Magnetic Phase Transition of the Mixed Antiferromagnets

Ni$_{1-x}$M$_x$Cl$_2$·2H$_2$O (M=Co, Mn)

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Abstract. Mixed antiferromagnets Ni$_{1-x}$M$_x$Cl$_2$·2H$_2$O (M=Co, Mn) were prepared. The crystal structure of NiCl$_2$·2H$_2$O is a little different from that of CoCl$_2$·2H$_2$O and MnCl$_2$·2H$_2$O. In order to examine how Co or Mn spins in NiCl$_2$·2H$_2$O crystal structure behave, we determined precisely the phase transition temperatures by measuring the specific heats and have obtained the concentration dependence of the phase transition temperature. Substitution of Co for Ni increases a little the transition temperature and contrary to this the substitution of Mn decreases the transition temperature rapidly. The results are discussed on the basis of molecular field theory. In the case of M=Co, the concentration dependence of the phase transition temperature is well explained by molecular field theory. But, in the case of M=Mn, the molecular field theory cannot explain it sufficiently. Thus Mn spins in NiCl$_2$·2H$_2$O crystal show the peculiar behavior. We suppose that this may be attributed to a kind of the instability of Mn spins.

1. Introduction

Mixed antiferromagnets systems exhibit various magnetically ordered states such as an oblique antiferromagnetic phase and a spin glass phase and so on. For example, the mixed crystal of FeCl$_2$·2H$_2$O and CoCl$_2$·2H$_2$O is known as a typical transition metal dichloride dihydrate which shows the oblique antiferromagnetic state [1-3]. In the mixed crystal of MnCl$_2$·2H$_2$O and CoCl$_2$·2H$_2$O, the re-entrant spin glass phase appears [4-6]. The existence of an intermediate ordered phase is pointed out in the mixed crystal of FeCl$_2$·2H$_2$O and MnCl$_2$·2H$_2$O [7,8].

NiCl$_2$·2H$_2$O has the same chemical formula as CoCl$_2$·2H$_2$O, FeCl$_2$·2H$_2$O and MnCl$_2$·2H$_2$O, but it takes a different crystal structure from the others [9-11]. It is interesting to introduce these Co or Mn spins into in the NiCl$_2$·2H$_2$O crystal structures. Although the magnetic susceptibility measurements on the systems of Ni$_{1-x}$Co$_x$Cl$_2$·2H$_2$O or Ni$_{1-x}$Mn$_x$Cl$_2$·2H$_2$O is already reported, two neighboring magnetic transitions seen in pure NiCl$_2$·2H$_2$O are not observed separately in Ni-rich samples [12,13]. From this, we had a plan to measure the specific heats of Ni$_{1-x}$M$_x$Cl$_2$·2H$_2$O (M=Co, Mn) mixed crystal systems to determine the magnetic transition temperatures precisely.

2. Sample preparation and experiment

The samples were prepared by slow evaporation from an aqueous solution of proper amount of CoCl$_2$·6H$_2$O and NiCl$_2$·6H$_2$O or MnCl$_2$·4H$_2$O at 75 °C. The prepared samples were checked by X-ray diffraction. Even though the very slight diffraction pattern of tetrahydrate salts etc. was observed, we judged that this does not disturb the observation of the transition temperatures of the mixed dihydrate salts because of their low transition temperatures and very slight amounts. Ni and Co or Mn
concentrations of the prepared samples were determined by ICP emission spectrometry. Magnetizations were measured by using a SQUID magnetometer of Quantum Design, and specific heats were measured using the heat capacity measuring option of PPMS of Quantum Design.

3. Results

Figure 1 shows the typical results of the magnetic specific heat and magnetic susceptibility measurements on the samples of Ni$_{1-x}$Co$_x$Cl$_2$·2H$_2$O in Ni-rich side. The specific heat measurements have distinguished two close transitions apparently in comparison with the measurement of the susceptibility. (see the inset in figure 1 (a)) A little swell appearing at low-temperature near 2.5K is due to the contamination of the tetrahydrate Ni salt.

![Figure 1. (a) Magnetic specific heat and (b) magnetic susceptibility of Ni$_{1-x}$Co$_x$Cl$_2$·2H$_2$O (x=0.17).](image1)

In figure 2, the representative results of the magnetic specific heat and magnetic susceptibility measurements of Ni$_{1-x}$Mn$_x$Cl$_2$·2H$_2$O in Mn-rich side are shown. No maximum in the susceptibility due to a transition is observed clearly, which is the same results obtained by DeFotis et al. [13]. Contrary to this, as the magnetic specific heat shows the $\lambda$-type anomalies, the transition point can be determined clearly.

![Figure 2. (a) Magnetic specific heat and (b) magnetic susceptibility of Ni$_{1-x}$Mn$_x$Cl$_2$·2H$_2$O (x=0.94).](image2)

Figure 3 shows the Co concentration dependence of the transition temperatures of Ni$_{1-x}$Co$_x$Cl$_2$·2H$_2$O. The samples in the Ni-rich side keep the same crystal structure as NiCl$_2$·2H$_2$O and are considered to have the same magnetic structure as NiCl$_2$·2H$_2$O because the two neighboring transitions are observed. The transition temperatures increase slightly with the increasing substitution of Co and the difference between two neighboring transition temperatures gets closer. Another new peak of the specific heat appears in the sample of x=0.76 which is due to the mixing of CoCl$_2$·2H$_2$O structure. The crystal structure of x=0.82 sample changes to one of CoCl$_2$·2H$_2$O and the only one $\lambda$ type anomaly is observed in the specific heat. In Co-rich side the transition temperatures become a little higher with the increasing Ni substitution.

The Mn concentration dependence of the transition temperatures of Ni$_{1-x}$Mn$_x$Cl$_2$·2H$_2$O is shown in figure 4. Two transitions can be observed clearly until x=0.38. The sample with x=0.78 exhibits no transition in the measuring temperature range. (The transition temperature is considered to be lower than 2 K.) The samples with the Mn concentration more than x=0.89 have a MnCl$_2$·2H$_2$O-type magnetic structure and the only one $\lambda$ type transition is observed. The substitution of Co does not make the transition temperature change so much, but the Mn substitution causes the transition temperature decrease rapidly. In the Mn-rich side, the transition temperatures decrease rapidly, too.
4. Discussion
In the case of Ni-CoCl₂·2H₂O systems, the x dependence of the transition temperatures is plotted in figure 5 which are normalized by the transition temperature of x=0 pure crystal. T_N1 and T_N2 mean the two neighboring transition temperatures seen in Ni-type magnetic structure and the transition temperature T_N means that of the Co-type structure. Now we will discuss the concentration dependence of T_N(x) by use of simple molecular field theory.

We consider two magnetic ions A and B. When a part of A ions is replaced by B ions, the transition temperature T_N(x) is given as [14]

\[
\frac{T_N(x)}{T_N(0)} = \frac{1}{2} [\left(1 - x\right) + x p_1] + \frac{1}{4} \left[\left(1 - x\right) + x p_1\right]^2 + x(1 - x)(p_2^2 - p_1^2),
\]

where \(p_1 = T_A/T_B\) and \(p_2 = T_{AB}/T_A\). \(T_A\) and \(T_B\) are the transition temperatures of A and B ions, respectively and \(T_{AB}\) is the transition temperature determined by the interaction between A and B ions. The solid lines in figure 5 are drawn by use of best fit parameters \(p_1\) and \(p_2\). The values of \(p_1\) and \(p_2\) are written in the figure. The \(p_1\) and \(p_2\) values of \(T_{N1}\) and \(T_{N2}\) are different. This may reflect the mechanism causing this transition. But the precise is unclear.

In the case of Ni-MnCl₂·2H₂O systems, the x dependence of the normalized transition temperatures is shown in figure 6. In this case, there are no best fit parameters. Contrary to Ni-CoCl₂·2H₂O systems, the x dependence of \(T_{N1}\) and \(T_{N2}\) is the same. From such, Ni-MnCl₂·2H₂O systems cannot be explained in the simple molecular field approximation. In this system we seem to need to discuss by considering the large fluctuations of Mn ions [15-18].

5. Summary
The results are summarized as follows. 1) By measuring the specific heats, we were able to accurately determine the magnetic transition temperatures of Ni₁₋ₓMₓCl₂·2H₂O (M=Co, Mn). 2) The x dependence of the transition temperatures of Ni-CoCl₂·2H₂O systems can be well explained by the simple molecular field theory, in the other hand, Ni-MnCl₂·2H₂O systems are not. Since the transition...
temperature rapidly decreases with a small amount of substitution, we need to discuss in account of the fluctuation of Mn ions.

Figure 5. The concentration dependence of the normalized transition temperatures of Ni-CoCl$_2$·2H$_2$O systems. Solid lines are the best fit lines calculated by the simple molecular field theory.

Figure 6. The concentration dependence of the normalized transition temperatures of Ni-MnCl$_2$·2H$_2$O systems. There are no best fit lines calculated by the simple molecular field theory.

6. References

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