

Magnetic-field-induced martensitic transformation in MnNiAl:Co alloys

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A series of Heusler-type MnNiCoAl alloys have been prepared, and the composition dependence of the martensitic transformation has been investigated. Due to the formation of a local Mn-Co-Mn ferromagnetic structure in the antiferromagnetic matrix, a large magnetization difference of 48 Am²/kg and a driving efficiency of 2.14 K/T can be observed in Mn₅₀Ni₃₂Co₆Al₁₂ sample in which a field-induced transformation can be realized. X-ray diffraction results further indicate that the high temperature phase has a high level of atomic disorder which causes an increase of the thermal hysteresis of the transformation when increasing Co content. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3701136>]

Since ferromagnetic shape memory alloys (FSMAs) have become attractive candidates for high-performance magnetic-actuator materials, many new Heusler-type FSMAs with the important property of a field-induced martensitic transformation, such as NiMnX (X = In, Sn, Sb),¹⁻⁴ NiCoMnIn,⁵ NiCoMnSn,⁶ NiCoMnSb,⁷ NiCoMnGa,⁸ have been discovered. Their magnetic properties exhibit a great perspective for multifunctional applications. Mn₂YX-type FSMAs with the Hg₂CuTi structure possess the highest Curie temperatures (T_C),⁹ but their low magnetization, due to the antiferromagnetic structure formed in a Mn-rich environment, obstructs the application of these materials. A magnetic-field-induced martensitic transformation in these compounds has only been observed in MnCoNiGa.¹⁰

In this work, we report a magnetic-field-induced martensitic transformation realized in off-stoichiometric Mn₂NiAl. By substituting a small amount of Co for Ni, a local ferromagnetic structure is achieved in the antiferromagnetic matrix and the magnetization of the high temperature phase is effectively enhanced. Based on this, a large magnetization difference (ΔM) is obtained, which endows the system with a metamagnetization behavior.

All alloys have been prepared by arc-melting high-purity (3N) elements under argon atmosphere. Because for some samples with high Ni content ($\geq 38\%$) or high Co content ($\geq 5\%$) single-phase materials cannot be obtained by arc-melting, the melt-spinning method was utilized in these composition ranges to prevent presence of the γ phase. All as-prepared materials were annealed at 1273 K for 72 h and subsequently quenched in ice water. Structural examination was performed by x-ray diffraction (XRD) with Cu-K α radiation. A superconducting quantum interference device (SQUID) was used to determine the magnetic properties in the magnetic-field range of 0–13 T. The transformation

temperature was measured by differential scanning calorimetry (DSC) or by the magnetic method.

A series of Mn₅₀Ni_xCo_yAl_z samples with $x + y + z = 50$ and $z = 7 \sim 13$ was prepared to investigate the structural-transformation behavior. Figure 1 shows the phase diagram of the alloys on the Mn50 section. One can see that the FSMAs are localized in a narrow composition range where the Al content is relatively constant, while the contents of Co and Ni can vary in a relatively large range. In this area, when the composition changes, the change of valence-electron-to-atom ratio (e/a) resulting from the variation of the Co and Ni contents is much smaller than that resulting from Al. This implies a dependence of the martensitic transformation on the e/a ratio which dominates the structural transition by affecting the stability of the phonon mode.^{11,12} On the other hand, the Al content mainly dominates the strength of the covalence bond in this kind of intermetallic compounds.¹³ Therefore, these two factors make the FSMAs localized in a stripe-like area in the pseudo-ternary phase diagram.

Figure 2 shows the XRD patterns at room temperature for the alloys Mn₅₀Ni₃₆Co₂Al₁₂ and Mn₅₀Ni₃₀Co₈Al₁₂ with martensitic transformation temperatures above and below the room temperature, respectively. For Mn₅₀Ni₃₀Co₈Al₁₂, all diffraction peaks can be indexed well to a body centered cubic (BCC) structure with a lattice parameter $a = 5.8787 \text{ \AA}$. No superlattice reflections are found, which indicates a high level of atomic disorder. With a relatively low Co content, Mn₅₀Ni₃₆Co₂Al₁₂ has the body-centered tetragonal structure with lattice parameters $a = b = 5.4053 \text{ \AA}$ and $c = 6.8088 \text{ \AA}$. This is the same structure type as observed for Mn₂NiGa.⁹

Figure 3 shows the Co-content dependence of the martensitic phase transformation temperature (T_M), the reverse transformation temperature (T_A) and the thermal hysteresis (δT) for Mn₅₀Ni_{39-x}Co_xAl₁₁ alloys. Similar to the MnNiCoGa alloys,¹⁰ T_M in the MnNiCoAl system also decreases with increasing Co content. On average, T_M decreases about 30 K when 1 at. % Co is added. In view of the influence of

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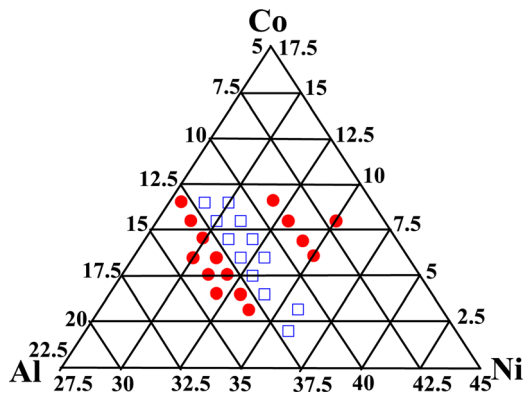


FIG. 1. Pseudo-ternary phase diagram of Mn50 cross-section of Mn₅₀ (NiCoAl)₅₀ alloys. The square and dot symbols represent the samples with and without martensitic transformation property, respectively.

the e/a ratio on T_M , this is consistent with the observation reported in previous work.¹⁴ However, we have found that, with increasing Co content, T_A increases instead of decreasing. This is quite different from other Heusler-type FSMA in which T_M and T_A usually change consistently.^{15,16} As the Co content increases to 9%, this opposite dependence of T_M and T_A on the Co content results in a significant increase of δT ($=T_A - T_M$) up to 183 K, which implies the absence of thermoelastic behavior at the transformation.

The DSC measurement indicates that the martensitic transformation and reverse transformation of the mother alloy Mn₅₀Ni₃₈Al₁₂ occur at 369 K and 383 K, respectively, where the alloy is paramagnetic. Substitution of Co for Ni in the mother parent alloy increases T_C and decreases T_M , so that the martensitic transformation can be modified to occur in the ferromagnetic region of the high temperature phase. As shown in the inset of Figure 3, T_C of the high temperature phase of Mn₅₀Ni₃₄Co₄Al₁₂ can just be observed, but it tangles with T_M at about 341 K. In Mn₅₀Ni₃₂Co₆Al₁₂, T_M and T_C become 318 K and 378 K, respectively. In the present paper, the emphasis will be on the investigation of Mn₅₀Ni₃₂Co₆Al₁₂.

Figure 4 shows $M-T$ curves of Mn₅₀Ni₃₂Co₆Al₁₂ measured in various magnetic fields. In the magnetic field of 7 T, A high magnetization of 63.1 Am²/kg can be obtained in the

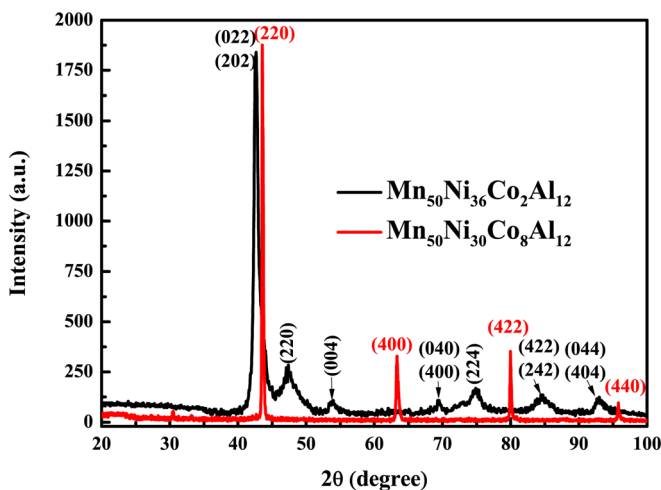


FIG. 2. XRD patterns at room temperature of arc-melted Mn₅₀Ni₃₆Co₂Al₁₂ sample and Mn₅₀Ni₃₀Co₈Al₁₂ ribbon sample.

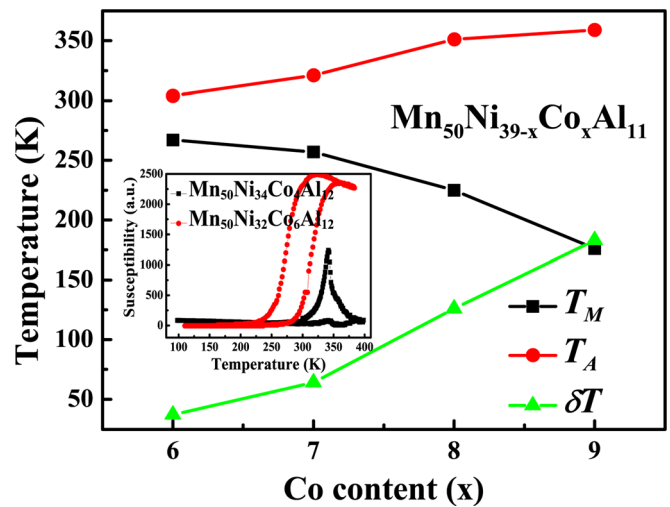


FIG. 3. Co-content dependence of T_M , T_A , and δT of Mn₅₀Ni_{39-x}Co_xAl₁₁ alloys. The inset shows the temperature dependence of the ac susceptibility of Mn₅₀Ni₃₄Co₄Al₁₂ and Mn₅₀Ni₃₂Co₆Al₁₂s.

high temperature phase. With respect to the low magnetization of the martensite, a large ΔM of 47.6 Am²/kg is achieved in this alloy. Meanwhile, compared with the $M-T$ curves measured at a low field of 0.1 T, T_M has obviously shifted to lower temperature by about 15 K with a driving efficiency of about 2.14 K/T. This value is comparable to that in the materials Ni₄₃Co₇Mn₃₉Sn₁₁ (3.6 K/T; Ref. 6) and Ni₄₁Co₉Mn₃₉Sb₁₁ (3.5 K/T).⁷ This implies that a field-induced martensitic transformation can be expected in Mn₅₀Ni₃₂Co₆Al₁₂.

Figure 5 shows the magnetization behavior ($M-B$) of Mn₅₀Ni₃₂Co₆Al₁₂ measured at different temperatures. At 10 K, the martensite is antiferromagnetic with a low magnetization, while the high temperature phase is ferrimagnetic at 350 K with a high magnetization. In between, the $M-B$ curve at 310 K exhibits an apparent loop behavior, suggesting a metamagnetic process. This is a typical field-induced transformation from low magnetization martensite to the high magnetization high temperature phase. Looking again at the $M-T$ curves in Figure 4, one may see that, in the demagnetized state, the parent and martensitic phase coexist. This means

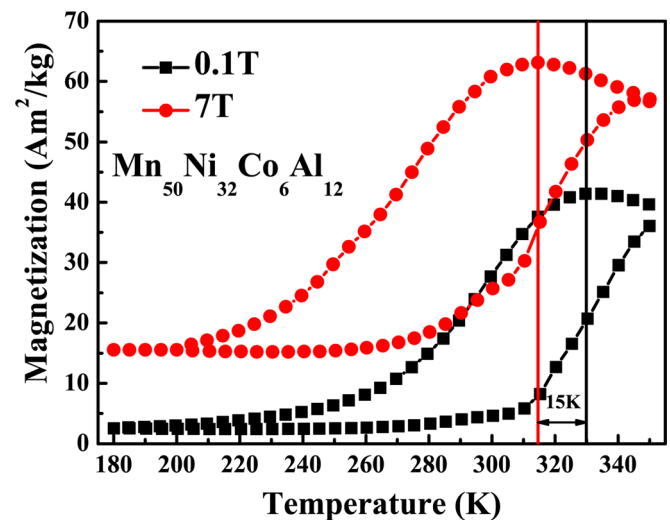


FIG. 4. $M-T$ of Mn₅₀Ni₃₂Co₆Al₁₂ measured in magnetic fields of 0.1 and 7 T. The vertical lines indicate the change of T_m upon application of a magnetic field.

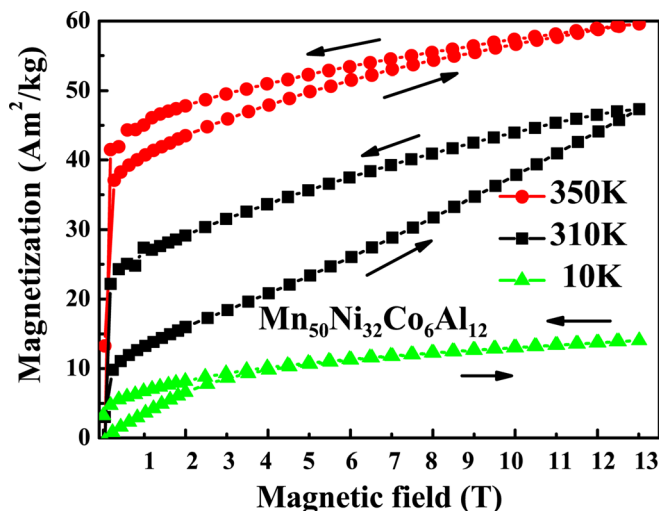


FIG. 5. Magnetization of $\text{Mn}_{50}\text{Ni}_{32}\text{Co}_6\text{Al}_{12}$ measured in heating run.

that the martensitic phase cannot completely be transformed to the high temperature phase by the applied magnetic field of 13 T and also that the high temperature phase induced by the field does not completely transform to the martensitic phase when the magnetic field is decreased to zero. Obviously, this is due to the large hysteresis of the system.

Figure 6 shows the magnetization of a series of $\text{Mn}_{50}\text{Ni}_{38-x}\text{Co}_x\text{Al}_{12}$ alloys. The saturation magnetization of the mother alloy $\text{Mn}_{50}\text{Ni}_{38}\text{Al}_{12}$ and of the material with 2–6 at. % added Co is less than $6.0 \text{ Am}^2/\text{kg}$ at 5 T, indicating that the martensite is antiferromagnetic. At $x=8$, where the alloy has lost the martensitic-transformation property, the high temperature phase shows a saturation magnetization of at 5 K up to $85.8 \text{ Am}^2/\text{kg}$. Our systematic investigation¹⁷ indicates that, when Co atoms are substituted, a special atomic configuration, a local Mn-Co-Mn ferromagnetic structure, is achieved in the antiferromagnetic matrix of the high temperature phase. However, the deformed lattice in the martensite makes the distance of Mn-Mn too short to form the ferromagnetic structure, as happens in the high temperature phase. This physical mechanism gives rise to the large ΔM upon Co doping. The inset of

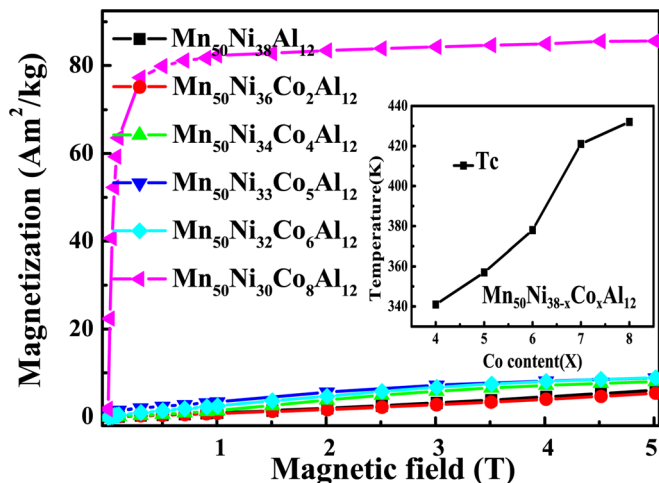


FIG. 6. M - H curves for $\text{Mn}_{50}\text{Ni}_{38-x}\text{Co}_x\text{Al}_{12}$ alloys measured at 5 K. The inset presents the dependence of T_C of the high temperature phase on the Co content.

Figure 6 shows the dependence of T_C of the high temperature phase on the Co content. The rapid increase of T_C indicates that the localized ferromagnetic structure enhances the exchange interaction. A similar property has also been observed in the samples shown in Fig. 3.

In summary, a series of Heusler-type MnNiCoAl alloys has been prepared and the composition dependence of the martensitic transformation has been investigated. Two factors, the e/a ratio and the covalent bond, affect the phase stability of the high temperature phase and, thus, dominate the martensitic transformation. The martensitic phase in this system has the body-centered tetragonal structure which is the same as in Mn_2NiGa . Different from other FSMA systems is that, when the Co content in the alloy increases, T_M and T_A vary in opposite direction, which results in a significant increase of the δT ($= T_M - T_A$). This may be due to the high level atomic disorder in the alloys. By substituting 6 at. % Co, a large ΔM up to about $48 \text{ Am}^2/\text{kg}$ is found in $\text{Mn}_{50}\text{Ni}_{32}\text{Co}_6\text{Al}_{12}$, which effectively gives rise to a field-induced martensitic transformation in this alloy. The present study indicates that the large ΔM obtained upon addition of Co arises from substantial enhancement of the magnetization of the high temperature phase due to a local Mn-Co-Mn ferromagnetic structure which is formed in the antiferromagnetic matrix.

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- ¹Y. Sutou, Y. Imano, N. Koeda, T. Omori, R. Kainuma, K. Ishida, and K. Oikawa, *Appl. Phys. Lett.* **85**, 4358 (2004).
- ²K. Oikawa, W. Ito, Y. Imano, Y. Sutou, R. Kainuma, K. Ishida, S. Okamoto, O. Kitakami, and T. Kanomata, *Appl. Phys. Lett.* **88**, 122507 (2006).
- ³T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Manosa, and A. Planes, *Nature Mater.* **4**, 450 (2005).
- ⁴K. Koyama, K. Watanabe, T. Kanomata, R. Kainuma, K. Oikawa, and K. Ishida, *Appl. Phys. Lett.* **88**, 132505 (2006).
- ⁵R. Kainuma, Y. Imano, W. Ito, Y. Sutou, H. Morito, S. Okamoto, O. Kitakami, K. Oikawa, A. Fujita, T. Kanomata, and K. Ishida, *Nature (London)* **439**, 957 (2006).
- ⁶R. Kainuma, Y. Imano, W. Ito, H. Morito, Y. Sutou, K. Oikawa, A. Fujita, K. Ishida, S. Okamoto, and O. Kitakami, *Appl. Phys. Lett.* **88**, 192513 (2006).
- ⁷S. Y. Yu, L. Ma, G. D. Liu, Z. H. Liu, J. L. Chen, Z. X. Cao, G. H. Wu, B. Zhang, and X. X. Zhang, *Appl. Phys. Lett.* **90**, 242501 (2007).
- ⁸S. Y. Yu, Z. X. Cao, L. Ma, G. D. Liu, J. L. Chen, G. H. Wu, B. Zhang, and X. X. Zhang, *Appl. Phys. Lett.* **91**, 102507 (2007).
- ⁹G. D. Liu, J. L. Chen, Z. H. Liu, X. F. Dai, and G. H. Wu, *Appl. Phys. Lett.* **87**, 262504 (2005).
- ¹⁰L. Ma, H. W. Zhang, S. Y. Yu, Z. Y. Zhu, J. L. Chen, and G. H. Wu, *Appl. Phys. Lett.* **92**, 032509 (2008).
- ¹¹P. Entel, V. D. Bucheikinov, V. V. Khovailo, A. T. Zayak, W. A. Adeagbo, M. E. Gruner, H. C. Herper, and E. F. Wassermann, *J. Phys. D* **39**, 865 (2006).
- ¹²A. T. Zayak, W. A. Adeagbo, P. Entel, and K. M. Rabe, *Appl. Phys. Lett.* **88**, 111903 (2006).
- ¹³J. Kübler, A. R. William, and C. B. Sommers, *Phys. Rev. B* **28**, 1745 (1983).
- ¹⁴T. Krenke, X. Moya, S. Aksoy, M. Acet, P. Entel, L. Manosa, A. Planes, Y. Elerman, A. Yücel, and E. F. Wassermann, *J. Magn. Magn. Mater.* **310**, 2788 (2007).
- ¹⁵Z. D. Han, D. H. Wang, C. L. Zhang, H. C. Xuan, B. X. Gu, and Y. W. Du, *Appl. Phys. Lett.* **90**, 042507 (2007).
- ¹⁶W. Ito, Y. Imano, R. Kainuma, Y. Sutou, K. Oikawa, and K. Ishida, *Metal. Mater. Trans. A* **38A**, 759 (2007).
- ¹⁷L. Ma, W. H. Wang, C. M. Zhen, D. L. Hou, X. D. Tang, E. K. Liu, and G. H. Wu, *Phys. Rev. B* **84**, 224404 (2011).