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Magnetic transitions and magnetocaloric effects in $Fe_{0.75}Mn_{1.35}As$

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Abstract In $Fe_{0.75}Mn_{1.35}As$ compound, a metamagnetic transition from an antiferromagnetic phase to a ferrimagnetic phase can be induced above its phase transition temperature $T_s = 165$ K by an external magnetic field, which leads to large magnetocaloric effects around T_s. The sign of the magnetic entropy change ΔS_M in the $Fe_{0.75}Mn_{1.35}As$ compound is negative, not as expected as an inverse magnetocaloric effect, and the maximum value of ΔS_M is 4.2 J/kg K at 167.5 K for a magnetic field change of 5 T. Although it induces an irreversible lattice expansion, the cycling of a magnetic field does not induce an irreversible change in the magnetic transitions and magnetocaloric behaviors. The antiferromagnetism-related metamagnetic transitions with a large magnetic entropy change may provide with an opportunity in searching novel materials for magnetic refrigeration.

Introduction

The magnetic refrigeration based on magnetocaloric effect (MCE) has attracted a great deal of interest in the prospect of an energy-efficient and environment friendly alternative to the common vapor cycle refrigeration technology [1–5]. MCE means the isothermal entropy change or the adiabatic temperature change by application or removal of a magnetic field. Recently, several ferromagnets were found to exhibit a large MCE, such as $MnFeP_{0.45}As_{0.55}$ [4], $Mn_{1-x}Fe_xAs$ [5], $La(Fe,Si)_{13}H_x$ [6, 7], for large magnetic entropy changes ΔS_M can happen in the vicinity of magnetic-phase transitions from paramagnetism (PM) to ferromagnetism (FM). On the other hand, several antiferromagnetic (AF) systems show temperature/field-induced AF/FM [8–10], AF-collinear/AF-triangular [11, 12], or AF/FI (ferrimagnetic) transitions [13] involving large magnetic entropy changes. It is worthwhile noting that the sign of the entropy change in these AF systems is positive, as known as an inverse MCE. Recently, we reported a large room-temperature MCE originated from a field-induced metamagnetic transition (AF/FI) in $Fe_{0.8}Mn_{1.5}As$ compound. Instead of showing inverse MCE, the sign of the entropy change in the compound is unexpectedly negative [14]. Here we investigate a MCE originated from a similar AF/FI transition in $Fe_{0.75}Mn_{1.35}As$ compound. As opposed to the AF systems stated above, the sign of the entropy change ΔS_M in the $Fe_{0.75}Mn_{1.35}As$ compound is also negative, revealing a different mechanism of MCE.

The first-order AF to ferrimagnetic (FI) transitions on cooling were reported for $Fe_{a-x}Mn_xAs$ system with $a = 1.95$ [15]. The transition temperature T_s can be set at any temperatures up to 345 K by a proper combination of metal/arsenic ratio, a ($1.95 \leq a \leq 2.35$) and Mn/Fe ratio [15–17]. The transitional metals in these solid solutions occupy two different sites, i.e., site 1 and site 2, and the magnetic structure can be regarded as a stacking of triple-layers of site 2–site 1–site 2. 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 [15]. The change of the spin

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configuration from the AF to the FI state in the systems involves a spin reversal of the triple-layer magnetic sublattice. In our previous work [18], anomalous electrical transport and magneto-transport behaviors have been systematically explored for the $Fe_{0.75}Mn_{1.35}As$ compound of this $Fe_{a-x}Mn_xAs$ family. Here we focus on the magnetic transitions and magnetocaloric effects in the $Fe_{0.75}Mn_{1.35}As$ compound.

Experimental

Polycrystalline $Fe_{0.75}Mn_{1.35}As$ compound was synthesized by a method described elsewhere [18]. X-ray diffraction (XRD) was carried out to verify that the sample yielded diffraction peaks characteristic of a single phase with 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 at temperatures from 5 K to 350 K. The change of the magnetic entropy was calculated from the *M–H* plots at various temperatures close to 165 K, with a temperature step of 5 K.

Results and discussion

The temperature dependence of the magnetization from 5 K to 350 K for the $Fe_{0.75}Mn_{1.35}As$ compound has been investigated in our previous work [18]. 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. A large thermal hysterisis of about 5 K between the transitions on warming and cooling processes is clearly observed [18]. An abrupt drop in magnetization and its thermal hysterisis at T_s are characteristic of a first-order magnetic phase transition. Meanwhile, it is reported that when the temperature is increased from T_s, the susceptibility versus temperature curve has a "knee" at about 415 K, which is considered the Néel temperature of the $Fe_{0.75}Mn_{1.35}As$ compound [17]. To explore a possible MCE and an influence of external magnetic fields on the FI–AF transition, the magnetization *M* (*H*) curves at a temperature range of 150–185 K at a step of 5 K are shown in Fig. 1a. At temperatures below 165 K, the magnetization rises abruptly at a rather low field, suggesting that the compound is in FI state. It is worthwhile noting that even at a field of up to 5 T the magnetization does not saturate. In sharp contrast, at 170 and 175 K, there exists an initial sharp increase of magnetization in weak fields. Then with further increasing the field, after a linear increase at low fields, which reveals that the compound is in an AF state, the magnetization increases

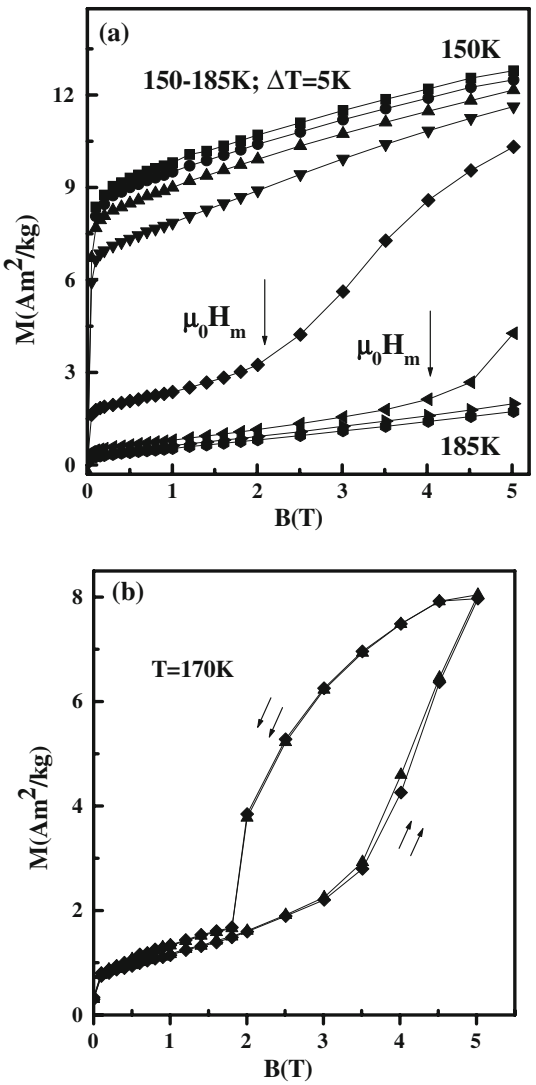

Fig. 1 **a** Field dependence of the magnetization of $Fe_{0.75}Mn_{1.35}As$ at the temperatures indicated. **b** Field dependence of the magnetization of $Fe_{0.75}Mn_{1.35}As$ at 170 K for the successively first and second field cycles

abruptly at critical fields $\mu_0 H_m$ of about 2 and 4 T, respectively, indicating a field-induced AF–FI transition. The similar initial sharp increase of magnetization in weak fields before PM or AM state can be seen in many well-known MCE materials, such as $Mn_{1-x}Fe_xAs$ [5] and Ni–Mn–In [19], which might be ascribed to that the samples are not completely homogeneous. The *M* (*H*) curves at 180 and 185 K show a typical AF behavior.

In our previous work, a positive magnetoresistance (MR) ratio as large as 12% for the first magnetic-field cycles was observed at 170 K at 5 T in the $Fe_{0.75}Mn_{1.35}As$ compound [18]. The maximum positive MR ratios at 5 T, however, were only 1.6 and 0.6% for the second and third magnetic-field cycles, respectively. These results indicated that at 170 K, magnetic fields induce an irreversible lattice

expansion and the amplitudes of the lattice expansion decrease with increasing the number of magnetic-field cycles. In order to explore the influence of magnetic-field cyclings on the field-induced AF–FI transition, the M (H) curves at 170 K for the successively first and second field cycles are shown in Fig. 1b. It can be clearly seen that the magnetization curve of the second cycle is virtually superimposed on that of the first one. This means that the cycling of a magnetic field does not induce an irreversible change in the magnetic transitions and magnetocaloric behaviors. This is different from the behavior in $Fe_{0.49}Rh_{0.51}$, in which large volume changes during the AF/FM transition lead to the irreversible MCE in alternating magnetic fields (i.e., it disappears after one cycle) [20]. Next, we shall try to explain the seemingly contradiction between the irreversible lattice expansion of the material and the reversible change of the magnetocaloric effect. On cooling in the $Fe_{2.1-x}Mn_xAs$ ($1.29 \leq x \leq 1.52$) system, it was observed that in $Fe_{0.75}Mn_{1.35}As$ there was a first-order change in the cell constants with a large expansion of the c axis by 2% and a comparatively smaller contraction of the a axis by 0.5% [16]. Our previous work showed that after several thermo-cycles, the irreversible lattice expansion of c axis was only 0.18% and even a lattice change of a axis was not observed. [18] Namely, the lattice parameter c of the FI state is about 2% larger than that of the AF state. However, the amplitude of the irreversible lattice change is only 0.18%. Consequently, the conclusion can be safely drawn that the partly irreversible lattice expansion (induced by a magnetic field or temperature) is not large enough, which cannot influence the magnetic transitions in the present compound. A similar irreversible lattice expansion was observed in the antiperovskite $ZnNMn_3$ [21], and in spite of the irreversible lattice expansion, a clear AF transition could still be seen after several thermo-cycles. From Fig. 1b, we can also see a quite large magnetic hysteresis over a large field range from 2 T to 5 T, revealing a coexistence of the AF and FI phases. This further confirms the first-order nature of the field-induced metamagnetic transition.

A large magnetic-field-induced ΔS_M is expected in $Fe_{0.75}Mn_{1.35}As$ from the magnetization curves in Fig. 1a, for a large MCE usually occurs at the magnetic transitions. The value of the isothermal $\Delta S_M(T,H)$ can be given by the following expression associated with the Maxwell relationship:

$$\Delta S_M(T,H) = S(T,H) - S(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \qquad (1)$$

As shown in formula (1), the sign of ΔS_M is determined by the sign of $\partial M/\partial T$. Figure 2 represents $\Delta S_M(T)$ curve of $Fe_{0.75}Mn_{1.35}As$ compound with a magnetic field change of 5 T. Here the sign of ΔS_M is negative. Namely, the present

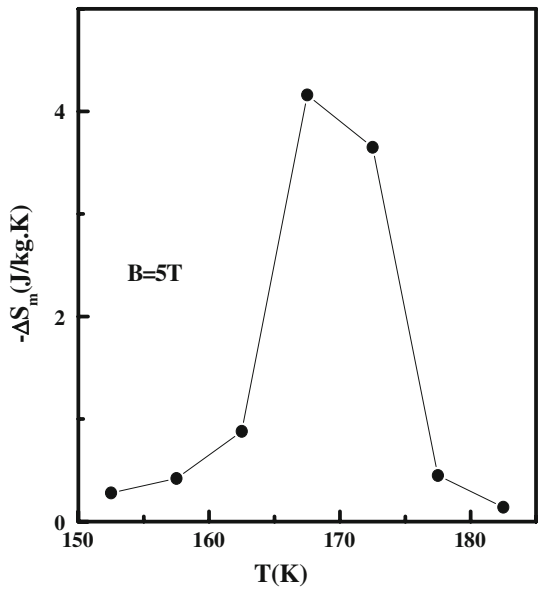

Fig. 2 Magnetic entropy changes of $Fe_{0.75}Mn_{1.35}As$ in an external field change of 5 T

compound shows a conventional MCE, cooling by adiabatic demagnetization. Since almost all the AF-related metamagnetic transitions show an inverse MCE, the MCE in $Fe_{0.75}Mn_{1.35}As$ is unusual, not as expected. Some authors tried to explain the origin of the field-induced inverse MCE near the transition temperature, there occurred a magnetically inhomogeneous state. Due to the presence of mixed magnetic exchange interactions, the application of an external magnetic field led to further spin disorder in those systems, which made the configurational entropy increase [22]. This interpretation is obviously unsuitable for MCE in $Fe_{0.75}Mn_{1.35}As$. As opposed to those AF systems showing an inverse MCE, the spin arrangement in the $Fe_{0.75}Mn_{1.35}As$ compound is FI at low temperatures and AF at high temperatures. In addition, as shown in Fig. 1a, the critical fields increase with increasing temperature. In the AF systems with inverse MCE, however, the critical fields decrease with increasing temperature. For a first-order phase transition, one could employ an approximation based on the Clausius–Clapeyron equation [23]:

$$-\left(\frac{dH}{dT}\right)_{eq} = \left(\frac{\Delta S}{\Delta M}\right)_T \qquad (2)$$

The left-hand side derivative of formula (2) is taken under the equilibrium conditions. For the right-hand side, $\Delta S = S_f - S_i$ and $\Delta M = M_f - M_i$, where the subsripts i and f correspond to phases in the initial and final magnetic field states, respectively. Obviously, according to the formula (2), if the low temperature phase is the FI and the critical fields increase with increasing temperature, it is understandable that the sign of the magnetic entropy change (ΔS_M) in $Fe_{0.75}Mn_{1.35}As$ is negative. Due to

magnetization measurements made at discrete temperature intervals, the magnetic entropy change is calculated by using the numerical approximation

$$\Delta S_{\mathrm{m}}(T_{\mathrm{av}}, B) = \sum_i \frac{M_{i+1}(T_{i+1}, B) - M_i(T_i, B)}{T_{i+1} - T_i} \Delta B \qquad (3)$$

where $M_{i+1}(T_{i+1}, B)$ and $M_i(T_i, B)$ represent the values of the magnetization in a magnetic field B at the temperatures T_{i+1} and T_i, and T_{av} is the average of T_{i+1} and T_i. The maximum ΔS_{M} (calculated using formula (3)) with a magnetic field change of 5 T is 4.2 J/kg K at 167.5 K. It indicates clearly that the field-induced metamagnetic transition is responsible for the large ΔS_{M} in $Fe_{0.75}Mn_{1.35}As$. A larger ΔS_{M} near room temperature can be expected in the $Fe_{a-x}Mn_xAs$ ($1.95 \leq a \leq 2.35$) system by increasing the saturation magnetization through increasing the Fe/Mn ratio or replacing As with other elements. Meanwhile, the transition temperature T_{s} in the present FeMnAs system can be set at any temperature from 153 K to 345 K [14–18]. This is practically meaningful, because one can expect large MCE in this quite wide temperature range.

Conclusion

The tetragonal $Fe_{0.75}Mn_{1.35}As$ compound exhibits a first-order phase transition at $T_{\mathrm{s}} = 165$ K from a FI phase to an AF phase with increasing temperature, while a large MCE has been observed near the magnetic transition temperature. The maximum value of ΔS_{M} is 4.2 J/kg K at 167.5 K in a magnetic field change of 5 T and the sign of ΔS_{M} is negative, revealing a different mechanism from the inverse MCE usually observed in the AF-related systems. The cycling of a magnetic field does not induce an irreversible change in the magnetic transitions and magnetocaloric behaviors. The large MCE associated with field-induced metamagnetic transitions in relation to AF, as shown in $Fe_{0.75}Mn_{1.35}As$, may open an important field in searching novel materials for room-temperature magnetic refrigeration.

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