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Electron Paramagnetic Resonance of Manganese in Gallium Arsenide

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The paramagnetic spin-resonance spectra of manganese in GaAs have been studied at 77°K. Isotropic values for the spectroscopic splitting factor g and for the hyperfine interaction constant A have been measured to be 2.004 and 56 G, respectively. Fine structure lines were not found, even at 4°K. A spin Hamiltonian describing the resonance spectra is given. An estimate of the cubic splitting constant a is deduced from the angular variation of the spectrum.

I. INTRODUCTION

IN this paper we describe the paramagnetic resonance of manganese in single-crystal gallium arsenide. The work was undertaken to see if spin-resonance techniques could be used in the study of defect and impurity interactions in GaAs involving manganese. It was found that the resonance spectra were not appropriate for such interaction studies. Only very broad hyperfine lines were observed while the fine structure lines, which ordinarily may be used to determine the charge state of the paramagnetic atom, were not resolved even at 4°K. In subsequent sections we present and discuss the spin resonance parameters we have measured and calculated.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Manganese was introduced into the crystal either by diffusion or by directly doping the melt during the growth process. The crystals containing manganese were grown vertically or by the horizontal Bridgeman technique with concentrations between 10^{17} and 10^{18} atoms/cm^3. In GaAs manganese behaves as an acceptor, and based on its electronic configuration it is presumed to be a substitutional impurity replacing gallium. This is further substantiated by our finding that the activation energy for manganese diffusion in GaAs (2.75 eV) is very close to that found for other impurities which replace gallium.

The acceptor impurity level obtained from Hall and optical absorption measurements[1] were found to be about 0.09 eV above the valence band. Consequently, at liquid-nitrogen temperature, where the spin-resonance data were obtained, nearly all the manganese atoms are un-ionized and contain a bound hole. The model for substitutional manganese described above would lead one to expect that the ground state is an S state and that the resonance behavior would stem from the five $3d$ electrons.

In the experiments reported here a paramagnetic resonance spectrometer was used operating at about 9.1 kMc/sec. The samples were oriented, cut to a size of 0.02 in.×0.02 in.×0.5 in. and etched in aqua regia before mounting in the resonant cavity.

The spectrum at 77°K consisted of six hyperfine lines, characteristic of the manganese nuclear spin $I=5/2$, which are very broad, about 28 G in half-width. Figure 1 shows the spectra taken with the magnetic field varying in a (110) plane from the $\langle 100\rangle$ direction through the $\langle 110\rangle$ direction. The central components of the spectrum are found to disappear when the field is parallel to a cube axis whereas the best resolution of the six lines occurs when the field is 35° from the $\langle 100\rangle$ axis. This variation is unexpected and is discussed later on. Although the pattern changes continuously with angle, the center of each observable hyperfine line remains fixed. Thus, the hyperfine interaction constant, A, is isotropic. Its value is found to be equal to 56 ± 2 G. Note that this value for A lies between that found for manganese in germanium, 48 G, and that found for manganese in ZnS, 68 G. This behavior is consistent with the observation made by van Wierengen[2] that the more ionic the bond, the greater the hyperfine interaction. The g value is 2.004 ± 0.003, close to that for the free electron as one would expect for an S-state ion.

At 4°K, no change in the spectrum was observed from that at 77°K. We were unable to detect any fine structure or any change in the linewidths at this temperature. This would suggest that the effects of spin-lattice interactions on the breadth of the lines, which should be strongly temperature dependent, is negligible.

Spin-resonance spectra have been reported for manganese in a number of different cubic crystals.[3–5] Generally, the spectra are composed of five fine structure lines centered around each of the six hyperfine lines. The spin Hamiltonian which describes manganese in this case is

$$\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}+A\mathbf{S}\cdot\mathbf{I}+\tfrac{1}{6}a[S_x^4+S_y^4+S_z^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)], \quad (1)$$

where the first term is the Zeeman term, the second describes the interaction of the electron spin with the nuclear spin of manganese, and the last is the interaction of the electron spin with the cubic crystal field. The transition energies for the fine structure lines calculated by Matarrese and Kikuchi[5] to second order in the hyperfine terms is given by

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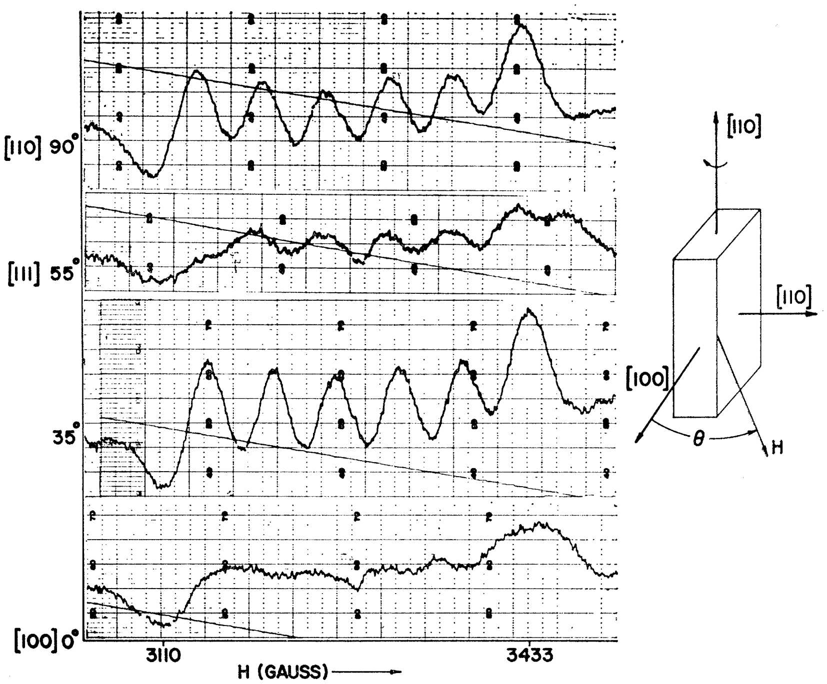

FIG. 1. Angular variation of EPR spectra at 77°K of manganese in gallium arsenide.

$$\Delta E = g\beta H_0 - Am - \frac{A^2}{2g\beta H_0}\left[\frac{35}{4} - m^2 + m(2M-1)\right] + \frac{a}{64}\left[(35\cos^4\theta - 30\cos^2\theta + 3 + 5\sin^4\theta\cos 4\psi) \times (56M^3 - 84M^2 - 134M + 81)\right]. \quad (2)$$

When the magnetic field is rotated about the ⟨110⟩ axis, then θ is the angle between the ⟨100⟩ axis and the magnetic field, and $\psi = 45°$. In Fig. 2 a plot of the spreading of the fine structure lines as a function of θ about the central component is shown which was obtained from Eq. (2). It can be seen from the figure that the maximum separation between the outermost lines is produced when the field is parallel to the ⟨100⟩ axis, at which point the separation is equal to $30|a| - 2A^2/g\beta H_0$. The lines have a minimum separation when $\theta = 31°$.

The experimental results we have obtained for manganese in gallium arsenide (Fig. 1) can be explained by the angular variation of the fine structure lines, if it is assumed that the broad hyperfine structure lines are in fact the envelopes of the fine structure pattern. In the spectra we have observed, the four central lines disappear at $\theta = 0°$, the same angle which produces the largest separation of the fine lines. The best resolution of the hyperfine lines is at 35° which is close to the angle of minimum separation of the fine lines. This strongly suggests that the degree of resolution results mainly from the overlap of the adjacent groups of unresolved fine structure lines. Additional evidence for this is obtained when the crystal is mounted in the resonant cavity so that the field is rotated in the (111) plane. The pattern is independent of angle as one would expect from Eq. (2).

Within the context of this explanation we can estimate an upper limit for the cubic splitting constant a. This estimated upper limit is 3.5 G if it is assumed that

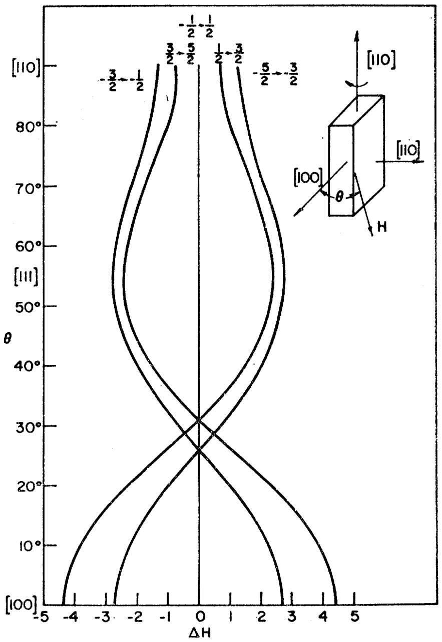

FIG. 2. Angular variation of fine structure line separation from the central component for manganese in a zinc blende lattice (from reference 5).

the maximum separation of the fine lines, which is $30|a|-2A^2/g\beta H_0$, has a value between A and $2A$. This is the value required to produce the disappearance of the hyperfine lines. Using this value, a half-width of about 20 G for the fine lines can be inferred from the spectra at the angle of minimum separation, $\theta=31°$. This line width cannot be accounted for by the effects of spin-spin interactions at concentrations of $10^{17}/\text{cm}^3$. Since, as mentioned earlier, the spin-lattice interactions contribute negligibly to the linewidth, it is suggested that the unusual width of the lines results from the hyperfine interactions with nearest-neighbor As atoms[6] and next-nearest-neighbor Ga atoms, all isotopes of which have a nuclear spin of 3/2.

III. CONCLUSIONS

The paramagnetic resonance spectra of manganese in GaAs have been observed at 77°K. The measured g and A are isotropic with values of 2.004 and 56 G, respectively. The spin Hamiltonian describing manganese in GaAs is expressed by Eq. (1). The angular variation of the fine structure lines obtained from this expression accounts for the unusual angular dependence of the spectrum. Finally, a maximum value of 3.5 G is estimated for the cubic anisotropy constant.

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Specific Heat of Single-Crystal $MnCl_2$ in Applied Magnetic Fields

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The specific heat of a single-crystal sample of $MnCl_2$ has been measured, in the liquid-helium temperature region, in applied magnetic fields extending up to 7.26 kOe. In all cases the magnetic field was applied parallel to an a axis of the hexagonal cell. The two specific heat maxima, which have been previously reported at 1.81 and 1.96°K in zero field, are associated with antiferromagnetic transitions. Both transition temperatures are found to be field dependent. The upper transition temperature increases with applied field while the lower transition temperature decreases. These results are correlated with neutron diffraction studies of the magnetic structure transitions.

INTRODUCTION

THE magnetic and thermal properties of $MnCl_2$ in the liquid-helium temperature region have been reported previously.[1–3] Briefly stated, $MnCl_2$ is paramagnetic at temperatures greater than 1.96°K, at which temperature a transition to an antiferromagnetic state occurs. At a slightly lower temperature, 1.81°K, the spin moments reorient to a different structure, and the magnetic system undergoes another phase transition to the low-temperature antiferromagnetic state. A well-defined λ-type anomaly in the specific heat is observed at each of these critical temperatures. The complex order of the Mn^{++} spin system in both the high-temperature and low-temperature antiferromagnetic state has been studied by the methods of neutron diffraction, as reported by Wilkinson, Cable, Wollan, and Koehler.[3] Interpretation of the neutron diffraction results is based, in a large part, on diffraction patterns from oriented single crystals, especially in an external magnetic field. In this regard, it is of considerable interest to examine the dependence of the transition temperatures on an external field which is applied along a known direction of a single crystal. For this purpose a series of specific-heat measurements in various applied fields has been performed. The two transition temperatures are identified by sharp λ-type maxima in the specific heat, and both are found to be a function of the magnetic field. In all measurements reported here, the external field was applied parallel to an a axis of the hexagonal cell.

EXPERIMENTAL PROCEDURE

A large crystal was grown from anhydrous $MnCl_2$ powder by the Stockbarger-Bridgman method in a quartz crucible. A final dehydration was performed by heating in vacuum immediately prior to crystal growth. A cylindrical crystal was machined from a section of the ingot which was optically clear and free from visible flaws. The final cylinder was 7.8 mm in diameter by

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