Anomalous positive magnetoresistance in $Fe_{0.75}Mn_{1.35}As$

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With increasing temperature, tetragonal $Fe_{0.75}Mn_{1.35}As$ compound exhibits a first-order phase transition at $T_s=165$ K from a ferrimagnetic (FI) phase with a large unit-cell volume to an antiferromagnetic (AF) phase with a small unit-cell volume. An external magnetic field induces a metamagnetic transition from the AF to the FI state above T_s, stabilizing the phase with the larger cell volume. With increasing the number of warming and cooling cycles, the resistivity curve, $\rho(T)$, shifts to higher values, and this shift is ascribed to a pronounced reduction of the mean-free path of electron scattering. After several thermocycles, a large, irreversible lattice expansion of c axis of 0.18% occurs. The positive magnetoresistance ratios as large as 12% and 6% for the first magnetic-field cycles are observed at 170 and 167 K, respectively, at 5 T. The overall magnetotransport behaviors on the subsequently second and third magnetic-field cycles at 170 K are similar to that in the first magnetic-field cycle, but with MR ratios of only 1.6% and 0.6%, respectively, at 5 T.

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The intermetallic compounds Fe_2As and Mn_2As are known to have the crystal structure of Cu_2Sb-type and the antiferromagnetic (AF) spin structure with their Néel temperatures of 353 and 573 K, respectively.[1–3] The first-order AF to ferrimagnetic (FI) transitions on cooling were reported for a $Fe_{a-x}Mn_xAs$ system with $a=1.95$.[4] The composition-controlled transitions, which take place below 153 K, occur with no change in the $P4/nmm$ crystal symmetry and are accompanied by volume increases up to 1.9%. The transition temperature T_s can be set at any temperature up to 345 K by a proper combination of metal/arsenic ratio, a $(1.95\leq a\leq 2.35)$ and Mn/Fe ratio.[4–6] The transitional metals in these solid solutions occupy two different sites. Below $x=1$ Mn occupies only one of the two different sites; instead, when $x>1$ Mn appears also in the second site, leading to a sharp increase in the c axis, which might be related to the appearance of the FI state at low temperatures as well. On the basis of neutron diffraction analysis by Yoshii and Katsuraki,[7] it is believed that the AF state at high temperatures has a spin structure of Mn_2As type, while the spin structure in the FI state at low temperatures is of the Mn_2Sb type.[4] The simultaneous occurrence of the structural change and the magnetic and order-disorder phase transitions is one of the most intriguing features of magnetic materials. Meanwhile, a strong correlation among spin, charge, and lattice type often exists in the first-order magnetic phase transitions.[8] Here we report another magnetically correlated phenomenon in the $Fe_{0.75}Mn_{1.35}As$ compound. With every warming and cooling cycle, the resistivity shifts to progressively higher value, which is ascribed to a pronounced reduction of mean-free path of electron scattering. The maximum positive magnetoresistance (MR) ratio of 12% at 170 K (or 6% at 167 K) for the first magnetic-field cycles suggests that an external field induces a large irreversible lattice expansion. There have been some previous reports on the structure and magnetism.[1–7] We report on the electrical transport and magnetotransport behaviors of the $Fe_{a-x}Mn_xAs$ $(1.95\leq a\leq 2.35)$ system.

Polycrystalline $Fe_{0.75}Mn_{1.35}As$ compound was synthesized from FeMn powders with purity of 99.9% and As powders of 99.99% purity. The starting materials were mixed in the desired proportion and then pressed into pellets. To prevent the volatilization of the As, the pellets were first slowly heated to and held at 580 °C for 2 days in an evacuated silica tube. Then the samples were heated at 900 °C for 2 days. After cooling down to room temperature, they were pulverized, mixed, pressed into pellets again, and heated at 900 °C for another 2 days, and then gradually cooled to room temperature. X-ray diffraction (XRD) was subsequently carried out to certify that the sample yielded peaks characteristic of a single phase with the Cu_2Sb-type tetragonal structure. The magnetic properties were measured by using a superconducting quantum interference device (SQUID) magnetometer at applied magnetic fields up to 5 T over the temperature range from 5 to 350 K. Transport properties were measured using a fourprobe dc method and a sweeping model at increasing and decreasing temperature rates of 3 K/min.

As stated above, the spin structure of $Fe_{0.75}Mn_{1.35}As$ is of the AF Mn_2As type at high temperatures and of the FI Mn_2Sb type at low temperatures. There are two different crystallographic sites for transition metal atoms, i.e., site 1 and site 2. The magnetic structure can be regarded as a stacking of triple layers of site 2–site 1–site 2. The moments of all triple layers would be parallel in the FI state, while the arrangement becomes antiparallel in the AF state, as shown in Fig. 1.[9,10]

The temperature dependence of the magnetization from 10 to 350 K, recorded at a magnetic field of 0.01 T, is presented in Fig. 2(a) for $Fe_{0.75}Mn_{1.35}As$. It can be clearly seen that with increasing temperature the magnetization drops abruptly at a temperature (defined as the phase transition temperature, T_s) of about 165 K, showing a magnetic phase transition from the FI to the AF state. The inset of Fig. 2(a) shows the thermomagnetic curves during both warming and cooling processes. A clear temperature hysterisis of about 5 K is observed. The abrupt drop in magnetization and its temperature hysterisis at T_s are characteristic of a first-order magnetic phase transition. To explore the influence of external fields on the FI-AF transition, the $M(H)$ curves are

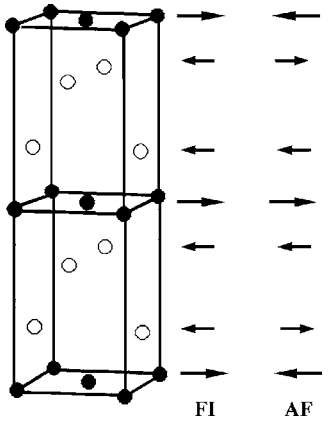

FIG. 1. The spin structure of Cu_2Sb-type $Fe_{0.75}Mn_{1.35}As$. The solid and open circles, respectively, represent site 1 and site 2 for the transition metal atoms.

shown in Fig. 2(b). At 160 K, the magnetization rises abruptly at a rather low field and shows a rapid tendency to saturate, suggesting that the compound is in FI state. In sharp contrast, at 170 K, after an initially linear increase at low fields, revealing that the compound is in an AF state at the zero field, the magnetization rises abruptly at a critical field, B_m, of about 2.8 T, indicating a field-induced AF-FI transition. The $M(H)$ curve for 180 K shows a typical AF behavior.

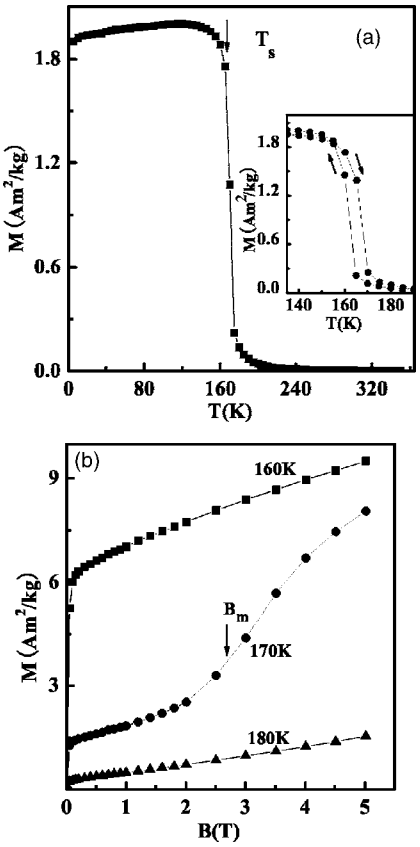

FIG. 2. (a) Temperature dependence of the magnetization at 0.01 T and (b) field dependence of the magnetization of $Fe_{0.75}Mn_{1.35}As$ at the temperatures indicated.

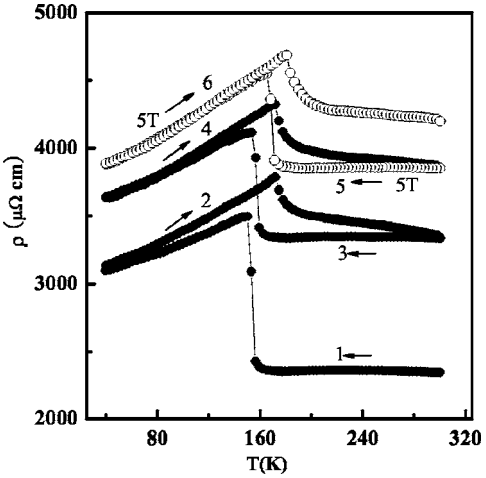

FIG. 3. Temperature dependence of the resistivity of $Fe_{0.75}Mn_{1.35}As$ measured during successive cycles of cooling and warming. The solid circles represent resistivity data at a zero field, and the open circles represent resistivity data at a magnetic field of 5 T.

Figure 3 represents the temperature dependence of resistivity for different thermal cycles n. The most striking characteristic of the transport behavior of the $Fe_{0.75}Mn_{1.35}As$ compound is that the resistivity curve varies with the number of thermal cycles n. On cooling, the initial resistivity (solid circles 1) sharply increases at a temperature of about 160 K (defined as the phase transition temperature on cooling $T_{s\downarrow}$) to a peak at 150 K, and then decreases almost linearly down to 45 K. With increasing temperature, the resistivity (solid circles 2) drops abruptly, but with a much smaller magnitude as compared to the increase on cooling, and at about 170 K (defined as the phase transition temperature on warming $T_{s\uparrow}$). The large temperature hysteresis of about 10 K further confirms the first order nature of the transition. Upon subsequent cooling and warming processes, the $\rho(T)$ curves exhibit similar behaviors. It is noteworthy that the magnitude of resistivity shifts to higher values as the number of thermal cycles increases. The $\rho(T)$ curves at a magnetic field of 5 T (open circles 5 and 6) show very similar behaviors to those at zero field. The only difference is that $T_{s\downarrow}$ and $T_{s\uparrow}$ shift to higher temperatures of 170 K and 180 K, respectively. Thus, a magnetic field of 5 T suppresses the AF phase, with its small unit cell volumes, and stabilizes the FI phase, having large unit cell volumes. If it is assumed that the scattering rate, $1/\tau$, and the effective number of carriers, n_{eff}, can be separated,[11] the resistivity can be described as $\rho = m/e^2 \tau n_{eff}$. For magnetic metal compounds, the total scattering rate can be expressed as $1/\tau = 1/\tau_0 + 1/\tau_{ph} + 1/\tau_{mag}$, where $1/\tau_0$ is the temperature independent scattering rate from imperfections in the crystal structure, $1/\tau_{ph}$ arises from electron-phonon scattering, and $1/\tau_{mag}$ is the magnetic scattering rate. Hence, for different thermal cycles, only the $1/\tau_0$ component can be responsible for the pronounced increase of resistivity at low temperatures. Moreover, it can be clearly seen in Fig. 3 that on cooling the resistivity shows a sharp increase of about 45% in the initial $\rho(T)$ curve at $T_{s\downarrow}$. Generally, in intermetallic compounds, when compared with a ferromagnetic (F) or

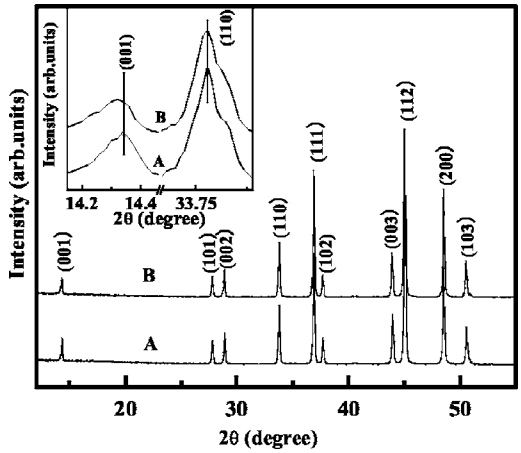

FIG. 4. XRD patterns of the initial sample (A) and the sample experienced five warming and cooling cycles (B). The inset shows an expanded view of the (001) peak and the (110) peak.

FI state, AF is a state with greater resistivity because of so-called super-zone gap effect.[12–16] Super-zone boundaries can make some part of the Fermi surface disappear and lead to a decrease in the effective number of conduction electrons, n_{eff}, consequently giving rise to larger resistivity in the AF state. In sharp contrast, in the present compound, the FI phase corresponds to a state with greater resistivity, which rules out the super-zone gap effect as the main mechanism of the large increase of resistivity. Consequently, the abrupt 45% increase of resistivity should be ascribed to an increase in $1/\tau_0$. As reported earlier,[6] on cooling in the $Fe_{2.1-x}Mn_xAs$ $(1.29 \leq x \leq 1.52)$ system, a first-order change in the cell constants with a large expansion of the c axis by 2%, a comparatively smaller contraction of the a axis by 0.5%, and a net volume increase by 0.5% were observed in $Fe_{0.75}Mn_{1.35}As$. It is expected that such a large lattice expansion of c axis could result in an irreversible increase of the lattice constant c and induce microcracks in the present compound. Figure 4 shows the XRD patterns for both the initial sample (A) and the sample (B) experienced five thermal cooling and warming cycles. The XRD patterns reveal that both the samples display peaks characteristic of a single phase with the Cu_2Sb-type tetragonal structure. As clearly seen in the inset of Fig. 4, compared to the initial sample A, the position of the (001) peak of the sample B shifts to a lower angle, indicating an increase of the lattice constant c. Meanwhile, the position of the (110) peak does not change, showing that the lattice constant a remains constant. The calculated lattice constants c and a are, respectively, 6.170 Å and 3.747 Å (for A), and 6.181 Å and 3.747 Å (for B), revealing that after several cycles a large irreversible lattice expansion of the c axis of 0.18% occurs. It is believed that the irreversible lattice expansion induces microcracks in the present compound. These microcracks, generated at every irreversible lattice expansion, can be considered as new scattering centers of charge carriers, leading to a reduction of the mean-free path of charge carriers. Consequently, the $1/\tau_0$ value is increased with increasing the number of thermal cycles. A similar phenomenon was observed in the antiperovskite $ZnNMn_3$,[8] where the transmission electron microscopy image clearly revealed the presence of microcracks in the material.

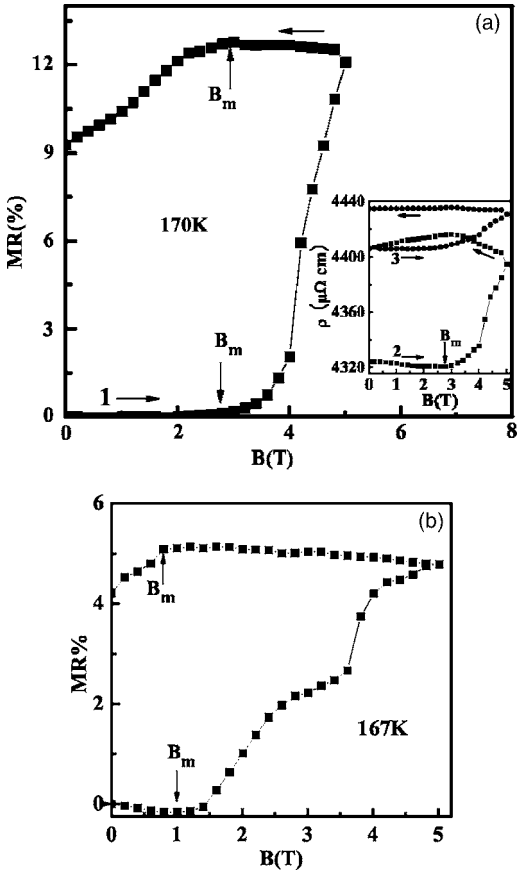

FIG. 5. Magnetic field dependence of the MR ratios at (a) 170 K and (b) 167 K for $Fe_{0.75}Mn_{1.35}As$. The inset of (a) shows the magnetic field dependence of the resistivities on the subsequently second and third magnetic-field cycles at 170 K.

A vast number of compounds in the family of perovskites, such as $La_{1-x}Sr_xMnO_3$ (Ref. 17) or $LaMn_{1-x}Ga_xO_3$ (Ref. 18), exhibit the structural phase transitions induced by an external magnetic field, leading to the colossal magnetoresistance (CMR) effects. Recently, Mira *et al.*[19] directly observed that a field induced a structural transition from the orthorhombic B31 phase to the hexagonal $B8_1$ phase in MnAs. In order to observe the influence of an external field on the structure transition and to better understand the magnetotransport behavior in the present compound, the tested sample in Fig. 3 was then lowered to different temperatures to test the magnetic-field dependence of the MR ratios. The MR ratios of both the stable AF state (at 5 K) and FI state (at 185 K) are expectedly negative (did not show here), because an external field suppresses the spin fluctuation in magnetic metals. The magnetotransport behaviors are similar at 170 and 167 K (shown in Fig. 5). The resistivity first expectedly decreases at low fields and then increases abruptly at a critical field, B_m, of 2.8 T at 170 K (or 1 T at 167 K), leading to a positive MR as large as 12% (or 6%) for a field of 5 T. Then, with decreasing the fields, the resistivity remains essentially constant until the same critical field, B_m, as for the ascending-field half cycles, and this was followed by a

gradual reduction in resistivity. This critical field B_m for 170 K exactly corresponds to the critical field shown in the $M(H)$ curves, indicating that the appearance of such a large positive MR effect is related to the metamagnetic transition. The overall magnetotransport behaviors on the subsequently second and third magnetic-field cycles at 170 K [see the inset of Fig. 5(a)] are similar to that in the first cycle. However, the magnitude of resistivity change sharply decreases. The maximum positive MR ratios at 5 T are only 1.6% and 0.6% for the second and third cycles, respectively. In general, positive MR effects are ascribed to the Lorentz contribution to resistivity. In pure metals and single crystals, a large positive MR (even a few hundred percent) is observed on the condition of $\omega_c\tau \gg 1$ (where ω_c and τ are the cyclotron frequency and the conduction electron relaxation time, respectively). The above condition holds good for many pure elemental metals at low temperatures (where τ is large, which means that resistivity is quite small, $\sim n\Omega$ cm).[20] For example, a positive MR ratio of about 100% was observed in polycrystalline Cu at 4 K in a field of 5 T.[21] Moreover, Yamada and Takada predicted theoretically that a positive MR can arise in an antiferromagnetic system with localized magnetic moments, due to the enhancement of spin fluctuations in one of the magnetic sublattices, and is usually small.[22,23] Tsui *et al.*[24] reported a large positive MR in Dy/Sc superlattices, which was speculated to originate from the multiple reflections of carriers from the interface before scattering, thereby increasing the sensitivity of resistance to momentum loss upon reflection. The large positive MR reported subsequently in $RE_2Ni_3Si_5$ (RE=Tb, Sm, Nd) was interpreted in the same manner because the structure of these materials can be viewed as a naturally occurring layered structure containing sheets of rare earth atoms.[20] The resistivity of the present $Fe_{0.75}Mn_{1.35}As$ compound is higher than 2000 $\mu\Omega$ cm. Certainly, the Lorentz contribution to resistivity is not the mechanism. Considering that the appearance of the large positive MR effects in the present compound is associated with a metamagnetic transition from AF to FI state, the other two mechanisms stated above are also not suitable for this material. Furthermore, it is noteworthy that the ascending-field and descending-field half cycles in Figs. 5(a) and 5(b) do not overlap, indicating an irreversible resistive state. As certified by the XRD results (shown in Fig. 4), a temperature-induced AF to FI transition is concomitant with an irreversible lattice expansion. Consequently, the conclusion can be safely drawn that the external magnetic fields induce a metamagnetic transition from the AF to the FI state and simultaneously induce an irreversible lattice expansion. This expansion results in the formation of microcracks in the material, leading to an irreversible switching of the resistive state as well as a large positive MR.

In conclusion, $Fe_{0.75}Mn_{1.35}As$ has an unusual tetragonal-to-tetragonal structural phase transition near 165 K. The phase transition involves a large irreversible lattice expansion and is accompanied by a large upturn in resistivity curves. An external field of 5 T shifts the transition temperature to a higher temperature by about 10 K, inducing a structural transformation from a tetragonal phase with small volumes to a tetragonal phase with large volumes, and simultaneously, a large resultant difference in resistivity at zero field as well as large positive MR ratios of 12% and 6% in the first magnetic-field cycles at 170 and 167 K, respectively, at 5 T.

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