MAGNETIC ANISOTROPY OF Zn-Cr ALLOYS AT VERY LOW TEMPERATURES*

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ABSTRACT

The temperature dependent magnetization of Zn-Cr single crystals was measured from 2K down to 10 mK using a SQUID magnetometer. A large anisotropy is observed for the magnetization along the parallel and perpendicular axes of the crystal. For low concentrations impurity-impurity reactions do not dominate the behavior of the system, although they are still present even in the 10 ppm impurity concentration range. The anisotropy in the magnetization, $M_{\parallel}-M_{\perp}$, is negative which is in contrast with the Mn in Zn system where the anisotropy is positive. The results are analyzed in terms of crystal field splittings and exchange. These results have important implications for the Kondo effect in this system.

INTRODUCTION

An important aspect of the study of dilute magnetic alloys is the behavior of a magnetic impurity in the limit of infinite dilution, i.e. single-impurity behavior. Although many experiments on such alloys are interpreted to be in this limit, it is only for impurity concentrations of the order of a few p.p.m. or less in most systems that impurity-impurity interactions can be neglected.[1] In the high temperature limit, where most magnetic alloy experiments are performed, the magnetic behavior of many systems follows a Curie-Weiss law, and the effect of impurity-impurity interactions appears as a second order term, the Curie-Weiss temperature. At low temperatures, however, when kT becomes comparable to the interaction energy of interest, single-impurity effects can be discerned from impurity-impurity effects by studying a system for various concentrations of magnetic impurities. Such studies on dilute single crystals of Zn-Mn have shown that for a few ppm of magnetic impurities, single-impurity effects are indeed observed. In that system, of interest because of the hexagonal symmetry of the host, a large anisotropy is observed in the magnetization of the impurities.[2] The magnetization along the a-axis saturates at approximately 0.1K while the c-axis magnetization continues to increase as the temperature is lowered. Although the free Mn^{+2} is an S-state ion, one possible interpretation of the anisotropy is in terms of crystal field effects. In order to pursue this line of study, which has been unexplored, we have measured the magnetization of Cr impurities in Zn single crystals. The Cr^{+2} is a non S-state ion and crystal fields should have a strong influence on the behavior of this system. A study of this system down to 10 mK is presented in this paper.

EXPERIMENTAL DETAILS AND RESULTS

The Zn-Cr samples were made by preparing a master alloy of Zn (6N) containing 500 ppm of Cr (4N purity). Upon further dilution to the desired concentration, the alloy was kept molten in a N_2 atmosphere (approximately 35 Torr). A single crystal was formed by the Bridgman technique in which the molten sample cooled slowly over a period of 2-3 days. After X-ray orientation, a sample along the c-axis and one along the a-axis were spark cut from the single crystal alloy. The two orientation samples were cut from adjacent positions in the large alloy sample in order to minimize concentration differences. Final preparation consisted of an acid etch of each sample to a diameter of 2.29 mm from the initial 4 mm diameter. An analysis of the alloy was made with an atomic absorption spectral photometer which gave a Cr concentration of 10.5 ppm for the sample discussed here. This value is in good agreement with the concentration determined from the high temperature Curie-Weiss behavior of the sample.

The magnetization measurements are made with a SQUID magnetometer mounted inside the mixing chamber of a ^3He-^4He dilution refrigerator. One of the oriented Zn-Cr samples and a similar sample of pure Zn are placed in each side of an astatically wound pair of coils which comprise the primary of a flux transformer going to the SQUID sensor. The measured magnetization is the contribution of the magnetic impurities, with minimal background effects. The temperature is measured with a CMN thermometer located also inside the mixing chamber.

The magnetization is measured from 2 K down to 10 mK in a field of 82 Oe trapped in a Nb cylinder surrounding the sample. Such a field is necessary to maintain the sample in the normal state. The magnetometer has been previously calibrated against the nuclear magnetization of indium and aluminum as well as that of CMN.[3]

In figure 1 the magnetization results for the 10 ppm single-crystal samples are presented as a function of reciprocal temperature for the two orientations. At high temperatures both samples show a Curie-like behavior, although the a-axis Curie constant is larger than that of the c-axis. This fact can be attributed to some anisotropy in g and also to a difference in concentration between the two samples. At low temperatures, the magnetization is anisotropic. Such behavior has been observed in Zn-Mn[2] but it is significant that the anisotropy is opposite in sign for the two alloy systems.

DISCUSSION

The results in figure 1 present a very interesting aspect of the ground-state behavior of transition impurities. Symmetry of the host plays an important role in the very low temperature behavior of magnetic impurities, which do retain some ionic character. In the high temperature regime, the Cr moment is 2.8 μ_B which for g = 2 corresponds to an effective spin S = 1. The free-ion state of Cr^{+2} is S = 2, L = 2 but the orbital angular momentum is expected to be mostly quenched in Zn. In Cu the measured[4] g for Cr^{+2} is

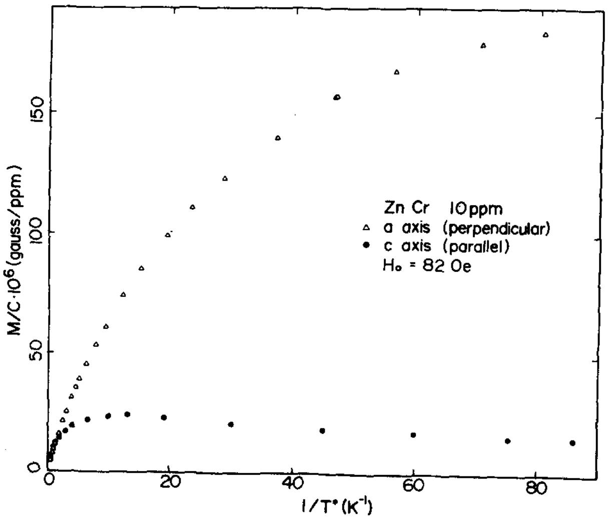

Fig. 1. Magnetization per impurity of single crystal ZnCr measured along parallel and perpendicular crystal axes.

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very nearly 2. A reduced effective spin is due to the strong mixing between impurity states and the host conduction electrons. Our value is in reasonable agreement with other workers[5].

The exchange interaction between impurities and conduction electrons plays a major role in the effects observed in dilute magnetic alloys. It is usually represented by a Hamiltonian of the form

$$\mathcal{H} = J\vec{S}\cdot\vec{s} \ . \tag{1}$$

Due to this exchange, impurities can couple to one another via the RKKY interaction, which will give concentration dependent effects. In data not presented here, $M_\perp/c$, the perpendicular magnetization per impurity ion, of a 138 ppm sample of Cr in Zn becomes completely saturated near T = 0.1K whereas in the 10 ppm sample there is no moment saturation even for temperatures as low as 0.01K. From more extensive data on Zn-Mn alloys, which show similar concentration effects, we have shown that impurity-impurity interactions are becoming small in the few ppm range. Hence neglect of RKKY interactions in the discussion of the 10 ppm Zn-Cr results appears to be valid.

A large magnetic anisotropy as shown in figure 1 is suggestive of a contribution from the orbital angular momentum. Even though the latter may be quenched, spin-orbit coupling can cause fine structure splittings of the degenerate spin levels by the crystal field. For axial symmetry, the Hamiltonian that would represent such splitting is written in the form

$$\mathcal{H} = D[S_z{}^2 - \tfrac{1}{3}S(S+1)] \ , \tag{2}$$

where D is the fine structure splitting resulting from 2nd order spin-orbit interaction. For a spin of 2 and D > 0 as observed here, the splitting would give a singlet as the lowest state with two doublets above it. The Hamiltonian in equation (2) has been applied successfully to insulators, however there is no justification in using it for transition impurities in metals. Since the effective spin for Cr^{+2} in Zn is measured to be approximately 1, it is not clear which spin value one should use in the Hamiltonian, especially if it is not an exact multiple of half. At this stage it is not clear what is the significance of crystal fields in alloys. The crystal field concept has been successful in interpreting the results for rare earth impurities[6]. For transition impurities Hirst[7] has advocated that the ionic model may be valid in many cases, however, there is a lack of experimental data at this stage. He has proposed a model based on the configurational energy of the impurity electrons.

For positive splitting D, the ground state should be a singlet (assuming S = 2 configuration). This is in direct contrast with Mn^{+2} in the same host, where D < 0. A difference is expected as Cr^{+2} is a non S-state ion, even though its orbital momentum L is quenched. Hirst has pointed out that L may not be entirely quenched in highly symmetric systems. The sign of D obtained here agrees with the results of Hedgecock et al[8] obtained at high temperatures for quite concentrated samples. They fitted their data with D = 0.083K assuming a spin of 3/2. The departure from ionic behavior was attributed to the Kondo effect with a Kondo temperature of 0.29 K, but impurity-impurity interactions were completely neglected.

Usually an isotropic exchange is assumed (equation 1) for most studies of alloys, however an anisotropic exchange has been proposed[9] to explain certain results on rare earth impurities. Such anisotropy arises from orbital contributions and may well be applicable to our results. The exchange interaction depends on $S_z{}^2$ which would give a behavior similar to fine structure, eq. 2.

The results presented here have an important bearing on the relation of the Kondo effect to the magnetization. There is no evidence for a Kondo spin-compensated state. The perpendicular magnetization is still increasing at temperatrres much below a reported T_k near 1K. It may be that the Kondo effect will be anisotropic, however, before taking such an approach, the important problem of crystal fields and exchange in metals must be better understood. The implications for resistivity measurements are interesting. Depending on the energy scheme, spin-flip scattering may not be possible and no Kondo effect will be observed at temperatures below the splitting of the fine structure. Cornut and Coqblin[9] discuss this point with regard to rare earth impurities. Measurements of resistivity on single crystals would clarify this problem while EPR studies would describe the state of the impurities.

Our results show the ground state behavior at very low temperatures of Cr^{+2} in Zn and lead to a new approach toward the magnetic impurity problem of transition ions which in the past has been dominated by the Kondo spin-compensated state. Two possible sources of magnetic anisotropy in the system studied here emerge from this study: crystal field effect and exchange. A fuller analysis of this problem will be published elsewhere.

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REFERENCES

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(1) J. C. Doran and O. G. Symko, Proc. of 19th Magnetism Conf., Boston, 980 (1973).
(2) S. Kral, T. Steelhammer, and O. G. Symko, to be published.
(3) T. Steelhammer and O. G. Symko, to be published.
(4) P. Monod and S. Schultz, Phys. Rev. 173, 645 (1968).
(5) Ford, P. J., Rizzuto, C., and Salamoni, E., Phys. Rev B. 6, 1851 (1972)
(6) G. Williams and L. L. Hirst, P.R. 185, 407 (1969). L. J. Tao, D. Davidov, R. Orbach, D. Shaltiel and C. R. Burr, Phys. Rev. Lett. 26, 1438 (1971).
(7) L. L. Hirst, Z. Physik, 241, 9 (1971).
(8) F. T. Hedgcock, S. Lewis, P. L. Li, J. O. Strom-Olsen and F. F. Wassermann, Can. J. of Phys. 52, 1759 (1974).
(9) B. Cornut and B. Coqblin, Phys. Rev. B. 5, 4541 (1972).