Magnetic phase transitions in the dilute antiferromagnet $Co_{0.5}Zn_{0.5}F_2$

A. N. Bazhan, Ali Ya. Amin,[1)] and S. V. Petrov

Institute of Physical Problems, Academy of Sciences of the USSR

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Single crystals of $Co_{0.5}Zn_{0.5}F_2$ have been grown, and their magnetic properties have been studied at magnetic fields from 0 to 60 kOe and at temperatures from 1.7 to 20 K. At $T < T_N = 12.5 \pm 0.5$ K these crystals have the properties of a uniaxial antoferromagnet with a strong Dzyaloshinskiĭ interaction. The perpendicular magnetic susceptibility has an unusual temperature dependence in weak magnetic fields.

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Single crystals of CoF_2, of D_{4h}^{14} tetragonal symmetry, belong to the group of well-known "easy-axis" antiferromagnets exhibiting a Dzyaloshinkiĭ interaction.[1–5] In a study of the magnetic properties of $Mn_{1-x}Zn_xF_2$ single crystals, Foner[3] showed that the replacement of the magnetic Mn^{++} ion in a tetragonal crystal lattice by a nonmagnetic Zn^{++} ion lowers the temperature of the transition to the ordered state, T_N, and reduces the magnetic field of the phase transition which results from a flipping of the magnetic moments of the Mn^{++} sublattice. It seemed interesting to study the magnetic properties and phase transitions in the system $Co_{1-x}Zn_xF_2$, in which some of the magnetic Co^{++} ions of pure CoF_2 crystals are replaced by nonmagnetic Zn^{++} ions.

The $Co_{1-x}Zn_xF_2$ ($x = 0.5$) samples were synthesized from anhydrous CoF_2 and ZnF_2 which had been melted beforehand in an atmosphere of *HF*. The resulting samples were then used to grow single crystals in a helium atmosphere, in the apparatus described in Ref. 7. The magnetic properties were measured with a vibrating-sample magnetometer[8] at temperatures from 1.7 to 20 K and at magnetic fields from 0 to 60 kOe.

Figure 1 shows the dependence of the magnetic moment on the applied magnetic field, **H**, for the cases in which this field is oriented along the [100] binary axis (curve 1), along the [110] binary axis (curve 2), and along the [001] tetragonal axis (curve 3). It can be seen from Fig. 1 that with $\mathbf{H} \parallel [100]$ and $H < 10$ kOe the field dependence $M(H)$ is described by $M(H) = \chi_\perp^* H$, where $\chi_\perp^* = (1.3 \pm 0.1) \times 10^{-1}$ emu/mole. As H is increased, the behavior $M(H)$ becomes nonlinear, and at $H > 35$ kOe it can be described by $M(H) = \sigma_D + \chi_\perp H$, where $\sigma_D = (2.5 \pm 0.2) \times 10^3$ emu/mole and $\chi_\perp = (5.2 \pm 0.3) \times 10^{-2}$ emu/mole. The value of σ_D was found by extrapolating the linear function $M(H)$ from strong fields $H > 35$ kOe, to $H = 0$. With $\mathbf{H} \parallel [110]$ and $H < 10$ kOe, the magnetic moment is a linear function of the field, described by $M(H) = \chi^* H$, where $\chi^* = (1.1 \pm 0.2) \times 10^{-1}$ emu/mole. With increasing H, the dependence $M(H)$ becomes nonlinear, and at $H > 35$ kOe it can be described by $M(H)$

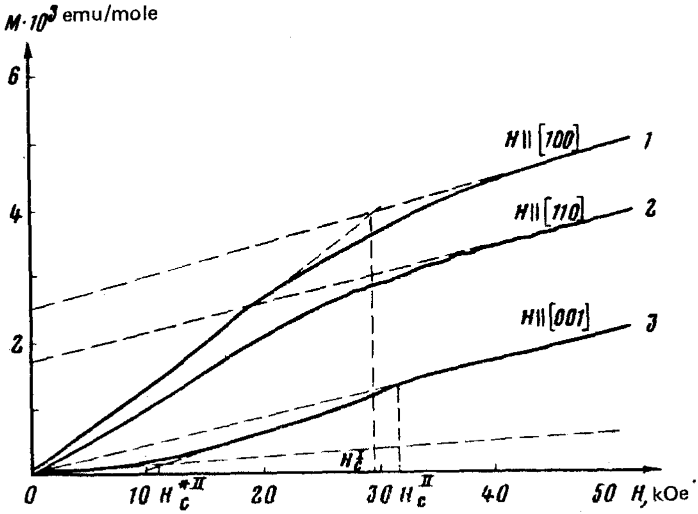

FIG. 1. Dependence of the magnetic moment on the applied magnetic field in $Co_{0.5}Zn_{0.5}F_2$. 1–**H** ∥ [100]; 2–**H** ∥ [110]; 3–**H** ∥ [001].

$= \sigma_D^* + \chi_\perp^{**}$ **H**, where $\sigma_D^* = (1.8 \pm 0.2) \times 10^3$ emu/mole and $\chi^{**} = (4.0 \pm 0.3) \times 10^{-2}$ emu/mole. In a magnetic field oriented along the [001] tetragonal axis in weak magnetic fields, $H < 5$ kOe, we find $M(H) = \chi_{\parallel} H$, where $\chi_{\parallel} = (1.2 \pm 0.2) \times 10^{-2}$ emu/mole. In fields $5 < H < 30$ kOe, the slope of the $M(H)$ curve increases smoothly, and at $H > 30$ kOe the curve can be described by $M(H) = \chi H$, where $\chi = (3.8 \pm 0.2) \times 10^{-2}$ emu/mole.

Figure 2 shows the temperature dependence of the magnetic moment σ_D for the case **H** ∥ [100]. Figure 3 shows the temperature dependence of the magnetic susceptibility in weak magnetic fields ($H < 5$ kOe) for **H** ∥ [001] [curve 1, $\chi_{\parallel}(T)$ and

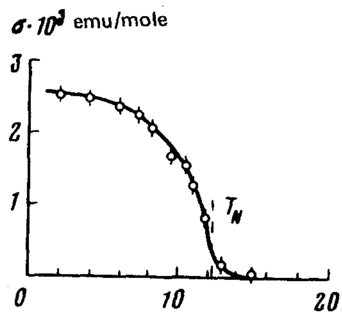

FIG. 2. Temperature dependence of the ferromagnetic moment $\sigma_D(T)$.

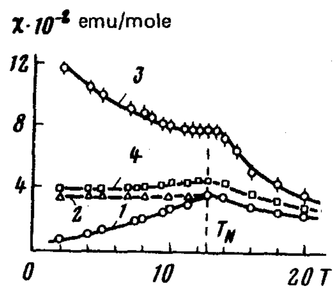

FIG. 3. Temperature dependence of the magnetic susceptibilities. 1–weak $\chi_{\parallel}(T)$ in magnetic fields ($H < 5$ kOe) with **H** ∥ [001]; 3–$\chi_\perp^*(T)$ in weak magnetic fields, **H** ∥ [100]; 2–$\chi(T)$ in strong magnetic fields ($H > 40$ kOe) with **H** ∥ [001]; $\chi_\perp(T)$ in strong magnetic fields, **H** ∥ [100].

for **H** || [100] [curve 3, $\chi_\perp^*(T)$] and in strong magnetic fields ($H > 40$ kOe) for **H** || [001] [curve 2, $\chi(T)$] and for **H** || [100] [curve 4, $\chi_\perp(T)$]. The temperature of the phase transition to the ordered state is found from the disappearance of the magnetic moment σ_D (Fig. 2) and from the maximum of the susceptibility $\chi_{||}(T)$ in weak magnetic fields (Fig. 3) to be $T_N = 12.5 \pm 0.5$ K.

It follows from the temperature dependence of the susceptibility that in the absence of a magnetic field the $Co_{1-x}Zn_xF_2$ single crystals convert to a magnetically ordered state at a temperature $T < T_N = 12.5 \pm 0.5$ K. This state is analogous to one with an antiferromagnetic vector **L** oriented along the tetragonal axis. When the field **H** along the [100] or [110] binary axes is strengthened, there is a phase transition from a purely antiferromagnetic state to one with a slight ferromagnetism, σ_D. The phase transition to the slightly ferromagnetic state occurs in a field $H_c^I \approx 30$ kOe. This value was determined from the intersection of the linear plots of $M(H)$ for $H < 20$ kOe and $H > 40$ kOe. A strengthening of the field **H** when oriented along the [001] tetragonal axis is accompanied by a phase transition, probably involving a flipping of the magnetic moments of the sublattices. This transition occurs in fields 10 kOe $< H < H_c^{II} \approx 32$ kOe and is related to a rotation of the antiferromagnetic vector **L**. The thermodynamic theory of weak ferromagnetism developed by Dzyaloshinskiĭ[1] was used in Refs. 4 and 9 to derive expressions relating the magnetic fields for the phase transitions, H_c^I for **H** || [100] and H_c^{II} for **H** || [001], with the effective fields of various interactions in the crystal. From these relations we find that H_c^I and H_c^{II} are related by

$$H_D H_c^I = H_D^2 - \left(1 - \frac{\chi_{||}}{\chi_\perp}\right) {H_c^{II}}^2 , \qquad (1)$$

where $H_D = \sigma_D/\chi_\perp$ is the Dzyaloshinskiĭ interaction, and $\chi_\perp$ and $\chi_{||}$ are the transverse and longitudinal susceptibilities. Equation (1) holds quite well for a variety of antiferromagnetic crystals. In the our case of a dilute antiferromagnet with a random distribution of interacting magnetic ions, it is not clear whether the thermodynamic potential of Ref. 1 and expression (1) can be used for calculations, but when we substitute in (1) the magnetic fields found from Fig. 1 ($H_c^I = 30 \pm 1$ kOe, $H_c^{II} = 32 \pm 1$ kOe, $H_D = 48 \pm 4$ kOe) and $1 - \chi_{||}/\chi_\perp = 0.77$ we see that this relation holds within ~10%. It should be pointed out that the magnetic field H_c^{II} is determined here from the point at which the linear dependence $M(H) = \chi H$ sets in.[10]

It can be seen from Figs. 2 and 3 that the temperature dependence observed experimentally for the ferromagnetic moment, $\sigma_D(T)$, and those for the magnetic susceptibilities, $\chi_{||}(T)$, are the same as in an ordinary antiferromagnet. On the other hand, the increase in the susceptibility $\chi_\perp^*(T)$ in weak magnetic fields, $2 < H < 5$ kOe, in the case **H** || [100] differs from that of ordinary antiferromagnets. This dependence is analogous to that which we found in Ref. 6 for $\chi_\perp^*$ in $Mn_{1-x}Zn_xF_2$ in weak magnetic fields ($H < 3$ kOe) with **H** || [100].

In summary, the replacement of the magnetic Co^{++} ion by the nonmagnetic Zn^{++} ion in the system $Co_{0.5}Zn_{0.5}F_2$ reduces T_N (the temperature of the phase transition to the ordered state), H_c^I (the magnetic field of the phase transition from the antiferromagnetic state to a state with a slight ferromagnetism), and H_c^{II} (the field of the transition involving a flipping of the magnetic moments of the Co^{++} sublattices) to values significantly lower than in pure CoF_2. The magnetic moment σ_D, on the other hand, remains constant, if we take into account the relative concentration of Co^{++} ions. The nonlinear increase in the susceptibility $\chi_\perp^*(T)$ with the temperature in weak fields **H** || [100] is difficult to explain on the basis of a purely antiferromagnetic model, as in Ref. 6. It should be assumed that this temperature dependence of the susceptibility results from a random distribution of magnetic Co^{++} ions in the tetragonal lattice.

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1)Physics Department, Helsinki University, Helsinki, Finland.

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