Experimental phase diagram of a random mixture of two anisotropic antiferromagnets

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Specific heat, susceptibility, and magnetization measurements were performed on a random mixture of two antiferromagnets with competing spin anisotropies, $FeCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 2H_2O$. From these experiments, the concentration versus temperature phase diagram is obtained, which shows clearly the existence of a tetracritical point. The phase diagram is compared with those obtained by recent renormalization-group analysis and mean-field theories.

Tetracritical phase transitions have received considerable theoretical attention in the past few years.[1-7] Recent renormalization-group analysis[4,6] and mean-field theories[5,7-10] have shown that the tetracritical points usually occur when a system has two order parameters, with competing interactions. Good examples of the system are quenched random mixtures of two kinds of magnets with different types of magnetic ordering. In the experimental phase diagrams hitherto obtained in a variety of random mixtures such as some rare-earth metal alloys,[5,7,11] $Ni_xCo_{(1-x)}Cl_2 \cdot 6H_2O$,[12] $Fe(Pd_xPt_{1-x})_3$,[13] $UAs_{1-x}S_x$,[14] $(Fe,Mn)WO_4$,[15] and $K_2Mn_{1-x}Fe_xF_4$,[16] the boundaries between a paramagnetic phase and an ordered phase are clearly found. However, the low-temperature phase separation lines between two ordered phases are less clear[14,16] or are not observed.[12,13,15] It is thus highly desirable to get experimental phase diagrams which show clearly the existence of a tetracritical point.

In this paper, we report an experimental concentration versus temperature phase diagram of a random mixture of two anisotropic antiferromagnets, $FeCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 2H_2O$, which demonstrates a

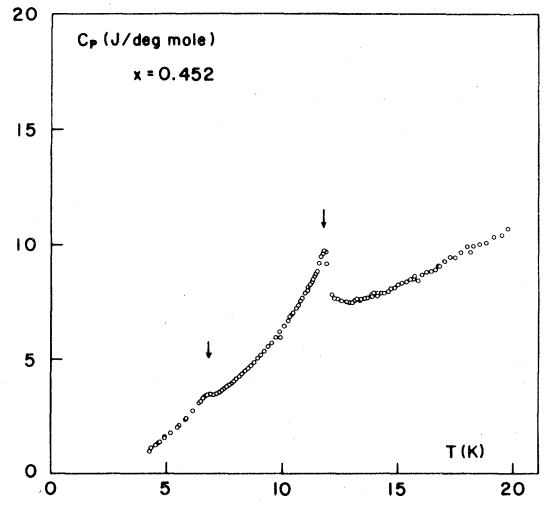

FIG. 1. Specific heat, including a contribution of the lattice, vs temperature.

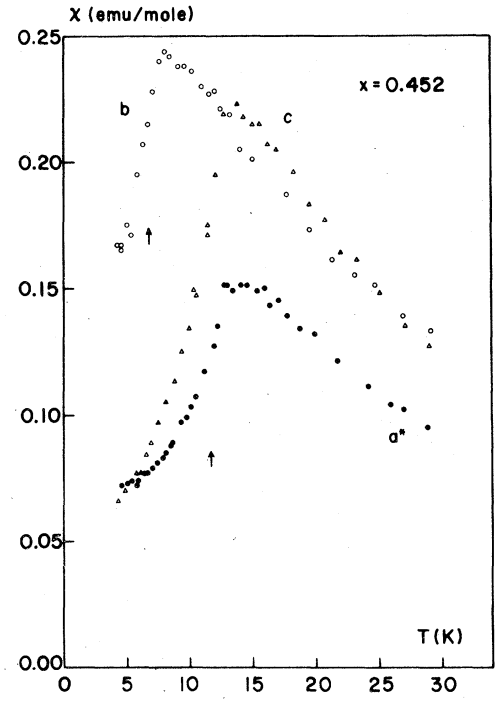

FIG. 2. Temperature dependences of the susceptibilities of $x = 0.452$ sample.

tetracritical phase transition. The magnetic properties of $FeCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 2H_2O$ have been studied extensively[17] and are now well known. The two crystals have the same monoclinic structure, the lattice parameters being only slightly different from each other. Therefore, we can expect that they make a solid solution over the entire range of concentration. In fact, an x-ray analysis on powdered samples shows that the crystals are homogeneous. The ordered state spin structures of $FeCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 2H_2O$ are the same except for the directions of the easy axes; the easy axis of $CoCl_2 \cdot 2H_2O$ points along the b axis, while that of $FeCl_2 \cdot 2H_2O$ along the α axis which lies in the ac plane and makes an angle of 32° with the c axis.[17] Thus, the system, $Fe_{(1-x)}Co_xCl_2 \cdot 2H_2O$, serves as a good example of a quenched random mixture with competing spin anisotropies.

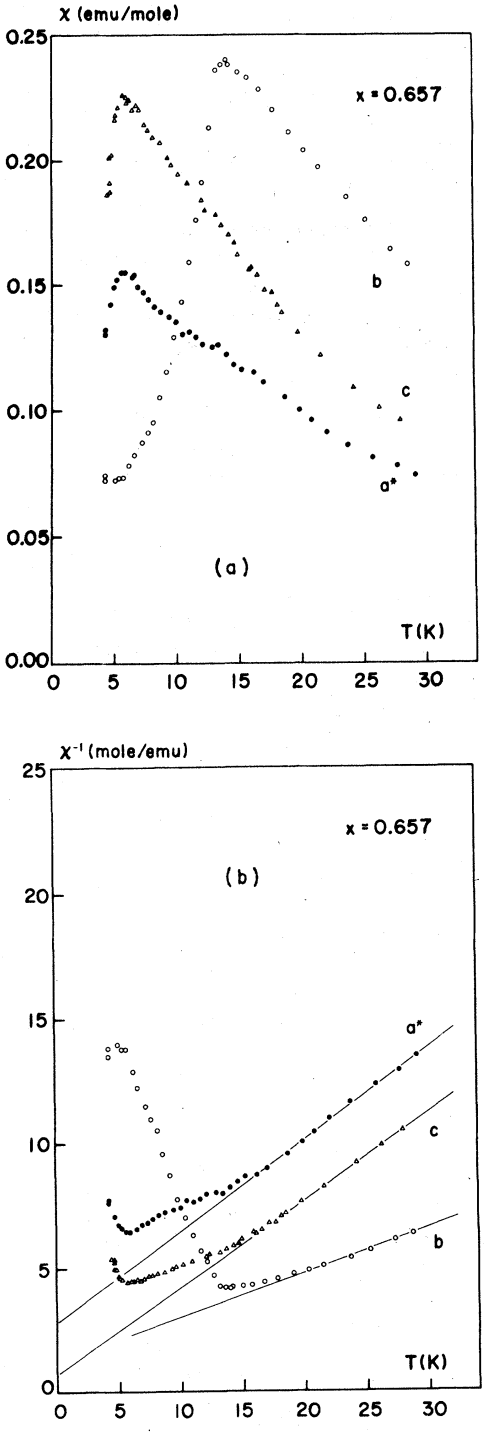

FIG. 3. Temperature dependences of the susceptibilities (a) and of the inverse of the susceptibilities (b) of the $x = 0.657$ sample.

The phase diagram was determined from the measurements of specific heat(C_p), susceptibility(χ), and magnetization on single crystals of $Fe_{(1-x)}Co_xCl_2 \cdot 2H_2O$. The specific heat was measured by a conventional adiabatic calorimeter. The susceptibility data were taken by an ac method. The temperature of a sample was measured in this magnetometer by a Au(Co)-Cu thermocouple which was attached directly on the sample. The M-H curve of a sample was displayed on an X-Y recorder by the use of the apparatus developed by the present authors.[18] The method of the single-crystal growth is the same as that reported previously.[17] The concentration, x, was determined by means of a chemical analysis.

In Fig. 1 is shown the temperature dependence of C_p of an $x = 0.452$ sample. The anomaly in the C_p at 11.8 K indicates a phase transition from a paramagnetic to an antiferromagnetic state, while a small peak around 6.8 K corresponds to a transition from the antiferromagnetic to an ordered phase. In order to see what is meant by these two successive phase transitions, we have measured the single crystal χ as

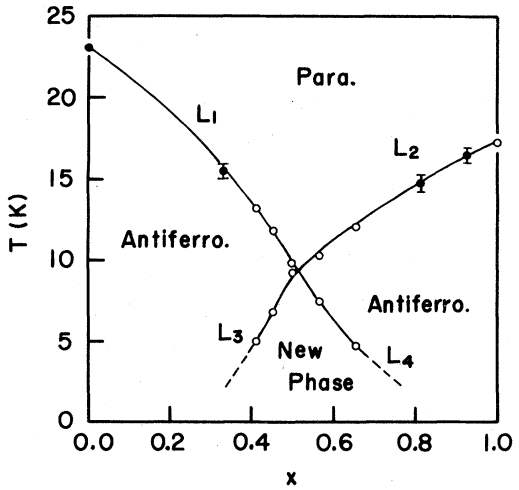

FIG. 4. Concentration vs temperature phase diagram of $Fe_{(1-x)}Co_xCl_2 \cdot 2H_2O$. The open and filled circles show the critical points determined from the measurements of C_p and χ, respectively.

a function of temperature (T). The result for an $x=0.452$ sample is shown in Fig. 2. The two transition points observed in $C_p(T)$ are shown in this figure by the arrows. The higher transition temperature agrees with the temperature at which $d\chi_{a^*}/dT$ and $d\chi_c/dT$ have their maximum values, while the lower transition temperature coincides with the temperature where $d\chi_b/dT$ is maximum (here, the a^* axis is perpendicular to both the b and c axes and should not be confused with the α axis). Even in a mixed magnet, the transition temperature determined from C_p seems to agree with the temperature at which $d\chi/dT$ diverges, as in the case of pure antiferromagnets.[19] From Fig. 2, it is seen that an ordering of the spin component in the a^*c plane in which the easy axis of pure $FeCl_2\cdot 2H_2O$ lies, occurs first, followed by an ordering of the spin component along the b axis which is the easy direction of pure $CoCl_2\cdot 2H_2O$. For the mixed crystals in the Co^{2+} rich region, the situation is reversed, i.e., the ordering of the b component occurs first, followed by that of the spin component in the a^*c plane, as shown in Fig. 3(a).

The experimental phase diagram obtained from the measurements of C_p and χ is shown in Fig. 4. This figure demonstrates clearly the existence of a tetracritical point. From Figs. 2 and 3(a), the critical lines L_1 and L_4 indicate the ordering of the a^*c component of the spin system, while L_2 and L_3 that of the b component. Thus the line L_1 is connected to the line

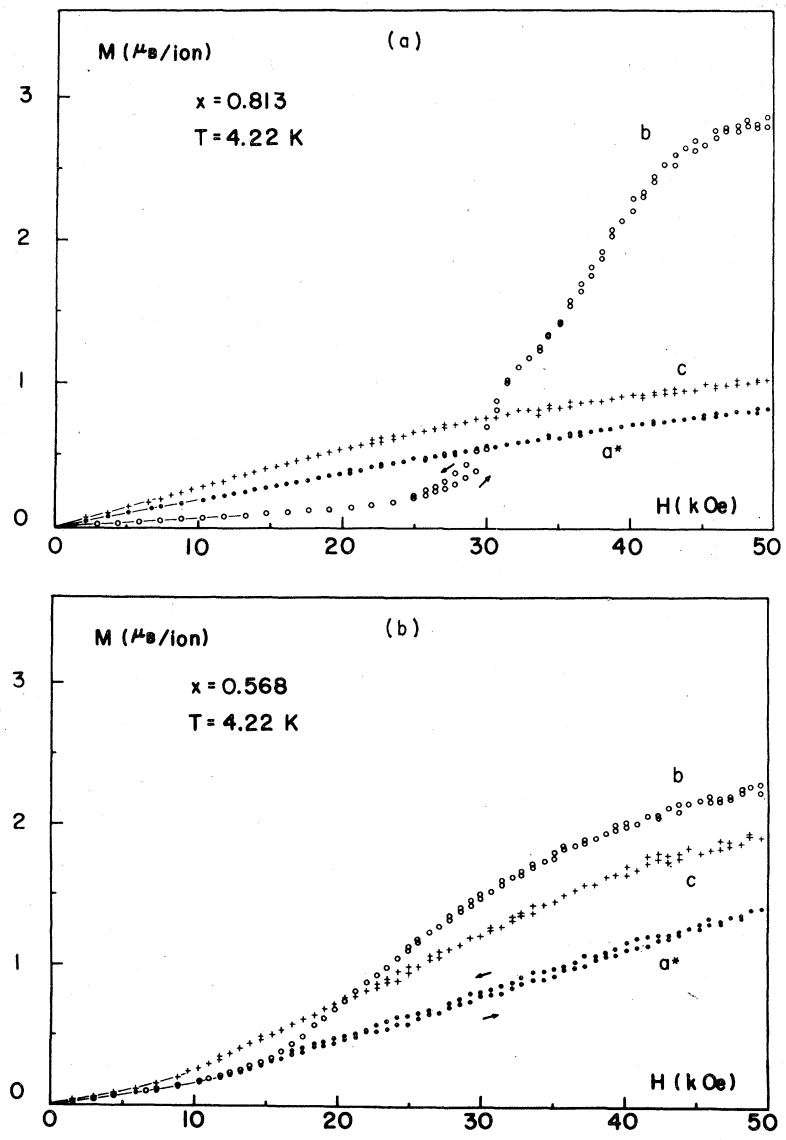

FIG. 5. Magnetization vs external field of $x=0.813$ (a) and $x=0.568$ (b) samples, measured at $T=4.22$ K.

L_4, and L_2 is connected to L_3 as in Fig. 4. The agreement of the qualitative feature of this phase diagram with the result of Aharony and Fishman (AF)[6] in the case of decoupled tetracritical points is remarkable. The critical lines in Fig. 4 become roughly straight ones near the tetracritical point, and meet at an angle, not tangentially, as predicted theoretically.[6] According to the theory of AF, near the decoupled tetracritical point, one of the spin components which is associated with competing spin anisotropies orders at the higher transition temperature and a simultaneous ordering ("mixed ordering") of the components occurs at the lower critical point. This is observed experimentally as shown in Figs. 2 and 3(a). However, the temperature dependences of the inverse of χ_{a^*} and χ_c deviate from the straight lines (Curie-Weiss law) in Fig. 3(b) in the temperature range between the higher and lower critical points, indicating that the decoupling is not complete but that there exists a weak coupling between the two subsystems in this temperature region.

Magnetization measurement at $T=4.22$ K on $x=0.813$ and 0.568 samples shows clearly a difference between the Co^{2+} rich antiferromagnetic phase and the intermediate phase, as in Figs. 5(a) and 5(b). In the Co^{2+} rich region [Fig. 5(a)], the measured M-H curve is reminiscent of the two-stepped metamagnetic transition observed in pure $CoCl_2 \cdot 2H_2O$.[17] While in the intermediate concentration region [Fig. 5(b)], the magnetizations along the a^*-, b-, and c-axes, whose magnitudes are nearly the same, increase gradually with the external field. This implies that the directions of the spins in the intermediate phase distribute widely in the crystal.

Recently, Matsubara and Inawashiro (MI)[8] have shown theoretically the existence of a new ordered phase, called "oblique antiferromagnetic (OAF) phase" which is intrinsic in the random mixture of two anisotropic antiferromagnets with different orientations of easy axes. The OAF phase corresponds to the "mixed ordering" phase of AF. In the mean-field theory of MI, the directions of the sublattice magnetizations in the OAF phase are at an angle from the easy axes of the pure substances. One of the experimental pieces of evidence for identifying the low-temperature phase located in the intermediate concentration region in Fig. 4 with the OAF phase, is seen in Figs. 2 and 3(a); all of the χ_{a^*}, χ_b, and χ_c do not go to zero when extrapolated to $T=0$ K. Further study, including NMR and neutron-diffraction experiments, is needed for the determination of the spin arrangement in the intermediate phase.

The dynamic properties of this mixed magnet are also worth studying in view of the long relaxation time for the spin reversals observed in pure $FeCl_2 \cdot 2H_2O$[17] and the very short one in pure $CoCl_2 \cdot 2H_2O$.[20]

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