Crystal-Field Splitting and Kondo Effect in Zn-Mn†

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Magnetic-anisotropy measurements show evidence for the existence of crystal-field splitting of the transition-metal ion in zinc-manganese single crystals. Assuming the manganese ion has a spin value of 2, the maximum energy splitting Δ is $0.3°K$. On the condition that Δ/T, $T_K/T < 1$, the Kondo behavior as indicated by the experimentally measured magnetic susceptibility is not seriously affected.

Evidence for the coexistence of crystal-field splitting and the Kondo effect has been reported for single crystals of rare-earth metal alloys, e.g., Y-Ce, La-Ce.[1,2] However, no observations have been reported indicating the existence of crystal-field splitting of transition-metal ions in a Kondo alloy. In studies of the magnetic susceptibility and the magnetic anisotropy of Zn-Mn single crystals, we have found evidence for a crystal-field splitting of the manganese ion in the presence of the Kondo effect.

The magnetic susceptibility $\chi_\perp$ was measured using Curie's method, and the magnetic anisotropy $\Delta\chi = \chi_\perp - \chi_\parallel$ was measured using a torque method. The single crystals were grown from the melt by slow cooling in a temperature gradient and subsequently annealed in argon for 17 h at $390°C$.[3] The manganese concentration was determined from the room-temperature susceptibility using the value[4] of $(1.55 \pm 0.15) \times 10^{-6}$ emu/g at.%. Figure 1(a) shows the inverse of the magnetic anisotropy per unit Mn concentration, $\Delta\chi^i(T)/c = [\Delta\chi(T)^{Zn-Mn} - \Delta\chi(T)^{Zn}]/c$, as a function of temperature for the range of manganese concentrations studied.[5] Values of $\Delta\chi(T)$ were measured to better than 2% so that $\Delta\chi^i/c$ has a precision of better than 10%.

Hirst[6] has discussed the energy splitting of a manganese ion in a hexagonal close-packed lattice and suggests that the lowest-lying level of an S-state ion is subject to an energy splitting of less than $0.1°K$. The g value for manganese in zinc is 2.05 ± 0.01 and is temperature independent below $90°K$,[7,8] which suggests that the manganese ion is predominantly s-like and hence will experience only a small energy splitting. The observed reduction of the manganese spin value from $\frac{5}{2}$ to 2 is presumably due to the s-d mixing which is also responsible for small orbital contributions resulting in the observed g value of 2.05.

With the use of a spin-only Hamiltonian for a manganese ion in a hexagonal matrix, the magnetic susceptibility, if one neglects the contribution due to conduction-electron polarization, would be[9]

$$\chi_\perp^i = \frac{Ncg_\perp^2\beta^2 S(S+1)}{3kT}\left[1 - \frac{A(2S-1)(2S+3)}{30kT}\right], \quad (1)$$

$$\chi_\parallel^i = \frac{Ncg_\parallel^2\beta^2 S(S+1)}{3kT}\left[1 + \frac{A(2S-1)(2S+3)}{15kT}\right], \quad (2)$$
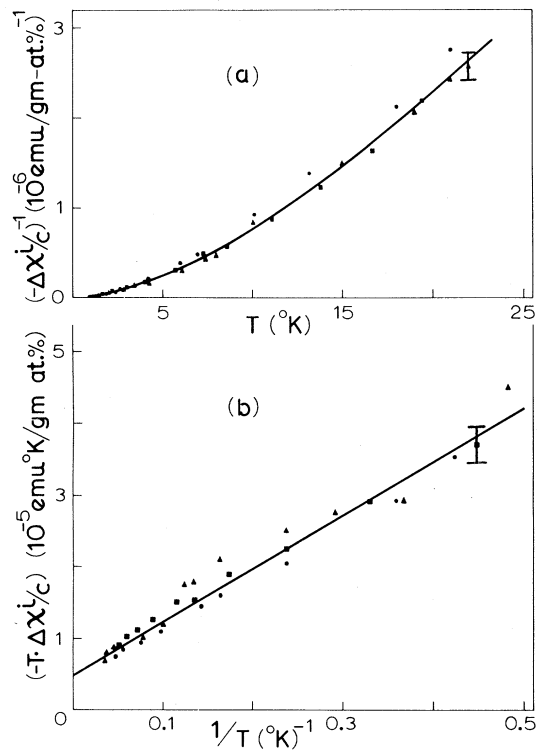

FIG. 1. Magnetic anisotropy for Zn-Mn single crystals; circles, 135 ppm; squares, 280 ppm; and triangles, 475 ppm. (a) Inverse magnetic anisotropy per unit Mn concentration as a function of temperature. (b) $-(T \Delta\chi^i)/c$ as a function of inverse temperature.

so that

$$\Delta\chi^i = \frac{Nc\bar{g}^2\beta^2 S(S+1)}{3kT}\left[\frac{g_\perp^2 - g_\parallel^2}{\bar{g}^2} - \frac{A(2S-1)(2S+3)}{30kT}\frac{2g_\parallel^2 + g_\perp^2}{\bar{g}^2}\right], \tag{3}$$

where A is the crystal-field parameter (positive A implies the c axis is the easy axis of magnetization). $g_\parallel$ and $g_\perp$ are the g factors parallel and perpendicular to the hexagonal axis, respectively; $\bar{g}^2 = \frac{2}{3}g_\perp^2 + \frac{1}{3}g_\parallel^2$; β is the Bohr magneton; and c is the concentration of Mn ions in atomic percent.

From Eq. (3) we see that $(T\Delta\chi^i)/c$ should vary linearly with T^{-1} if $\Delta\chi^i$ is due predominantly to crystal-field effects. From Fig. 1(b) we see that this relationship is indeed obeyed with an anisotropy in the g factor, $(g_\perp - g_\parallel)/\bar{g} = 0.5\%$, and a crystal-field parameter $A/k = 0.078 \pm 0.008°K$ using an effective spin[10] of 2 for the Mn ion. This corresponds to a maximum energy splitting Δ of $0.3°K$.

Crystal-field effects alone cannot reproduce the observed magnetic susceptibility χ^i. This is illustrated in Fig. 2 where curve b is calculated from Eq. (1) using the previously determined values of A and $(g_\perp - g_\parallel)/\bar{g}$. The large discrepancy between curves a and b in Fig. 2 must be

due to the neglect of the conduction-electron contribution to the susceptibility. A graph of the inverse of the difference δ between the experimental points and the crystal-field curve plotted against $\ln T$ is shown in the inset of Fig. 2. If δ is a measure of the conduction electron susceptibility in a Kondo system, then the inverse of δ indeed should vary as $\ln T$.[11] This experimental evidence suggests that a combined susceptibility for the manganese ions in the presence of crystal-field effects plus the Kondo effect can be written as

$$\chi = \chi_0 + \chi_{CF} + \chi_{s-d}, \tag{4}$$

where χ_0 obeys the high-temperature Curie law, χ_{CF} is the term coming from the splitting of the Mn ground state due to the crystal field, and χ_{s-d} is the term due to the exchange interaction between the impurity d electron and the screening conduction electrons. This means that Eqs. (1) and (2) become

$$\chi_\perp^i = \frac{Ncg_\perp^2\beta^2 S(S+1)}{3kT}\left[1 - \frac{A(2S-1)(2S+3)}{30kT} - \frac{1}{\ln(T/T_K)}\right], \tag{5}$$

$$\chi_\parallel^i = \frac{Ncg_\parallel^2\beta^2 S(S+1)}{3kT}\left[1 + \frac{A(2S-1)(2S+3)}{15kT} - \frac{1}{\ln(T/T_K)}\right], \tag{6}$$

so that

$$\Delta\chi = \frac{Nc\bar{g}^2\beta^2 S(S+1)}{3kT}\left[\frac{g_\perp^2 - g_\parallel^2}{\bar{g}^2}\left(1 - \frac{1}{\ln(T/T_K)}\right) - \frac{A(2S-1)(2S+3)}{30kT}\frac{2g_\parallel^2 + g_\perp^2}{\bar{g}^2}\right]. \tag{7}$$

If the anisotropy in the g factor is small enough to make the term

$$\frac{g_\perp^2 - g_\parallel^2}{\bar{g}^2}\frac{1}{\ln(T/T_K)},$$

an order of magnitude smaller than the other term, then Eq. (7) reduces to Eq. (3) and the anisotropy is due solely to crystal-field effects. In addition, if the crystal-field-splitting term obtained from the magnetic-anisotropy measurement is an order of magnitude smaller than the s-d exchange interaction term, then Eqs. (5) and (6) will reduce to the Scalapino[11] expression for the susceptibility.

Figure 3 shows a graph of $(\chi_\perp^i)^{-1}$ versus T. The solid line is the calculated curve based on Eq. (5) using $A/k = 0.078°K$ and using T_K as a fit-
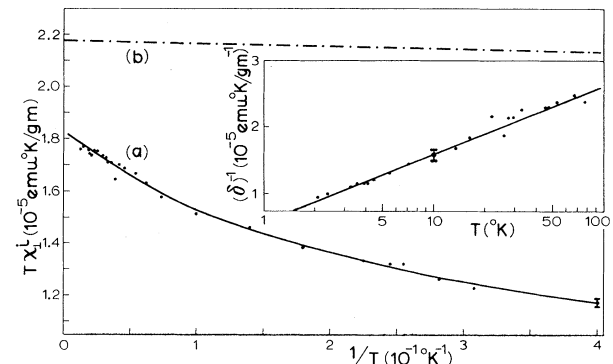

FIG. 2. $T\chi_\perp^i$ as a function of inverse temperature for the 475-ppm Zn-Mn sample. Curve a, smoothed experimental curve. Curve b, calculated curve based on Eq. (1) for a Mn spin of 2 and $A/k = 0.078°K$. The inverse of the difference between curves a and b is plotted as a function of $\ln T$ in the inset.
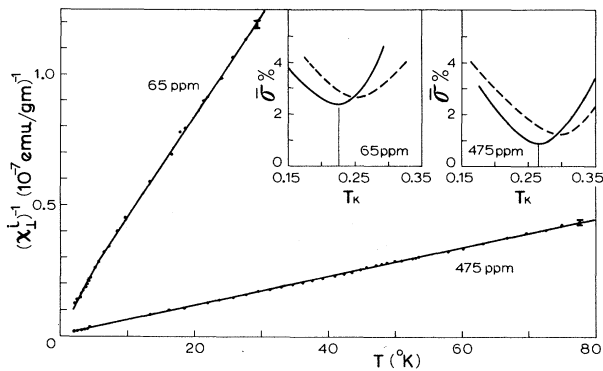
FIG. 3. $(\chi_\perp{}^i)^{-1}$ as a function of temperature for Zn-Mn samples containing 65- and 275-ppm impurity. Solid line through the experimental points, calculated by using $A/k = 0.078°K$ and choosing T_K as a fitting parameter in Eq. (5). Inset, standard deviation for varying T_K. Solid line, standard deviation for the combined Kondo and crystal-field effects with $A/k = 0.078°K$; broken line, for the Kondo effect only.

ting parameter for best fit. The inset in the figure shows that the standard deviation is minimized for a value of T_K of $0.23 \pm 0.04°K$ and a value of T_K of $0.27 \pm 0.04°K$ for the samples containing 65- and 475-ppm impurity, respectively. Although the fit is sensitive to the value of T_K, T_K itself is insensitive to the value of A. It should also be pointed out that the standard deviation is lower when a finite value of A is used in the region of best fit for T_K. The average value of T_K for these two Zn-Mn single crystals is $0.25 \pm 0.04°K$, which agrees with the value reported for polycrystalline samples.[10,12]

Recent[2] theoretical calculations for the La-Ce system point out that the Kondo effect can coexist with crystal-field splittings only when the crystal field does not completely remove the degeneracy of the rare-earth ground state. In contrast to the large crystal-field splitting of a rare-earth ion, for a transition metal ion the splitting, as reported here, is extremely small, indicating that the Kondo effect should be little affected. In fact, from the success in fitting the data by Eqs. (3) and (5) one can say that the contributions due to the s-d exchange interaction and the crystal-field splitting can be considered independent and separable effects provided $\Delta/T < 1$ and $T_K/T < 1$. In conclusion, we suggest that by using an isotropic Kondo temperature and a

crystal-field splitting it is possible to explain the magnetic anisotropy and magnetic susceptibility of Zn-Mn single crystals.

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