maximum in χ'') is shifted to higher temperatures with increased frequency.

[6]The influence of impurity-clothed dislocations has been discussed by R. W. Shaw and D. E. Mapother, Phys. Rev. 118, 1474 (1960), in connection with filamentary structure observed in magnetic transitions. Dislocations as a possible source of filamentary structure have also been discussed by others, e.g., J. E. Kunzler, Rev. Modern Phys. 33, 501 (1961); J. J. Hauser and E. Buehler, Phys. Rev. 125, 142 (1961).

DOUBLE ACCEPTOR DEFECT IN CdTe†

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In the course of studying the electrical properties of high-purity single crystals of CdTe, a new center, thought to be a native double acceptor, has been observed. It is believed to be the first of its kind in compound semiconductors identified by electrical transport measurements. This center is formed during heat treatment in a Cd atmosphere. The doubly ionized acceptor level lies 0.056 eV below the conduction band, and when this level is filled the center contains two electrons and is an effective hole trap at low temperatures. In fact, the singly negatively charged center has such a low cross section for electron capture that it is impossible to observe a normal freeze-out of electrons into the second level when the samples are cooled below a critical temperature region. A similar level about 0.09 eV below the conduction band has also been found in CdS.

CdTe samples were prepared by techniques already described.[1] High-purity crystals having a residual impurity donor concentration of about 10^{15} cm^{-3} were used.[2] Hall bars of approximately $3\times3\times10$ mm^3 were sealed in small evacuated quartz ampoules to which Cd metal was added. These were heated to various temperatures for varying lengths of time and then quenched. The surface regions of the samples were removed by grinding, etching, and a final chemical polish. The crystals were then studied using conventional dc techniques to measure the Hall coefficient, resistivity, and Hall mobility from 350°K to 12°K. There were provisions for exciting the samples with a small incandescent lamp mounted inside the cryostat.

The temperature dependence of the Hall constant for electrons in several samples is shown in Fig. 1. Curve *A* represents an unfired sample; curve *B*, a sample fired at 900°C for 30 min; and curve *C*, a sample fired at 900°C for 285 h. The solid curves correspond to measurements without light, and the dashed curves show the effects following photoexcitation at the lowest temperature. Freeze-out of electrons into the level of interest starts near 300°K and is most pronounced in curve *B*. The thermal activation energy is 0.056 eV. At about 110°K the electronic equilibrium

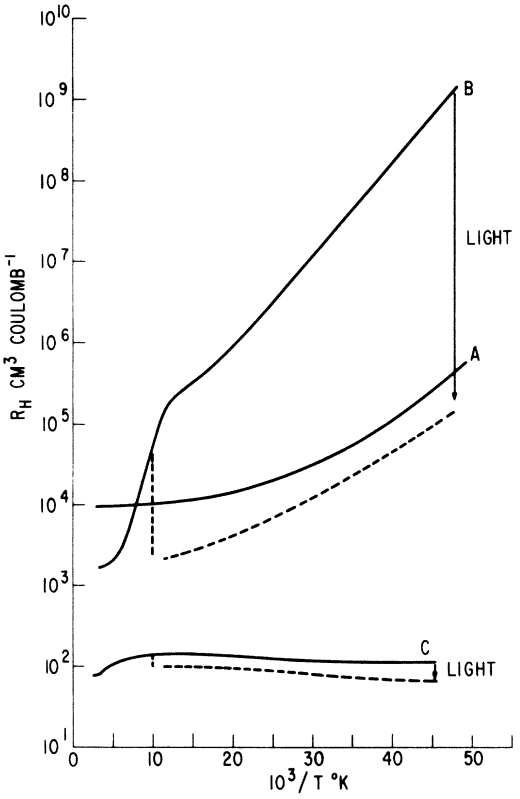

FIG. 1. The temperature dependence of the Hall coefficient, R_H, of n-type CdTe samples. The dashed curves show R_H after photoexcitation at the lowest temperature. *A*: original high-purity material; *B*: Cd fired for one-half hour at 900°C; *C*: Cd fired for 285 hours at 900°C.

starts to lag the thermal equilibrium. The lag increases as the temperature is lowered, and at 85°K it is necessary to wait several hours to establish electronic equilibrium. At lower temperatures it becomes impossible to reach equilibrium with regard to the 0.056-eV level. This sluggishness was observed for the heating as well as the cooling of samples in this temperature region.

The peculiarity of the above behavior suggests that a barrier is associated with the 0.056-eV level. The decay of conduction electrons following photoexcitation was measured at four temperatures in the critical temperature region, i.e., 95 to 115°K. The simple relation $\Delta n = c \exp(-t/\tau)$ was observed over three decades at each temperature, and over the limited temperature region the lifetime can be expressed as $\tau = \tau_0 \times \exp(0.27\ \mathrm{eV}/kT)$, where $\tau_0 = 3.2 \times 10^{-12}$ sec.

In Fig. 2 the Hall mobilities are shown corresponding to the Hall constants of Fig. 1. Curve *A* again is the unfired sample which also exhibits the intrinsic mobility over the range shown.[2] Photoexcitation did not change the mobility for this sample. There is, however, a pronounced effect on the mobility of the fired samples, as seen from the dashed curves. After photoexcitation at the lowest temperature, the mobility shows a marked increase. The original

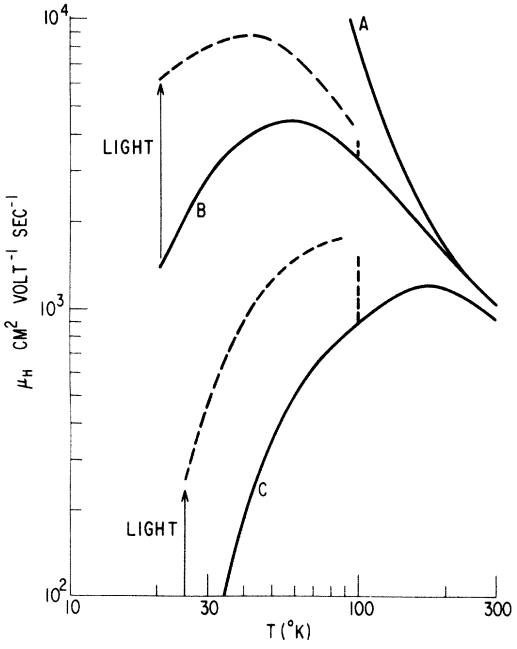

FIG. 2. The electron Hall mobility, μ_H, of the samples shown in Fig. 1.

mobility curve is rejoined at about 100°K, the temperature at which the excess electrons, thrown out of equilibrium at the lowest temperature, are able to freeze into the 0.056-eV level.

We conclude that the 0.056-eV level, although close to the conduction band, is the doubly ionized state of a two-level acceptor defect. The singly ionized state has a charge of -1 and is responsible for the barrier observed. Photoexcitation at the lowest temperature produces hole-electron pairs. The holes are captured (trapped) by the filled double acceptor centers resulting in a change of the charge state of the centers from -2 to -1. The excess electrons are unable to reach electronic equilibrium with the centers because of insufficient kinetic energy to surmount the barrier about the singly occupied defect. When the temperature is raised to the critical region, the Hall constant increases and the mobility decreases to their original values as electronic equilibrium is re-established.

The explanation of the behavior observed in these crystals is based on a double acceptor model analogous to that established for many impurities in Ge.[3] Qualitatively, the observed effects on mobility and Hall coefficient with and without light show a one-to-one correspondence between the effects reported here and those reported, for example, for Mn-doped Ge.[4] A quantitative difference appears to be that in the present case, the ratio of the barrier to the second (thermal) ionization energy is much greater than the ratio seen for double acceptors in Ge. This prevents thermal equilibrium from being established as the CdTe samples are cooled, but causes no difficulty for the double acceptor centers seen in Ge.

It is to be emphasized that the double acceptor centers described here are not necessarily the dominant defects in the CdTe system. Under the present preparative conditions, their formation is accompanied with a concurrent formation of donor centers. The results indicate that for short firing times the samples are slightly more *n* type than they were originally but are also more compensated. Hence, the 0.056-eV level appears to be dominant. After long periods of firing the concentration of both acceptor and donor defects increase, but the latter more than the former. There is an additional peculiarity in this system. Short firing times of about one-half hour produce, after surface region removal, a homogeneously changed sample. Long firing times of several hundred hours also yield homo-

geneous samples. However, treatment times of intermediate periods result in inhomogeneous crystals. This suggests that at least two processes occur during heat treatment. The fast one is essentially complete after a short time and then is succeeded by a much slower process.

The following evidence strongly suggests that the double acceptor center described here is a native defect. It is observed only when samples were quenched and is seen in excess of the number of donors and acceptors normally found in slow cooled or annealed samples. Spectroscopic analysis on CdTe has revealed that likely common metal impurities are below the defect concentrations observed. After heat treatment in excess Cd, a similar double acceptor defect with the doubly ionized level 0.09 eV below the conduction band has also been seen in CdS. Its electrical properties are identical to the center described here in CdTe. Furthermore, CdTe samples showing the behavior illustrated in curve *B* of Fig. 1 go to high resistance within several days on standing at room temperature. This decay is suggestive of recombination of Frenckel defects or precipitation of Schottky centers. The present results, however, do not permit an unambiguous identification of the native double acceptor center. Although we beleive that the center is a simple native defect, we cannot rule out the possibility that the actual defects involved may be complexes of interstitials and/or vacancies or even chemical impurities that are not normally electrically active. However, such complexes must maintain the properties of a double acceptor.

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[1]M. R. Lorenz and R. E. Halsted (to be published).

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

[3]See, for example, W. W. Tyler and H. H. Woodbury, Phys. Rev. 102, 647 (1956).

[4]Compare Figs. 11 and 10 of reference 3 with Figs. 1 and 2, respectively, of this Letter.

STRUCTURE IN THE DENSITY OF STATES OF SUPERCONDUCTING INDIUM FILMS*

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Giaever, Hart, and Megerle,[1] and more recently Rowell, Chynoweth, and Phillips,[2] have reported humps in the conductance vs voltage curves for electrons tunneling between a normal metal and a superconductor through a thin insulating barrier. If one assumes (see Bardeen[3]) that the matrix element, M, that appears in the transition probability for electrons tunneling through the barrier is constant for small energy differences, then the reported humps in the conductance curves indicate structure in the density-of-states distribution. Solutions of the integral equation which gives the energy gap parameter, Δ, as a function of the excitation energy E have been carried out by Swihart[4] and Culler, Fried, Huff, and Schrieffer.[5] Both of these predict structure in the density of states, in particular, two humps occuring at energies near $k\Theta_D$ and $2k\Theta_D$, where Θ_D is the Debye temperature. However, Rowell, Chynoweth, and Phillips[2] observed far more extensive harmonic structure in the density of states of lead than had been theoretically predicted. They observed this structure at engeries $\Delta + nE_T$, where E_T is the energy of the transverse acoustic phonon in lead, and n is an integer. Since such structure until now has only been observed in lead, it is of interest to examine other superconductors. As one expects such structure to be most readily observed in superconductors having a low Θ_D, the most suitable choices appear to be mercury, indium, and tin. The purpose of this Letter is to describe the conductance vs voltage curve for indium obtained from our tunneling experiments with In-Al_2O_3-Al junctions.

The relative conductance, $(dI/dV)_{ns}/(dI/dV)_{nn}$,