cm^2/volt sec,

$$\mu \cong 50(m/m^*)^{3/2}(300/T)^{1/2} \text{ in ZnO}$$

and

$$\mu \cong 120(m/m^*)^{3/2}(300/T)^{1/2} \text{ in CdS.}$$

The piezoelectric scattering appears ample for the requirement of large phonon drag with a small effective mass. This calculation and these consequences will be discussed elsewhere.

Electrical conductivity in these piezoelectric materials results in a relaxation-type dispersion for the elastic constant c_{33} and also for c_{44} when propagation is perpendicular to the c axis. A theory of this dispersion has been developed and it successfully predicts the magnitude of the peak as well as the directional dependence of the photosensitive ultrasonic attenuation recently reported by Nine.[11] (K. Dransfeld of these Laboratories has observed that this attenuation does go through a maximum with light intensity.)

It also appears likely that the observations of luminescence occurring when excited (metastable) CdS is given an impact in the c-axis direction[12] have their origin in piezoelectric field ionization of shallow traps.

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PRESSURE DEPENDENCE OF CUBIC CRYSTALLINE FIELD SPLITTINGS OF S-STATE IONS*

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The detailed nature of the interaction between paramagnetic ions with half-filled shells (S ground states) and crystalline electric fields has been the subject of considerable discussion. The theoretical analysis of Watanabe[1] in particular has stimulated a good deal of experimental work. Recently Watanabe[2] has reviewed much of the pertinent experimental data and suggested that hydrostatic pressure might be used to clarify the problem. We had arrived at the same conclusion some time ago and had already performed such experiments prior to his suggestion. The majority of the results were presented at the Cambridge Meeting of the American Physical Society.[3] Complete reports on these and related investigations are to be submitted to the Physical Review in the near future. This note will summarize only those details which are pertinent to Watanabe's calculation.

Using apparatus similar to that previously described,[4,5] the paramagnetic resonance (PMR) spectra of Mn^{2+} and Fe^{3+} ($3d^5$, ^6S) present as trace ($\lesssim 0.01\,\%$) impurities in an MgO crystal have been observed as functions of hydrostatic pressure to 10 000 kg/cm^2 at room temperature. Details of these spectra and their analysis have been given by Low.[6,7] Of present interest is the cubic anisotropy energy represented by the spin-Hamiltonian term $(a/6)(S_x^4+S_y^4+S_z^4)$. The pressure-induced variations of the a parameters of both ions are shown in Fig. 1. Within experimental error the ratio $a_{\mathrm{Fe}}/a_{\mathrm{Mn}} = 10.70 \pm 0.02$ is independent of pressure. The fractional variation of a per kg/cm^2 is

$$(\partial \ln a/\partial P)_T = 4.03 \times 10^{-6} \ (\mathrm{kg/cm^2})^{-1}. \qquad (1)$$

In comparing this result with microscopic

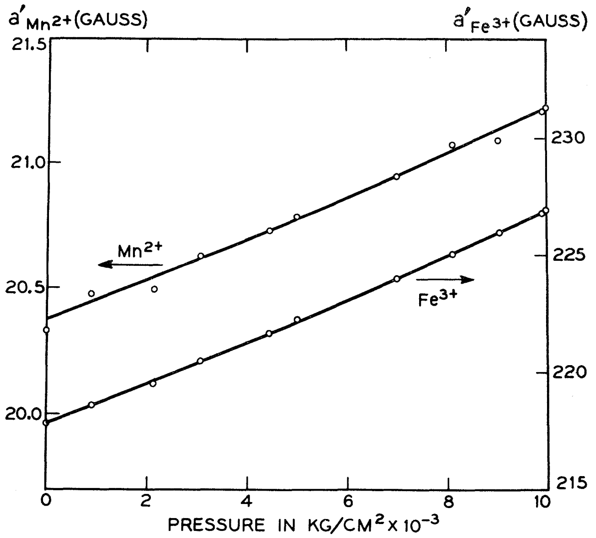

FIG. 1. Pressure dependence of the cubic field splitting parameters of Mn^{2+} and Fe^{3+} in MgO at room temperature. The units are "electron gauss": $a' \equiv a/g\beta$. (The g values are independent of pressure to at least 1 part in 10^5.)

crystalline field theory two principal assumptions are made: (I) The local compressibility in the immediate vicinity of the magnetic impurity is essentially unchanged from that of the undisturbed host lattice. (II) The effective electrostatic potential seen by the magnetic cation may be computed from a simple ionic model. The observed equality of $\partial \ln a/\partial P$ for both a doubly and a triply charged ion in the same lattice supports (I). Further confirmation of both (I) and (II) has been obtained from the pressure dependences of the g values of Cr^{3+} and Ni^{2+} in MgO.[8]

The volume dependence of a is computed using Bridgman's value[9] for the bulk compressibility of crystalline MgO:

$$(\partial \ln a/\partial \ln V)_T = -7.08 \quad (Mn^{2+} \text{ and } Fe^{3+} \text{ in MgO}). \quad (2)$$

According to Watanabe[1,2] the parameter a should be closely proportional to the square of the strength of the cubic potential. In the limit of zero overlap, such a potential varies as interionic distance to the inverse fifth power or $V^{-5/3}$, which means

$$(\partial \ln a/\partial \ln V)_T = -3.33 \quad \text{(theory)}. \quad (3)$$

While a number of cavils may be raised regarding the accuracy of Eq. (3) in the case of real complexes, our data on the better understood F-state ions indicate that for MgO Eq. (3) is valid to within ± 20% at least. The disagreement between Eqs. (2) and (3) greatly exceeds such a margin and suggests that the cubic field splittings are more nearly proportional to the fourth power of the cubic potential in this lattice. Though consistent with Watanabe's conclusion that even powers of the cubic potential are dominant in determining a, this result conflicts with his numerical estimates for Mn^{2+} which indicate that any fourth power contribution is negative and much weaker than the positive second power term.

The pressure variation of a for Mn^{2+} in cubic ZnS has also been measured. Analysis similar to that described above leads to the volume dependence of the cubic field splitting,

$$(\partial \ln a/\partial \ln V)_T = -3.2 \quad (Mn^{2+} \text{ in ZnS}). \quad (4)$$

This apparently second-power-of-the-potential variation cannot safely be considered to support Watanabe's theory since the ionic model is not even approximately adequate in this case.[10] Failure of the simple model in tetrahedral coordination has been most clearly demonstrated by observations of a for Mn^{2+} in CdTe.[11] This splitting proves to be almost four times larger than for ZnS:Mn^{2+} whereas Watanabe's calculations lead to a value more than five times smaller.

A further indication that our understanding of crystalline field effects on the S-state ions is still quite incomplete has come to light in studying the temperature dependences of a for Mn^{2+} and Fe^{3+} in MgO. It is found that the effect can be accurately accounted for simply on the basis of Eq. (2) and the thermal expansion coefficient of the host lattice, i.e., there is no measurable explicit effect of lattice vibrations at constant crystal volume. This can be shown to imply an anomalous frequency dependence of the cubic field splitting[12] which is inconsistent with existing theory.

The constant support and encouragement of Professor N. Bloembergen is gratefully acknowledged as are numerous stimulating conversations with Dr. Jean Jeener and other associates. The MgO crystals used in these experiments were provided by the Norton Company. Professor C. Kikuchi of the University of Michigan kindly made available a natural zincblende crystal.

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EVIDENCE FOR AN ANTIFERROMAGNETIC-FERRIMAGNETIC TRANSITION IN Cr-MODIFIED $\mathrm{Mn_2Sb}$

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We wish to report an unusual magnetization behavior found in the compound $\mathrm{Mn}_{2-x}\mathrm{Cr}_x\mathrm{Sb}_{1-y}\mathrm{In}_y$, where $0.025 \leqq x \leqq 0.20$ and $0 \leqq y \leqq 0.05$. With decreasing temperature, the saturation magnetization undergoes a transition within about a 10° interval from a strongly ferrimagnetic state ($\sigma = 20$ to 30 gauss-cm^3/g) to a weakly magnetic state ($\sigma \simeq 1$ gauss-cm^3/g). This transition, which occurs in the temperature range 120 to 385°K depending on the amount of chromium present, is not accompanied by a change in crystal structure. At high temperatures, the magnetic properties of these compounds are similar to those of the parent compound $\mathrm{Mn_2Sb}$,[1] but the saturation magnetization is too low to be accounted for entirely by the amount of chromium and indium present. As the temperature is lowered, transition to the weakly magnetic state takes place. This behavior is illustrated in Fig. 1, where the saturation magnetization is plotted as a function of temperature for two compounds, $\mathrm{Mn_{1.87}Cr_{0.13}Sb_{0.95}In_{0.05}}$ and $\mathrm{Mn_{1.95}Cr_{0.05}Sb_{0.95}In_{0.05}}$. The saturation magnetization for $\mathrm{Mn_2Sb}$ is included for comparison.

Below the transition temperature T_S, the materials exhibit an average saturation magnetization of 1 gauss-cm^3/g. Metallurgical studies have shown, however, that there is a tendency toward nonstoichiometry on the manganese-deficient side resulting in precipitation of a small amount of MnSb. If the modified $\mathrm{Mn_2Sb}$ is formed with excess manganese, the residual magnetization is reduced but not eliminated completely. We attribute this residual magnetization to ferromagnetic MnSb precipitate. It appears then that the compound of interest may have no net magnetic moment below the transition temperature. The indium present in these compositions has but little effect on their magnetic properties and can in fact be eliminated without loss of the magnetic transition. However, in the absence of indium during the synthesis, it becomes even more difficult to avoid precipitation of MnSb.

The composition region in which ferrimagnetism occurs is designated by the cross-hatched area in Fig. 2. This area is bounded at high temperature by the normal Curie temperature and at low temperature by the transition at T_S. It is to be

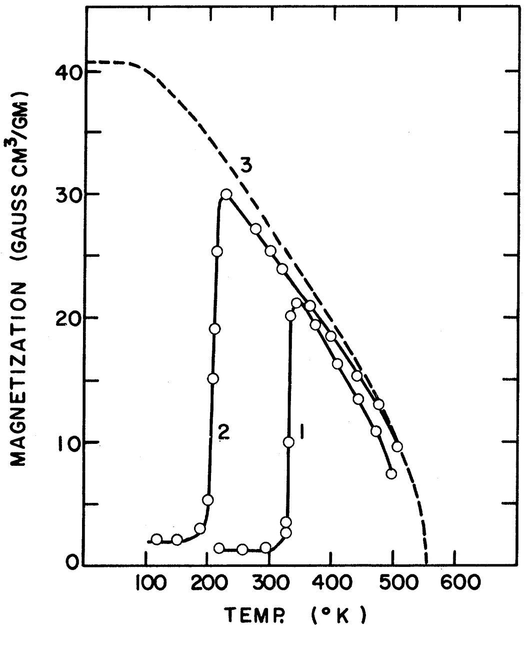

FIG. 1. Saturation magnetization of $\mathrm{Mn}_{2-x}\mathrm{Cr}_x\mathrm{Sb}_{1-y}\mathrm{In}_y$. Curve 1, $x = 0.13$, $y = 0.05$; curve 2, $x = 0.05$, $y = 0.05$; curve 3, $\mathrm{Mn_2Sb}$ ($x = 0$, $y = 0$).