respectively.[29] With these values the

[28] See, for example, H. Brooks, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7, p. 87.

[29] The difference in the deformation potentials for the s-like conduction band and the p-like valence bands is nearly the same ($\sim$6 eV) for all group IV and III–V semiconductors [see W. Paul, J. Appl. Phys. **32**, 2082 (1962)]. Thomas' values of 4.5 eV [J. Appl. Phys. **32**, 2298 (1961)] and Langer's value of 3.8 eV (to be published) for CdTe suggest that this crude relation also holds for the II–VI compounds. Also, for Ge it has been shown [H. R. Philipp, W. C. Dash, and H. Ehrenreich, Phys. Rev. **127**,

calculated mobilities are

$$\mu_{dp}(ZnTe)=4\times10^3(300/T)^{1/2}\ cm^2/V\ sec,$$

$$\mu_{dp}(ZnTe)=2\times10^4(300/T)^{1/2}\ cm^2/V\ sec.$$

Since these values are about a factor of 40 times larger than the measured values, it appears that acoustic mode scattering is not important for these compounds. Of course, if the deformation potentials are much larger than our estimated values (say by a factor of five), our conclusion would be in error. However, it seems rather unlikely in light of present knowledge that these quantities can be so huge.

The expression for the mobility of holes in degenerate p-like bands scattered by the nonpolar interaction with the optical phonons, μ_{npo}, can be obtained from the work of Ehrenreich and Overhauser.[30] From their study of the mobility of holes in Ge, it can be readily shown that

$$\mu_{npo}=\frac{1.35\times10^{17}\rho a^2\theta^3}{C_4^2T^{5/2}}\left[\frac{m^{5/2}(m_1^{1/2}+m_2^{1/2})}{(m_1^{3/2}+m_2^{3/2})^2}\right]$$

$$\times\int_0^\infty\frac{x\exp(-\theta T^{-1}x)dx}{\varphi(x^{-1})}\ cm^2/V\ sec\quad(6)$$

with

$$\varphi(t)=n(1+t)^{1/2}+(n+1)(1-t)^{1/2}\quad for\quad t<1$$

$$=n(1+t)^{1/2}\quad\quad\quad\quad for\quad t>1.$$

Here n is the usual optical phonon occupation number given by $[\exp(\theta/T)-1]^{-1}$, θ is the Debye temperature, m_1 and m_2 are the masses of the light and heavy hole, respectively, a is the lattice constant (in cm), and C_4 is the coupling constant (in eV). The constant C_4 is analogous (but not equal) to the deformation potential for the optical modes in say Conwell's formulation.[31] In line with our limited knowledge about the masses for ZnTe the factor involving the masses is replaced by $m^{*-5/2}=(0.6m)^{-5/2}$. The biggest uncertainty, however, is in the magnitude of the optical mode coupling parameter C_4, about which little is known. To our knowledge the only semiconductor for which the strength of this coupling has been determined is Ge. In their recent study of the mobility of p-type Ge, Brown and Bray[32] have determined coupling parameters for the different modes (so-called optical and acoustic deformation potentials). From their results it is possible to deduce that the value of C_4 is 20 eV, which corresponds to their optical mode deformation potential of 8.8 eV. On the

763 (1962)] that the deformation potential for the valence band ($\Gamma_{25'}$) edge is opposite and equal to roughly half that for conduction band (Γ_{21}) edge at $k=0$.

[30] H. Ehrenreich and A. W. Overhauser, Phys. Rev. **104**, 331 and 649 (1956).

[31] E. Conwell, J. Phys. Chem. Solids **8**, 236 (1959).

[32] D. M. Brown and R. Bray, Phys. Rev. **127**, 1593 (1962).

other hand, it is possible to make a rough estimate of the upper limit of this parameter for InSb. We find the value to be 15 eV.[33] Using the value of 15 eV for ZnTe we find that μ_{npo} has the values of 790, 2000, and 1800 cm²/V-sec at $T=300$, 200, and 100°K, respectively. These values are too large by a factor of about 8 at 300°K and 25 at 100°K.

With significantly larger values for the mass and C_4 than the estimates that we have used, μ_{npo} could yield values comparable to the observed values. On the other hand it is important to note that the temperature dependence of μ_{npo} also is not in very good accord with the data, as it increases too rapidly with decreasing temperature. Thus, while we cannot at present definitely rule out the possibility that this type of scattering contributes significantly to the total, these observations suggest that it does not dominate the scattering.

This mechanism can be completely ruled out for n-type ZnSe for two reasons. First, the effective mass is small and $\mu_{npo} \propto (m^*)^{-5/2}$. The second and more important reason is that for the Γ_1 (s-like) conduction band minimum the matrix element for scattering between electronic states $\mathbf{k}$ and $\mathbf{k}'$ vanishes to lowest order in the phonon wave vector $\mathbf{q}=\mathbf{k}-\mathbf{k}'$. The reduction in the scattering due to this selection rule is $\sim 10^{-3}$.

The last mechanism to be considered is the scattering of the carriers by the electric polarization associated with the optical modes. The strength of the interaction is indicated by the polar coupling constant α which is

$$\alpha = (m^*/m)^{1/2}(\text{Ry}/\hbar\omega_l)^{1/2}(\epsilon_\infty^{-1} - \epsilon_s^{-1}),$$

where Ry is the Rydberg of energy, $\hbar\omega_l$ is the energy of the longitudinal optical mode for long wavelength, and ϵ_∞ is the high-frequency or optical dielectric constant.[34] Using the relevant parameters, which are given in Table I and the assumed values of m^*/m we find that $\alpha = 0.41$ and 0.39 for electrons in ZnSe and holes in ZnTe, respectively. By noting that the factor which more properly reflects the relative magnitude of succeeding terms for the weak coupling case is $\alpha/6$, it is evident that the weak coupling approach is probably adequate for these materials. The perturbation theory result for simple parabolic bands obtained by Howarth and Sondheimer[35] and in which the Callen effective

charge[36] is used can be written as

$$\mu_{\text{polar}} = \frac{0.870(m/m^*)}{\alpha\hbar\omega_l}\left[\frac{e^z - 1}{z^{1/2}}\right]G(z)e^{-\xi} \text{ cm}^2/\text{V sec}, \quad (7)$$

where $z = \hbar\omega_l/kT = \theta T$, $\hbar\omega_l$ is in eV, and $G(z)e^{-\xi}$ is a tabulated function. A more general result having the same form as Eq. (7) but in which the screening by the carriers is taken into account was given by Ehrenreich.[37] His $G(z)$ is a function of the carrier concentration through the plasma frequency ω_p defined by $\omega_p^2 = 4\pi e^2 n/m^*$. The difference between the $G(z)$ for the screened and unscreened interactions vanishes as $\omega_p/\omega_l \to 0$. Since $\omega_p/\omega_l \ll 1$ for all ZnSe and ZnTe crystals considered in this context, the screening can be neglected.

The values obtained from Eq. (7) are shown as the solid curves in Figs. 5 and 6. In contrast to the previous mechanisms considered, polar scattering leads to results which are quite close to the experimental mobilities. It is noteworthy that there are no adjustable parameters in μ_{polar} except perhaps the m^*s (which, in fact, have not been varied). There is an apparent small discrepancy in that the calculated curves exhibit a small positive curvature at the higher temperatures while the data do not. However, recent investigations of CdTe[38] and the silver halides[39] have suggested that such differences may be due to the temperature dependences of the relevant parameters in the coupling constant (i.e., ϵ_s, ϵ_∞ and $\hbar\omega_l$). For example, a small relative change in ϵ_∞ and ϵ_s would have an appreciable effect on α because of considerable cancellation in $\epsilon_\infty^{-1} - \epsilon_s^{-1}$. Since the variation of ϵ_s with temperature is expected to be larger than that of ϵ_∞,[38] we will neglect the latter in considering the nature of the correction arising from the temperature dependence of α. The variation of ϵ_s with temperature, which is unknown for ZnSe and ZnTe, will be assumed to be similar to that of CdTe. It is to be noted that the dashed curves which include this correction, have a temperature dependence which more closely resembles the data in the intrinsic range.

In summary, the polar optical mode scattering clearly dominates the intrinsic scattering of electrons in ZnSe, the scattering from all other mechanisms being very much weaker. This mechanism is undoubtedly also very important for p-type ZnTe as the estimated mobility due to it alone has the correct magnitude and temperature dependence. The other scattering mechanism that possibly could be important in the scattering of the holes is the nonpolar interaction with the optical phonons. This could be the case if the appropriate coupling parameter is considerably larger than the values we have considered. Finally, it should be noted

[33] As C. Hilsum and A. C. Rose-Innes (reference 25) have already noted, polar optical mode scattering apparently accounts for the room temperature hole mobility (750 cm²/V-sec) of InSb. Using this fact, the limit on C_4 is then arrived at by applying Eq. (6) and requiring $\mu_{npo} > 10^3$ cm²/V sec. A value of $m^* = 0.4$ m [F. Stern, Proceedings International Conference on Semiconductor Physics, Prague 1960 (Czechoslavakian Academy of Sciences, Prague, 1961), p. 363] was used. The larger values of $m^* = 0.5$ m and 0.6 m suggested by H. Ehrenreich [J. Phys. Chem. Solids 2, 131 (1957)] and Hilsum and Rose-Innes would lead to lower values for C_4.

[34] See, for example, A. R. Hutson, Semiconductors, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), p. 541.

[35] D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) A219, 53 (1953).

[36] H. Ehrenreich, J. Phys. Chem. Solids 2, 131 (1957).

[37] H. Ehrenreich, J. Phys. Chem. Solids 8, 130 (1959).

[38] B. Segall, M. R. Lorenz, and R. E. Halsted (to be published).

[39] R. van Heynigen, Phys. Rev. 128, 2112 (1962); and F. C. Brown (private communication).

that high-temperature data would be very helpful in assessing the roles of these two mechanisms since $\mu_{npo} \propto (\theta/T)^{3/2}$ while $\mu_{polar} \propto (\theta/T)^{1/2}$ for $T \gg \theta$.

IV. CONCLUSION

The present study of the electrical transport properties of ZnSe and ZnTe has shown that shallow impurity states, observed in materials like Si, Ge, and the more thoroughly studied compounds of the III–V compound family are more widespread in the II–VI compounds than has been believed in the past. Furthermore, it was found that the processes controlling the electrical conduction of the investigated compounds are similar to those that have been shown to be important in such compounds as InSb and GaAs. Thus, in spite of their less covalent character, the II–VI compounds are in these respects quite similar to the more conventional semiconductors.

The method of firing the crystals in liquid Zn has enabled us, by sufficiently suppressing the concentration of compensating impurity and native defects, to observe a shallow donor level in ZnSe with ionization energy of ~0.01 eV. It has also proved possible to prepare heavily Al-doped ZnSe crystals which are degenerate.

The discovery of shallow acceptors in ZnTe represents the first case in which uncompensated acceptor levels of near hydrogenic depths have definitely been observed in any of the II–VI semiconductors. Acceptor levels correlated with Cu, Ag, and Au dopants were identified and found to have ionization energies of 0.15, 0.11, and 0.22 eV, respectively. The levels are most probably simple acceptors resulting from the substitutional replacement of Zn atoms by noble metal atoms; although more complex models cannot presently be excluded. A level at 0.048 eV in undoped crystals has been identified as being due to a Zn vacancy. Some evidence is presented for what is believed to be the second charge state of the vacancy.

The Hall mobility data on lightly doped ZnSe and ZnTe strongly suggest that the mobilities for $T \gtrsim 100°$K are determined by the intrinsic properties of the crystals. Analysis of the intrinsic (or lattice) mobility indicates that in the case of ZnSe polar optical mode scattering strongly dominates over the scattering by the piezoelectric activity of the acoustic modes, the deformation potential, and the nonpolar interaction with the optical modes. Similarly, the polar scattering of the optical phonons appears to be the important mechanism determining the mobility of holes in ZnTe. It is possible, however, that the nonpolar optical mode interaction could also contribute appreciably to the scattering of the holes if the relevant coupling parameter is significantly larger than the corresponding parameters for Ge and InSb.