Random spin disorder of antiferromagnetic long-range order in a spin-glass system: proton nuclear magnetic resonance study of $Co_{1-x}Mn_xCl_2.2H_2O$

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Random spin disorder of antiferromagnetic long-range order in a spin-glass system: proton nuclear magnetic resonance study of $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$

H Kubo and K Zenmyo
Fukuoka Institute of Technology, Wajiro, Fukuoka 811-02, Japan

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Abstract. The proton NMR spectrum of the magnetically ordered phase of $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$ for $0.25 \lesssim x \lesssim 0.47$ is not given by a simple symmetric line. The deviation is due to spin disorder of Co or Mn spins in the antiferromagnetic long-range order. The fraction of spin disorder depends on the concentration x and temperature. The spin disorder is observed in the antiferromagnetic phase as well as in the re-entrant spin-glass phase.

1. Introduction

Spin-glass behaviour is widely seen in compounds with competing exchange interactions [1]. In the re-entrant spin-glass phase, the spins in the spin-glass state coexist with the ordered spins of the (anti)ferromagnetic state. Recently, Ito *et al* [2] and Katori *et al* [3] have shown that the antiferromagnetic long-range order in the spin-glass system $Fe_{1-x}Mn_xTiO_3$ is not that of a complete antiferromagnet. DeFotis *et al* [4] and Deguchi *et al* [5] have also shown that the antiferromagnetic state in the compound $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$ is a 'frustrated' antiferromagnet. These results suggest that the antiferromagnetic long-range order in the spin-glass system is not always a simple antiferromagnet. Deviations from a completely ordered antiferromagnetic system are directly reflected in the NMR spectra. From this viewpoint, proton NMR measurements have been carried out on the compound $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$ which has the Ising character [6]. The purpose of this work is to clarify the nature of the long-range antiferromagnetic order, and to show that frustration due to the competing exchange interactions generates randomly disordered spins.

2. Experimental results

The NMR measurements were carried out on $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$ by the conventional spin-echo method. The samples were grown from an aqueous solution. Although it is not easy to check the homogeneity of the mix of Co and Mn atoms, the concentration dependence of the NMR linewidth [6] is consistent with random mixing.

The re-entrant spin-glass phase of this compound is found below 2.4 K for a wide concentration range $0.2 \lesssim x \lesssim 0.9$ [6, 7]. In the re-entrant spin-glass phase the spins in the spin-glass state coexist with the spins of the antiferromagnetic long-range order. The spins in the spin-glass state freeze randomly with a concentration-dependent weight [6]. The spin structure of the antiferromagnetic spins is that of $CoCl_2 \cdot 2H_2O$ [8] for $x \lesssim 0.47$ and that of

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$MnCl_2 \cdot 2H_2O$ [9] for $x \gtrsim 0.73$. In the intermediate region $0.47 \lesssim x \lesssim 0.73$ [7], both spin structures coexist. In this paper we discuss only the region where $x \lesssim 0.47$.

Typical proton NMR spectra of the re-entrant spin-glass phase are shown in figures 1(*a*)–1(*c*). The spectrum consists of well separated lines at about 18 and 24 MHz. The proton NMR frequency is proportional to the magnitude of the dipole field due to the surrounding moments. Although the dipole interaction itself is a long-range interaction, the dipole field experienced by a proton nucleus depends strongly on whether its nearest neighbour is Co or Mn. The lines at about 18 and 24 MHz are due to proton nuclei having Co and Mn moments, respectively, at the nearest-neighbour site.

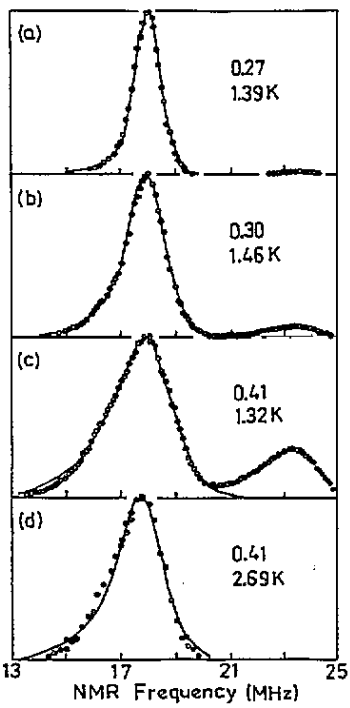

Figure 1. Proton NMR spectra in $Co_{1-x}Mn_xCl_2 \cdot 2H_2O$. The full curves are the calculated lines with random disordered spins of (*a*) 1.9%, (*b*) 3.2%, (*c*) 6.4% and (*d*) 4.5%.

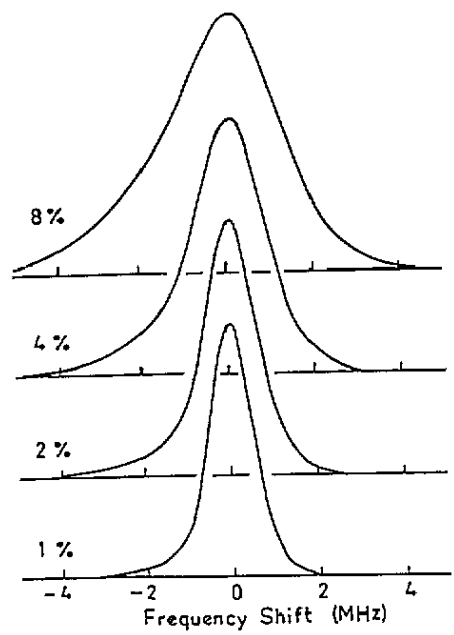

Figure 2. Calculated NMR spectra of proton nuclei in the antiferromagnet with random disordered spins at $x = 0.5$. The frequency 0 MHz means a NMR frequency of antiferromagnetic order without disorder. The percentages show the amounts of disordered spins.

As seen in figure 1, the lines at about 18 MHz are not symmetric but are expanded on the low-frequency side of the peak. We previously suggested [6] that the origin of this deviation from symmetry may be due to nuclei in the spin-glass region of the sample, but we can now show that this is not the case. To clarify this point, we measured the spectra in the antiferromagnetic phase at a temperature above the re-entrant spin-glass phase transition temperature. A typical result is shown in figure 1(*d*). The line at about 24 MHz disappears. The NMR line at about 24 MHz is due to proton nuclei with a Mn nearest neighbour. As already shown [6], the proton NMR line about 24 MHz in the antiferromagnetic region of the sample is not observed. This is probably due to the short spin–spin relaxation time. Hence the observed line at about 24 MHz at low temperatures is due solely to the nuclei in the spin-glass region of the sample. Therefore, the disappearance of this line at high

temperatures is reasonable because there is no spin-glass spins in the antiferromagnetic phase. However, the expansion to the lower-frequency side of the line at about 18 MHz is observed even at a temperature where only the antiferromagnetic spin state exists. Hence it is reasonable to conclude that the expansion to the low-frequency side is not due to proton nuclei in the spin-glass region of the sample.

3. Model and calculation

Although the random mixture of Co and Mn moments will in principle lead to a deviation in the symmetry of the line, because of the difference between the magnitudes of the moments, the calculated spectra show this deviation to be very small. The existence of the spin-glass spins cannot be the main origin as the deviation from the symmetric line is observed even in the antiferromagnetic phase. However, Ito *et al* [2] and Katori *et al* [3] have pointed out that some spins may not be perfectly ordered in the antiferromagnetic regions of the material. This disorder will lead to a deviation from the symmetric NMR lineshape. Here we assume that this disorder consists of random spin disorder in the antiferromagnetic long-range order. Considering the Ising character of this compound [6], we also assume that the disordered spin orients to just the opposite direction expected from the long-range order. Following these assumptions the expected NMR spectra are calculated and compared with the observed results.

The NMR frequency f is obtained directly from the relation $f = \gamma|\boldsymbol{H}_d|$, where γ is the nuclear gyromagnetic ratio 4.2575 MHz kOe^{-1} for proton nuclei and $|\boldsymbol{H}_d|$ is the magnitude of the dipole field. Initially we calculate the frequency difference between the ideal antiferromagnetic state and a state with one disordered spin. A system of about 500 spins within a sphere of radius 23 Å was chosen for the calculation and is usually of sufficiently high magnitude for the present purpose. We used the averaged lattice parameters and the averaged moment of Co and Mn for the appropriate Mn concentration [8, 9]. The frequency difference is divided into 200 groups on both sides of the ideal peak. These groups then run from -5 to $+5$ MHz with an interval of 0.05 MHz. The calculated frequency of each spin then determines the group which the spin is placed in. Finally we obtain a set of groups m ($m = 1, 2, \ldots, 200$) with number of spins N_m, and frequency difference from the ideal case $\mathrm{d}f_m$. The NMR spectrum for one spin disorder is calculated by summing 200 Gaussian lines with centre frequency $\mathrm{d}f_m$ and relative intensity N_m. The intrinsic linewidth is assumed to be 1 MHz.

Using the results of the calculation for one disordered spin, we obtain the spectrum for two disordered spins. If the two defective spins belong to the groups m and n, respectively, such a case occurs N_mN_n times (if $m \neq n$) and the frequency difference is approximated by $\mathrm{d}f_m + \mathrm{d}f_n$. By considering all cases of two defective spins, we get a new set of 200 groups with relative intensity $I_{m'}$ ($m' = 1, 2, \ldots, 200$) and frequency difference $\mathrm{d}f_{m'}$. The NMR spectrum is then obtained in a manner similar to the case of one disordered spin. Repeating the process we calculated a total of seven cases (disorder from $1, 2, 4, \ldots, 64$ spins). Spectra with an arbitrary concentration of spin disorder are obtained from linear combinations of two adjacent spectra. Typical results are shown in figure 2. The spectra are not symmetric and are expanded on the low-frequency side of the peak.

4. Comparison with observation and discussion

The results from the procedure described above were fitted to the experimental data. For

comparison with the observations, the concentration of the disordered spins and the position of the line were treated as adjustable parameters. We considered only the line at about 18 MHz because the line at about 24 MHz is well separated. The best-fitted results are shown in figures 1(*a*)–1(*c*). The agreement with the observed results is quite satisfactory. The calculated results were also compared with a number of other observed spectra in the re-entrant spin-glass phase for the region $x \lesssim 0.47$ and good agreement was also obtained. Hence we conclude that, in the re-entrant spin-glass phase for the region $x \lesssim 0.47$, some spins disorder randomly in the antiferromagnetic long-range order. The number of disordered spins increases from 1.9% ($x = 0.27$) to 8.0% ($x = 0.46$) depending on the Mn concentration. This result agrees with the conclusion of Ito *et al* [2] and Katori *et al* [3].

The calculated results are also compared with the observed spectra in the antiferromagnetic phase shown in figure 1(*d*). Although slight deviations are seen, the expansion to the low-frequency side agrees well with the experimental results. The percentage of the disordered spins is calculated to be 4.5% at 2.69 K which is less than 6.4% at 1.32 K. The random disordered spins gradually decrease as the temperature increases. The existence of the random disordered spins could therefore be the origin of the 'frustrated' antiferromagnet reported by DeFotis *et al* [4] and Deguchi *et al* [5]. The random spin disorder of this mixture will also correspond to the deviation from antiferromagnetic long-range order in $Fe_{1-x}Mn_xTiO_3$ found by Ito *et al* [2] and Katori *et al* [3].

It should be emphasized that the observed random spin disorder is essentially different from the spin disorder caused by the local environments in which the spins sit and whether the neighbouring moments are Co or Mn moments. If the observed spin disorder is caused by such local exchange interactions, the amount of disordered spins will be essentially independent of the temperature. However, the amount of random spins depends on the temperature. Furthermore, although even for $x = 0.16$ some disordered spins would be expected, no deviation from a symmetric line is observed. These facts show that the random spin disorder in this compound is due to frustration between the competing exchange interactions and therefore is an essential phenomenon in the spin-glass system.

In the re-entrant spin-glass phase, we conclude that two kinds of spin coexist: the spins participating in the antiferromagnetic long-range order with some degree of random disordered spins, and the random spin-glass spins with the concentration-dependent weights [6]. These results suggest a picture of the coexistence of spin-glass spins and antiferromagnetic spins. As the antiferromagnetic spins are subject to long-range order [1], the randomly disordered spins and the clusters of random spin-glass spins are distributed in the antiferromagnetic long-range order. In this picture, even if there are many random disordered spins and spin-glass spins, the antiferromagnetic long-range ordering itself is always maintained.

References

[1] Huang C R 1985 *J. Magn. Magn. Mater.* **51** 1
[2] Ito A, Ebii S, Katori H A and Goto T 1992 *J. Magn. Magn. Mater.* **104–7** 1635
[3] Katori H A, Goto T, Ebii S and Ito A 1992 *Physica* B **177** 323
[4] DeFotis G C, Mantus D S, McGhee E M, Echols K R and Wiese R S 1988 *Phys. Rev.* B **38** 11 486
[5] Deguchi H, Takahashi K, Kubo H and Takeda K 1990 *J. Phys. Soc. Japan* **59** 1071
[6] Zenmyo K and Kubo H 1992 *J. Phys. Soc. Japan* **61** 1025
[7] Zenmyo K and Kubo H 1993 *J. Phys. Soc. Japan* **62** 1025
[8] Narath A 1964 *Phys. Rev.* **136** A766
[9] Spence R D and Rama Rao K V S 1970 *J. Chem. Phys.* **52** 2740