Temperature dependence of spin reversal in ordered Ni_3Mn: Evidence for anomalous behavior

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(Received 9 August 1993; revised manuscript received 25 October 1993)

A neutron-diffraction experiment on a partially ordered $Ni_{78}Mn_{22}$ sample shows a temperature dependence of the average magnetic moment of the Mn atoms in the Ni site reminiscent of a critical phenomenon. This effect has been attributed to the change with temperature of the number of Mn atoms antiferromagnetically aligned with the bulk magnetization. The possibility of a correlation between the observed phenomenon and the ferromagnetic ordering transition in fully disordered samples is also proposed.

The variety of magnetic structures exhibited by $Ni_{1-x}Mn_x$ alloys around the Ni_3Mn composition in the disordered phase has been ascribed[1] to the competition between ferromagnetic and antiferromagnetic interactions. As shown by the phase diagram in Fig. 1, the disordered alloys around the composition Ni_3Mn are ferromagnetic for $x \leq 0.24$ and above a composition-dependent temperature, below which a reentrant spin-glass state has been identified.[2] The transverse spin-correlation function determined by Cable, Nicklow, and Tsunoda[1] shows that in the spin-glass phase the magnetic short-range-order parameters have an alternate sign for the first four shells. On the other hand, at large distance the short-range-order parameters remain positive. This complex behavior suggests the coexistence of short-range antiferromagnetic order with long-range ferromagnetic order. Previous studies[3-5] of a Ni_{78} Mn_{22} alloy have shown that, as one could anticipate, the effects of the competing interactions can be easily detected even in the case of small deviations from perfect chemical order. This feature may be easily understood considering that Mn atoms carry a rather high magnetic moment,[5] so that even a small number of Mn atoms occupying Ni sites can give rise to a relatively large effect on the average magnetic moment of these sites. These studies have shown that Mn atoms in this alloy have a magnetic moment of about 4 μ_B with fluctuating sign (spin reversal) as far as the z-component of the magnetic moment is concerned. Of course, since the investigations of Refs. 3–5 have been performed employing polarized neutron diffraction, the results do not rule out the possibility of noncollinear components of the magnetic moment, which have been observed in the reentrant state,[1] but whose presence in the ferromagnetic state has never been reported. Considering that in the same alloy anomalous features have also been detected[6] in the temperature dependence of the bulk magnetization, we have decided to perform a study of the Mn magnetic moment in this alloy as a function of temperature in order to ascertain the existence of a temperature-dependent trend of the spin reversal process.

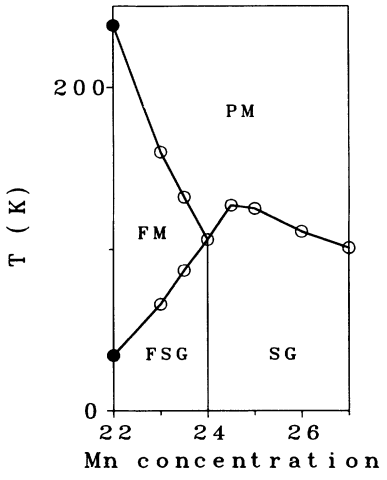

FIG. 1. Phase diagram of disordered NiMn alloys around Ni_3Mn composition showing ferromagnetic (FM), reentrant ferro-spin-glass (FSG), normal spin-glass (SG), and paramagnetic (PM) phases. Circles are from Ref. 2, dots are present data.

The present neutron-diffraction experiment has been performed using the polarized-neutron diffractometer installed at the 1-MW Training, Research, and Isotope Production Reactor of Centro Ricerche Energia, Casaccia (Rome). The polarized monochromatic neutron beam was obtained using a $Co_{92}Fe_8$ monochromator, the neutron spin was reversed at 3 Hz frequency, the sample was magnetized at saturation by a vertical magnetic field of 0.7 T, and the diffracted beam was detected in the horizontal plane. The sample, already used in the experiments reported in Refs. 3–5, was in the shape of a slab having dimensions $1 \times 1.8 \times 0.07$ cm^3.

The room-temperature chemical and magnetic state of the present sample has been reported in Ref. 5. The value of the long-range-order parameter S is 0.553(4), where S is defined as the ratio between the measured scattering amplitude of a superlattice reflection and the

scattering amplitude expected from the ideally ordered *stoichiometric* sample. Since the sample is not fully ordered, the Mn atoms can occupy both crystallographic sites, namely, the Mn atoms can be located at the corners (site 1, ideally Mn sites) as well as at the face centers (site 2, ideally Ni site) of the cell. The Mn occupation probabilities, as deduced by composition and S are 0.634(10) and 0.082(10) at sites 1 and 2, respectively. The distribution of the Mn atoms between the two sites is an important parameter in the present study: site 1 has indeed a small average number of Mn atoms first nearest neighbors, $n_{\mathrm{Mn}}=0.98(12)$, while the corresponding figure for site 2 is 3.19(12).

In order to determine the average magnetic moment of Mn, μ(Mn), in each site, we have measured the ratio between the neutron intensities for up and down spin neutrons from which magnetic structure factors can be obtained. The two reflections (100) and (200) as a function of temperature from 40 up to 523 K have been studied. The temperature of the sample was held constant within ± 1 K and the measurements have been restricted to this temperature range in order to avoid any change of the state of order of the sample during the neutron measurements, the ordering temperature being about 640 K. In any case S has been measured again after the high-temperature measurements with no detectable change of its value within experimental errors. The measured structure factors, after standard corrections for incomplete polarization and incomplete spin reversal of the neutron beam and half-wavelength contamination, are reported in Table I. Inspection of this table shows for both structure factors an appreciable temperature dependence, which, considering that the Curie temperature T_C of the present sample, is about 750 K, cannot be described by a Brillouin-type variation of the bulk magnetization. Neglecting any change with temperature of the magnetic form factors, at least for the present values of T/T_C, one may suppose that the observed variation of the structure factors must reflect a rearrangement with temperature of the magnetic moments. Under the hypothesis that the spin-reversal model of the Mn magnetic moment[5] is valid in the whole temperature range of this experiment one can deduce the average Mn magnetic moments at the two sites μ_1 (Mn) and μ_2 (Mn). This can be done considering

TABLE I. Structure factors of the (100) and (200) reflections measured in the present sample as a function of temperature.

T (K)	(100) $F(Q_S)$ (μ_B/cell)	(200) $F(Q_F)$ (μ_B/cell)
40	1.394±0.040	1.726±0.016
288	1.199±0.047	1.495±0.031
301	1.238±0.040	1.568±0.033
363	1.231±0.030	1.384±0.020
373	1.225±0.040	1.342±0.027
383	1.221±0.021	1.307±0.012
395	1.191±0.018	1.219±0.012
436	1.071±0.023	1.094±0.021
473	1.133±0.036	1.027±0.028
523	0.979±0.054	0.813±0.035

that the magnetic structure factor of the (100) reflection, which is a superlattice reflection for the $L1_2$ structure, is

$$F(\mathbf{Q}_S)=A_1(\mathbf{Q}_S)-A_2(\mathbf{Q}_S) \tag{1a}$$

while that of the (200) reflection, which is a fundamental one, is

$$F(\mathbf{Q}_F)=A_1(\mathbf{Q}_F)+3A_2(\mathbf{Q}_F)\ . \tag{1b}$$

$\mathbf{Q}_S$ and $\mathbf{Q}_F$ are the exchanged wave vectors of the (100) and (200) reflections and A_1 and A_2 are the magnetic scattering amplitudes of the two sites 1 and 2, respectively, and $F(\mathbf{Q}_S)$ and $F(\mathbf{Q}_F)$ the corresponding measured magnetic structure factors. The magnetic scattering amplitudes of the two sites can be written in terms of occupation probabilities, magnetic moments and form factors of Mn and Ni atoms in the two sites. Using the values reported in Ref. 5 for the Ni and Mn form factors and $\mu(\mathrm{Ni})=0.306\,\mu_B$ for the Ni magnetic moment, one has

$$\begin{aligned} A_1(Q)&=p_{\mathrm{Mn}}(\mathrm{Mn})\mu_1(\mathrm{Mn})f_{\mathrm{Mn}}(Q) \\ &\quad +p_{\mathrm{Mn}}(\mathrm{Ni})\mu(\mathrm{Ni})f_{\mathrm{Ni}}(Q)\ , \\ A_2(Q)&=p_{\mathrm{Ni}}(\mathrm{Mn})\mu_2(\mathrm{Mn})f_{\mathrm{Mn}}(Q) \\ &\quad +p_{\mathrm{Ni}}(\mathrm{Ni})\mu(\mathrm{Ni})f_{\mathrm{Ni}}(Q)\ . \end{aligned} \tag{2}$$

In Eq. (2) $p_l(X)$ is the probability of finding the atom X at site l, $f_{\mathrm{Mn}}(Q)$, and $f_{\mathrm{Ni}}(Q)$ are the spherical form factors of Mn and Ni. The aspherical contributions to the structure factor are neglected in Eq. (2) because Q_S and Q_F are small.

The temperature dependence of μ_1(Mn) and μ_2(Mn) is shown in Fig. 2. The most interesting result concerns the

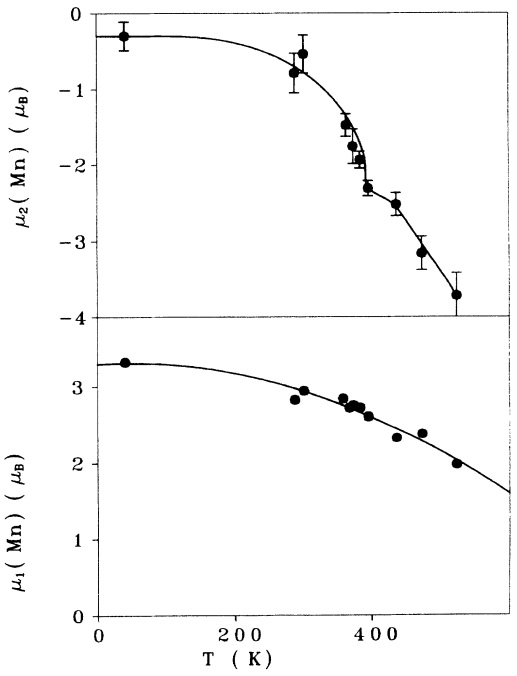

FIG. 2. Average magnetic moments of Mn atom at the two sites versus temperature. μ_1(Mn) refers to the Mn site, μ_2(Mn) refers to the Ni site. The full line is a guide to the eye.

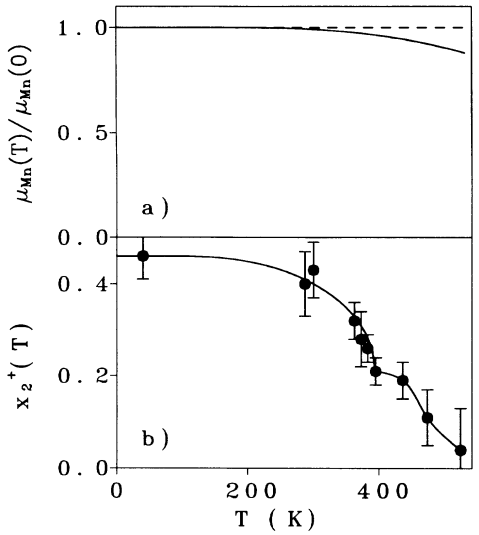

FIG. 3. Absolute value of the Mn magnetic moment versus temperature as deduced using the approximation described in the text. (b) Percentage of positively aligned Mn magnetic moments at the Ni site.

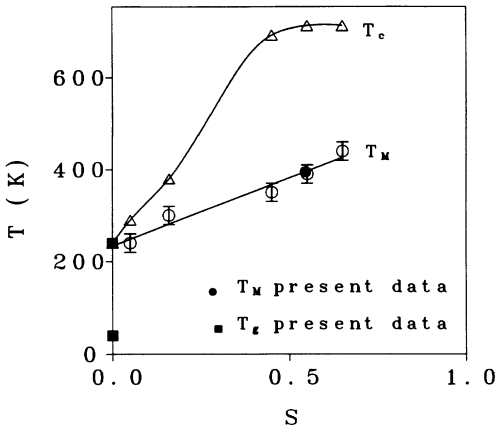

FIG. 4. Transition temperatures measured in $Ni_{78}Mn_{22}$ as a function of S. Curie temperature T_C as measured in Ref. 6 (triangles); temperature T_M as deduced from the inflection point in bulk magnetization curves presented in Ref. 6 (circles); temperature T_M as deduced from the present neutron-diffraction experiment (dot); Curie temperature T_C and glass transition temperature T_g as deduced from ac susceptibility measurements in a fully disordered sample (squares).

behavior of the magnetic moment of Mn atoms located at the Ni site, which, as shown in Ref. 5, are on the average antiferromagnetically coupled to the bulk magnetization because of their high number of Mn nearest neighbors. The magnetic moment μ_2(Mn) shows a clear discontinuity of its temperature derivative at about 395 K. Therefore, following the model of Ref. 5, we have interpreted the temperature dependence of μ_2(Mn) as due to a temperature-dependent spin-reversal of the Mn atoms having a number of Mn nearest neighbors higher than some given number. According to this model one can write

$$\begin{aligned}\mu_1(\mathrm{Mn})&=\mu_{\mathrm{Mn}}(T)[2x_1^+(T)-1]\,,\\ \mu_2(\mathrm{Mn})&=\mu_{\mathrm{Mn}}(T)[2x_2^+(T)-1]\,,\end{aligned}\tag{3}$$

where $\mu_{\mathrm{Mn}}(T)$ is the absolute value of the Mn magnetic moment in the present fcc environment, which , according to Ref. 5, is about 4 μ_B. $x_1^+(T)$ and $x_2^+(T)$ are the percentages of ferromagnetically coupled Mn atoms at Mn and Ni sites, respectively. In order to deduce $x_1^+(T)$ and $x_2^+(T)$ from Eq. (3) we have determined $\mu_{\mathrm{Mn}}(T)$ using a Brillouin function[7] with parameters $\mu_{\mathrm{Mn}}(0)=4\ \mu_B$, $J=\frac{1}{2}$, and a Curie temperature equal to 750 K. The temperature dependence of $\mu_{\mathrm{Mn}}(T)$ thus obtained is shown in Fig. 3(a) while $x_2^+(T)$ deduced from Eq. (3) is shown in Fig. 3(b). In conclusion, one has that x_2^+ versus T is reminiscent of a critical behavior with a critical temperature of about 395 K.

The anomalous trend of the magnetic moment of Mn at site 2, which is quite clear in the present neutron-diffraction experiment, is also seen in the bulk magnetization measurements versus temperature,[6] though in this case it is less evident because the fraction of Mn atoms at site 2 is rather small. Indeed, in Ref. 6 one sees that the bulk magnetization has an inflection point at a temperature T_M dependent on the state of order. The value of T_M deduced from Ref. 6 for the present value of S, $T_M=395$ K, agrees quite well with the temperature determined using our diffraction results so that the inflection point in the bulk magnetization curves of Ref. 6 appears to be associated with enhanced antiferromagnetic ordering of Mn atoms in the Ni site. From the curves of Ref. 6 one can deduce the value of T_M for different degrees of long-range order. These values are reported in Fig. 4 as a function of S.

In order to complete the analysis, a sample having dimensions $0.6\times0.5\times0.1$ cm^3 has been cut from the ingot used for the neutron-diffraction sample. This sample has been heated up to 1000 K and then quenched in ice water to get a disordered phase. Indeed, a complete disordered state has been obtained and the sample has been used to measure the ac susceptibility in the temperature range 4.2–293 K. It has been observed a clear transition from the spin-glass state below 34 K to the reentrant ferromagnetic phase at 238 K. These two temperatures are also shown in Fig. 4.

The most remarkable feature of Fig. 4 is that the extrapolation at $S=0$ of the values of T_M is very close to the transition temperature to the paramagnetic phase of the disordered alloy thus pointing out to the existence of a connection between the two phenomena in a fully disordered sample. This connection can be justified considering that, as the degree of order decreases, the structural difference between the two lattice sites decreases as well, so that the anomalous phenomenon described by T_M merges with the critical phenomenon described by T_C.

The authors wish to thank D. Fiorani, A. M. Testa, and E. Agostinelli for having provided us with the ac-susceptibility data.

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