

# Specific heat of $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$ compounds at low temperatures

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The specific heat of five  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  compounds in the concentration range corresponding to values of  $x$  between 0 and 0.7 has been measured between 2 and 27 K. The phase diagram and the spin-wave dispersion laws have been studied in these compounds, for which the initial components are layered antiferromagnets with a strong competing anisotropy.

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This letter reports measurements of the specific heat of  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  compounds with concentrations  $x$  between 0 and 0.7 over the temperature range from 2 to 27 K.

The layered antiferromagnets  $\text{FeCl}_2$  and  $\text{CoCl}_2$  have isomorphic crystal structures  $R_{3d}^5$  with similar lattice constants. Their mixed compounds form substitutional solid solutions of similar structure. In them, hexagonal layers of metal ions alternate with two layers of chlorine ions; the  $c_3$  principal symmetry axis runs perpendicular to the plane of a layer.

Calorimetric data put the antiferromagnetic-transition temperature of  $\text{CoCl}_2$  at  ${}^1T_N = 24.7$  K and  $\text{FeCl}_2$  at  ${}^2T_N = 23.5$  K. The specific heats of these halides have been studied at liquid-helium temperature.<sup>3</sup>

The ferromagnetic interaction between the metal ions in a layer in these materials is much stronger than the antiferromagnetic between layers. There is a pronounced anisotropy of the exchanger interaction, and the spins in the  $\text{CoCl}_2$  are oriented in the plane of the layer, while those in the  $\text{FeCl}_2$  are directed along the  $c_3$  principal axis. The energy gap in the spin-wave spectrum of  $\text{FeCl}_2$  is large,<sup>4</sup>  $\Delta K_B \sim 25$  K; the gap in the high-frequency branch of the  $\text{CoCl}_2$  spectrum is of the same order of magnitude.<sup>4</sup> The  $\text{CoCl}_2$  and  $\text{FeCl}_2$  exhibit the properties of three-dimensional antiferromagnets up to rather high temperatures; in  $\text{CoCl}_2$ , for example, the sublattice magnetization exhibits a quadratic behavior<sup>5</sup> up to 14 K.

Our purpose in this study was to determine the ordering of mixed compounds  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  and the temperature dependence of the magnetic specific heat.

The specific heat was measured for  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  compounds with several concentrations:  $x = 0.08$  (I),  $x = 0.14$  (II),  $x = 0.51$  (III),  $x = 0.59$  (IV), and  $x = 0.70$  (V).

The compounds were synthesized by melting mixtures of anhydrous halides of iron and cobalt in a sealed ampoule at  $T = 1000$  °C; the melt was held several hours at the temperature and then cooled slowly. Chemical analysis puts the accuracy of the concentration ( $x$ ) determination at  $\sim 0.005$ .

The behavior of mixed compounds with a random distribution of components

with competing anisotropies has recently been studied theoretically.<sup>6,7</sup> It has been shown that there are two lines of second-order phase transitions which separate phases on the  $x$ - $T$  phase diagram. These lines correspond to the ordering of only one or the other of the spin components, and they intersect at an angle at the tetracritical point  $T_4$ . A simultaneous ordering (a mixed ordered phase) of the spin components is predicted at intermediate concentrations.

The mixed compounds  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  are solid solutions of components with competing anisotropies.

Recent neutron-diffraction studies of  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  compounds<sup>8</sup> have shown that one line on the phase diagram corresponds to an ordering of the spin component in the easy plane, while a second line corresponds to an ordering of the spin component along the  $c$  axis. The lines intersect at a concentration  $x \sim 0.7$  at the tetracritical point,  $T_4 \sim 15$  K. The mixed ordered phase exists for  $x$  between 0.8 and 0.55; the sublattice magnetization directions make an angle with the  $c$  axis and with the easy plane.

Figure 1 shows the results of our measurements of the specific heat between 4 and

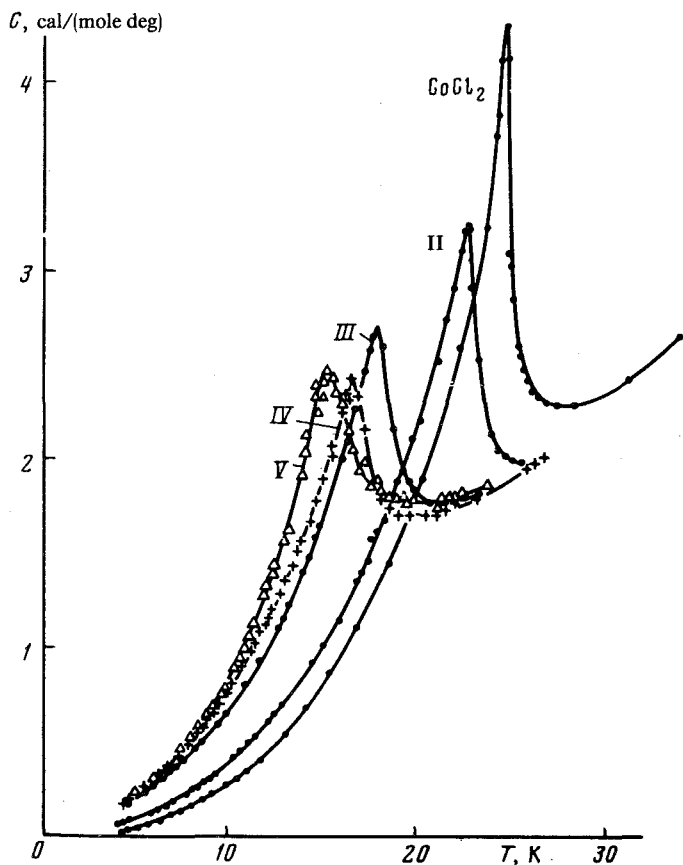


FIG. 1.

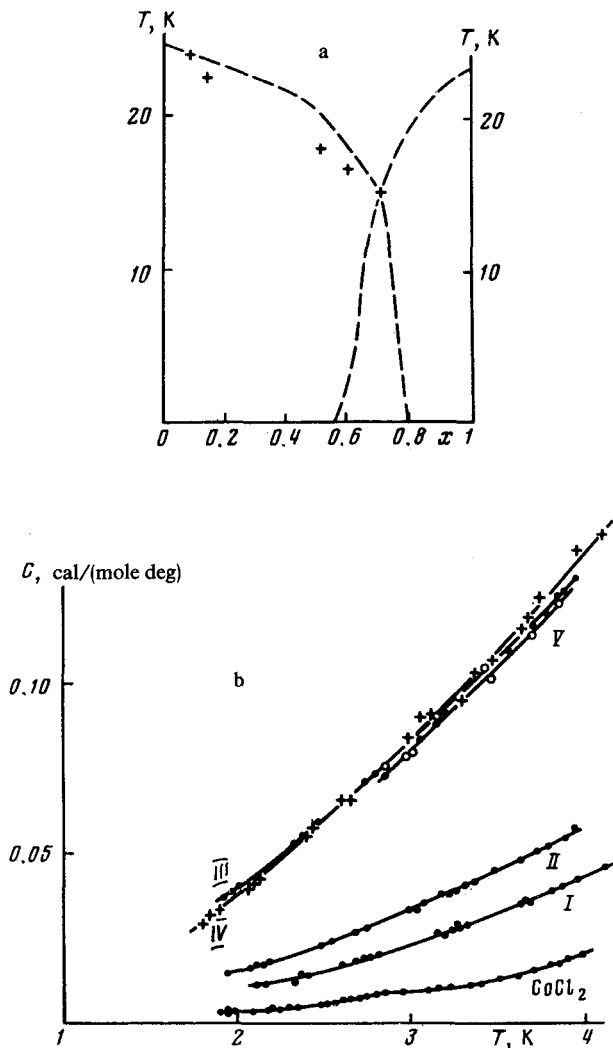


FIG. 2.

27 K for four compounds  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  with concentrations  $x$  between 0 and 0.7. Also shown in this plot of  $C$  vs  $T$  are data for pure  $\text{CoCl}_2$ , for which we used the results of Ref. 1 above 11 K. As for the pure  $\text{CoCl}_2$ , the mixed  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  compounds show a sharp specific-heat peak at the transition to the paramagnetic state. As  $x$  is increased,  $T_N$  decreases.

It can be seen from Fig. 1 that the compounds studied in the present experiments exhibit no additional specific-heat peaks on the curves of  $C$  vs  $T$  at temperatures from 4 K to  $T_N$ . The only change is that the specific-heat peak on the curve of  $C$  vs  $T$  for the concentration  $x = 0.70$  is slightly broader than in the other compounds. For this concentration, the maximum at  $T = 15.3$  K is observed near the tetracritical point.

Figure 2a shows the  $x$  dependence of the antiferromagnetic transition temperature  $T_N$  for the  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  compounds with  $x$  between 0 and 0.70. The data from the present experiments are shown by the plus signs, while the dashed curves show the data from Ref. 8. Our values of  $T_N$  are slightly lower than Ref. 8.

Figure 2b shows the specific heat of the  $\text{Fe}_x\text{Co}_{1-x}\text{Cl}_2$  compounds in a plot of  $C$  vs  $T$ , along with the specific heat of  $\text{CoCl}_2$ , at liquid-helium temperature.

The specific heat of these compounds increases substantially at low temperatures. In compounds III, IV, and V the magnetic specific heat is much higher (by a factor of about 8) than the specific heat of  $\text{CoCl}_2$  at liquid-helium temperature. This result is evidence that low-frequency excitations in these compounds are very important.

None of the compounds exhibit an additional peak on the  $C(T)$  curve at liquid-helium temperature. A possible explanation for the absence of a maximum in the compound with  $x = 0.59$  is the circumstance that the additional hump is small and is washed out by a composition inhomogeneity  $x \sim 0.01$  of the sample.

Figure 3 shows the specific heat of compounds III, IV, and V in a plot of  $C/T^{3/2}$  vs  $T^{3/2}$ . We see that for compound V ( $x = 70$ ) the experimental points conform to a straight line over a broad temperature interval between 2.8 and 11 K. In other words, the specific heat in the new phase is described well by

$$C \left[ \frac{\text{cal}}{\text{mole deg}} \right] = 4.3 \cdot 10^{-4} T^3 + 1.3 \cdot 10^{-2} T^{3/2} .$$

The first term in this expression is larger than the cubic terms in the specific heat in  $\text{CoCl}_2$  and  $\text{FeCl}_2$  (Ref. 3) (for  $\text{CoCl}_2$ , we have  $C = 3.1 \times 10^{-4} T^3$  cal/(mole deg), and

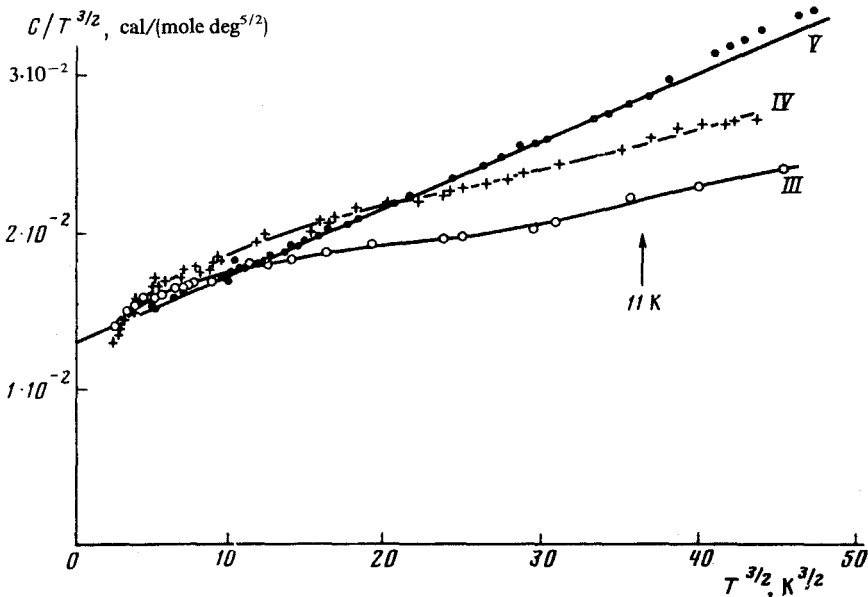


FIG. 3.

in  $\text{FeCl}_2$  we have  $C = 3.7 \times 10^{-4} T^3$  cal/(mole deg). This first term thus exceeds the lattice component of the specific heat. It might be suggested in this connection that the spin-wave spectrum of the new phase contains spin waves of a ferromagnetic type, which give rise to a term  $T^{3/2}$  in the specific heat, and (apparently) waves of an antiferromagnetic type, which, along with the lattice specific heat, contribute to the  $T^3$  term.

For the compounds III ( $x = 0.51$ ) and IV ( $x = 0.59$ ), which belong to a phase in which the spin component in the easy plane is becoming ordered, the experimental points do not conform to straight lines, so that they are not described by a dependence  $C = AT^3 + BT^{3/2}$ . It should be noted that the spin-wave spectrum of compounds of this type has not been derived theoretically.

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