Electrical Properties of n-Type CdTe†

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Transport measurements are reported on high-purity and doped n-type single-crystal CdTe with 300°K carrier concentrations ranging from 6×10^{14} to 2×10^{18} cm^{-3}. Variations of Hall coefficient (R_H) and resistivity (ρ) with temperature are investigated. The magnetoresistance ($\Delta\rho/\rho$) and magnetic field dependence of R_H are also examined. The Hall mobility (μ_H) of high-purity CdTe exhibits a region of intrinsic behavior as it rises rapidly with decreasing temperature from 1050 cm^2/V sec at 300°K to values as high as 57 000 cm^2/V sec at 30°K. The contributions of acoustic, piezoelectric, and nonpolar optical mode scattering are found negligible. Polar optical mode scattering, however, provides quantitative agreement with the experimental μ_H assuming a $\mathbf{k}=0$ minimum, $m^*=0.11m$ and correcting for the temperature dependence of the static dielectric constant. Corrections to the lattice mobility arising from the nonparabolicity of the conduction band, admixture of p component in the wave function, screening by the carriers, and electron-electron scattering are considered and are shown to be negligible. At low temperatures μ_H is limited by impurity scattering. Carrier concentration, donor depth, and low-temperature mobility data are attributable to a simple singly charged donor impurity. At 300°K $\Delta\rho/\rho H^2<10^{-11}$ G^{-2}. The angular dependence and magnitude of the magnetoresistance is found to be subject to demonstrable but as yet unavoidable electrode effects and hence not useful in providing information about the band structure.

INTRODUCTION

PROGRESS in understanding the basic properties of II–VI semiconducting compounds has been hindered by the difficulty of obtaining definitive transport measurements. To a large extent this has been the result of problems associated with single-crystal growth, purification, and stoichiometric control in these large band gap semiconductors. In this context, CdTe is of considerable interest. It has the zinc blende structure and can be grown from the melt in both n- and p-type forms. In addition, fairly high mobilities could be anticipated in materials that are suitably prepared.

In the course of his broad survey of the properties of CdTe, deNobel[1] investigated the electrical properties of both n- and p-type crystals. In his material, electron mobilities up to 1200 cm^2/V sec (170°K) were observed.[2] The mobility did not exhibit the strong temperature-dependence characteristic of intrinsic behavior. More recently Yamada has reported electrical measurements on p-type[3] and n-type[4] single crystals. The highest mobilities achieved in his n-type material were slightly higher than deNobel's, the peak being $\sim$1500 cm^2/V sec at 90°K. Yamada also studied the magnetoresistance and its angular dependence. From an analysis of this data, he suggested that the conduction band does not have a simple minimum at the center of the Brillouin zone, but has a multivalley structure with minima on the ⟨111⟩ axes. In both of the above-mentioned studies of n-type materials the results for the mobility did not permit unambiguous conclusions concerning the scattering mechanisms operative in various temperature ranges.

This paper reports a study of the electrical properties of n-type CdTe with emphasis on crystals of higher purity than previously achieved. A sealed-ingot zone refining technique has been found effective for preparing high purity n-type CdTe single crystals.[5] Doped crystals have also been prepared. In the following section of this paper, Hall coefficient and resistivity measurements on these materials are presented. Magnetoresistance measurements are also described. The zone-refined material exhibits intrinsic mobility over a substantial temperature range. Low-temperature mobilities are observed which are much higher than previously attained.

An analysis of these results is presented in a subsequent section. Information concerning the concentrations of effective donors and acceptors is obtained. The effective ionization energy of the donors is determined. Theoretical estimates are made of the contribution of various scattering mechanisms to the mobility of electrons in CdTe. Comparison with experiment establishes the nature of the dominant scattering processes over the entire temperature range. Analysis of the transport data further provides information regarding the nature of conduction band minimum and the value of the effective mass. Conclusions concerning the nature of the donor are also derived and discussed.

EXPERIMENTAL

Electrical measurements were performed on two groups of samples. The first group were donor-doped samples. These were prepared by sealing CdTe and a suitable dopant into a quartz ampoule and effecting crystal growth by the Stockbarger technique. The second group of samples came from ingots of multiple zone-refined high-purity CdTe. The method of preparation is described in detail elsewhere.[5] These zone-refined

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[1] D. deNobel, Philips Res. Rept. **14**, 361, 430 (1959).

[2] We cite here the experimentally determined Hall mobility (R_H/ρ).

[3] S. Yamada, J. Phys. Soc. Japan **15**, 1940 (1960).

[4] S. Yamada, J. Phys. Soc. Japan **17**, 645 (1962).

[5] M. R. Lorenz and R. E. Halsted, J. Electrochem. Soc. (to be published).

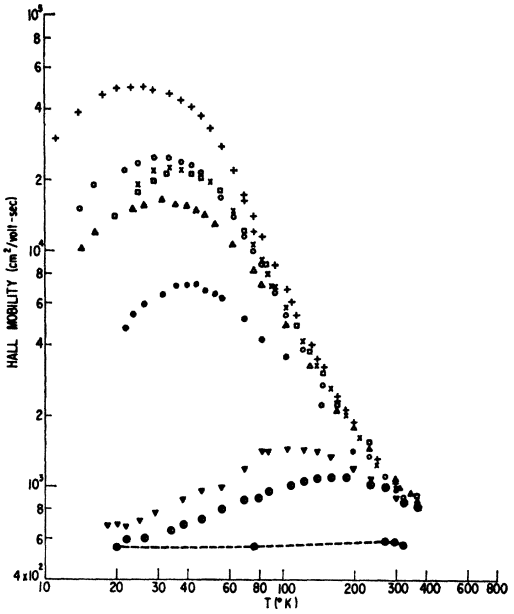

FIG. 1. Temperature dependence of Hall mobility of various n-type CdTe samples. +, ○, ×, □, and △: samples of multiple zone-refined, undoped CdTe; ●: sample of multiple zone-refined CdTe, annealed in excess Cd; ▼ Nd, ⊗ In, and -●- I doped samples.

ingots generally exhibited n-type conductivity without any intentional impurity doping.

Hall samples were cut from single crystals with a diamond blade into bars roughly 2 mm×2 mm×10 mm bars. Some crystals were truly single while others contained (111) twin planes. In agreement with deNobel no evidence of inhomogeneity in electrical properties associated with twin planes has been observed. After sawing, the bars were lightly ground with fine grained abrasive powder. This was followed by a chemical polish. The specimens were etched first in a solution of one part HF, one part HNO_3, and two parts water and then treated in a solution consisting of seven parts of saturated $K_2Cr_2O_7$ solution and three parts of concentrated H_2SO_4.[6] The resultant surface is shiny black and indistinguishable from a cleaved surface except for the inevitable step pattern characteristic of cleaved CdTe. Sometimes it is necessary to repeat the two-step polish treatment before the surface is ready for electroding. Indium beads on 5-mil Pt wire leads were soldered to the bars. Good low-resistance Ohmic contacts were obtained if electroding was done immediately after the chemical polish and providing the indium made an alloy rather than a mechanical contact. It would seem that the indium has to dissolve, diffuse, or cut through a thin high-resistance surface layer for good electrode contacts.[7]

[6] T. Ichimiya, T. Niimi, K. Mizuma, O. Mikami, Y. Kamiya, and K. Ono, in *Solid State Physics in Electronics and Telecommunications (Proceedings of the International Conference held in Brussels June 2–7, 1958)*, edited by M. Desirant and J. L. Michielo (Academic Press Inc., New York, 1960), Vol. 2, p. 845.

[7] H. D. Coghill, R. K. DiCerbo, R. E. Halsted, and M. R. Lorenz, Bull. Am. Phys. Soc. 6, 312 (1961).

The specimens were then subjected to resistivity and Hall measurements by a standard dc method. Magnetic field strengths up to 7.3 kG were employed. The dependence of the Hall coefficient on the magnetic field strength was checked at 298°K, liquid N_2 and liquid H_2 temperatures.

For magnetoresistance measurements untwinned crystals were used. The sample arrangement was the same as for the Hall measurement except for the omission of Hall probes. Since it is known that size and shape of electrodes have a strong influence on the experimental results,[8] various size electrode contacts were tried. The effect of varying the positioning of the contacts relative to the crystal axes was also investigated.

RESULTS

The temperature dependence of Hall mobilities for a number of samples is shown in Fig. 1. Impurity donor doped samples exhibit relatively low mobilities. Relatively small changes are observed with temperature. The carrier concentration of these samples was calculated from the relation $n=r(R_H ec)^{-1}$, where r is the ratio of the Hall mobility μ_H to the drift mobility μ_D and was assumed for simplicity to be unity. The carrier concentrations for the impurity doped samples are plotted in Fig. 2. These results are similar to the earlier work of deNobel and Yamada. As the carrier concentration increases, the electron Hall mobility is reduced and is less dependent on temperature. The highest carrier concentration was 2×10^{18} cm^{-3} in the iodine-doped sample. Characteristic of such heavily doped samples are precipitated phases which can be seen by transmitted infrared radiation with the aid of an ir image tube.

In contrast to the first group of samples, zone-refined crystals are free of precipitates, have low carrier concentration and have strongly temperature-dependent

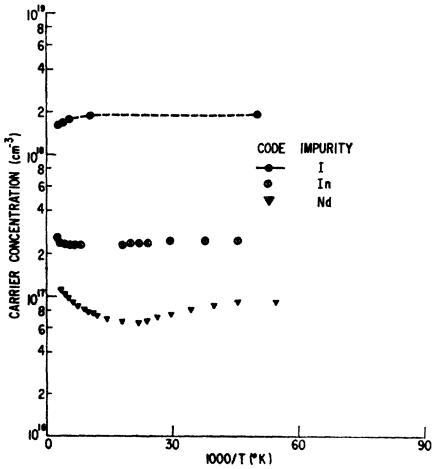

FIG. 2. Electron concentration as a function of temperature for several impurity doped samples. ▼ Nd, ⊗ In, and -●- I.

[8] M. Glicksman, J. Phys. Chem. Solids 8, 511 (1959).

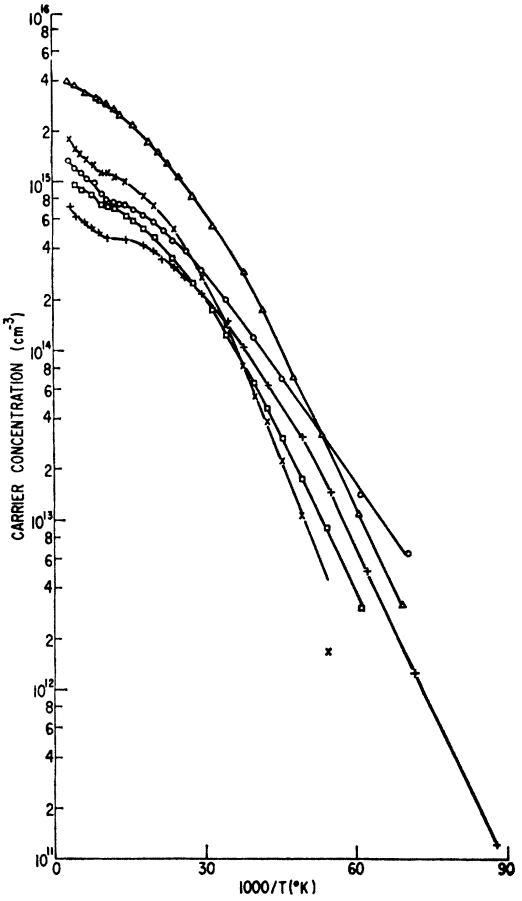

FIG. 3. Electron concentration as a function of temperature for various zone-refined, undoped samples whose Hall mobilities are shown in Fig. 1.

Hall mobilities (see Fig. 1). The highest Hall mobility of 57 000 cm^2/V sec is much greater than any value previously reported for CdTe. Carrier concentrations of these samples at 298°K are of the order of 10^{15} per cm^3. Their variation with temperature is shown in Fig. 3. The results of this group of samples will be analyzed in detail in the following section.

In Fig. 4 the dependence of the Hall coefficient on the magnetic field strength is illustrated at various temperatures.

Difficulty was encountered in achieving reproducible magnetoresistance measurements. An effect proportional to H^2 is readily obtained. However, a strong dependence of the magnetoresistance on the size of the voltage probes was observed. Experimental values for the transverse magnetoresistance of 1.5×10^{-12} to 8.5×10^{-12} G^{-2} were observed on different samples. However, comparable variations in magnitude were obtained by re-electroding a given sample. Lower values were correlated with small area contacts. A second effect which was noted involved the positioning of contacts. This is illustrated by the following behavior obtained with an oriented single-crystal bar. The long axis ⟨211⟩ corresponded to the current direction. The two other axes were ⟨110⟩ and ⟨111⟩. First the two voltage probes, i.e., indium dots of about 1-mm diam, were fused onto the (110) face. The transverse magnetoresistance was measured. The voltage probes were then removed and fused onto the (111) face. Again the magnetoresistance was measured. The results are shown in Fig. 5. It is evident that altering the position of the contacts relative to the crystal orientation changes the apparent angular dependence of the results.

ANALYSIS OF DATA AND DISCUSSION

Assumptions of Theory

In the work that follows, we make two important assumptions regarding the structure of the conduction band. First, we assume that there is a simple s-like minimum at the center of the Brillouin zone (i.e., at $\mathbf{k}=0$). Secondly, we will take the effective mass to be 0.11 m, where m is the free electron mass.

The first assumption is in disagreement with conclusions drawn in two recent publications on CdTe. On the basis of his magnetoresistance measurements, Yamada[4] suggests that the absolute minimum of the conduction band is not at $\mathbf{k}=0$, but, in fact, is on the ⟨111⟩ axes. As previously noted, magnetoresistance measurements can be obscured by contact effects. From our experience with this type of measurement in CdTe, we believe this to be the case with Yamada's results. This point will be examined in more detail in the discussion of the present magnetoresistance measurements. The other work which tends to argue against a $\mathbf{k}=0$ minimum is that of Davis and Shilliday[9] who studied the absorption near the band edge. From the energy and temperature dependence of the absorption constant in the range of about 10 to a few hundred cm^{-1}, they conclude that there is an indirect transition at about 0.1-eV lower energy than the direct transition.

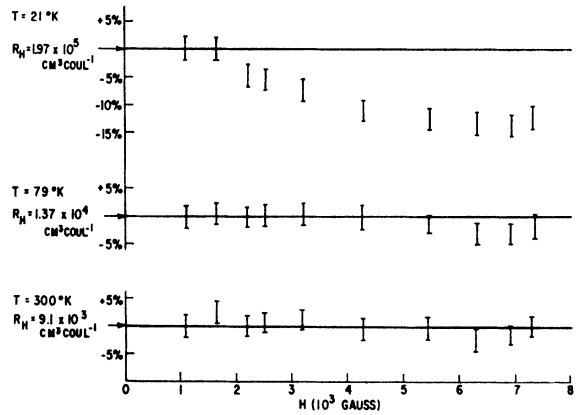

FIG. 4. Magnetic field dependence of the Hall coefficient in a zone-refined, undoped CdTe sample at 21, 79, and 300°K.

[9] P. W. Davis and T. S. Shilliday, Phys. Rev. 118, 1020 (1960).

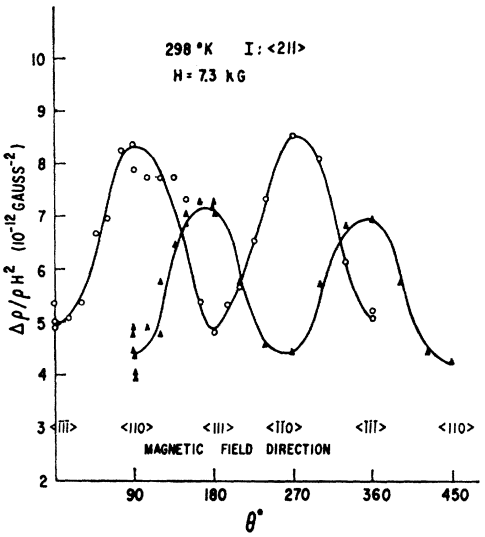

FIG. 5. Effect of altering orientation of contacts with respect to magnetic field direction in transverse magnetoresistance measurements on CdTe. ⊙ voltage probes on (110) face, △ voltage probes on (111) face.

Since all group IV, group III–V and group II–VI semiconductors for which the band structures are known have their valence band maximum at $\mathbf{k}=0$, such an indirect transition would probably mean that the conduction band does not have its minimum at $\mathbf{k}=0$. However, it should be realized that before data at such low absorption constants can be interpreted properly, one must investigate the effects of impurities, and in addition take into account the role of the phonon-assisted "direct" exciton as has been done by Dietz, Hopfield, and Thomas[10] for ZnO. Neither of these effects were considered by Davis and Shilliday. Thus, both the magnetoresistance and optical studies fail to present a strong case for a nonsimple conduction band.

On the other hand, the sharp exciton lines seen in absorption and the fluorescence spectra which exhibit sharp lines close ($\sim$0.01 eV) to the direct band edge[11] argue in favor of a direct transition. The sharp line emission at energies almost 0.1 eV above the supposed indirect gap would be particularly hard to understand. Furthermore, Thomas' exciton studies on uniaxially-stressed crystals show that the excitons are associated with the bands around $\mathbf{k}=0$.[12] We thus tend to believe the $\mathbf{k}=0$ minimum picture. A more direct confirmation of this would, of course, be desirable. Probably the most important consequence for the subsequent work of assuming that the minimum is at the center of the Brillouin zone is that intervalley scattering is thereby excluded.

The assumed value of the effective mass is on firmer footing. Using Faraday rotation and reflection measurements, Marple[13] has determined the mass to be $(0.11\pm0.01)\,m$. In addition, the 0.11 value is consistent with the extrapolation of electron masses for CdS and CdSe as a function of the ($\mathbf{k}=0$) band gaps. This was, in fact, the basis of our first estimate. It corresponds to using a two band model in which the interband momentum matrix element is constant for these II–VI compounds as has been shown to be the case for the III–V compounds.[14] It is interesting to note the agreement of the measured value with the value estimated on the basis of the bands at $\mathbf{k}=0$. This would appear to be additional support for the simple model of the conduction band.

Analysis of the Carrier Concentration

The data that we are going to consider are those for the more lightly doped samples which are shown in Fig. 3. The cases in which impurity banding comes in at fairly high temperatures, typical examples of which are given in Fig. 2, will not be analyzed in detail.

The constant $r\equiv\mu_H/\mu_D$ in the relation $R_H=r(\text{nec})^{-1}$ lies between 1 and 2 depending on a number of factors including the nature of the operative scattering mechanism. The values of n plotted in Figs. 2 and 3 were obtained using the simplifying approximation that $r=1$ for all T. This approximation is, in fact, not as bad as it might seem. In the high T region ($T\gtrsim\theta\equiv$Debye temperature) where optical mode scattering is dominant (see below) r is close to unity.[15] The constant r tends to increase somewhat as T drops below θ. However, the mobility is increasing rapidly so that, at $T\sim100$°K and $H=7.3$ kG, $\omega\tau=\mu H/c$ is about 1. This indicates the onset of the "high-field" regime, and as a consequence, r would be closer to one than it is for $H\rightarrow0$. The argument also holds at still lower temperatures where $\omega\tau$ is definitely larger than unity, even though $r(H=0)$ might be somewhat larger.[16]

An indication of the field dependence can be obtained from Fig. 4 which shows plots of $R_H(H)$ vs H for $T=21$, 79, and 300°K. At the lowest temperature it appears that the "high-field" condition prevails at $H=7.3$ kG; however, measurements at higher fields would be required to be certain that saturation had been reached. At $T=79°$ the data just suggests the onset of field effects at $H=7.3$ kG.

From the curves of n vs $1/T$ it is apparent that as the contribution to the carrier concentration from the level determining the low-temperature behavior is saturating at about 80°K or so, a deeper level begins to contribute appreciably. A relatively sharp break, occurring at around 100°K in the carrier concentration curve, is common to all the samples being considered

[10] R. E. Dietz, J. J. Hopfield, and D. G. Thomas, J. Appl. Phys. **32**, 2282 (1961).
[11] R. E. Halsted, M. R. Lorenz, and B. Segall, J. Phys. Chem. Solids **22**, 109 (1961).
[12] D. G. Thomas, J. Appl. Phys. **32**, 2298 (1961).
[13] D. T. F. Marple, preceding paper [Phys. Rev. **129**, 2466 (1963)].
[14] H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961).
[15] R. T. Delves, Proc. Phys. Soc. (London) **73**, 572 (1959).
[16] The characteristic values of $r(H=0)$ calculated from the Brooks-Herring formulas for the concentrations in the samples considered are about 1.5 (see Table II).

TABLE I. Donor depths and donor and acceptor concentrations derived from the electron concentration data of Fig. 3. The results obtained by applying the statistics appropriate to the single and double donor cases are tabulated.

Sample identification	Single donor N_a (10^{15} cm^{-3})	N_d (10^{15} cm^{-3})	ϵ_d (eV)	Double donor N_a (10^{15} cm^{-3})	N_d (10^{15} cm^{-3})
A(+)	0.24	0.7	0.011	0.8	1.2
B(○)	2.4	3.2	0.007	8.9	9.8
C(△)	1.7	5.2	0.010	5.2	7.9
D(×)	1.5	2.7	0.011	5.4	6.6
E(□)	1.3	2.0	0.010	4.0	4.6

except perhaps sample C in which it is less pronounced. From these curves one can readily estimate the "saturation" contribution (N_d-N_a) for the shallower level. In the present work we do not consider the deeper level any further as the data at present are not sufficiently extensive.

To obtain desired information about the donor ionization energy E_d and the concentrations of donors N_d and compensating acceptors N_a, the carrier concentrations are analyzed according to the well-known statistics for a single level and nondegenerate carrier densities. That is, the carrier concentration n is given by

$$n(N_a+n)/(N_d-N_a-n)=gN_c\exp(-E_d/kT), \quad (1)$$

where $N_c=2(m^*kT/2\pi\hbar^2)^{3/2}$ and g is a degeneracy factor which depends upon the nature of the impurity state and of the band edge. For the simple Γ_1 minimum that we are assuming, g has the values $\frac{1}{2}$ or 2 depending on whether the level involved is a single donor (e.g., Al) or the shallow level of a double donor (e.g., a Cd interstitial). Both cases must be considered since the analysis provides our best basis for determining whether foreign impurities or native defects dominate the transport properties of the crystals studied.

The analysis of the data is carried out in a straightforward manner. First n is studied in the "freeze-out" region where (1) leads to $n=g(N_d-N_a)N_a^{-1}N_c\times\exp(-E_d/kT)$. By fitting this expression to the data, E_d and the ratio $(N_d-N_a)N_a^{-1}$ can be obtained. The saturation value of carrier concentration, N_d-N_a, can be readily estimated from the curves of Fig. 3. Therefore, N_d and N_a are individually determined. Finally n is computed according to Eq. (1) for the full range of temperatures with minor adjustments being made in N_d-N_a until a satisfactory fit of the data is obtained. The values for E_d, N_d, and N_a for the five samples considered are given in Table I, both for the simple and double donor cases. The $n(T)$ computed from the parameters in Table I differ from the observed n arising from the lower level by less than 10% for all relevant temperatures except for the double donor case for samples A and C, where the deviations are somewhat larger. It should be noted that the tabulated N_a corresponds to the concentration of "accepted" electrons and that if some of the compensating acceptors are double acceptors, N_A would deviate accordingly from the actual acceptor concentration.

The values of ϵ_d are seen to be about 0.010 eV with the exception of one sample for which it is somewhat lower. This value is to be compared with the one obtained from the hydrogenic model, $13.6\ (m^*/m)\epsilon_s^{-2}=0.013$ eV, where ϵ_s is the static dielectric constant for which we have employed a value of 10.6.[17,1,3] Since CdTe has some polar character, there will be additional binding due to the polar coupling of the electron to the longitudinal optical modes. As we will see below, the coupling is relatively weak, and since in addition the binding is also weak, we can say that an electron in its orbit will interact with the polar lattice very much as a free "polaron" does. The binding energy is then still given by the hydrogenic model except that the appropriate mass is that of the "polaron"[18] which is $\approx m^*(1+\alpha/6)$ where α is the conventional polaron coupling constant. As α will be shown to have a value of about 0.4, the binding energy is about 0.014 eV. The values deduced from the data are significantly lower than this. It seems probable that this difference is a concentration effect similar to that found in Ge.[19] In analogy with the Ge case, it would appear that the concentrations of ionized impurities are sufficiently high so that a reduction of 30% in ϵ_d is possible. It would, of course, be desirable to study ϵ_d over a wider range of concentrations than has been done in this work. It is also interesting to compare the deduced ϵ_d values with that expected for a double donor. From the analogy with atomic H and He and by the use of the effective mass approach, ϵ_d for a double donor is estimated to be about 0.025 eV. That this is considerably larger than the hydrogenic value is due to the incomplete shielding by the electrons. It would seem very difficult to understand the large reduction from this value to those found in the present samples in terms of the concentration effect noted above for defect concentrations involved here.[20]

It is noteworthy that the N_d and N_a are distinctly larger for the double donor case. The saturation value of n from both levels of a double donor is $2N_d-N_a$. The experimental curves indicate lower saturation

[17] P. Fisher and H. Fan, Bull. Am. Phys. Soc. 4, 409 (1959).
[18] P. M. Platzman, Phys. Rev. 125, 1961 (1962).
[19] P. P. Debye and E. M. Conwell, Phys. Rev. 93, 693 (1954).
[20] A sizable lowering could, of course, result if there were some correlation between acceptors and donors at distances $\gtrsim\epsilon_s a_0(m/m^*)\approx 50$ Å, where a_0 is the Bohr radius. However, we have no definite evidence concerning pairing in these samples.

values than those determined from Table I. This then argues further against the double donor model.

On the other hand, from the values of N_d and N_a in Table I it would seem that the values for the simple donor case are not unreasonable for these zone-refined samples. Furthermore, they are not inconsistent with the results of chemical analysis of these crystals.

Analysis of the Mobility

There are several important features to be noted in the mobility curves shown in Fig. 1. One is the high values that have been achieved for the zone-refined samples. Another is the low mobilities at low temperatures for the heavily doped crystals. This is presumably due to impurity scattering. A significant feature is the fact that the mobility data for samples containing various concentrations of defects are observed to converge to a common curve at moderate to high temperatures. The temperature dependence and the extent of the range over which the curves converge strongly indicate that in that range the measured mobilities of the samples with highest mobility are intrinsic; that is, are determined by the properties of the perfect crystal. For the best samples the range is from the highest measured temperature, about 400°K, down to about 80°K. It will be shown that the magnitude and the temperature dependence of the lattice mobility are adequately accounted for by a lattice scattering mechanism. For low temperatures, the mobility is limited largely by the defects.

As will be shown below, these mobility data are amenable to theoretical analysis comparable in detail with the more favorable cases among the compound semiconductors. The analysis generally parallels Ehrenreich's[21] detailed treatments of GaAs and InSb where it was demonstrated that the polar nature of the compounds plays a major role in the transport properties. A similar conclusion would be expected to hold for CdTe which is thought to be more polar than these two III–V semiconductors.

The intrinsic scattering mechanisms that could come into play are acoustic mode (or deformation potential), piezoelectric, and the polar and nonpolar scattering associated with the optical modes. The nonpolar optical mode scattering is very weak for the Γ_1 electrons since the matrix element between electron states with wave vectors $\mathbf{k}$ and $\mathbf{k}'$ vanishes by symmetry to lowest order in the phonon wave vector $\mathbf{q}=\mathbf{k}-\mathbf{k}'$. The contribution to the scattering from this source is thus reduced roughly by a factor k^2a^2 (where a is the lattice constant) which is $\sim 10^{-3}$ at room temperature. Of the remaining three scattering mechanisms, it is generally felt that the last one is the most important. However, the other two have often been thought to contribute appreciably in the II–VI compounds.

Deformation potential scattering arises from the changes in the crystal potential $V(\mathbf{r})$ introduced by the local strains associated with the acoustic modes. The theory for this mechanism is simple and well known for the case of a nondegenerate band. The mobility for this case is[22]

$$\mu_{dp}=3.0\times 10^{-5}(m^*/m)^{5/2}C_l T^{-3/2}E_c^{-2}\ \text{cm}^2/\text{V sec}, \quad (2)$$

where E_c is the deformation potential for the conduction band (in eV) and $C_l=\rho\langle u_d^2\rangle$ (in d cm^{-2}) with ρ the density and $\langle u_d^2\rangle$ being the square of the longitudinal sound velocity averaged over direction.[23] As the mobility, Eq. (2), for this scattering varies with T in a manner crudely similar to the observed μ for materials of this type, this mechanism has occasionally been thought to contribute appreciably. Since we know m^* and can determine $\rho\langle u_d^2\rangle$ from the elastic constants which have been measured by McSkimin and Thomas,[24] the only unknown parameter is E_c. From experiments on the behavior of the exciton spectra in CdTe under uniaxial stress, Thomas[12] has found the difference in the deformation potential for the conduction and valence bands, E_c-E_v, to be about 4.8 eV. Langer[25] has found E_c-E_v to be about 3.5 eV from studies of the optical properties of the band edge under pressure. To obtain an idea of the value of E_c above, we recall the results of the pressure experiments on the group IV and III–V semiconductors. It has been found that the pressure coefficients for the various direct gaps are fairly constant for all these semiconductors.[26] In addition, it has been found that for Ge the coefficients for the conduction and valence bands have comparable magnitudes but opposite signs.[27] If, as appears likely, a similar relationship holds for CdTe, E_c is roughly 2–3 eV. With $E_c=2.5$ eV the mobility due to this type scattering would be given by

$$\mu_{dp}=1.5\times 10^5(300/T)^{3/2}\ \text{cm}^2/\text{V sec}, \quad (3)$$

which is over a factor of 100 larger than the observed mobilities. In order for deformation potential scattering to be contributing appreciably, i.e., about 20%, E_c would have to be more than five times the value assumed. As this seems excessively high, it appears that this mechanism does not play a significant role.

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[21] H. Ehrenreich, J. Phys. Chem. Solids **2**, 131 (1957); **9**, 129 (1959); Phys. Rev. **120**, 1951 (1960). See also C. Hilsum and A. C. Rose-Innes, *Semiconducting III–V Compounds* (Pergamon Press, New York, 1961).

[22] See, e.g., H. Brooks, in *Advances in Electronics Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7, p. 85.

[23] The average over directions was obtained by averaging the values of ρu_l^2 in the [100], [111], and [110] directions using the weighting factors 6, 8, and 12, respectively. The result is $\rho\langle u_l^2\rangle = C_{11}+17/39[C_{12}+C_{44}-C_{11}]$, where the C_{ij} are the elastic constants.

[24] H. J. McSkimin and D. G. Thomas, J. Appl. Phys. **33**, 56 (1962).

[25] D. W. J. Langer (private communication).

[26] W. Paul, J. Appl. Phys. **32**, 2082 (1961).

[27] H. R. Philipp, W. C. Dash, and H. Ehrenreich, Phys. Rev. **127**, 762 (1962).

Piezoelectric scattering, which occurs for crystals with the zinc blende structure because of the nonvanishing polarization associated with the acoustic mode, has been studied by Meyer and Polder[28] and Harrison.[29] The mobility due to this type of scattering alone is given by

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

where ϵ_s is the static dielectric constant and e_{14} is the piezoelectric constant. Unfortunately, e_{14} is not known for CdTe. However, the constant is known for three other II–VI compounds with the zinc blende structure: ZnS,[30] ZnSe,[31] and ZnTe,[32] for which it has the values 4.2×10^4, 1.90×10^4, and 8.8×10^3 esu/cm^2, respectively. On the basis of the trend of these constants, which is at least in part due to the decreasing ionic nature of crystals in the sequence, we can reasonably assume that e_{14} for CdTe would be about that for ZnTe, or, at least, not much more.[33] Using the value for ZnTe we find

$$\mu_{\text{piezo}}\approx 1.9\times10^6(300/T)^{1/2}\ \text{cm}^2/\text{V sec}, \quad (5)$$

which is again, at least, a factor of 100 larger than the measured values of μ in the intrinsic range. Thus, this mechanism also does not contribute significantly.

The preceding results imply that the polar optical mode scattering, which results from the interaction of the electron with the electrical polarization associated with the optical phonons, must essentially account for all the scattering in the intrinsic range. When the coupling between the electrons and phonons is relatively weak, it suffices to study the mobility of the "bare" electron interacting with the phonon field by a weak coupling treatment. If, on the other hand, the interaction is strong, the problem becomes more complicated as it is then necessary to consider the mobility of the "polaron," the electron with its associated polarization cloud. A measure of the strength of the coupling is given by the so-called coupling constant

$$\alpha=(m^*/m)^{1/2}(\text{Ry}/\hbar\omega_l)^{1/2}(\epsilon_\infty^{-1}-\epsilon_s^{-1}), \quad (6)$$

where $\hbar\omega_l$ is the energy of the longitudinal optical mode, Ry is the rydberg, and ϵ_∞ and ϵ_s are the high- and low-frequency dielectric constants, respectively. Using the measured values of these quantities, i.e., $\hbar\omega_l=0.0213$ eV,[11] $\epsilon_\infty=7.13$,[17,1,3] and $\epsilon_s=10.6$, we find that $\alpha=0.39$. Since the parameter whose smallness (compared to unity) determines the quantitative accuracy of the weak-coupling approximation[34] appears to be $\alpha/6$, and since $\alpha/6\ll1$, we can expect the perturbation approach to give quantitatively correct results for this material.

The weak-coupling result for a nondegenerate semiconductor having a simple band, which we will use, is essentially the result obtained by Howarth and Sondheimer.[35] Taking into account the fact that the Callen charge should be used,[21] the mobility can be written as

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

if $\hbar\omega_l$ is in eV. Here $z=\theta/T$ where θ is the Debye temperature defined by $\hbar\omega_l=K\theta$ and $G(z)e^{-\xi}$ is a function which has been evaluated by Howarth and Sondheimer and generalized by Ehrenreich[36] to include the effects of the screening by the carriers. It is to be noted that for the carrier concentrations that we are concerned with, $\hbar\omega_p/\hbar\omega_l\ll1$ where the plasma frequency, ω_p, is defined by $\omega_p^{2}=4\pi e^2n/\epsilon_\infty m^*$. Thus, the screening effects are negligible for the present samples.

Other corrections to the mobility arising from nonparabolicity of the conduction band and from the p component of the conduction band wave function for nonvanishing $\mathbf{k}$ vectors were shown to be significant in the study of InSb.[21] On the basis of Kane's results for the energy bands in a zinc blende crystal resulting from interaction of the conduction and valence bands[37] it can be shown that for kinetic energies small compared to the band gap E_g one has

$$E(\mathbf{k})=E_g+\epsilon_k\left\{1+\epsilon_k\left(1-\frac{m^*}{m}\right)^{2}(E_g+\tfrac{2}{3}\Delta)^{-1}\times\left[1-\frac{(E_g+\tfrac{2}{3}\Delta)(2E_g+\Delta)}{E_g(E_g+\Delta)}\right]+\cdots\right\},$$

where Δ denotes the spin-orbit splitting of $\Gamma_{25'}$ and where $\epsilon_k=\hbar^2k^2/2m^*$. For kinetic energies equal to kT the nonparabolic terms introduce a correction of only about 1%, which is negligible for our purposes. Similarly, the admixture of p function in the wave function of a thermal electron can be estimated, and is found to be about 0.1. Admixtures of this magnitude lead to corrections of the order of 1% in the relevant matrix element because of the orthogonality of the s and p functions. That both corrections, which are significant in InSb, are negligible in CdTe is a consequence of the

[28] H. J. G. Meyer and D. Polder, Physica **19**, 255 (1953).
[29] W. A. Harrison, Phys. Rev. **101**, 903 (1956).
[30] W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946), p. 229.
[31] D. Berlincourt, H. Jaffe, and L. R. Shiozawa (to be published).
[32] L. R. Shiozawa, Clevite Corporation Final Technical Report. Contract No. AF33(616)-6865 (unpublished).
[33] After this work was completed the results of electro-elastic measurements by D. Berlincourt, H. Jaffe, and L. R. Shiozawa (reference 31) were made available to us. They found the 77°K value of e_{14} to be 1.01×10^4 esu/cm^2 and obtained an extrapolated room-temperature value of 0.91×10^4 esu/cm^2. Inasmuch as our assumption is in accord with their results, our estimate for μ_{piezo} needs no revision.
[34] This inference is based on the fact that for couplings such that $\alpha/6\ll1$ the self-energy and effective mass of the free polaron [see R. P. Feynman, Phys. Rev. **97**, 660 (1955)] and the binding to a Coulomb potential (reference 18) are given correctly by the weak coupling approximation.
[35] D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).
[36] H. Ehrenreich, J. Phys. Chem. Solids **8**, 130 (1959).
[37] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).

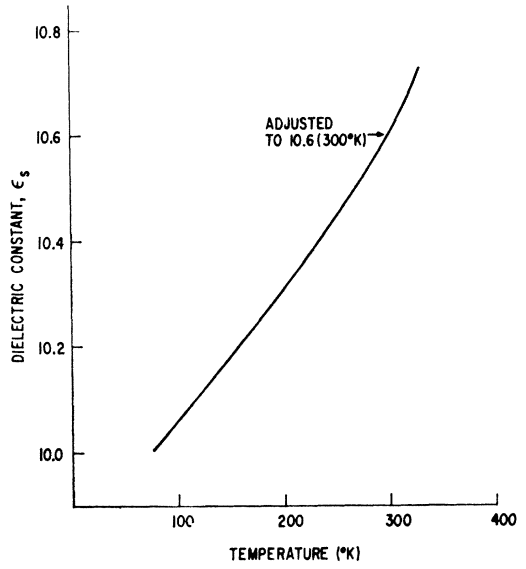

FIG. 6. Temperature dependence of the static dielectric constant of CdTe measured at 5 kc/sec on polycrystalline CdTe films.

fact that the band gap is relatively much larger in the latter.

Carrier-carrier scatterings are also known to affect the mobility. Since the concentration of holes is extremely small, electron-hole scattering is completely negligible. As has been noted earlier,[38] electron-electron (*e–e*) scattering for simple bands cannot alter the total momentum, and hence the current, but it can produce an effect on the conduction through a redistribution of carrier momenta. The magnitude of this effect depends on the energy dependence of the primary scattering process, as well as the carrier concentration and temperature, being larger where the energy dependence is stronger. The energy dependence of polar scattering has been shown to be as weak if not weaker than that for deformation potential scattering at least for $T>\theta$.[14] The reduction in the mobility for deformation potential scattering due to *e-e* scattering has been shown to be virtually nil for $T\gtrsim 60°K$.[39,40] The neglect of this scattering mechanism is, therefore, amply justified for polar scattering in the intrinsic temperature range.

The mobility given in Eq. (7) is the drift mobility, while the experimental quantity plotted in Fig. 1 is the Hall mobility. The ratio $r=\mu_H/\mu_D$ for this case has been obtained by Delves[15] who solved the Boltzmann equation numerically for the weak field case.

Another point, which to our knowledge has not previously been taken into account when μ_{polar} has been compared with measured values for semiconductors, is that (7) was derived under the assumption that the parameters ϵ_s, ϵ_∞, $\hbar\omega_l$, and m^* are constant. In actuality all these parameters may vary somewhat with T.[41] Arguments can be given to suggest that the effect on μ_{polar} from changes in ϵ_∞ and m^* are small.[42] As we will show below, present information also points to a very small change in $\hbar\omega_l$. The variation of the remaining parameter, ϵ_s, could have an appreciable effect on α for this semiconductor since there is considerable cancellation in the factor $\epsilon_\infty^{-1}-\epsilon_s^{-1}$. We propose to consider the effect of the variation of this parameter on the mobility by the simple phenomenological means of inserting its T dependence in (7).

A measurement of the temperature dependence of the static dielectric constant of polycrystalline CdTe films for $T=80$ to 325°K is reproduced in Fig. 6.[43] The data are normalized to an absolute value for ϵ_s of 10.6 at 300°K, a value compatible with film and single-crystal measurements[17,1,3] and probably accurate within several percent. A change of 6% is observed between 80 and 300°K. The error limits of prior measurements indicating no temperature dependence of the reflectivity of CdTe in the far infrared are sufficiently great to allow this result.[44] Direct measurement of $\hbar\omega_l$ has been possible only at low temperature. From phonon-structured band edge emission spectra, $\hbar\omega_l(20°K)=0.0213$ eV.[11] Mitsuishi[44] has determined by Kramers-Kronig analysis of reststrahl data that $\omega_t(90°K)=144$ cm^{-1} and $\omega_t(300°K)=140$ cm^{-1} in CdTe. It is interesting to note that with these values the temperature dependences of ϵ_s and ω_t roughly cancel out in the Lyddane, Sachs, Teller relation $\hbar\omega_l=(\epsilon_s/\epsilon_\infty)^{1/2}\hbar\omega_t$. Therefore, if one makes the previously discussed assumption of a negligible temperature dependence for ϵ_∞,[42] the temperature dependence of $\hbar\omega_l$ can also be neglected for this material. It should also be noted that a small change in $\hbar\omega_l$ would only produce a small change in the mobility. The value $\hbar\omega_l=0.0213$ eV will subsequently be taken as a constant over the temperature range of interest.

In Fig. 7 we show μ_{polar} calculated from Eq. (7)

[38] See, for example, Debye and Conwell, reference 19.
[39] J. Appel, Phys. Rev. **122**, 1760 (1961).
[40] T. P. McLean and E. G. S. Paige, J. Phys. Chem. Solids **16**, 220 (1960).

[41] It has come to our attention that similar effects have been considered in the alkali and silver halides by R. Van Heynigan, Phys. Rev. **128**, 2112 (1962); and F. C. Brown (private communication).
[42] The high frequency dielectric constant is given in terms of the classical expression for the bound oscillator, involving oscillator strengths and energy differences, summed over the bands. The T dependence of ϵ_∞ would come from the variations in the momentum matrix elements and in the energy differences for a given $\mathbf{k}$. It should be noted that the largest contributions to the sum comes at energies of ≈ 4 or 5 eV while the shifts in the band gaps are approximately 0.1 eV in the range of 100 to 300°K. Furthermore, the correction arising from the change in the momentum matrix element is of the opposite sign. These considerations suggest a small variation in $\epsilon_\infty(T)$. Unfortunately, experimental data on the question are unavailable. Similar considerations also lead to the conclusion that effective mass should change by the order of a percent in the relevant temperature interval. [See M. Cardona, Phys. Rev. **121**, 752 (1961) for a discussion of $m^*(T)$ for GaAs which has comparable band gap and m^*.] The resulting change in the mobility would be correspondingly small.
[43] R. E. Halsted and H. D. Coghill (to be published).
[44] A. Mitsuishi, J. Phys. Soc. Japan **16**, 533 (1961).

using the room temperature value of ϵ_s as the dashed curve. The solid curve shows the corresponding Hall mobility[45] which also includes the correction for the temperature variation of $\epsilon_s(T)$. Also included for comparison purposes are the measured values of μ_H for the highest mobility sample augmented by a few values for other crystals at higher temperatures to increase the temperature range. We note that while the uncorrected mobility curve is in rough accord with experimental data, the corrected mobility is in quantitative agreement down to about 100°K. At high temperatures the uncorrected μ_{polar} exhibits a greater curvature than the measured or the corrected mobility. The explanation for this is simply that due to the T dependence of ϵ_s the strength of the interaction increases as T increases and as a result the mobility decreases. At the low-T end of the intrinsic range (~80–100°K) the measured values fall below the theoretical curve. There are two reasons for this. Scattering due to the defects is becoming increasingly important and tends to reduce μ. Also important is the fact, mentioned earlier, that at these mobilities and fields, we are getting into the "high-field" region, and here $\mu_H(H) \rightarrow \mu_d$. The fairly large correction factor ($r \approx 1.3$ for these temperatures) included in the solid curve is the "low-field" value of μ_H/μ_d. Therefore, the actual agreement with theory is even better than indicated by the curves. The small discrepancies are understandable in view of the uncertainties in the experimental values and in the approximations involved in the theory.

The quantitative agreement found for μ in the intrinsic range is significant in several ways. First, it provides additional support for the validity of μ_{polar} [Eq. (7)] when appropriately employed. Secondly, the agreement and the fact that μ being proportional to $(m^*)^{-3/2}$ is moderately sensitive to the mass value, tends to confirm our initial estimate of $m^*=0.11m$. This value is in agreement with Marple's direct and probably more precise determination of $m^*=(0.11\pm0.01)m$ obtained by means of Faraday rotation and free carrier reflectivity measurements. In turn, the fact that $m^*=0.11m$ was estimated on the basis of the $\mathbf{k}=0$ minimum throws additional (albeit indirect) support behind this picture of the conduction band.

TABLE II. A comparison of mobilities calculated for CdTe at 23°K (impurity scattering range) with experiment. The results of assuming different scattering mechanisms are illustrated.

Sample identification	Measured and computed mobilities (10^{+4} cm²/V sec)					
		Single donor		Double donor		Neutral
	Measured	Drift	Hall	Drift	Hall	impurity
A(+)	5.7	4.7	7.7	2.0	3.3	35
B(○)	2.3	0.7	1.1	0.33	0.51	19
C(△)	1.5	1.1	1.7	0.35	0.57	4.4
D(×)	1.7	1.1	1.7	0.19	0.29	12
E(□)	1.6	1.2	1.9	0.42	0.62	21

[45] Since Delves (reference 12) gives the factor $r=\mu_H/\mu_D$ for only a few values of θ/T, only a rather approximate interpolation was possible.

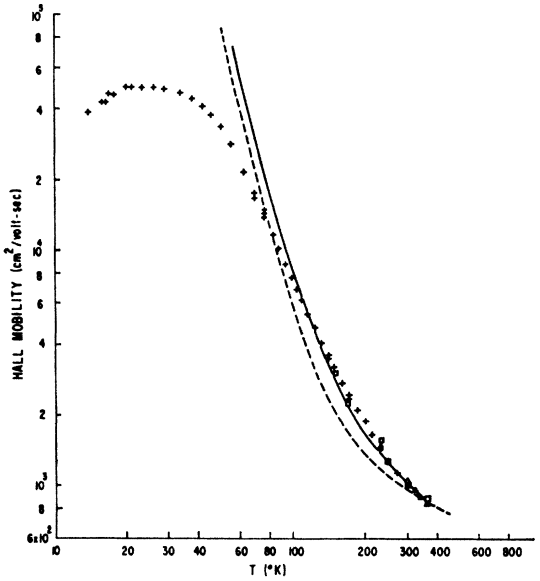

FIG. 7. Comparison of CdTe electron mobility data with theory for polar optical scattering. Dashed curve shows effect of neglecting correction for temperature dependence of the static dielectric constant.

Mobility in the Defect Limited Range

For T below about 70°K the mobilities of the samples considered are obviously strongly affected by the crystal imperfections. Undoubtedly, charged impurity scattering becomes very important here. Also, if there are a sufficiently large number of neutral impurities with large orbits, they too can contribute appreciably to the reduction of μ.

We have calculated the mobilities associated with each of these mechanisms separately. For the mobility limited by charged impurity scattering, we have used the well-known Brooks-Herring formula[22] and have taken into account the temperature variation of the number of ionized centers N_I and the number of screening electrons, n_i. Both the single and double donor cases were examined. The mobility for neutral impurity scattering was evaluated from the formula derived by Erginsoy[46] using the computed number of neutral impurities N_n at the given temperature. The quantities N_I, n_i, and N_n were determined for the different samples on the basis of the N_a and N_d given in Table I.

Typical results for these calculations are given in Table II for $T=23$°K. Calculations for other low temperatures ($T<35$°) were also performed. We have restricted ourselves to this temperature range since for higher T the combined effect of impurity and polar

[46] C. Erginsoy, Phys. Rev. **79**, 1013 (1950).

scattering must be considered as is evidenced by the bending over of μ at about 25 to 40°K. There are a number of points to be noted from the results in Table II. One is that the mobility associated with the neutral impurity scattering is much higher than that for charged impurity scattering. Another is that the computed mobility associated with the charged impurity scattering for the double donor case is quite a bit lower than the observed mobilities, while the computed mobilities for the simple donor case are in fair accord with experiment. Finally, the calculated drift and Hall mobilities for the simple donor model generally bracket the measured quantity. Similar results were obtained for the other low temperatures considered. As we have noted before, for these temperatures and the field of 7.3 kG, we are not in the low-field regime, so that the measured Hall mobility should be between the low-field Hall mobility and the drift mobility values. Since we would expect the Brooks-Herring theory to give results which are at least semiquantitatively correct, this result yields support to the simple donor picture. It was previously noted that the donor depth and saturation value of n obtained from $n(T)$ analysis could best be interpreted in terms of a simple donor. It would therefore seem quite likely that a residual simple impurity and not a doubly ionizable intrinsic defect is controlling the transport behavior of these zone-refined samples.

Several comments on the limitations of the theory are appropriate. First of all, the simple theory of impurity scattering is not as well founded as would be desirable.[47] Also, Erginsoy's formula is based on the assumption that the wave function of the impurity is hydrogenic. Since our results for ϵ_d suggest that concentration effects are lowering the ionization energy, it is not unlikely that the wave functions are more diffuse than that predicted by the hydrogenic model. If this were so, the neutral scattering would be correspondingly stronger. Finally, as we noted before, there may be some double acceptors compensating the donors. As a double acceptor scatters four times more effectively than does a single acceptor, the mobility would be reduced. If these acceptors represented a large fraction of the total, the agreement noted above would be poorer.

Magnetoresistance

The magnetoresistance effect in CdTe was found relatively small, $\Delta\rho/\rho H^2 < 10^{-11}$ G^{-2}. This is an order of magnitude smaller than observed, e.g., in GaAs and InP.[8] Unhappily, it was found to be complicated by contact effects which we have been able to reduce, but not eliminate to date, by attempts at reducing the contact area. Measured values of the transverse magnetoresistance have ranged from 1.5×10^{-12} to 8.5×10^{-12} G^{-2} in different samples at room temperature. Contact effects which could be as large as the bulk magnetoresistance were described in the work with InP and GaAs. So perhaps it is not surprising to observe similar behavior in CdTe. Figure 5 shows that contact effects can yield spurious information on the apparent angular dependence of magnetoresistance in CdTe. Because of this uncertainty in angular dependence data, we believe that our present results are of questionable value in elucidating the band structure of CdTe. Their similarity with prior results would also lead us to question the experimental basis of Yamada's suggestion that the conduction band minimum is not at $\mathbf{k}=0$.

[47] C. Herring, in *Proceedings of the International Conference on Semiconductor Physics, Prague, Czechoslovakia, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 60.

SUMMARY

Transport measurements have been performed on high purity and doped n-type single crystal CdTe with 300°K carrier concentrations ranging from 6×10^{14} to 2×10^{18} cm^{-3}. The temperature dependence of the Hall coefficient and resistivity was investigated. The magnetoresistance and magnetic field dependence of the Hall coefficient were also examined. The temperature dependence of the free electron concentration in high-purity CdTe samples is consistent with theoretical curves calculated for a simple donor with a depth of 0.010 eV. The data reveal the presence of a deeper level which was not considered further in this investigation. The Hall mobility of high-purity CdTe exhibits a region of intrinsic behavior as it rises rapidly with decreasing temperature from 1050 cm^2/V sec at 300°K to values as high as 57 000 cm^2/V sec at 30°K. These data proved amenable to analysis comparable in detail to the more favorable cases among the compound semiconductors.[21] It was shown that acoustic, piezoelectric, and nonpolar optical mode scattering make a negligible contribution to the observed intrinsic scattering. Polar scattering by the longitudinal optical phonons, however, provides quantitative agreement with the experimental Hall mobility assuming a $\mathbf{k}=0$ minimum, $m^*=0.11\,m$ and correcting for the temperature dependence of the static dielectric constant. Corrections to the polar optical mode scattering due to the nonparabolic terms in the conduction band $E(\mathbf{k})$, the admixture of p component in the conduction band wave function for $\mathbf{k}\neq0$, screening by the carriers, and electron-electron scattering are found to be negligible. The electron effective mass used in the mobility analysis is in agreement with Marple's[18] result from Faraday rotation and free carrier reflectivity measurements. The compatibility of the results with the $\mathbf{k}=0$ hypothesis and the agreement of the mass estimated from the $\mathbf{k}\cdot\mathbf{P}$ approach for a $\mathbf{k}=0$ minimum with Marple's value is considered additional evidence in favor of this disputed point.

At low temperatures the mobility is limited by impurity scattering. The possible contributions of neutral,

double donor and simple donor scattering are examined. The experimental results best conform to scattering calculated for a simple singly charged donor impurity.

In addition, the donor ionization energies and the saturation values of $n(T)$ appear to be more satisfactorily understood in terms of a simple donor than a double donor (e.g., native defect). It, therefore, seems quite probable that the donor defect controlling the electrical properties of these zone-refined crystals is a residual simple impurity.

Magnetoresistance effects proportional to H^2 were readily observed. This was found due in part to contact effects which obscured both the magnitude and angular dependence of the true effect for CdTe. The magnitude for CdTe is, however, $<10^{-11}$ G^{-2} at 300°K. The uncertainty of the angular dependence must be removed before definitive conclusions concerning band structure can be drawn from this type of measurement.

ACKNOWLEDGMENTS

The authors employed instrumentation developed by H. H. Woodbury for the transport measurements and are indebted to him also for much helpful advice. We also thank Professor F. C. Brown for helpful discussions, Miss E. L. Kreiger who performed much of the computational work, and B. B. Binkowski and L. H. Esmann who ably assisted with sample preparation and measurement.

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Knight Shifts in Niobium-Molybdenum Alloys

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Measurements of the Knight shift of Nb^{93} in Nb-Mo alloys are reported. For alloys containing less than 40 at.% Mo, the shift is equal to the Nb metal shift of 0.83%. For higher Mo concentrations, the shift decreases linearly with concentration to a value of 0.57% at 95 at.% Mo. The possible meaning of these results and their relation to other measurements on these alloys are discussed.

WE have measured the Knight shift (K_S) of Nb^{93} nuclei in alloys of Nb and Mo as a function of concentration. The results are shown in Fig. 1. It can be seen that the shift is constant within experimental accuracy up to about 40% Mo and is equal to the Nb metal shift of 0.83%. For higher Mo concentration K_S decreases linearly as the molydenum concentration is increased.

The resonance frequencies were determined from the position of the zero-slope point on the resonance line, i.e., from the point where the derivative changes sign. For high Nb concentration (above 30% Nb) the resonance lines were asymmetric with long tails towards high fields and about 30 G wide. At lower Nb concentrations the lines narrowed, becoming 2 G wide in the 5% Nb alloy. The shifts were measured by comparison with the Br^{79} nuclear resonance in water solution of KBr, assuming the nominal values of 1040.7 and 1066.7 cps/G for the gyromagnetic ratios of Nb^{93} and Br^{79}, respectively. From the intensity of the observed resonance lines it seems that one only sees the $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition of the Nb nucleus.

The measurements were carried out on a Varian spectrometer. Most alloys were measured at room temperature in a field of 15 kOe. A number of alloys were, however, measured also at fields of 12 and 8 kOe. No significant changes in the fractional shift or in the linewidths were found at these fields (see Fig. 1). It, therefore, seems clear that quadrupole effects are not important either for the measured shift or for the linewidth. No temperature dependence of K_S was found down to 4°K.

Niobium-molybdenum alloys have been investigated extensively in recent years. Hulm *et al.*[1,2] have measured

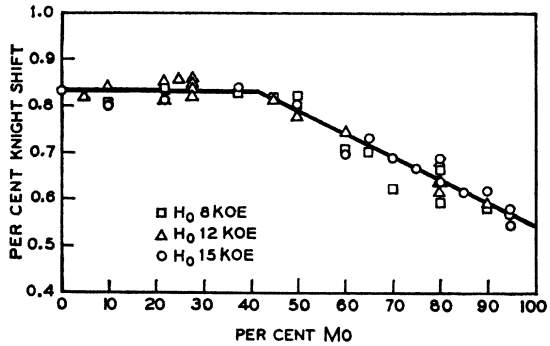

FIG. 1. The percentage Knight shift of Nb^{93} in Nb–Mo alloys as a function of Mo concentration. Measurements at 15, 12 and 8 kOe are included.

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[1] J. K. Hulm and R. D. Blaugher, Phys. Rev. 123, 1569 (1961).
[2] J. K. Hulm, R. D. Blaugher, T. H. Geballe, and B. T. Matthias, Phys. Rev. Letters 7, 302 (1961).