MAGNETIC BEHAVIOR OF SINGLE CRYSTAL EPILAYERS OF THE

DILUTED MAGNETIC SEMICONDUCTOR $\text{Zn}_{1-x}\text{Co}_x\text{Se}$

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ABSTRACT

SQUID magnetometry (6-100 K, 4 Tesla) and 9.3 GHz EPR studies have been carried out on thin single crystal films of $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ as a function of Co concentration for $0.0076 \leq x \leq 0.094$. The samples were grown by molecular beam epitaxy on GaAs(001) substrates and were also characterized by RHEED, AUGER, x-ray fluorescence, and several x-ray diffraction techniques. At low temperatures, the magnetic behavior is dominated by the isolated paramagnetic Co^{2+} ions ($S = 3/2$) in Zn sites. The reduction of the measured magnetization from that calculated shows that nn (and perhaps nnn) Co^{2+} pairs are antiferromagnetically coupled with an exchange constant exceeding 20 K. For higher x samples, EPR at 5 K gives an isotropic $g=2.27$ Co^{2+} line with an x-dependent linewidth. For $x = 0.0076$, strong angularly dependent EPR lines are seen which are thought to arise from Co^{2+} ions in low symmetry sites, probably in the neighborhood of dislocations. Their contribution to the magnetization also is reduced relative to isolated Co^{2+} ions.

INTRODUCTION

Diluted magnetic semiconductors (DMS) are typically II-VI zincblende-structure semiconducting compounds for which transition metal ions are substituted into the site of the column II element. They exhibit a number of interesting properties including giant magneto-optic and magneto-resistance effects which offer potential for device applications [1]. These properties arise from the fact that the strong exchange interactions between the magnetic ions and the conduction/valence band electrons serve as an enhancement factor for externally applied magnetic fields [2].

To date most of the work on these materials has concerned DMS's with Mn^{2+} as the magnetic element [1]. However, in the past several years Fe-containing DMS's have received increasing attention [3], and recently Co-bearing DMS compounds have been produced [4]. Both $(\text{Zn,Fe})\text{Se}$ and $(\text{Zn,Co})\text{Se}$ single crystals have now been produced in thin film form by molecular beam epitaxy (MBE) on GaAs [4,5].

The present paper describes the results of SQUID magnetometry and magnetic resonance studies which probe the magnetic behavior of MBE-grown single crystal $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ films. Since the ground state of Co^{2+} in ZnSe is a spin-degenerate orbital singlet (4A_2), $(\text{Zn,Co})\text{Se}$ is expected to resemble $(\text{Zn,Mn})\text{Se}$ (6A_1) in its magnetic properties. We find this to be true, although the relatively strong sensitivity of Co^{2+} to low symmetry crystal fields has important effects on the behavior of $(\text{Zn,Co})\text{Se}$ at low Co concentration.

EXPERIMENTAL

The samples examined in this study were grown by MBE using elemental source ovens. The $\text{Zn}_{1-x}\text{Co}_x\text{Se}$ crystals grew as (001) layers on GaAs(001) substrates. Details of the growth methods are given elsewhere [4]. The source fluxes were monitored with a quadrupole mass analyzer during deposition. Actual film thicknesses and Co concentrations x were determined by x-ray fluorescence methods after removal from the MBE system. The samples had x values ranging from 0.0076 to 0.094 and thicknesses from 0.3 to 2.6 μm . Auger spectroscopy showed no measurable impurities.

A variety of x-ray techniques were used to characterize the film quality as discussed in [4]. The thicker, lower x samples showed well-ordered single crystal growth of $(\text{Zn,Co})\text{Se}$ under the growth conditions used. For the larger x values good quality crystals could be grown only up to about 0.3 μm thick and exhibit tetragonal distortions which are perpendicular to the film plane. This suggests that the substitutional incorporation of Co is more disruptive of the ZnSe host lattice than is that of Fe. This may be due to a tendency to form CoSe, which has the hexagonal NiAs structure, at higher Co concentrations. Additional work in this area is clearly needed.

Suitable samples of $(\text{Zn,Co})\text{Se}$ were cleaved from the 1 cm x 1 cm platelets grown and were examined by SQUID magnetometry and electron paramagnetic resonance (EPR). Magnetic moment data were taken on each sample in applied fields of 3 or 4 Tesla using a BTi Model 900 susceptometer. The EPR data were taken at 9.3 GHz in a Varian E-9 spectrometer using a flowing He gas to permit measurements down to 4.5 K.

RESULTS AND DISCUSSION

The magnetization (M) data for an $x = 0.016$ sample are shown plotted as a function of H/T in Fig. 1. It should be noted that the temperature-independent diamagnetic contribution of the GaAs substrate has been removed from the raw data. Although the substrate moment is always at least several times that of the $(\text{Zn,Co})\text{Se}$ film, the characteristic temperature dependence of the paramagnetic Co^{2+} signal makes this procedure straightforward and reliable.

An isolated Co^{2+} ($3d^7$) ion in a tetrahedral Zn site has an orbital singlet ground state [6] with a spin $S = 3/2$. Our own EPR results agree with early studies [7] of Co-doped ZnSe which found an isotropic EPR line

Fig. 1 The magnetization M vs H/T for an $x = 0.016$ (Zn,Co)Se sample. Data were taken at 3 Tesla ($\times$) and at 4 Tesla ($\square$). The solid line is a fit of Eqn. (1) to the data and yields $A = 0.61$.

due to Co^{2+} with a g -value of 2.27. The magnetization of a dilute $\text{Zn}(1-x)\text{Co}(x)\text{Se}$ sample can then be calculated [8] as

$$M = ANxg\mu_B \langle S_z \rangle \quad (1)$$

where N is the number of Zn ions per unit volume in ZnSe, $g = 2.27$, μ_B is the Bohr magneton, $\langle S_z \rangle$ is the thermal average value of the component of the Co^{2+} spin along the applied field and the reduction factor A lies between 0 and 1. It is well known that $\langle S_z \rangle = SB_S(y)$, where $B_S(y)$ is the Brillouin function for spin $S = 3/2$ and $y = g\mu_B H/kT$. Equation (1) is valid for a set of non-interacting Co^{2+} ions with concentration x when $A = 1$. Following the data analysis of Mn- and Fe-bearing ZnSe-based DMS materials [1,9], we let A vary, since the number of exchange-coupled pairs and more complex groupings of Co^{2+} ions can be expected to become significant when x exceeds a percent or so, decreasing the net moment.

In Fig. 1, the data for $H = 3$ T and $H = 4$ T are both plotted. The fact that the two sets of data fall on the same curve indicates that M is a joint function of H/T as expected from Eqn. (1). This is similar to the behavior of (Zn,Mn)Se [1] and in marked contrast to the behavior of (Zn,Fe)Se [10] at low temperatures. The solid line in Fig. 1 represents a fit of Eqn. (1) to the data using only A as a fitting parameter. For $x = 0.016$ we find $A = 0.61$, i.e., only 61% of the Co^{2+} ions exhibit isolated ion magnetic behavior. Note that the shape of the curve is accurately predicted without any free parameters. This means that the remaining Co^{2+} ions must have magnetically inactive ground states, suggesting antiferromagnetic pairing.

We carried out a similar analysis of the M vs T data at 4 Tesla on all of the (Zn,Co)Se samples studied and in each case found a good

fit to the data by varying only A . Thus the data for $0 < x \leq 0.094$ and $T \leq 100$ K are well fit by a simple Brillouin function. In order for the antiferromagnetic pairs not to make a significant contribution to the temperature dependence of M for temperatures up to 100 K, which would have produced detectable deviations from the behavior observed as given by Eqn. (1), the Co-Co exchange coupling parameter J must be greater than roughly 20 K.

The values of A thus found are shown as a function of the concentration x in Fig. 2. Also shown are two curves labelled NN and NNN. These curves represent the probabilities that for a given Co^{2+} ion one will find no other Co^{2+} in the shell of 12 nearest neighbor (nn) Zn sites, or the 18 nn plus next nearest neighbor (nnn) Zn sites. If one assumes 1) random replacement of the Zn by Co, and 2) that the Co^{2+} ions which are nn or nnn form antiferromagnetically coupled pairs, then the curves represent the expected A values due to these interactions. In general, the nnn curve gives a better fit to the A values found, although the nn curve also behaves in a qualitatively correct manner. Thus the data indicate that nn and probably nnn Co^{2+} pairs are antiferromagnetically coupled with $J > 20$ K. Note, however, that the lowest concentration sample ($x = 0.0076$) has an A value which lies far below either of the above curves. The EPR data discussed next provides a possible explanation.

The X-band EPR signals from the (Zn,Co)Se films with $x = 0.016$, 0.036 and 0.040 confirm that for these concentrations the EPR spectrum is dominated by a single isotropic line at $g = 2.27$ which broadens with x as shown in Fig. 3. To date we have not been able to observe any EPR in higher x samples, probably due to increased line broadening (see Fig. 3) making

Fig. 2 Reduction factor A as a function of the Co concentration x . The solid lines are discussed in the text.

Fig. 3 EPR peak-to-peak linewidth vs cobalt concentration x for $T = 6$ K.

the signals too weak to see for the $0.3 \mu\text{m}$ samples available. When the temperature is raised above about 15 K the lines start to broaden and can not be observed above 150 K. It is likely that this behavior is due to relaxation broadening as the isolated Co^{2+} relax via the much faster relaxing exchange-coupled Co^{2+} pairs. In contrast to the isotropic behavior found for the samples described above, the $x = 0.0076$ sample shows a strongly angularly dependent spectrum which collapses into a strong narrow line for $H // [001]$, the normal to the film.

One possible explanation for these low symmetry EPR spectra for $x = 0.0076$ is that they are due to exchange coupled pairs. We rule this out since 1) all of the observed EPR lines have the same temperature dependence (falling uniformly with increasing temperature) in contrast to what would be expected for pairs, and 2) we would expect that any EPR lines due to pairs to be even stronger for $x = 0.016$, while only a few weak angularly dependent lines are found in this sample.

It should be noted that Co^{2+} in a Zn site has a rather large deviation (0.27) between its g value and that of the free electron. This large orbital contribution implies that the ground state of the ion is very sensitive to local low symmetry crystal fields. If, e.g., a low symmetry crystal field term leaves the $S = \pm 1/2$ doublet lower, as is consistent with the $x = 0.0076$ EPR results, and the zero-field splitting exceeds 30 K, then the contribution of Co^{2+} ions in such sites to the magnetic susceptibility will be greatly reduced in comparison to the Co^{2+} ions in cubic sites. We suggest that for $x < 0.01$ a substantial fraction of the Co^{2+} ions are associated with low symmetry sites with a consequent reduction in their magnetic moment in the temperature range studied. This is consistent with the low symmetry EPR signals

observed for $x = 0.0076$ and the high sensitivity of tetrahedrally coordinated Co^{2+} ions to local distortions. A possible origin for such behavior that we can not rule out is that for the lowest x sample there is a clustering of Co in the neighborhood of the dislocations.

CONCLUSIONS

We have successfully grown single crystal epitaxial films of the diluted magnetic semiconductor $(\text{Zn},\text{Co})\text{Se}$ for the first time. The observed paramagnetic behavior at low temperatures is dominated by those Co^{2+} ions which are isolated in Zn sites. There is clear evidence of antiferromagnetic coupling between nearest neighbor and probably next nearest neighbor Co^{2+} pairs at higher Co concentrations which removes their contribution from the measured magnetic moment. There also is evidence that for $x < 0.01$ the Co^{2+} ions tend to be found in low symmetry sites, probably near dislocations. The rich range of behavior observed in these $(\text{Zn},\text{Co})\text{Se}$ crystal films merits further work in the areas of their magneto-optic properties and the determination of both the antiferromagnetic exchange constant(s) and the optimum growth conditions to suppress dislocations.

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