PHYSICAL REVIEW B VOLUME 25, NUMBER 1 1 JANUARY 1982

Spin-glass behavior of a randomly mixed insulating ferromagnet and antiferromagnet

K. Katsumata, T. Nire, and M. Tanimoto
Research Institute of Applied Electricity, Hokkaido University, Sapporo 060, Japan

H. Yoshizawa
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan
(Received 29 July 1981)

Susceptibility, magnetization, neutron diffraction, and electron-spin-resonance experiments were performed on a random mixture of an insulating ferromagnet and an insulating antiferromagnet, $Rb_2Mn_{1-x}Cr_xCl_4$. These experiments have given evidence of spin-glass behavior for the intermediate concentrations. This spin-glass is of a new type, the origin of which is different from those found in metals and in the diluted insulating ferromagnet.

Since the pioneering works by Cannella and Mydosh[1] and by Edwards and Anderson,[2] many experimental and theoretical studies have been done on spin-glasses. It seems now to be widely accepted that a competition between ferromagnetic and antiferromagnetic exchange interactions plays an essential role in determining spin-glass properties. As the competition occurs not only in the case of the long-range Ruderman-Kittel-Kasuya-Yosida interaction but in near-neighbor exchange interactions, we expect that a spin-glass phase[3,4] exists in insulators where the short-range interaction dominates. In fact, recent experiment[5] has shown that $Eu_xSr_{1-x}S$ is an insulating spin-glass. The origin of the spin glass in the Eu compound has extensively been studied[5,6]: When ferromagnetic EuS is diluted at random with diamagnetic SrS, an imbalance between the nearest-neighbor ferromagnetic and the next-nearest-neighbor antiferromagnetic exchange interactions occurs which brings about a spin-glass. Another example of an insulating spin glass may be found in a random mixture of a ferromagnet and an antiferromagnet.[7–10] In this site random magnet, the exchange interaction between the ferromagnetic and antiferromagnetic ions is essential to the existence of the spin-glass. In spite of many theoretical efforts,[7–10] there has been no experiment on this kind of insulating spin-glass. We have found, for the first time, that a randomly mixed insulating ferromagnet and antiferromagnet, $Rb_2Mn_{(1-x)}Cr_xCl_4$ exhibits spin-glass behavior.

The antiferromagnet Rb_2MnCl_4 [$T_N \sim 55$ K (Ref. 11)] and the ferromagnet Rb_2CrCl_4[$T_C = 57$ K (Ref. 12)] have the same K_2NiF_4-type structure and the lattice constants are nearly the same. Thus, we can expect that the two compounds make a good solid solution over the whole range of concentration. We grew single crystals of $Rb_2Mn_{(1-x)}Cr_xCl_4$, with $0 < x < 0.6$, using a similar method described by Garton and Walker.[13] The concentration x was determined by a chemical analysis.

We have performed susceptibility, magnetization, neutron diffraction, and ESR experiments on the mixture to investigate magnetic properties. The susceptibility was measured by an ac method under zero external field. The operating frequency of the ac field was 200 Hz. The apparatus was fully automated by use of a Hewlett-Packard System 9835A desktop computer. The measured susceptibility was displayed versus the measured temperature on a Hewlett-Packard 7225A graphics plotter. The temperature of a sample was measured in this magnetometer by a Au(Fe)-Ag thermocouple, which was attached directly on the sample. The magnetization was measured by a sample extraction technique as a function of the external magnetic field. The magnetic fields were generated in a Nb-Ti superconducting solenoid. The neutron diffraction experiment was carried out on the triple-axis spectrometer of the Institute for Solid State Physics which is installed at JRR-2, Japan Atomic Energy Research Institute (JAERI), Tokai, Japan. The monochromator was pyrolytic graphite and the wavelength of the neutrons was 2.44 Å. The temperature of the specimen was measured by a Au(Fe)-Cu thermocouple attached to the aluminum sample holder. The powdered sample used in the neutron experiment was obtained by crushing sin-

gle crystals. The sizes of the grains were less than 500 μm. The ESR measurements at 24 and 35 GHz bands were performed with a conventional transmission-type spectrometer. The ESR experiment at 9 GHz region was done with a reflection-type spectrometer. A continuous flow system (Oxford Instruments ESR 10) was employed in this experiment in order to vary the temperature of only the sample.

In Fig. 1 we show temperature dependence of susceptibility for $x=0.38$ and $x=0.58$ single crystals. A sharp cusp is observed in the $x=0.38$ sample as in the cases of *Au*Fe (Ref. 1) and other metallic and insulating spin glasses. Because of the demagnetizing effect, the susceptibility in the $x=0.58$ sample shows a broad peak rather than a cusp.

In Fig. 2 we show the magnetic field dependence of the magnetization in the $x=0.58$ sample observed at 4.2 K (well below the temperature T_{SG} at which the susceptibility is maximum). The magnetization increases abruptly at low fields followed by a rather gradual change at high fields. This trend of field dependence is widely seen in spin-glasses, a part of which may be explained by the negative sign of the nonlinear susceptibility discussed theoretically by Suzuki.[14] A hysteresis is seen in an increasing and subsequently decreasing fields.

From the susceptibility and magnetization measurements mentioned above, we see that

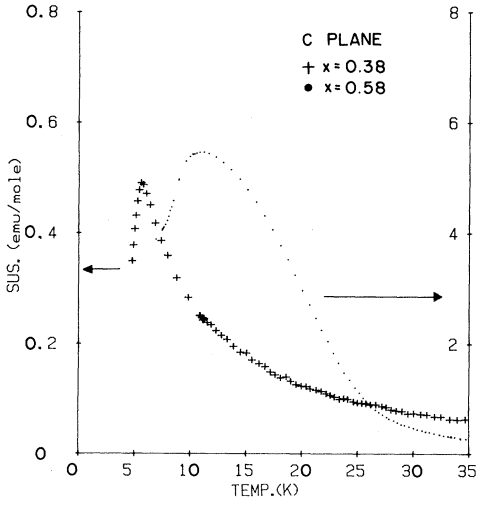

FIG. 1. Temperature dependence of the susceptibility in $Rb_2Mn_{(1-x)}Cr_xCl_4$. The single crystals were disk shaped with the ac field directed in the plane of the disk (*c*-plane).

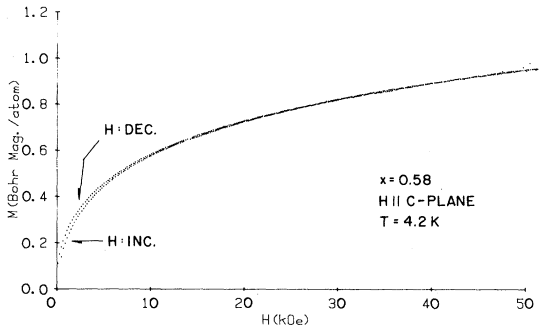

FIG. 2. Magnetization vs external magnetic field for $x=0.58$ disk-shaped sample.

$Rb_2Mn_{(1-x)}Cr_xCl_4$ behaves like a spin-glass. In order to examine further whether this compound is a spin-glass or not, we have performed a neutron diffraction experiment on powdered samples of $Rb_2Mn_{(1-x)}Cr_xCl_4$ with several values of x. If this compound is a spin-glass, magnetic long-range orderings should be absent. Figure 3(a) shows clearly that there is no antiferromagnetic long-range order in the $x=0.58$ sample at $T\simeq 7$ K. For comparison, we have plotted in Fig. 3(b) the result for the $x=0.21$ sample, which is antiferromagnetic below about 30 K. The reflections in Fig. 3 are indexed based on the K_2NiF_4-type magnetic unit cell after Birgeneau *et al.*[15] To check the absence of ferromagnetic long-range order, we also measured temperature dependence of the intensity of the (111) nuclear reflection in the $x=0.58$ sample. The intensity was temperature independent between 8 and 50 K within the experimental scatter. Thus, the mixture with $x=0.58$ exhibits neither antifer-

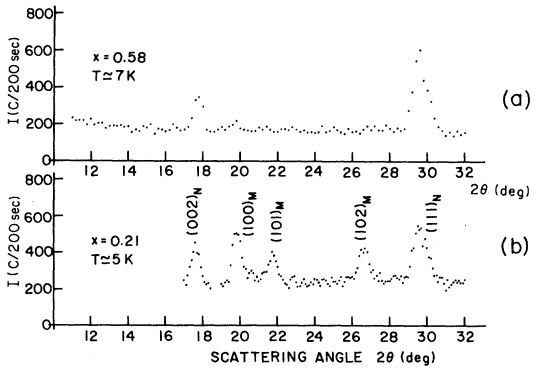

FIG. 3. Neutron diffraction patterns for powdered $Rb_2Mn_{(1-x)}Cr_xCl_4$ (a) in the spin-glass and (b) in the antiferromagnetic states.

romagnetic nor ferromagnetic long-range ordering below T_{SG}. The neutron experiment shows also that there is no chemical clustering of macroscopic size, i.e., that the crystal is not composed of macroscopic clusters of antiferromagnetic Rb_2MnCl_4 and ferromagnetic Rb_2CrCl_4. A conventional neutron diffraction technique, however, cannot exclude the possibility of a coexistence of the clusters of microscopic size.

For this reason, and in order to obtain microscopic information on the spin-glass, we have carried out ESR experiments on $Rb_2Mn_{(1-x)}Cr_xCl_4$. The results are summarized in Fig. 4. An intense resonance line was observed accompanied by a weak resonance line for both $x=0.38$ and $x=0.58$ samples below T_{SG}. The intensity of the weak line is about a hundredth of that of the main line in the case of $x=0.58$. The frequency versus magnetic field relation of the main resonance line is similar, as a whole, to that of an antiferromagnetic resonance line when the external field is directed perpendicularly to the easy axis of magnetizations. If the resonance comes from microscopic clusters of Rb_2MnCl_4, then we should observe ferromagnetic resonance from clusters of Rb_2CrCl_4 with similar intensity, contrary to the experiment. It is already clear that the weak resonance line does not correspond to the ferromagnetic one because the intensity is very weak. Thus, it can be said from the ESR experiment that we have no evidence for the existence of the clusters with a microscopic size, and that the main resonance comes from a coupled motion of Mn^{2+} and Cr^{2+} spins. The frequency versus field relation of the main resonance line is very similar to that observed in a metallic spin-glass *Cu*Mn (Refs. 16–18). This similarity demonstrates again that $Rb_2Mn_{(1-x)}Cr_xCl_4$ is a spin-glass. From Fig. 4, it seems that an excitation energy ($\sim$20 GHz) exists at zero external field and at 4.2 K. As spin-glass is very sensitive to external magnetic fields, it is important to see whether or not the zero field resonance really exists. For this purpose, we have tried to observe the absorption under a fixed frequency ($\sim$9 GHz) and in zero magnetic field with varying temperature. The frequency of the zero field resonance decreases with increasing temperature as in the case of an antiferromagnet, so we can observe the resonance in the low frequency ESR experiment at an elevated temperature. The result is shown in the inset of Fig. 4.

From the susceptibility, magnetization, neutron diffraction, and ESR experiments described above,

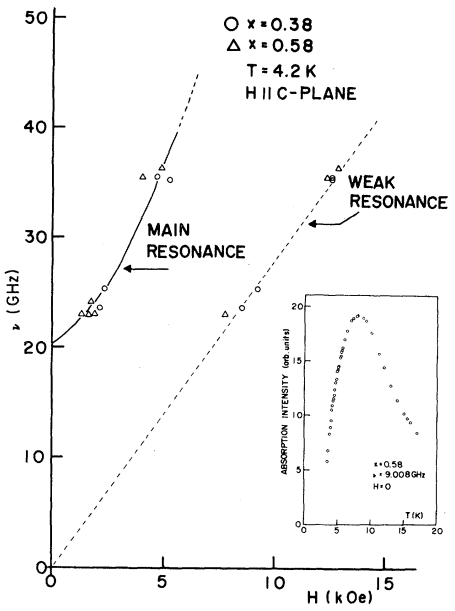

FIG. 4. Frequency vs external magnetic field relations for the magnetic resonances in $Rb_2Mn_{(1-x)}Cr_xCl_4$. The inset shows an absorption observed in zero magnetic field.

it becomes clear that a randomly mixed insulating ferromagnet and antiferromagnet $Rb_2Mn_{(1-x)}Cr_xCl_4$ exhibits spin-glass behavior. However, whether the freezing of this spin-glass is a phase transition or a nonequilibrium phenomenon is still controversial as in other spin-glasses. Recently, Morgenstern and Binder[19] have shown by an exact numerical calculation that the two-dimensional $\pm J$ spin-glass model does not exhibit a phase transition even at zero temperature, and that the spin-glass state is a metastable one with a long relaxation time, while Anderson[20] has pointed out that the real properties of spin-glass are similar to those in the two-dimensional XY model,[21] which has a phase transition. Although the compounds Rb_2MnCl_4 and Rb_2CrCl_4 are predominantly two-dimensional magnets, they exhibit three-dimensional orderings at relatively high temperatures. The former has a uniaxial, and the latter has an XY anisotropies. Thus, there is no reason to exclude the possibility of a phase transition in $Rb_2Mn_{(1-x)}Cr_xCl_4$ spin-glass. We hope that the present experiment will stimulate theoretical works. Further experiments are now in progress and the results will be reported later.

We would like to express our sincere thanks to Professor K. Hirakawa, Professor T. Oguchi, Professor M. Suzuki, Professor G. Shirane, Professor

K. Nagata, Professor S. Kobayashi, Professor H. Takayama, Professor Y. Miyako, Professor F. Matsubara, and Professor Y. Yokozawa for their many helpful discussions and useful comments.

Thanks are also due to the Agne Gijutsu Center for the chemical analysis. This work was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education in Japan.

[1]V. Cannella and J. A. Mydosh, Phys. Rev. B 6, 4220 (1972).
[2]S. F. Edwards and P. W. Anderson, J. Phys. F 5, 965 (1975).
[3]F. Matsubara and M. Sakata, Prog. Theor. Phys. 55, 672 (1976).
[4]Y. Ueno and T. Oguchi, J. Phys. Soc. Jpn. 40, 1513 (1976).
[5]H. Maletta and W. Felsch, Phys. Rev. B 20, 1245 (1979).
[6]K. Binder, W. Kinzel, and D. Stauffer, Z. Phys. B 36, 161 (1979).
[7]F. Matsubara, Prog. Theor. Phys. 52, 1124 (1974).
[8]M. V. Medvedev and E. L. Rumyantsev, Phys. Status Solidi B 85, 427 (1978).
[9]T. Oguchi and Y. Ueno, J. Phys. Soc. Jpn. 46, 729 (1979).
[10]S. Fishman and A. Aharony, Phys. Rev. B 19, 3776 (1979); 21, 280 (1980).
[11]A. Epstein, E. Gurewitz, J. Makovsky, and H. Shaked, Phys. Rev. B 2, 3703 (1970).
[12]M. J. Fair, A. K. Gregson, P. Day, and M. T. Hutchings, Physica 86-88B, 657 (1977).
[13]G. Garton and P. J. Walker, J. Cryst. Growth 33, 61 (1976) ; 36, 351 (1976).
[14]M. Suzuki, Prog. Theor. Phys. 58, 1151 (1977).
[15]R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, Phys. Rev. Lett. 22, 720 (1969).
[16]J. Owen, M. E. Browne, V. Arp, and A. F. Kip, J. Phys. Chem. Solids 2, 85 (1957).
[17]K. Okuda and M. Date, J. Phys. Soc. Jpn. 27, 839 (1969).
[18]S. Schultz, E. M. Gullikson, D. R. Fredkin, and M. Tovar, Phys. Rev. Lett. 45, 1508 (1980).
[19]I. Morgenstern and K. Binder, Phys. Rev. B 22, 288 (1980).
[20]P. W. Anderson, J. Appl. Phys. 49, 1599 (1978).
[21]J. M. Kosterlitz and D. J. Thouless, J. Phys. C 6, 1181 (1973).