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Nonmagnetic Impurity Effect in $CuF_2 \cdot 2H_2O$

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We have measured the magnetic susceptibilities of a $CuF_2 \cdot 2H_2O$ sample by means of the SQUID (superconducting quantum interference device) at the magnetic fields of 0.5 T and 1 mT, in the temperature range 5-300 K. The sample was found to contain some nonmagnetic calcium and magnesium impurities by the elemental analysis. Our measurements differ from known results for pure $CuF_2 \cdot 2H_2O$ and are well explained by the effect of the nonmagnetic impurities in our sample. The purity of our sample derived from the temperature dependence of the susceptibilities was compared with that from the elemental analysis.

I. Introduction

High purity $CuF_2 \cdot 2H_2O$ has a monoclinic crystal structure[1, 2] and is a spin $S=1/2$ two-dimensional Heisenberg antiferromagnet[3, 4] with a Neel temperature $T_N=10.9$ K[5]. In general, two-dimensional systems are known to show broad maxima in the magnetic susceptibilities[4, 6]. $CuF_2 \cdot 2H_2O$ has a broad susceptibility maximum around 26 K[7, 8]. However, when nonmagnetic impurities are introduced into the two-dimensional antiferromagnets, the antiferromagnetic transition temperature depends on the impurity concentrations and there is a drastic increase in the susceptibilities around the critical temperatures. In addition, the susceptibility can depend on the applied magnetic field in this case[6]. Hence, we may determine the impurity concentrations in a two-dimensional antiferromagnet by comparing the susceptibility measurements with those from the high purity samples.

A quasi-two-dimensional magnet with disordered magnetic system, that is, a random-site diluted magnet. In such a system, the magnetic ordering temperature T_c decreases with decreasing concentration p of the magnetic species, and the susceptibility undergoes a drastic increase around the transition temperature[9]. Besides, the susceptibility for the direction perpendicular to the applied field depends on the direction of that field[10]. The decrease of the transition temperature, $T_c(p)$, depends on the lattice symmetry and the interaction Hamiltonian. The variations of $T_c(p)$ for the Ising, XY, and Heisenberg model have been studied by the series expansion techniques, finite cluster approximation, and the numerical (Monte Carlo) calculation[11]. Such variations can be explained by the ferrimagnetic fluctuation effect of the total magnetic moments or the random field effect[12]. In typical 2-d system models, only the Ising model has a long-range order for $T_c > 0$ K. Although long-range magnetic order does not exist in ideal 2-d Heisenberg systems, it is possible for a system with a small Ising component and a weak interlayer interaction[6].

For a antiferromagnetic system the order parameter associated with long range order is the sublattice magnetization M_s. It follows that M_s^2 is proportional to the infinite-range correlation function Γ_∞. The finite range correlation functions Γ_r, on the other hand, show an inflection point at T_N [6]. Accordingly, dx_m/dT has a maximum at T_N.

The magnetic susceptibility follows the Curie-Weiss law $x_m = C_m/(T-\theta)$ above the T_c. For a concentration p of the magnetic ions, the Curie constant C_m and the temperature θ are given by

$$C_m = \frac{pNg^2\mu_B^2 S(S+1)}{3k},$$

$$\theta(p) = \frac{2pzJS(S+1)}{3k} \qquad (1)$$

where J is the exchange interaction constant and z is the number of nearest neighbors in the magnetic lattice.[10].

Ⅱ. Experimental

The powder sample of $CuF_2 \cdot 2H_2O$ of unspecified purity was commercially available. According to the elemental analysis, it includes the nonmagnetic calcium (Ca^{++}) (0.45 %) and magnesium (Mg^{++}) (0.18 %) ions. The magnetic susceptibility measurements at applied magnetic fields of 0.5 T and 1 mT were made using a SQUID manetometer (Quantum Design MPMS) in the temperature range 5-300 K as cooling the sample.

Ⅲ. Results and discussion

Fig. 1 shows the temperature dependence of the magnetic susceptibility for the applied fields of 0.5

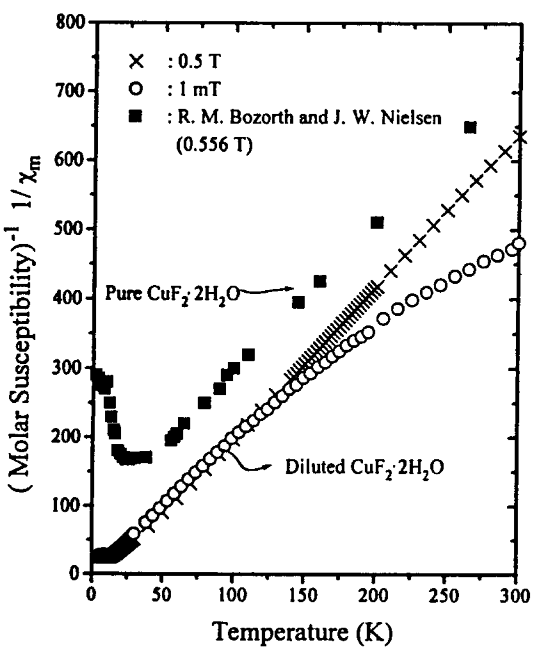

Fig. 1. Inverse molar susceptibilities as a function of temperature.

T and 1 mT below 100 K. It shows a drastic deviation from the results by Bozorth and Nielsen (0.556 T)[7] and Tazawa *et al.* (1.08 T)[8] for high purity $CuF_2 \cdot 2H_2O$ samples. Broad maxima around 26 K are seen in pure $CuF_2 \cdot 2H_2O$ above the Neel temperature $T_N = 10.9$ K in the measurements by Bozorth and Nielsen. From their measurements, an isotropic exchange energy $J = -13\ k_B$ was obtained by the 2-d Heisenberg high temperature series expansion, and an anisotropy factor $H_A/H_E = 3.7 \times 10^{-3}$ was obtained by the antiferromagnetic resonance below the T_N[3]. However, in our measurements the susceptibility maxima were observed at 11 K and the increase is much more rapid than in the reported results in pure samples. It is also seen that the maximum values are about seven times greater in our sample than in pure samples. These results are consistent with the nonmagnetic impurity case described in the Introduction and suggests that our sample is not pure enough for an ideal Heisenberg antiferromagnetic case. The measured T_c defined by the temperature at which $d\chi_m/dT$ is the maximum was 9.5 K and was independent of the applied field. This can be explained by the nonmagnetic impurity effect. Nonmagnetic impurities randomly distributed in the antiferromagnetic sheets upset the balance between the two sublattices and cause a mismatch in the couplings perpendicular to the antiferromagnetic sheets and thus disturb the sensitive interlayer order[6]. Then it gives rise to local fluctuations of the magnetic moments and a drastic increase in the magnetic susceptibilities[12]. Since the broad susceptibility maxima in the pure $CuF_2 \cdot 2H_2O$ are attributed to direct exchange interactions in the antiferromagnetic layers and weak interlayer ferromagnetic interactions, it is understood that nonmagnetic impurities can upset the intralayer antiferromagnetic order and the weak interlayer ferromagnetic order.

Our susceptibility data at 0.5 T gives $C_m = 0.450 \pm 0.001\ m^3K/mole$ and $\theta(p) = 9.0$ K for the Curie-Weiss law $\chi_m = C_m/(T-\theta)$. The value of $C_m = 0.45\ m^3K/mole$ is compared with that of $0.46\ m^3K/mole$ from the pure $CuF_2 \cdot 2H_2O$. Using these values and $z = 4$, the magnetic ion concentration $p = 0.980 \pm 0.002$ and the isotropic exchange energy

$J = 4.6\ k_B$ are obtained. This value of the magnetic ion concentration considerably deviates from the elemental analysis, which indicates a magnetic ion concentration of over 0.99. This difference seems to arise from the use of Eq. (1), which is derived from the three-dimensional molecular field theory. However, no comprehensible theory exists properly applicable to the two-dimensional nonmagnetic impurity cases such as our system.

Smaller low temperature susceptibilities at 1 mT than at 0.5 T are attributed to the external field dependence of the susceptibility component in the direction perpendicular to the applied field in diluted magnets[10, 12]. Fig. 2 shows the inverse of the susceptibility $1/\chi_m$ as a function of temeprature. It is seen that the high temperature behavior at 1 mT shows an anomalous deviation from the Curie-Weiss law. Such a deviation may be expected when the external field is not strong enough to overcome the exchange interactions between the unpaired electron spins, since the Curie-Weiss law is valid for paramagnets with negligible interactions other than the dipolar interactions.

In summary, we have made magnetic susceptibility measurements for a $CuF_2 \cdot 2H_2O$ sample at the external magnetic fields of 0.5 T and 1 mT using a SQUID magnetometer. From these measurements, it was possible to determine the effect of the nonmagnetic impurities in our sample by comparing our data with previous results in pure samples.

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$CuF_2 \cdot 2H_2O$에서의 비자성 불순물 효과

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SQUID를 이용하여 5-300 K의 온도 범위에서 0.5 T와 1 mT의 자기장에서의 $CuF_2 \cdot 2H_2O$ 시료의 자기감수율을 측정하였다. 원소분석에 의하면 이 시료는 비자성 불순물인 칼슘과 마그네슘 불순물을 포함하고 있다. 우리의 측정 결과는 순수한 $CuF_2 \cdot 2H_2O$에 대하여 알려진 결과와 차이가 나며 이는 우리 시료 내의 비자성 불순물 효과로 잘 설명된다. 자기감수율의 온도의존성으로부터 유도한 비자성 불순물 농도를 원소분석으로부터 얻은 값과 비교하였다.