Magnetic-field-induced transformation in FeMnGa alloys

W. Zhu,¹ E. K. Liu,¹ L. Feng,¹ X. D. Tang,¹ J. L. Chen,¹ G. H. Wu,¹,a) H. Y. Liu,² F. B. Meng,² and H. Z. Luo²

¹Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
²School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, People’s Republic of China

(Received 7 September 2009; accepted 7 November 2009; published online 3 December 2009)

A kind of ferromagnetic shape memory alloy with off-stoichiometric composition of Heusler alloy Fe₅₀Mn₂₂.₅Ga₂₇.₅ has been synthesized. By optimizing composition, the martensitic transformation has been modified to occur at about 163 K accompanying spontaneous magnetization, which enables a magnetic field-induced structural transition from a paramagnetic parent phase to a ferromagnetic martensite with high magnetization of 93.8 emu/g. The material performs a quite large lattice distortion through the transformation, (c−a)/c=33.5%, causing a shape memory strain up to 3.6%. Such large lattice distortions strongly influence the electron structures, and thus some special physical behavior related to the transport and conductive properties is investigated. © 2009 American Institute of Physics. [doi:10.1063/1.3269590]

Ferromagnetic shape memory alloys (FSMAs) (Refs. 1–6) with martensitic transformation (MT) is an important functional material system. In 2006, an important effect, magnetic-field-induced transformation was discovered in NiCoMnIn alloy⁷ and thus triggered more interest in the technology application about these materials. In recent years, a few kinds of similar systems have been developed.⁸–¹⁴ However, FeMn-based Heusler alloys, have been scarcely developed as FSMAs except Fe₄₃Mn₂₈Ga₂₉ alloy reported by Omori at al.¹⁵ recently. In this letter, we report that the off-stoichiometric Heusler alloys of Fe₂MnGa alloy have been synthesized as FSMAs in a quite wide composition range. Especially, a transformation from the paramagnetic parent phase to the ferromagnetic martensite can be achieved by modifying the alloy composition and thus generates a large magnetization difference (ΔM) to enable a magnetic field-induced MT. With a large intrinsic lattice distortion, the material performs a large shape memory strain up to 3.6% even in the polycrystalline samples. Moreover, other properties different from most developed FSMAs are discussed in the report.

FeMnGa alloys near the stoichiometric Heusler alloy of Fe₂MnGa are prepared by radio-frequency (RF) induction melting the elements of Fe and Ga with the high purity under argon atmosphere and then annealed at 1100 °C for three days with quenching in ice-water subsequently. The superconducting quantum interference device magnetometer is used for magnetic property measurements. The structures of the samples were determined by x-ray diffraction (XRD) examination. The shape memory effect is measured by the eddy sensor for the samples with the size of 10.2(L)×3(W)×3 mm³ in the free state without preloading. The resistivity versus temperature is measured by the standard four-point method on the FeMnGa samples cut in the appropriate size.

Figure 1 shows the phase diagram for the FeMnGa FSMAs. Around Fe₅₀Mn₂₂.₅Ga₂₇.₅ composition (★), the pure body-centered cubic (BCC) can be synthesized by RF induction melting method, while the coexistent phase (○) of BCC matrix and trace face-centered cubic (FCC) is found in a quite large composition range. Specially, in the area surrounded by the border line, the alloys have MT character and are FSMAs. One may see that FSMAs occupy a narrow area where the Ga content trends to remain a relatively constant value of about 29(±1) at. % and the ratio of Fe/Mn is allowed to be changed largely. It implies that the stability of BCC phase strongly relies on the valence-electron-to-atom ratio (e/a), which dominates the lattice structure transition by affecting the instability of phonon mode.¹⁶,¹⁷ In this letter, the FSMAs with composition near Fe₅₀Mn₂₂.₅Ga₂₇.₅ are emphatically investigated.

Figure 2 depicts the magnetic properties upon the MT of the Fe₅₀Mn₂₂.₅Ga₂₇.₅ alloy in the magnetic field of 5 T. The dramatic increase in magnetization for cooling and the decrease for heating apparently reveal the MT behavior with a large thermal hysteresis of about 81 K. The martensite of the alloy has a higher magnetization than the parent phase, which is different from other FSMAs, such as Co–Ni–Ga,⁴ Ni₂FeGa,⁶ Mn₂NiGa,¹⁸ and Ni₂MnAl (Ref. 19) alloy.

a)Author to whom correspondence should be addressed. Electronic mail: ghwu@aphy.iphy.ac.cn.

FIG. 1. (Color online) Phase diagram of FeMnGa alloys synthesized by RF melting method. Two phases, BCC and FCC (△) structures formed in the composition range. The FSMAs is in the area surrounded by the border line.
In a low field, as shown in the inset, the ac susceptibility of the Fe$_{51}$Mn$_{22}$Ga$_{27}$ alloy exhibits a sharp increase around 190 K, which reveals the Curie temperature ($T_C$) of the parent phase. The following decrease in susceptibility resulted from the large magnetocrystalline anisotropy of the martensite phase. The martensite of Fe$_{50}$Mn$_{22.5}$Ga$_{27.5}$ alloy at 300 K, as also seen in magnetic measurement of the Fe$_{50}$Mn$_{22.5}$Ga$_{27.5}$ sample. The inset is the shape memory effect of this sample measured in the free state without preloading.

The martensite of Fe$_{50}$Mn$_{22.5}$Ga$_{27.5}$ alloy exhibits a sharp increase around $T_C=197$ K and $T_C=227$ K. Comparing the parameters with those of the Fe$_{50}$Mn$_{22.5}$Ga$_{27.5}$ alloy, one could see that a slightly modified composition can seriously affect the MT through MT.22,23 This abnormal conductivity behavior may be attributed to the abrupt change of the electron structure due to the large lattice distortion.

Figure 3 shows the XRD patterns of the parent phase and the martensite of Fe$_{50}$Mn$_{22.5}$Ga$_{27.5}$ alloy. At 300 K, the characteristic peaks can be indexed well to a BCC structure with the calculated lattice parameters $a=5.8562$ Å for the parent phase. The martensite (with some traced parent phase measured at 90 K, as also seen in magnetic measurement) shows a body-centered tetragonal structure with the lattice parameters $a=b=5.3282$ Å and $c=7.1134$ Å. This transformation causes a large lattice distortion, $(c-a)/a=33.5\%$, which is the largest among all the reported FSMAs, much larger than that of Mn$_3$NiGa (21.3\%)$^{18}$ and Ni$_{48.8}$Mn$_{29.7}$Ga$_{21.5}$ (10.66\%).$^{20}$ Moreover, like most Fe-based shape memory alloys such as Fe–Ni–Co–Ti, the specific volume through MT increases about 0.85% by calculating the given lattice parameters, which is different from the negative value of volume changes for Ni$_3$MnGa (Ref. 1) and Mn$_2$NiGa.$^{18}$ Such transformation needs more energy to overcome the friction during the motion of the phase boundaries, which may explain the quite large thermal hysteresis of about 81 K in this system. The large lattice distortion generates a remarkable shape memory effect, as shown in the inset of Fig. 3.

Figure 4 shows the temperature dependence of ac susceptibility and electrical resistivity of the Fe$_{50}$Mn$_{22.5}$Ga$_{27.5}$ alloy. Two abnormal changes of the resistivity occurring at 216 and 263 K correspond to the MT and the reverse MT and are consistent with the magnetic susceptibility measurement. It reveals that the martensite has a lower resistivity in ferromagnetic state and the parent phase performs semimetal-like conducting behavior in paramagnetic state. Our $ab$ initio calculation indicates that, like Fe$_{50}$MnAl,$^{21}$ there is an energy gap in spin-down side localized at the Fermi energy level. These results strongly suggest that the parent phase is a half-metal-like compound. For the martensite, the electron density of states near the Fermi surface approximately increases an order of magnitude due to the serious degradation of antibonding. As a result, the resistivity decreases and shows a positive temperature coefficient. However, the resistance in almost all of the previous FSMAs apparently increases through MT.$^{22,23}$ This abnormal conductivity behavior may be attributed to the abrupt change of the electron structure due to the large lattice distortion.

Figure 5 shows the magnetization curves of the Fe$_{50}$Mn$_{22.5}$Ga$_{27.5}$ alloy at different temperatures on cooling. At 250 K, the parent phase states in the paramagnetism, but...
still shows a rather apparent magnetization behavior, which suggests a strong short term exchange interaction. For the martensite, the saturate magnetization of about 93.8 emu/g was measured at 5K. In the temperature range from 200 to 100 K, the magnetization curves become looplike shape. Especially, the MH curve shows a quite large hysteresis between the field-up and field-down at 170 K, and indicating a magnetic field-induced transformation in this system.

It should be emphasized that, due to the MT scuffles with the spontaneous magnetization transition in this sample, the observed field-induced transformation here proceeds just in this way: from the paramagnetic parent phase to the ferromagnetic martensitic phase, which is just opposite to those observed in all other FMSA systems.\textsuperscript{7-14} This performs a consistent entropy change between the magnetocaloric effect and the martensitic transformation. In addition, it seems that the martensitic phase induced by the applied field could not be completely recovered to austenite when the magnetic field decreases to zero, which can be attributed to the large hysteresis in this material. Further work will focus on improving the material properties, especially for decreasing the hysteresis of the transformation to realize the recoverable field-induced MT.

In summary, the FSMAs of FeMnGa have been synthesized in a large composition range close to the stoichiometric Heusler alloy of Fe\textsubscript{2}MnGa. A field-induced transformation from paramagnetic parent phase to ferromagnetic martensite has been observed, which achieves a consistent entropy change relationship between the magnetocaloric effect and MT. The material also shows a large lattice distortion of 33.5\% through the MT which performs a large shape memory strain up to about 3.6\%. The experimental results indicate that the large lattice distortion leads to some distinct physical behavior.

This work is supported by National Natural Science Foundation of China in Grant Nos. 10774178 and 50771103.