Correlation between Irradiation and Thermally Induced Defects in II-VI Compounds*

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Recently, two of us reported on a unique new double-acceptor defect produced in CdS and CdTe by heat-treating single crystals at 800–1000°C in Cd. An analogous defect has been observed in ZnSe fired in liquid Zn. This note reports on the production of this defect in CdTe, CdS, and ZnSe by electron irradiation.

IT has long been recognized that point-lattice defects in many solids can be generated in measurable concentrations at high temperatures and may, in part, be quenched into the solid by rapid cooling. It has also been recognized that such defects can be produced by the displacement of atoms from their normal lattice sites by irradiation with fast atomic particles. However, in most semiconductors, it has been difficult to interpret thermal quench and irradiation experiments mainly due to rapid annealing effects and the interaction of the primary defects with each other or with chemical impurities. Recently, two of us[1] reported on a unique new double acceptor defect produced in CdS and CdTe by heat-treating single crystals at 800–1000°C in Cd. An analogous defect has been observed in ZnSe fired in liquid Zn.[2] This article reports on the production of this defect in CdTe, CdS, and ZnSe by electron irradiation. The simplicity of these experiments provides a unique and unambiguous correlation between these two methods of producing imperfections in these crystals and indicates the intrinsic origin of the observed center.

ZnSe crystals showing n-type conductivity were prepared by firing them for 100–200 h at 1050°C in liquid Zn containing 10^{-3} mole fraction of Al. Crystals so treated will be referred to as fired crystals. A fired crystal that has been subsequently heated for 10–100 h in liquid Zn at 900–950°C will be referred to as an annealed crystal. Figure 1 shows the Hall coefficient versus reciprocal temperature for fired and annealed crystals. The annealed crystal shows very little effect with light. The low-temperature freeze-out indicates the presence of a shallow level at approximately 0.02 eV below the conduction band edge which is attributed to Al.

The fired crystals, in the dark, show in addition to the shallow 0.02 eV level seen in the annealed samples, a level approximately 0.1 eV from the conduction band edge. If these crystals are illuminated with incandescent light at low temperatures, the electrons frozen into the 0.1 eV level are released giving a persistent increase in conductivity even after the illumination is discontinued. Simultaneously, the mobility increases. At about 100°K the fired samples slowly recover from the effects of the light and at about 160°K light has no gross effect on either the Hall coefficient (see Fig. 1) or the mobility. These characteristics indicate that this level is analogous to the double acceptor defect previously described in CdS and CdTe.

An annealed ZnSe sample (1 mm thick) that has been irradiated for 30 min with 1.5-MeV electrons (total dosage of 6×10^{16} electrons/cm^2) shows the same characteristics as the fired sample shown in Fig. 1. On reannealing, the irradiated samples revert back to the condition in which the 0.1 eV levels are absent or greatly reduced in concentration, and in which illumination produces little or no effect on the Hall coefficient. The cycling of crystals between the fired and the annealed states or between the irradiated and annealed states can be repeated reproducibly any desired number of times. It is, thus, evident that both the firing at 1050°C and the irradiation with electrons are capable of

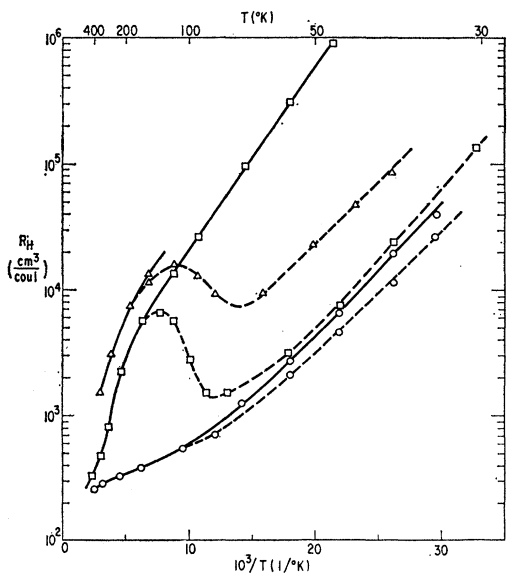

FIG. 1. Temperature dependence of the Hall coefficient for annealed (circles), fired (squares), and irradiated (triangles) ZnSe crystals. The solid lines represent measurements taken in the dark; the dashed lines represent measurements taken under illumination.

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[1] M. R. Lorenz and H. H. Woodbury, Phys. Rev. Letters **10**, 215 (1963).

[2] M. Aven (to be published).

introducing the 0.1 eV levels into ZnSe in comparable concentrations.

The ZnSe crystals were doped with Al to produce high n-type conductivity samples. Undoped crystals often show high resistivity after heat treatment or irradiation which makes it difficult to perform electrical measurements at low temperatures.

The correlation between irradiation and thermal treatments has also been observed in CdS and CdTe. For example, comparable electron irradiation of an unfired CdTe sample (characterized by curve A of Fig. 1, Ref. 1) produces a crystal showing the same characteristic behavior as a sample fired for 30 min at 900°C in saturated Cd vapor (curve B of Fig. 1, Ref. 1). CdS crystals appear to require much larger irradiation dosages to produce the double acceptor center in similar concentrations.

The defect described in Ref. 1 and this letter appears to be the dominant electrically active defect produced in the n-type II-VI compounds by short metal vapor firing or by electron damage. If other defects are produced, they are either unstable at room temperature or are not electrically active in n-type material. The observation of the described double acceptor center in CdS, CdTe, and ZnSe suggests the general nature of this defect in the II-VI family of compounds.

It has been suggested that a defect of the type reported here may be responsible for part of the edge emission spectra seen in II-VI compounds.[3] However, a relationship between the emission intensity of the optically observed center and the defect concentrations obtained from electrical transport measurements has not yet been established.

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Magnetic Properties of the Hexagonal Antiferromagnet $CsMnF_3$†

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The magnetic properties of the hexagonal antiferromagnet $CsMnF_3$ have been investigated by magnetic susceptibility, torsion, electron resonance, and nuclear-antiferromagnetic double resonance. Torsion measurements establish a transition to an antiferromagnetically ordered state at 53.5°K. A weak sixfold anisotropy in the transverse plane and a large axial anisotropy along the c axis corresponding, respectively, to the fields $36K_3/M=1.1$ Oe and $K_1/M=-7500$ Oe are detected. Susceptibility measurements at 4.2°K establish an exchange field $H_E=3.5\times10^5$ Oe. The temperature dependence of K_3 was observed from 4.2°K to the transition temperature and compared with spin-wave and molecular field theory. From paramagnetic resonance measurements an isotropic g value of 1.9989 ± 0.003 is determined. Magnetic resonance measurements below the transition temperature with the applied field in the transverse plane show a weak sixfold anisotropy consistent with the torsion measurements. Measurements out of the transverse plane confirm the large axial anisotropy. In the temperature range from 0.3 to 4.2°K there is an additional temperature dependent anisotropy field $H_{A,T}=9.15/T$ Oe directed along the sublattices. This field arises from the hyperfine interaction with the Mn^{55} nuclear magnetization. Assuming parallel ordering within the transverse planes with adjacent planes alternately magnetized, a calculation of the classical dipolar interactions and of the ligand field anisotropy arising from the displacement of the nearest neighbor fluorines gives a combined axial anisotropy field $K_1/M=-7965$ Oe. The in-plane anisotropy due to second-order dipolar interactions is estimated to be ≈2 Oe in reasonable agreement with observation. The strong coupling between the nuclei and electrons affords an opportunity to observe the Mn^{55} nuclear resonance indirectly by monitoring the position of the electron resonance field. A saturation of the nuclear magnetization is observed at 668 Mc/sec which is $(3\pm1)\%$ smaller than the calculated average hyperfine field of 689 ± 7 Mc/sec. This indicates the presence of a zero-point reduction in the electron spin.

I. INTRODUCTION

SINCE the late 1940's, great strides have been taken in the discovery and experimental observations of antiferromagnetic compounds. In the last few years the compounds $XMnF_3$, where X represents Na, K, and Rb, have been of considerable interest. Like many other double fluorides, these compounds exist in the perovskite-type structure.[1,2] Extensive crystallographic[3–5] and magnetic[6–16] investigations have been

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[2] Yu. P. Simanov, L. R. Batsanova, and L. M. Kovba, Zh.