Magnetic properties and martensitic transformation in quaternary Heusler alloy of NiMnFeGa

Z. H. Liu, M. Zhang, W. Q. Wang, W. H. Wang, J. L. Chen, and G. H. Wu[a)]
State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

F. B. Meng, H. Y. Liu, B. D. Liu, J. P. Qu, and Y. X. Li
Center of Magnetic Materials and Magnetic Technology, Hebei University of Technology, Tianjin 300130, People's Republic of China

(Received 18 February 2002; accepted 13 August 2002)

Quaternary Heusler alloy $Ni_2(Mn,Fe)Ga$ has been studied systematically for the structure, martensitic transformation, and magnetic properties in two systems of $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ and $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$. Substituting Fe for Mn up to about 70%, the pure $L2_1$ phase and the thermoelastic martensitic transformation still can be observed in these quaternary systems. Iron doping dropped the martensitic transformation temperature from 220 to 140 K, increased the Curie temperature from 351 to 429 K, and broadened the thermal hysteresis from about 7 to 18 K. Magnetic analysis revealed that Fe atoms contribute to the net magnetization of the material with a moment lower than that of Mn. The temperature dependence of magnetic-field-induced strains has been improved by this doping method. © *2002 American Institute of Physics.*
[DOI: 10.1063/1.1511293]

I. INTRODUCTION

$Ni_{50}Mn_{25}Ga_{25}$ exhibits a shape-memory effect upon the martensitic transformation and magnetic-filed-induced strains[1–5] at martensite state. It has been attracting strong interest for potential applications as magnetic-field-controlled actuators.[6] This application requires the material having a martensitic transformation property and also being ferromagnetic. For this purpose, some candidate materials, such as Ni_2MnAl,[7] Co_2NiGa, [8] and NiCoAl,[9] have been developed recently. As a better candidate, the material should be with a higher T_C than that of Ni_2MnGa, a higher M_s at working temperature, and a similar thermoelastic martensitic transformation property enabling the shape memory effect.

In this article, we report a pseudoquaternary Heusler alloy of NiMnFeGa. The material is also with cubic $L2_1$ structure and ferromagnetic, possessing a thermoelastic martensitic phase transition. We focused on the influences of the Fe content on the martensitic phase transformations and magnetic properties in two series samples of $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ and $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$. It was found that, the existence of Fe in this intermetallic compound caused a stronger magnetic exchange interaction leading to higher Curie temperature. The temperature dependence of magnetic-field-induced strains (MFIS) in single crystal $Ni_{52}Mn_{16}Fe_8Ga_{24}$ was discussed by comparing with $Ni_{52}Mn_{24}Ga_{24}$.

II. EXPERIMENTAL PROCEDURE

Two series samples of $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ and $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$ were prepared by the arc-melting method from metal elements Ni, Mn, and Ga with purity of 99.95%. As-cast ingots were subsequent annealed at 800 °C for four days for high chemical ordering. Single crystal $Ni_{52}Mn_{16}Fe_8Ga_{24}$ and $Ni_{52}Mn_{24}Ga_{24}$ were grown by the Czochralski method as reported previously.[3] Powder x-ray diffraction (XRD) was performed by Philip-Pert MPD diffractometer. The Curie temperature and martensitic transformation temperature were determined by an ac susceptibility measurement with an ac field of 796 A/m and a frequency of 77 Hz over a temperature range 77 - 500 K. The magnetization at 4 K was measured by a superconducting quantum interference device (Quantum Design MPMS).

III. RESULTS AND DISCUSSIONS

A. Structure

Figure 1 shows the XRD patterns for samples of $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ with $x=0,15,17$, and 19, respectively. When $x=15$ or less, the parent phase of the Fe doped samples has a pure cubic $L2_1$ structure [space group Fm3m as shown in Fig. 1(b)], showing the same XRD characteristic peaks with that of undoped sample [Fig. 1(a)]. This result agrees well with the results reported in Ref. 10 The substitution of Fe for some of the Mn makes the lattice shrunk because of the smaller ion diameter of Fe than that of Mn. For example, the lattice parameters of $Ni_{50.5}Mn_{16}Fe_8Ga_{24.5}$ are $a=b=c=5.792$ Å, which is about 0.55% less than 5.824 Å of $Ni_{50}Mn_{25}Ga_{25}$. When x is 17, some trace second phase can be observed from XRD patterns, which has been identified as the γ phase similar to that in NiFe alloys, as shown in Fig. 1(c). In the sample with $x=19$, the γ phase becomes more apparent and some characteristic peaks can be identified as shown in Fig. 1(d).

a)Electronic mail: userm201@aphy:phy.ac.cn

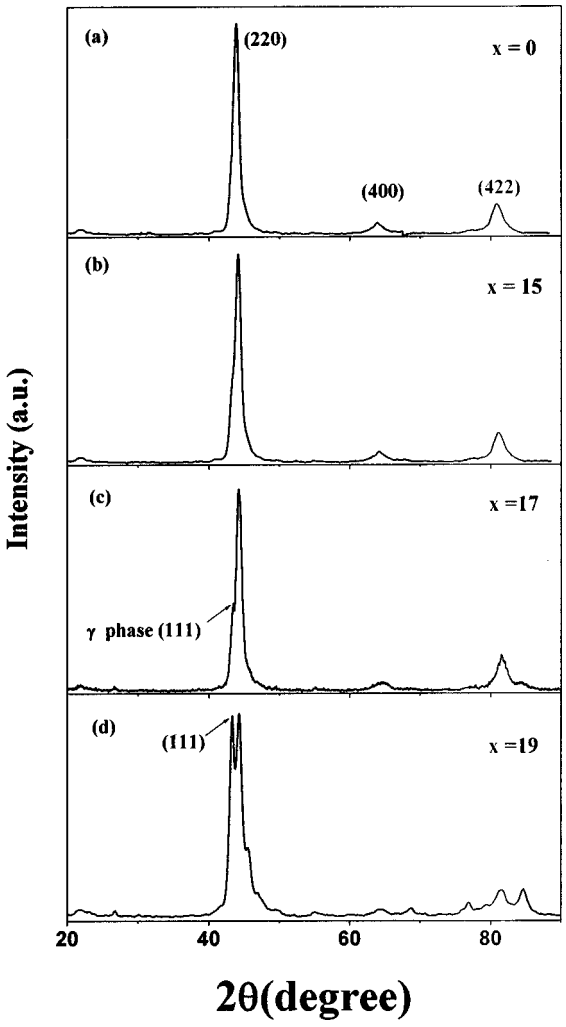

FIG. 1. XRD patterns of $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ alloy with (a) $x=0$, (b) $x=15$, (c) $x=17$, and (d) $x=19$ taken at 300 K.

Figure 2 shows the results from the metallographic observation in the present work. No second phase can be found in the sample with $x=15$. But in the sample with $x=19$, the γ phase is formed. The energy dispersion spectrum examination revealed that the composition of the γ phase is about $Ni_{49}Fe_{32}Ga_{19}$ and independent of the annealing temperature. Those examinations indicate that the maximum substitution of iron for manganese for keeping a pure $L2_1$ structure is about 70% in this pseudoquaternary intermetallic compound of NiMnFeGa.

B. Martensitic transformation

Figure 3 shows the ac susceptibility as a function of temperature measured from $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ ($x=2,6,13,17$) system. The martensitic transformation temperature and the Curie temperature of the samples have been precisely measured by this method. Clearly, the samples doped up to $x=17$ still exhibit a martensitic transformation similar to the undoped sample. Our low temperature XRD has confirmed that, during cooling, a structural transition from cubic to tetragonal occurred in this quaternary system, which is the same as the ternary alloy Ni_2MnGa. However,

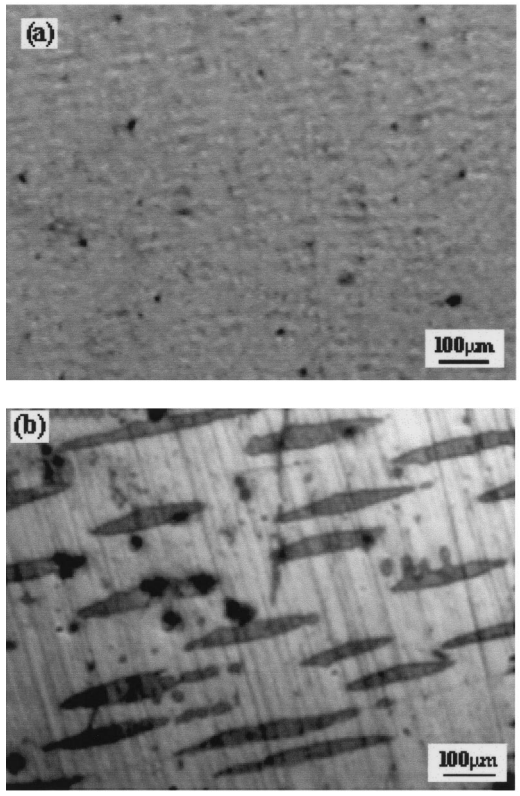

FIG. 2. Optical microscope photograph of (a) $Ni_{50.5}Mn_{10}Fe_{15}Ga_{24.5}$ and (b) $Ni_{50.5}Mn_6Fe_{19}Ga_{24.5}$.

the intermartensitic transformation that is usually observed in NiMnGa[11] could not be found in this NiMnFeGa alloy.

Table I lists the martensitic transformation temperature, T_m, thermal hysteresis between transformation and reversed transformation, δT, and Curie temperature, T_C measured from two systems of Fe doped compounds: $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ and $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$, in detail. Figure 4 illustrates these parameters vs iron doping level x in the system of $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$.

From Table I and Fig. 4, one can find that the martensitic transformation temperature, T_m, monotonously decreases with the increase of Fe content in the samples. It implies that the iron enhances the stability of the cubic parent phase, and

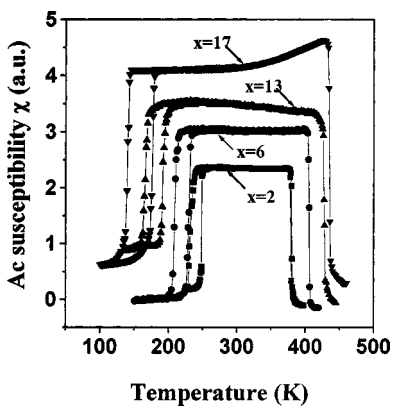

FIG. 3. Temperature dependence of low-field ac magnetic susceptibility for samples $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ ($x=2,6,13,17$).

TABLE I. Electron concentration, e/a, Martensitic transformation temperature, T_m, thermal hysteresis temperature, δT, Curie temperature, T_C, and saturation magnetization M_S, of Fe doped compounds: $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ and $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$

Compositions (in at. %)	e/a	T_m (K)	δT (K)	T_C (K)	M_S (emu/g)
$Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$					
$x=0$	7.535	233.6	6.6	350.9	62.75
$x=2$	7.555	230.6	6.8	377.6	63.75
$x=4$	7.575	228.4	7.6	391.5	64.10
$x=6$	7.595	215.6	8.9	403.5	64.99
$x=8$	7.615	207.5	9.8	415.3	66.88
$x=10$	7.635	194.2	12.8	420.1	66.72
$x=12$	7.655	181.9	14.0	424.3	64.88
$x=13$	7.665	169.6	15.4	427.1	63.65
$x=15$	7.685	153.9	16.7	428.0	62.33
$x=17$	7.705	143.7	17.7	429.2	60.51
$Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$					
$x=0$	7.648	355.1	4.0	363.8	57.74
$x=10$	7.748	296.4	7.5	406.8	66.13
$x=14$	7.788	257.9	19.3	421.5	63.30
$x=18$	7.828	197.4	26.2	433.1	61.60

lowering the transformation temperature. Chernenko investigated systemically the dopant dependence of Heusler alloy Ni_2MnGa based on the Hume-Rothery mechanism.[12] They found that the T_m shows a proportional relation with e/a in the range of 7.3-7.5, but having a complex dependence in the range of e/a = 7.5-7.7. The e/a values of Fe doped samples in this work are about 7.65-7.84, and crossing through these two ranges. Therefore, the dopant makes a different T_m variation, monotonous decrease with the increase of e/a. Furthermore, the variation of e/a for both systems is almost the same with 7.68-7.84 for $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ and 7.65-7.83 for $Ni_{50.4}Mn_{28-x}Fe_xGa_{24.6}$. But the T_m variations are very different from 143 to 233 K and from 197 to 355 K, respectively. It seems that the e/a dependence could not simply explain the T_m variation in our doping system. The other factor for the stability of parent phase, such as magnetic contribution, should be considered.

Figure 5 shows the temperature dependence of the ac susceptibility for $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$ ($x=0,10,14,18$) samples. Apparently, the change tendency of T_m and T_C agrees with those of the earlier samples. Comparing Figs. 3 and 5, one can see that the changes of T_m and T_C are larger in $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$ ($x=0,10,14,18$) than those in $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ when the variation of x is equal.

The data of thermal hysteresis, δT, shown in Table I and Fig. 4 exhibit the influence of the dopant of iron. The δT dramatically increases with the increase of the doped level in the system of $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$. Our recent investigation has indicated that the thermal hysteresis in the NiMnGa system originates from the friction of phase boundary motion, and being only a small part of the latent heat of martensitic transformation.[13] Obviously, the existence of Fe atoms in the NiMnGa systems increases the energy consumed for phase boundary motion. It may result in a decrease of the thermal elasticity in martensitic transformation. Comparing the results measured from the different Mn content systems of $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ and $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$, one can see that the δT also increased with the increase of the Fe content, but not so much like what happened in the related low Mn content system.

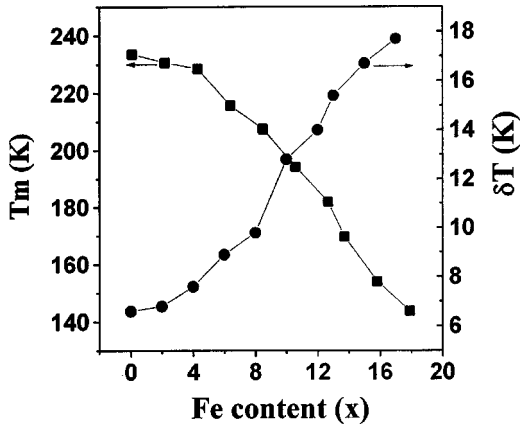

FIG. 4. Martensitic transformation temperature (T_m) and thermal hysteresis between transformation and reversed transformation (δT) for the different $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ samples as a function of Fe doping level.

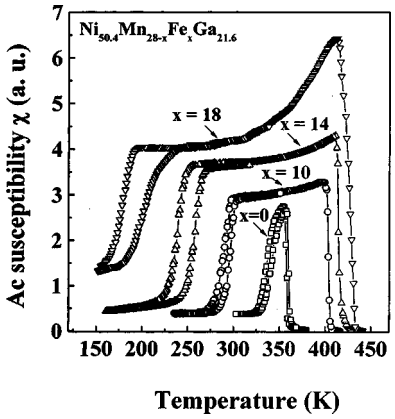

FIG. 5. Temperature dependence of low-field ac magnetic susceptibility for samples $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$ ($x=0,10,14,18$).

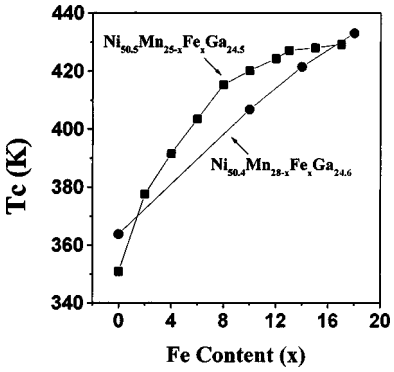

FIG. 6. Curie temperature (T_C) for the different samples as a function of Fe doping level.

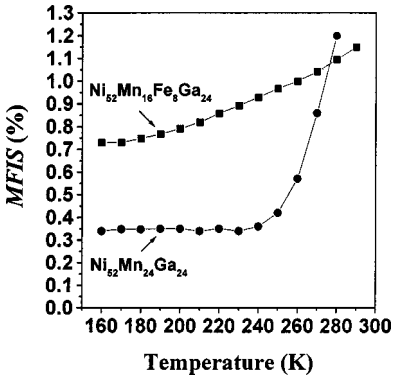

FIG. 8. The magnetic-field-induced strain in [001] direction of single crystal $Ni_{52}Mn_{16}Fe_8Ga_{24}$ and $Ni_{52}Mn_{24}Ga_{24}$ as a function of temperature.

C. Magnetic properties

Figure 6 shows the T_C as a function of the doping level listed in Table I. T_C increases with the increase of the content of Fe. In the $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ system, the T_C increases rather quickly at low doping level, and then becomes slow at high doping level. But in the $Ni_{50.4}Mn_{28-x}Fe_xGa_{24.6}$ system, the variation of T_C shows a near linear increase. These results clearly indicate that the exchange interaction of the systems is enhanced by doping iron. Enhanced exchange interaction results in an improvement of the magnetization at 300 K, as shown in Table I. One can see that, in two systems of $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ and $Ni_{50.4}Mn_{28-x}Fe_xGa_{21.6}$, the involvement of iron increases the magnetization in the almost all single phase ranges, and showing peak values at $x=8$ and $x=10$, respectively. The existence of the peak values indicates a competition between the increasing T_C and the decreasing content of Mn that has a larger moment than that of Fe. The magnetization measurement also indicates that the technical saturation is independent to the content of Fe, and showing the same achievement of about 2 kOe at 300 K.

Figure 7 shows the magnetic moment as a function of the doping composition in the $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ system. The moments for formula unit are calculated from the M-H curves measured at 4 K in the field up to 5 T, then extrapolating to 0 K. The result shows that the moments of $\mu_B/f.u.$ decreases monotonously with the increases of the content of iron. The kink of the curve reveals that the second phase appeared in samples as the content of iron being larger than $x=17$.

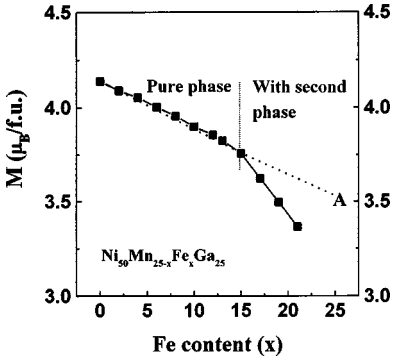

FIG. 7. Magnetic moment as a function of Fe doped level x in $Ni_{50.5}Mn_{25-x}Fe_xGa_{24.5}$ system measured at 4 K in the field up to 5 T.

In ternary alloy Ni_2MnGa, it has been confirmed by neutron scattering that the ferromagnetism mainly originates from the localized moment of Mn atoms, M_{Mn}, about 4.0 μ_B per Mn ion and the moment of Ni, M_{Ni}, is neglectable.[14] Recently, Brown *et al.*'s study shows that the magnetization of Ni and Mn will be redistributed with the variation of temperature. At martensite state, the Ni moment is 0.22 μ_B.[15] Buschow reported an lower value of $M_{Ni}=0.065\,\mu_B$ in the Heusler alloy of Ni_2CrAl. [16] The linear part of the moment curve in the range of $x=0-15$, as shown in Fig. 7, clearly indicates a substitution relation for Fe gradually replacing Mn in the compound. Fitting the experimental data linearly, the dot line A in Fig. 7 stands the substituting effect based on a fixed $M_{Mn}=4.13\,\mu_B$ (the value in Ni_2MnGa) and a zero M_{Ni} (based on the results from Ref. 15). Analyzing the slope of line A in Fig. 7, one can confirm that: (1) the iron atoms contribute a ferromagnetism to the material, but (2) the moment of Fe is less than that of Mn. Extrapolating the linear part of the measured data to $x=25$, however, the obtained Fe moment, $M_{Fe}=3.55\,\mu_B$ seems to be too big to be comparable to the value measured in other Heusler alloys with iron. Usually, iron has a quite consistent value about $M_{Fe}=2.5\,\mu_B$ in Co_2FeAl and Fe_2CoAl. [15] Although a clear magnetic structure cannot be completed confirmed only based on the experimental results at present time, earlier analysis indicates an interesting point: how to magnetically couple each other for three kinds of ferromagnetic atoms in this quaternary alloy. It has never been investigated in detail for ternary Heusler alloys. Further work will focus on the specific ferromagnetic structure related to three magnetic atoms including their atomic sites by means of neutron scattering and/or Mossbauer spectrum examinations.

D. Temperature dependence of MFIS

Figure 8 shows the MFIS in [001] direction of single crystal $Ni_{52}Mn_{16}Fe_8Ga_{24}$ and $Ni_{52}Mn_{24}Ga_{24}$ as a function of temperature. The MFIS was detected by applying a magnetic field of up to 1.5 T along the [001] direction then back to zero and the value was measured at a temperature interval of 10 K after the sample was cooled down to the martensite

finish temperature. For doped $Ni_{52}Mn_{16}Fe_8Ga_{24}$ single crystalline sample, the largest MFIS is 1.15% at T = 290 K. Decreasing the temperature to 170 K, the value of MFIS dropped to 0.75%, keeping a large MFIS in a quite large temperature interval of 120 K. On the other hand, for the undoped $Ni_{52}Mn_{24}Ga_{24}$ single crystal, the similar value of MFIS is 1.2% at 280 K, but dropped dramatically to 0.35%, about 70% decreasing in a very small temperature interval only 40 K. For all samples at all temperatures, however, the saturated magnetic fields for MFIS are the same at about 0.8 T. These results reveal that Fe substitution for Mn improves the temperature dependence of MFIS.

From Table I, one can see that the existence of Fe enhances the exchange interaction in this quaternary material. This results in an increase of the Curie temperature from 350 K for the undoped sample to 420 K for the doped sample. The improvement of magnetic property enables the actuator to work at a higher temperature.

IV. SUMMARY

We have found the quaternary alloys of Ni_2(Mn, Fe)Ga are a pure Heusler alloy phase and also possess thermoelastic martensitic transformation effect. The higher Curie temperature and magnetization can be attributed to an enhanced magnetic coupling due to the involvement of Fe. The discussion about the magnetic structure in this quaternary Heusler alloys confirmed that: (1) iron atoms contributed the ferromagnetism to the material and (2) Fe shows a lesser moment than that of Mn. A better temperature dependence of MFIS has been found in the doped $Ni_{52}Mn_{16}Fe_8Ga_{24}$ samples. These results imply that the quaternary alloys are candidate materials for actuators.

ACKNOWLEDGMENTS

The authors thank Professor Z. H. Cheng for the helpful discussions and comments on this manuscript. This work is supported by National Natural Science Foundation of China by Grant No. 50131010.

[1] K. Ullakko, J. K. Huang, C. Kantner, R. C. O'Handley, and V. V. Kokorin, Appl. Phys. Lett. **69**, 1966 (1996).
[2] R. D. James and M. Wuttig, Philos. Mag. A **77**, 1273 (1998).
[3] G. H. Wu *et al.*, Appl. Phys. Lett. **75**, 2990 (1999).
[4] R. Tickle, R. D. James, T. Shield, M. Wutting, and V. V. Kokorin, IEEE Trans. Magn. **35**, 4301 (1999).
[5] S. J. Murray, M. Marioni, S. M. Allen, and R. C. O'Handley, Appl. Phys. Lett. **77**, 886 (2000).
[6] O. Heczko, N. Glavatska, V. Gavriljuk, and K. Ullako, Mater. Sci. Forum **373-376**, 341 (2001).
[7] A. Fujita, K. Fukamichi, F. Gejima, R. Kainuma, and K. Isshida, Appl. Phys. Lett. **77**, 3054 (2001).
[8] M. Wuttig, J. Li, and C. Craciunescu, Scr. Mater. **44**, 2393 (2001).
[9] K. Oikawa *et al.*, Appl. Phys. Lett. **79**, 3290 (2001).
[10] B. Wedel, M. Suzuki, Y. Murakami, C. Wedel, T. Suzuki, D. Shindo, and K. Itagaki, J. Alloys Compd. **137**, 290 (1999).
[11] W. H. Wang, G.H. Wu, J.L. Chen, S.X. Gao, W.S. Zhan, G.H. Wen, and X.X. Zhang, Appl. Phys. Lett. **79**, 1148 (2001).
[12] V. A. Chernenko, Scr. Mater. **40**, 523 (1999).
[13] W.-H. Wang, J.-L. Chen, Z.-H. Liu, G.-H. Wu, and W.-S. Zhan, Phys. Rev. B **65**, 12416 (2002).
[14] P. J. Webster, K. R. A. Ziebeck, S. L. Town, and M. S. Peak, Philos. Mag. B **49**, 295 (1984).
[15] P. J. Brown, A. Y. Bargawi, J. Crangle, K.-U. Neumann, and K. R. A. Ziebeck, J. Phys.: Condens. Matter **11**, 4715 (1999).
[16] K. H. J. Buschow and P. G. van Engen, J. Magn. Magn. Mater. **25**, 90 (1981).