

Self-Compensation-Limited Conductivity in Binary Semiconductors. II. n -ZnTe†

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Paramagnetic resonance has been observed in Al-doped ZnTe grown in excess Te vapor. The resonance is due to a hole trapped at a defect consisting of a doubly negatively charged zinc vacancy V_{Zn}^{2-} and an Al^{3+} donor ion on one of the twelve zinc sites nearest the V_{Zn}^{2-} . The hole is trapped at the defect after irradiating the sample at 77°K with light of energy less than that of the band gap. The g tensor is orthorhombic, as expected for such a defect. Compensation of donor or acceptor impurities by doubly as opposed to singly ionized defects has been shown to be important in II-VI compounds. The observed resonance shows that compensation of Al donors in ZnTe by doubly charged zinc vacancies does indeed occur. A consequence of the self-compensation of donor impurities in ZnTe is that there is a limit to how n -type the material can be made. Similar attempts to dope ZnTe n -type were carried out with Ga, In, Br, and I. Only insulating crystals were produced, even after subsequent firing in Zn vapor. No analogous resonance signals were observed in these sample, however.

INTRODUCTION

IN this paper paramagnetic resonance measurements are presented for a defect found in Al-doped ZnTe grown in excess Te vapor. The resonance is due to a hole trapped at the defect which consists of a doubly negatively charged zinc vacancy, V_{Zn}^{2-} , and an Al^{3+} donor ion on one of the twelve zinc sites nearest the vacancy. The observation in ZnTe of a donor ion compensated by a vacancy, apart from any intrinsic interest, is important in that it is this mechanism of compensation of donor impurities by vacancies that has been proposed to explain the observed limit in n -type conductivity in ZnTe.¹⁻³

Limits in the conductivity have been observed in several II-VI compounds, particularly in p -type CdSe and in n -type ZnTe. Several authors have proposed that the limit in conductivity may be due to compensation of the added donor or acceptor impurities by vacancies or interstitial atoms.¹ Since a rearrangement of the host lattice is involved, this form of compensation is referred to as self-compensation. Brebrick outlined a theory for considering the process of self-compensation.² The theory has been extended by Mandel to enable the minimum amount of self-compensation in binary semiconductors to be calculated.³ He shows that, in II-VI compounds, self-compensation of added impurities by singly ionizable defects is insufficient to account for the observed limits in the conductivity. Self-compensation by *doubly* ionizable defects can, however, account for the limited conductivity.

The resonance and resistivity measurements reported herein do indeed show that compensation of Al donors in ZnTe by doubly negatively charged zinc vacancies

occurs. The defects observed by resonance represent a special case of self-compensation, namely that in which the Al donor and the vacancy are at closest possible sites. These centers represent a small fraction of all self-compensated centers.

Similar resistivity data have been obtained for crystals of ZnTe doped with Ga, In, Br, and I, respectively, although no analogous resonance signals have been observed in these samples.

The degree to which self-compensation limits the conductivity depends on the positions of the energy levels due to the vacancy. From the measured value of the g tensor for the resonance of the paired defect, it is inferred that the energy level due to the doubly charged zinc vacancy is close to the valence band, in agreement with the result derived from Hall effect data.⁴ The Fermi level can be no higher than approximately midway between the second ionization energy level of the compensating zinc vacancy and the conduction band. Since the second ionization energy level of the vacancy is close to the valence band, the Fermi level will be near the center of the band gap. Self-compensation in n -type ZnTe therefore results in material of comparatively low conductivity.

The g tensor for the resonance has orthorhombic symmetry as is expected for the defect involved and as had already been found for the same type of defect in Al-doped ZnS.⁵ The angles which the principal axes of the g tensor make relative to the cubic axes are considerably different in Al-doped ZnTe than in Al-doped ZnS. The difference in the direction of the axes will be shown to be consistent with a more covalent bond in ZnTe than in ZnS.

EXPERIMENTAL

J. A. Kucza of this Laboratory grew the crystals of ZnTe from the melt with aluminum added in metallic form. An excess of tellurium of up to 50% was used. This excess of tellurium lowers the melting point of

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¹ F. A. Kroger and H. J. Vink, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. III, p. 310.

² R. F. Brebrick, *Phys. Chem. Solids* 4, 190 (1958); 18, 116 (1961).

³ G. Mandel, *Phys. Rev.* 134, A1073 (1964).

⁴ M. Aven and B. Segall, *Phys. Rev.* 130, 81 (1963).

⁵ A. Rauber and J. Schneider, *Phys. Letters* 3, 230 (1963).

ZnTe to around 1200°C, so that quartz tubes may be used without softening.

Paramagnetic measurements were carried out at 77°K. No resonances were found for crystals in the dark. When the crystal was irradiated with light near 600 $m\mu$ for a few minutes, an anisotropic resonance was observed. Measurements taken with different orientations of the magnetic field in the (110) plane show that the g tensor of the resonance has orthorhombic symmetry. The values along the three principal axes are given by

$$g_1 = 2.045 \pm 0.001,$$

$$g_2 = 2.088 \pm 0.001,$$

$$g_3 = 2.091 \pm 0.001.$$

The axes of symmetry are similar to those found for the analogous defect in Al-doped ZnS. The resonance is due to a hole which because of the excitation with 600- $m\mu$ light has become trapped at a defect consisting of a doubly negatively charged zinc vacancy and an Al^{3+} ion occupying one of the twelve zinc sites closest to the vacancy. A zinc vacancy is a double acceptor in ZnTe and can accept two electrons. In this state it can compensate two singly ionized donors. In the observed resonance, one of the ionized donors Al^{3+} is in a neighboring site, whereas the other is more distant. The 600- $m\mu$ light excites an electron out of the zinc vacancy leaving a hole trapped at the site. A typical set of symmetry axes for the resonance due to the hole is shown in Fig. 1. g_1 and g_3 are in a type (011) plane and g_2 is along the [011] axis. There are twelve such sites corresponding to the twelve possible orientations of a zinc vacancy and an Al^{3+} ion at a zinc site nearest the vacancy. g_1 and g_3 are found to be rotated away from the [111] and [211] axes, respectively, by $15^\circ \pm 3^\circ$ in ZnTe:Al as compared to 2.5° in ZnS:Al. The g values along the axes of symmetry in ZnS:Al are

$$g_1 = 2.0030 \pm 0.0003,$$

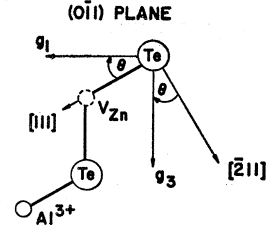
$$g_2 = 2.0513 \pm 0.0003,$$

$$g_3 = 2.0560 \pm 0.0003.$$

The crystals of Al-doped ZnTe did not show the microscopic twinning found in⁵ Al-doped ZnS and the resonances were therefore not as complicated as in that case.

The symmetry observed for the resonance is also consistent with a center involving a monovalent ion such as Li substituting for zinc and a trivalent ion such as Al on a neighboring zinc site. This type of defect is ruled out, however, since no intentional addition of monovalent atoms was made and more convincingly from the effect of heat treating the crystals in various atmospheres. The as-grown samples had a concentration of defects estimated from the resonance spectrum to be about $10^{14}/cm^3$. The resistivity of these samples was measured to be $10^8 \Omega$ -cm p -type at room temperature

FIG. 1. The orthorhombic axes for a hole trapped at a defect consisting of a zinc vacancy and an Al^{3+} ion on one of the twelve zinc sites nearest the vacancy. For simplicity only the bonds lying in the (011) plane are shown.



by use of a four-point probe. Electroless gold contacts were employed. As mentioned earlier, the defects observed by resonance do not represent all Al ions compensated by vacancies but rather only that fraction paired up on nearest possible sites. Chemical analysis of a clear transparent section of crystal showed the concentration of Al atoms in the crystal to be $\sim 10^{19}/cm^3$.

Heat treatment of the crystals in Zn vapor at temperatures above 600°C reduced the room-temperature resistivity to $10^6 \Omega$ -cm and the material became n -type as determined by a hot probe measurement (thermoelectric power). These crystals heat treated in Zn vapor showed no electron paramagnetic resonance (EPR) resonance spectrum indicating that the concentration of paired defects was below $10^{13}/cm^3$. To determine whether it was the temperature alone or the combination of temperature plus excess zinc vapor that had the effect, several crystals were heat treated in vacuum at temperatures between 600 and 1000°C. No effect on the concentration of paired defects was observed indicating that the excess zinc vapor must be present to reduce the number of paired defects. Finally, it was determined that heat treating the as-grown samples in Te vapor increased the number of defects observed. An order of magnitude increase was found for crystals heat treated in Te vapor at 800°C, and these samples were used in carrying out the anisotropy measurements previously described.

One crystal in which the resonance had been observed was taken through a cycle in which it was first heat treated in Zn vapor which caused the resonance to disappear. The same crystal was reheated in Te vapor and the resonance reappeared.

The response to the various heat treatments is consistent with the defect involving a zinc vacancy. This information along with the previously described symmetry measurements, leads to the model of the defect. This consists of a doubly negatively charged zinc vacancy and an Al^{3+} ion on one of the twelve zinc sites nearest the vacancy.

Similar samples were prepared from melts containing Ga, In, Br, and I. Chemical analyses indicated that each of these crystals contained in excess of $10^{19}/cm^3$ of the impurity involved. The results of resistivity measurements on these crystals were essentially identical to those on Al-doped ZnTe, again indicated essentially complete self-compensation. No resonances

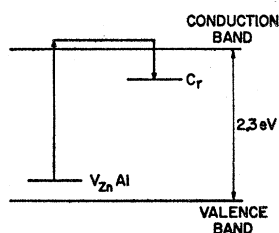


FIG. 2. The mechanism by which 600-m μ light causes a hole to be trapped at the V_{ZnAl} defect.

were observed, however, in any of these samples that were analogous to that observed in optically irradiated Al-doped ZnTe.

This does not imply that defect pairs involving these donors and zinc vacancies do not occur. They may form but because of some change in the nature of the resonance spectrum they are below the apparatus sensitivity. The spectra due to different donors will differ because of a hyperfine interaction between the hole and the donor nucleus.⁶ Because of the larger nuclear spin or larger number of isotopes in the case of Ga, Br, and In the resonance lines are probably broadened below the limit of detection. The case of I cannot so be explained and is also an anomalous case in the formation of defect pairs in ZnS.⁷

DISCUSSION OF THE RESULTS

As previously mentioned, the observation of a donor in ZnTe compensated by a doubly negatively charged zinc vacancy confirms the existence of self-compensation in this material. To trap a hole at the defect, the crystal is irradiated with 600-m μ light whose energy (2.07 eV) is less than the band gap (2.3 eV).⁸ A possible mechanism for this hole trapping process is shown in Fig. 2. The light excites an electron from the V_{ZnAl} defect to the conduction band leaving a hole. The electron is shown being trapped at a Cr site which acts as a deep acceptor in ZnTe.⁹ An actual increase in the number of Cr centers that have accepted an electron is observed by EPR. Unpaired Al^{3+} ions can also act as electron traps as well as other unknown centers. However, no resonance due to Al was observed at 77°K.

The hole that is trapped at the V_{ZnAl} defect is not centered at the zinc vacancy. Because the Al^{3+} ion has an extra positive charge compared to the Zn^{2+} for which it substitutes, it repels the hole. This results in the orthorhombic symmetry of the hole and also causes the g_1 axis to be rotated away from the [111] axis (Fig. 1). The amount it is rotated in ZnTe:Al, 15°, is considerably larger than for ZnS:Al, 2.5°. An explanation for this may be found in the degree of covalency of the

bonds. Because Te is more polarizable than S, ZnTe has more covalent bonds than ZnS. Figure 1 is drawn as if all the charge on the Te is concentrated at the lattice points. However, as the covalency in the bonds increases the charges will begin to occupy the regions along the bonds between lattice points. If some of the charge on the Te site nearest the hole moves toward V_{Zn} , the angle θ will increase.

The values of the g tensor along the principal axes are found to depart more from the g value of the free electron (2.0023) in the case of ZnTe:Al than for ZnS:Al. There are two models that have been used to explain the g values observed for this type of defect.¹⁰ One model considers the anion closest to the hole to have a missing p electron and the ground state is therefore a 2P state. The effect of charges of the surrounding ions on this state is calculated. The threefold degeneracy of the 2P is removed by the field produced by these ions and the g values along the principal axes may be calculated from the positions of the three energy levels.⁷ This model is found to give reasonable agreement with the observed g values for a defect involving a zinc vacancy and a Cl ion in ZnS.¹⁰ In an alternative model the bonding electrons are represented by a linear combination of atomic orbitals (LCAO). The effect on these orbitals of the charge distribution of the impurities is then considered. The g values calculated from this model are also in reasonable agreement with experiment but not quite as good as in the first model.¹⁰ A parameter that enters into the LCAO treatment is the energy required to lift an electron from a bonding orbital to the level in question.¹¹ This is equal to the separation of the energy level due to a vacancy from the valence band. The model shows that the departure of the g value from the free-electron value is inversely proportional to this energy. The larger departures of the g values from the free-electron values in the case of ZnTe:Al would indicate that the energy level due to the zinc vacancy is closer to the valence band in ZnTe than it is in ZnS. Hall-effect measurements by Aven and Segall⁴ have shown this level to be 0.13 eV from the valence band which is considerably smaller than the 0.8 eV observed in ZnS.¹² As mentioned previously, the effect of self-compensation of a donor by a low-lying second ionization energy level of a vacancy results in high resistivity crystals.

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¹² W. Van Gool, thesis, University of Amsterdam, 1961 (unpublished).