Mixed Phase of Spin-Glass Ordering and Antiferromagnetism in an Ising System, $Fe_xMn_{1-x}TiO_3$

H. Yoshizawa and S. Mitsuda
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

and

H. Aruga and A. Ito
Department of Physics, Faculty of Science, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan
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Neutron scattering demonstrates the coexistence of antiferromagnetic and spin-glass order in the Ising system $Fe_xMn_{1-x}TiO_3$ for $x=0.33$, 0.60, and 0.65. The behavior of the diffuse intensity as well as the inverse correlation length κ as functions of Fe-ion concentration x strongly suggests that there exists a phase boundary between the coexistence phase and the pure spin-glass phase. Thus the phase below the Almeida-Thouless line in an Ising spin-glass system should be distinguished from the pure spin-glass phase.

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Reentrant phenomena in spin-glass systems have been the subject of intensive studies for over a decade.[1-3] The phase diagram of the Sherrington-Kirkpatrick (SK) model[4] has provided a good guide to interpret the experimental results on the reentrant behavior. On the phase diagram of the SK model for the Ising spin-glass, the Almeida-Thouless (AT) line was thought to be the phase boundary where the system undergoes the reentrant transition from a ferromagnet to a spin-glass.[5] The discovery of the Parisi solution for the SK model renewed the interest in such an interpretation.[2,6] Toulouse[7] argued that the ferromagnetic order remains below the AT line and it coexists with the spin-glass ordering, because a region below the AT line is separated from the spin-glass phase by a vertical phase boundary. On the basis of a gauge transformation theory for the $\pm J$ Ising spin-glass system, Nishimori recently claimed the existence of a geometry-induced phase transition, where the vertical phase boundary again separates the pure spin-glass phase from the mixed phase.[8] A schematic phase diagram for the Ising SK model is depicted in Fig. 1, where we have introduced an antiferromagnetic phase as the ordered phase in order to make connection with the present experiments. The purpose of this Letter is to demonstrate that the reentrant phase of the Ising spin-glass system is indeed the mixed phase, and to suggest the existence of a vertical phase boundary between the mixed phase and the pure spin-glass phase in the Ising spin-glass system $Fe_xMn_{1-x}TiO_3$.

Most of the experimentally available spin-glass materials belong to the Heisenberg spin-glass category.[1] There is a good correspondence between spin-glass materials and the theoretical SK model with Heisenberg spins. Mössbauer experiments on FeAu by Campbell *et al.*[9] agree beautifully with the Gabay-Toulouse picture.[10] On the other hand, some of the neutron-scattering studies rather seem to favor a loss of the ferromagnetic order at the reentrant transition.[3,11] It should be noted, however, that the transverse components were observed separately from the ferromagnetic component in the recent small-angle neutron-scattering experiments,[12] and studies along this line might provide further information to elucidate the nature of the Heisenberg mixed phase. Returning to the Ising system, few materials are known as Ising spin-glasses. $Fe_xMg_{1-x}Cl_2$ is the only system where neutron-scattering experiments[13] were performed from a point of view similar to that of the present work. In this system it was found that the spin-glass ordering coexists with the antiferromagnetic long-range order, although the magnetic Bragg intensity showed no anomaly at or below the spin-glass freezing temperature. As is discussed later, the present experiments include identical behavior as part of their results, and lead to the understanding of such behavior.

To obtain the Ising spin-glass system, we chose a solid solution of Ising antiferromagnets, $Fe_xMn_{1-x}TiO_3$.

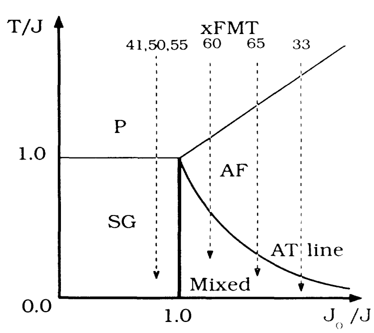

FIG. 1. Schematic phase diagram of the Ising SK model. "xFMT" denotes the Fe concentration, $100x$, of the Fe_x-$Mn_{1-x}TiO_3$ system.

Both $FeTiO_3$ and $MnTiO_3$ have a rhombohedral crystal structure $R\bar{3}$.[14] In this Letter, however, we employ the hexagonal notation ($a^*=1.422$ Å^{-1} and $c^*=0.442$ Å^{-1}) for the convenience of the scattering experiments. If we neglect the small translations of the magnetic ions along the hexagonal c axis, they form honeycomb layers which couple antiferromagnetically. Fe ions in $FeTiO_3$ align ferromagnetically in each layer, whereas Mn ions in $MnTiO_3$ couple antiferromagnetically. In the solid solution $Fe_xMn_{1-x}TiO_3$, a strong frustration within honeycomb layers leads to spin-glass behavior for the intermediate Fe concentration x. In recent experiments by Ito *et al.*,[15] clear cusps were observed in the longitudinal susceptibility for x=0.41, 0.50, and 0.55, whereas no anomaly was detected in the transverse susceptibility, suggesting the Ising spin-glass behavior. We note that magnetic[16] and neutron[14] studies established that $FeTiO_3$ and $MnTiO_3$ are good Ising antiferromagnets with their moments parallel to the hexagonal c axis.[17] In addition, the reentrant spin-glass phase is expected from the susceptibility measurements on samples for $x=0.65$, 0.60, and 0.33.[15]

Neutron-scattering experiments were performed on the triple-axis spectrometer ISSP-ND1 installed in JRR2 at the Japan Atomic Energy Research Institute, Tokai. The spectrometer was operated in a double-axis configuration with 40- and 80-min collimators for its double pyrolitic-graphite monochromators, and 50- and 40-min collimators before and after the sample, respectively. To satisfy the quasielastic condition, incident neutrons with $k_i=3.853$ Å^{-1} were selected, and a pyrolitic-graphite filter was used before the sample. Overall momentum resolutions (FWHM) were 0.148, 0.070, and 0.016 Å^{-1} for the vertical, longitudinal, and transverse directions, respectively.

Figure 2(a) shows the temperature dependence of the magnetic Bragg reflection of the $x=0.60$ sample. On decrease of the temperature, the intense magnetic Bragg reflection grows below T_N like an ordinary antiferromagnet. On further lowering of the temperature, however, it exhibits a drastic decrease. This anomaly occurs near the onset temperature of the hysteresis of the susceptibility.[15] The diffuse scattering also suggests reentrant spin-glass behavior. As seen from Fig. 2(b) the diffuse intensity measured near the (1,1,1.5) magnetic Bragg reflection increases rather than decreases below the regular critical scattering at T_N. It shows a broad maximum at $T\simeq 18$ K, but remains very intense at lower temperatures, below 10 K. The width of the Bragg reflection remains resolution limited down to the lowest temperature we studied. With the tightest collimation of our spectrometer, i.e., 10 and 20 min before and after the sample, respectively, the widths of the transverse scans at the mixed phase at $T=4.5$ K and at the reentrant regime $T=24$ K were identical, and agreed with that of the higher-order scattering at $T=40$ K. Since hysteresis is commonly seen in the spin-glass phase, we repeated the measurements of the Bragg intensity at (1,1,1.5) several times by cycling the temperature between 4 and 50 K in order to check if the persistence of the Bragg reflection was due to accidental freezing. Upon heating, however, the Bragg intensity increased again and always recovered the same maximum number of counts at $T\simeq 25$ K. We emphasize here that each temperature run gave an identical temperature dependence within the experimental accuracy; in other words, the Bragg intensity was reversible and reproducible versus the heat treatment. We also monitored the time dependence of the Bragg scattering at several temperatures, including 4.5 and 24 K, but no change was observed for over several hours. On the basis of these observations we believe that the effect is in equilibrium, and conclude that the antiferromagnetic long-range order persists below the reentrant transition in the Ising system $Fe_xMn_{1-x}TiO_3$.

Interestingly, a fraction of the decrease of the Bragg intensity is highly sensitive to the concentration of Fe ions. The decrease of the intensity of the $x=0.65$ sample is less prominent than that of the $x=0.60$ sample, and that of the $x=0.33$ sample was not detectable, as seen in Figs. 2(c) and 2(f). We emphasize that all of them exhibited the clear diffuse scattering which is associated with the spin-glass behavior. This tendency can be qualitatively understood by our recalling the phase diagram in Fig. 1. The spin-glass samples with $x=0.41$, 0.50, and 0.55 can be assigned somewhere in the spin-glass (SG) regime, whereas the coexistence samples should be located in the antiferromagnetic (AF)-mixed regime. Furthermore, the distance from the SG–mixed-phase boundary reflects the degree of influence of the spin-glass ordering on the antiferromagnetic order. We now understand that the results[13] on $Fe_{0.55}Mg_{0.45}Cl_2$ correspond to that of the $x=0.33$ sample in our case, where the distance from the SG phase boundary is large enough to "hide" the influence of the spin-glass ordering from the temperature dependence of the Bragg reflection.

The temperature dependence of the diffuse scattering for the $x=0.60$ sample is parametrized by fitting it with the Lorentzian $S(q)=A/(\kappa^2+q^2)$, and the results are shown in Figs. 2(d) and 2(e). The inverse correlation length κ has two distinct minima, one at the Néel temperature $T_N=32.5$ K and the other at the spin-glass transition temperature $T\simeq 20$ K. Namely, the spin-spin correlation length of the $FeTiO_3$-type structure diverges once at the antiferromagnetic phase transition, and almost diverges around the spin-glass transition. The amplitude A almost doubles around $T\simeq 20$ K, which means an increase of the number of spins contributing to the diffuse scattering. Combining the behaviors of the amplitude A and the Bragg intensity, we interpret this to mean that some spins are removed from the antiferromagnetic long-range order and are transferred to the diffusive component. In other words, the AT line is

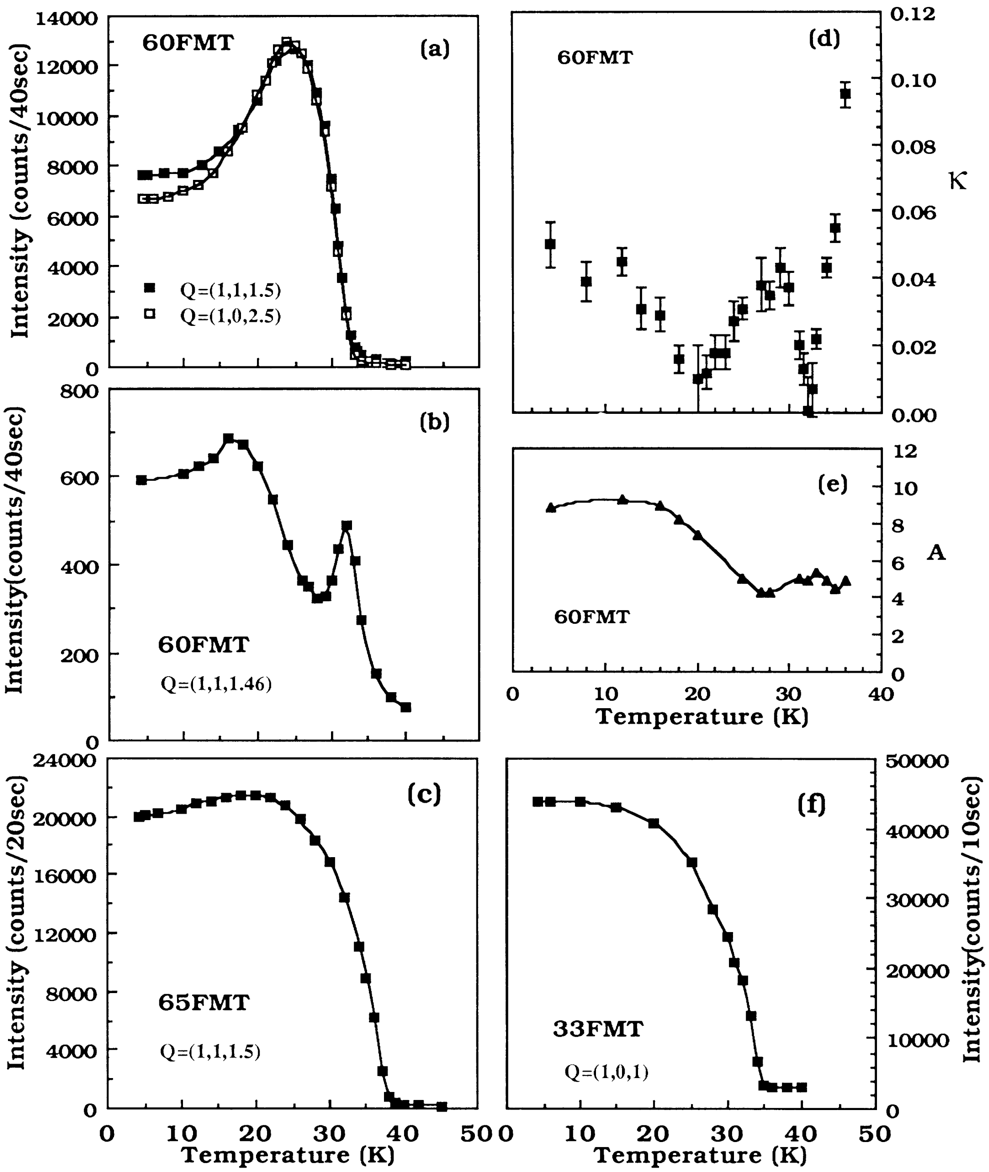

FIG. 2. (a) Peak intensity curves for the antiferromagnetic Bragg reflections observed at $Q=(1,1,1.5)$ and $(1,0,2.5)$ for the $s=0.60$ sample. The deviation of two curves at low temperatures is caused by the difference in the structure factors of the intense diffuse scattering. (b) Temperature dependence of the diffuse scattering observed at $Q=(1,1,1.46)$ for the $x=0.60$ sample. (c),(f) Temperature dependences of the peak intensities of the $x=0.65$ and 0.33 samples. (d),(e) Inverse correlation length κ (in inverse angstroms) and the amplitude of Lorentzian for the $x=0.60$ sample.

detected as the partial instability of the long-range order of the high-temperature phase.

Finally we examine the role of the possible vertical phase boundary between the spin-glass phase and the mixed phase. Consider a scan at $T=0$ K along the J_0/J axis in the SK phase diagram in Fig. 1, and assume that the transition from the spin-glass phase to the mixed phase is of second order. Then it is natural to expect a divergence of the correlation length at the boundary. To check this, we plot the full width at half maximum (FWHM) and the intensity of the diffuse scattering at low temperatures as functions of the Fe-ion concentration. The diffuse intensity of each scan is normalized against that of the $x=0.60$ sample by our taking account of the Fe-ion concentration and the weight of each sample. In Fig. 3, dashed lines separate the three regions: a region with the $MnTiO_3$-type long-range order (left), one with the $FeTiO_3$-type long-range order (right), and the spin-glass region (middle). As we expected, the diffuse intensity increases steeply near the dashed lines.

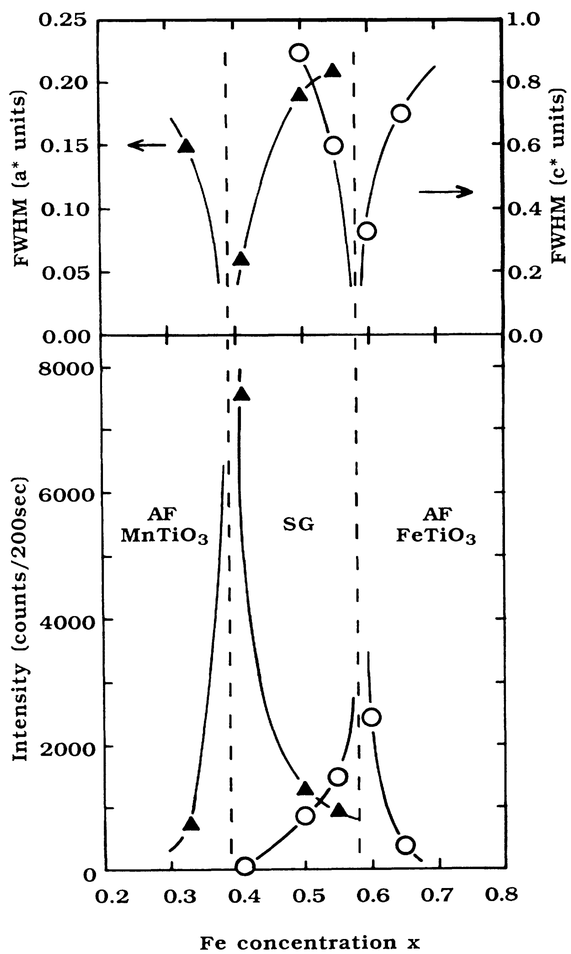

FIG. 3. Upper panel: FWHM measured along the c^* direction around the (1,1,1.5) reflection (circles) and the FWHM along the a^* direction around the (101) and (102) reflections (triangles). Lower panel: concentration dependence of the diffuse intensity at the low-temperature limit. Curves are drawn as guides to the eye.

The FWHM in the upper panel seems to vanish at these boundaries. Notice that the FWHM's can be compared without any normalization against the sample dependence. Therefore these results are consistent with the existence of the vertical phase boundary. We believe that the mixed phase is separated from others not only by the AT line but also by the vertical phase boundary. There seems to exist a complete qualitative correspondence between the phase diagram of the SK model and that of the Ising system $Fe_xMn_{1-x}TiO_3$.

In summary, we have performed quasielastic-neutron-scattering measurements on the Ising-type reentrant spin-glass system $Fe_xMn_{1-x}TiO_3$. The clear reentrant spin-glass transition was observed through the anomalies in the temperature dependences of both the Bragg reflections and the diffuse scattering. The persistence of the antiferromagnetic Bragg reflection below the reentrant transition suggests the coexistence of antiferromagnetism and spin-glass ordering. It is gratifying to find the critical behavior of the diffuse intensity as well as the inverse correlation length as functions of the Fe concentration at the low-temperature limit, which supports the existence of a vertical phase boundary for the geometry-induced phase transition in the $\pm J$ Ising spin-glass model.

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