

# Composition anisotropy compensation and spontaneous magnetostriction in $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$ alloys

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The possibility of the composition anisotropy compensating in  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$  is discussed phenomenologically, based on a single ion approach. The crystal structure, the easy magnetization direction, and the spontaneous magnetostriction of  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  ( $0 \leq x \leq 0.7$ ) alloys are studied. Single-phase  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  with cubic  $\text{MgCu}_2$ -type structure forms up to  $x=0.4$  and the magnetostrictive phase exists in all the alloys studied. A single (440) peak of  $x$ -ray diffraction of the Laves phase exists when  $0 \leq x \leq 0.3$ , but becomes doubly split when  $0.4 \leq x \leq 0.7$  because of a large spontaneous magnetostriction along its easy magnetization direction  $\langle 111 \rangle$ . Composition anisotropy compensation is realized in  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys.  $\text{Tb}_{0.2}\text{Dy}_{0.4}\text{Pr}_{0.4}(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloy with the single Laves phase has a large magnetostriction ( $\lambda_{111} \approx 1200$  ppm) and a low anisotropy, which may be a good candidate material for magnetostriction application. © 2003 American Institute of Physics. [DOI: 10.1063/1.1569651]

The discovery of the well-known magnetostrictive compound  $\text{Tb}_{0.27}\text{Dy}_{0.73}\text{Fe}_2$  (Terfenol-D)<sup>1</sup> was based on the Clark's proposal of alloying  $\text{RFe}_2$  compounds with the same magnetostriction sign but with the opposite signs of their anisotropy constants  $K_1$ .<sup>2</sup> Since then, pseudobinary systems of magnetostrictive compounds  $\text{R}_{1-x}\text{R}'_x\text{Fe}_2$  ( $\text{R}, \text{R}' = \text{rare earths}$ ) have been intensively investigated in order to find a novel compound having a high magnetostriction at low fields.<sup>3</sup> For this purpose, it is important to find a magnetostrictive system with composition anisotropy compensation. Since the anisotropy constants  $K_1$  of  $\text{PrFe}_2$  and  $\text{DyFe}_2$  have the same sign,  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$  used to be considered as a non-compensating system according to the Clark's lowest order theory.<sup>2</sup> In this letter, we propose that in some systems, like  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$  and its based compounds, the effects of the anisotropy constants  $K_2$  must be taken into account and we succeeded in achieving the composition anisotropy compensating in a  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  system. The composition anisotropy compensation in  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$  systems is first predicted phenomenologically by a single-ion approach and then realized experimentally by synthesizing the multi-component compounds  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$ .

The easy magnetization direction (EMD) of  $\text{DyFe}_2$  lies along  $\langle 100 \rangle$ ,<sup>4</sup> while that of  $\text{PrFe}_2$  lies along  $\langle 111 \rangle$  at room temperature, as proved by its Mössbauer spectrum.<sup>5</sup> Based on these experimental results, the anisotropy compensation should be achievable in the pseudobinary  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$  system. When both  $K_1$  and  $K_2$  are taken into account, the anisotropy compensating is attained in  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$ , as indicated by the following calculation.

According to the single-ion approach, the magnetocrystalline energy of  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$  at room temperature  $E_a(\text{Dy}_{1-x}\text{Pr}_x)$  can be phenomenologically expressed by<sup>6</sup>

$$\begin{aligned} E_a(\text{Dy}_{1-x}\text{Pr}_x) &= (1-x) \cdot E_a(\text{Dy}) + x \cdot E_a(\text{Pr}) \\ &= (1-x) \cdot [K_1(\text{Dy})(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_1^2\alpha_3^2) \\ &\quad + K_2(\text{Dy})\alpha_1^2\alpha_2^2\alpha_3^2] + x \cdot [K_1(\text{Pr})(\alpha_1^2\alpha_2^2 \\ &\quad + \alpha_2^2\alpha_3^2 + \alpha_1^2\alpha_3^2) + K_2(\text{Pr})\alpha_1^2\alpha_2^2\alpha_3^2], \quad (1) \end{aligned}$$

where  $E_a(\text{R})$  indicates the anisotropy energy of  $\text{RFe}_2$ ,  $K_1(\text{R})$ , and  $K_2(\text{R})$  are the anisotropy constants of  $\text{RFe}_2$ , and  $\alpha_i$  is the direction cosines of the direction of magnetization with respect to the cubic axes. At room temperature, only  $K_1$  and  $K_2$  are taken into account is acceptable<sup>6</sup>

$$\begin{aligned} E_a(\text{Dy}_{1-x}\text{Pr}_x) &= [(1-x) \cdot K_1(\text{Dy}) + x \cdot K_1(\text{Pr})](\alpha_1^2\alpha_2^2 \\ &\quad + \alpha_2^2\alpha_3^2 + \alpha_1^2\alpha_3^2) + [(1-x) \cdot K_2(\text{Dy}) \\ &\quad + x \cdot K_2(\text{Pr})](\alpha_1^2\alpha_2^2\alpha_3^2), \quad (2) \end{aligned}$$

hence,

$$K_1(\text{Dy}_{1-x}\text{Pr}_x) = (1-x) \cdot K_1(\text{Dy}) + x \cdot K_1(\text{Pr}), \quad (3a)$$

$$K_2(\text{Dy}_{1-x}\text{Pr}_x) = (1-x) \cdot K_2(\text{Dy}) + x \cdot K_2(\text{Pr}), \quad (3b)$$

because  $K_1(\text{Pr}) > 0$  and  $K_1(\text{Dy}) > 0$ ,  $K_1(\text{Dy}_{1-x}\text{Pr}_x) > 0$ . If the EMD of a compound  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$  lies along  $\langle 111 \rangle$ , one needs<sup>7</sup>

$$\frac{K_2(\text{Dy}_{1-x}\text{Pr}_x)}{K_1(\text{Dy}_{1-x}\text{Pr}_x)} < -9. \quad (4)$$

Then one gets the condition for the composition anisotropy compensation

$$\begin{aligned} 9K_1(\text{Dy}) + K_2(\text{Dy}) &= x \cdot [(9K_1(\text{Dy}) + K_2(\text{Dy})) \\ &\quad - (9K_1(\text{Pr}) + K_2(\text{Pr}))]. \quad (5) \end{aligned}$$

It was found that at room temperature, the EMD of  $\text{PrFe}_2$  lies along  $\langle 111 \rangle$ ,<sup>5</sup> while that of  $\text{DyFe}_2$  lies along  $\langle 100 \rangle$ ,<sup>4</sup> and thus one has

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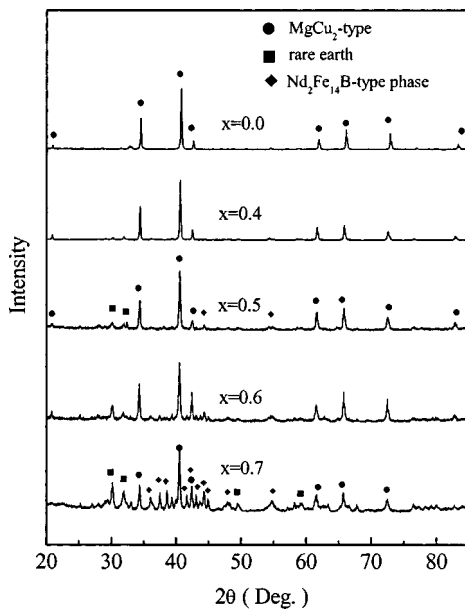


FIG. 1. XRD patterns of homogenized  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys.

$$9K_1(\text{Pr}) + K_2(\text{Pr}) < 0, \quad (6a)$$

$$9K_1(\text{Dy}) + K_2(\text{Dy}) > 0, \quad (6b)$$

from which one shows that

$$0 < x < 1. \quad (7)$$

This means the composition anisotropy compensating can be reached in  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$ , depending upon the ratios of  $K_1$  to  $K_2$ . But the anisotropy of  $\text{PrFe}_2$  is so small that the compensating point must be at the range of high Pr content. Unfortunately,  $\text{PrFe}_2$  cannot be synthesized at ambient pressure.<sup>8</sup> In this letter, a certain amount of Tb is introduced to compensate the partial anisotropy of Dy, and a small amount of B is used to stabilize Pr in  $\text{RFe}_2$ .

All polycrystalline samples of  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x \times (\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  with  $x = 0, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60,$  and  $0.70$  were prepared by arc melting the appropriate constituent metals in a high purity argon atmosphere. The purity of the constituents was 99.9% (Tb, Dy, and Pr), 99.8% (Fe), and 99.5% (B). The ingots were homogenized at  $700^\circ\text{C}$  for seven days in an argon atmosphere. X-ray diffraction (XRD) data were recorded at room temperature with  $\text{Cu } K\alpha$  radiation in a Rigaku D/max-2500pc diffractometer with a graphite monochromator. In order to investigate peak splitting induced by the spontaneous magnetostriction, a high-precision step scanning was performed for (440) peaks of XRD. The magnetostriction coefficient  $\lambda_{111}$  was determined after the effect of the  $K\alpha_2$  radiation was removed with a standard method.<sup>9</sup>

XRD patterns of homogenized samples of  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys are shown in Fig. 1. It is seen that the  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys with  $0 \leq x \leq 0.4$  are essentially single cubic Laves phases with a  $\text{MgCu}_2$ -type structure. When  $x = 0.5$ , the alloy consists predominantly of the cubic Laves phase in which a small amount of excess rare earth Pr, Dy, and  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type phase present. The amount of the cubic Laves phase decreases, while that of rare earth and  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type phase increase

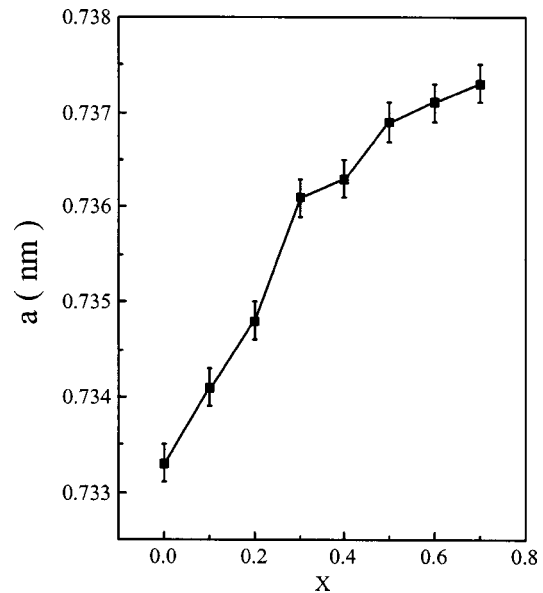


FIG. 2. Pr composition dependence of lattice parameter  $a$  of the cubic Laves phase in  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys.

with increasing nominal Pr content, when  $0.5 \leq x \leq 0.7$ . The  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type and cubic Laves phases coexist, together with a small amount of excess rare earth when  $x = 0.7$ . When  $x = 0.8$ , the Cubic Laves phase disappears. This rule has been found also in similar systems of alloys  $\text{Tb}_{1-x}\text{Pr}_x\text{Fe}_{1.93}\text{B}_{0.15}$ ,  $\text{Dy}_{1-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$ , and  $\text{Tb}_{0.15}\text{Dy}_{0.85-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  when  $x = 0.8$ .<sup>10</sup> No traces of the  $\text{PuNi}_3$ -type phase is found in all the alloys studied because of the introduction of boron.<sup>11</sup> The Pr composition dependence of the lattice parameter  $a$ , for  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  Laves phase, is shown in Fig. 2. The lattice parameter increases with increasing  $x$ , due to the bigger radii of the  $\text{Pr}^{3+}$  ion. The increase in the lattice parameter becomes less pronounced when  $0.5 \leq x \leq 0.7$  indicating that Pr content in Laves phase is lower than its nominal composition of the corresponding alloy because of the appearance of other Pr-containing phases according to the phase equilibrium conditions. But it is noticed that the lattice parameter still increases up to  $x = 0.7$ . This suggests a Pr solubility limit in the range of  $0.5 \leq x \leq 0.7$  in the multicomponent Laves phase.

Some alloys in powder form were step scanned with  $\text{Cu } K\alpha$  radiation at the (440) line of  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x \times (\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  cubic Laves phase, in order to study their EMD and spontaneous magnetostriction. XRD spectra after deduction of  $K\alpha_2$  with a standard method for the alloys are shown in Fig. 3. The EMD of Laves phase can be determined by the method of Dwight and Kimball.<sup>12,13</sup> In Fig. 3 the (440) line of the Laves phase is a single peak for the  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys with  $0 \leq x \leq 0.3$ . This means that the EMD lies along  $\langle 100 \rangle$  axes. Only a tiny crystal structure distortion originating from magnetostriction is realized ( $\lambda_{100} \approx 0$ ) and XRD splittings are not observed. Nevertheless, the double splitted (440) lines of the Laves phase are clearly observed in the alloys with  $0.4 \leq x \leq 0.7$ . This indicates the EMD lies along  $\langle 111 \rangle$  axes and a large rhombohedral distortion occurs due to magnetostriction, contributing to a large splitting of the (440) XRD line. In the  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys, the Tb content keeps in-

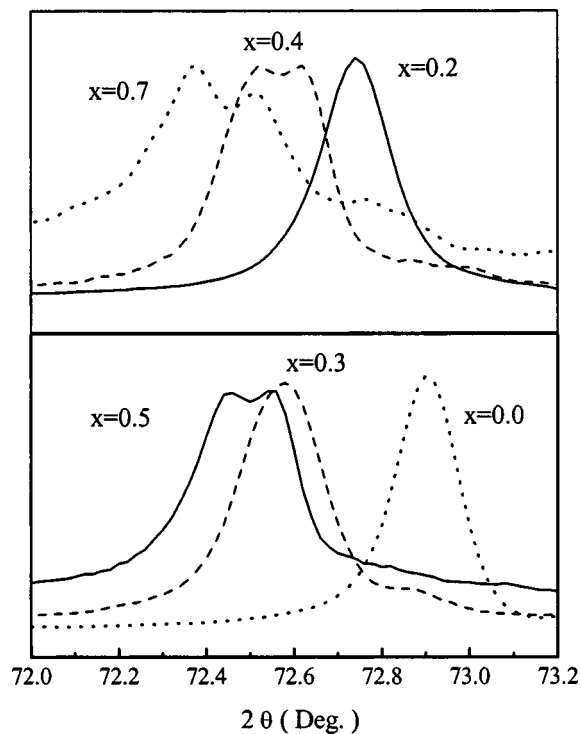


FIG. 3. Profiles of the (440) line of the cubic Laves phase in  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys.

variant. The change of the EMD is determined by the content change between Pr and Dy. This indicates that the anisotropy of  $\text{PrFe}_2$  and  $\text{DyFe}_2$  can compensate with each other, in correspondence with the theoretical analysis earlier. The anisotropy compensation point must be in the range of  $0.3 \leq x \leq 0.4$ . The magnetostriction coefficient  $\lambda_{111}$  of the Laves phase which the EMD lies along  $\langle 111 \rangle$  can be calculated from the double split distance of the (440) lines.<sup>11,14</sup> As plotted in Fig. 4,  $\lambda_{111}$  monotonically increases from about 1200 ppm with  $x=0.4$  to about 1800 ppm with  $x=0.7$ . According to the discussion of the lattice parameter earlier, the Pr content in Laves phase still increases (although it is lower than its nominal composition) in this composition range. We conclude that the  $\lambda_{111}$  of  $\text{Pr}(\text{Fe,B})_2$  Laves phase is larger than that of the  $\text{Dy}(\text{Fe,B})_2$  Laves phase. According to single-ion model, the magnetostriction  $\lambda_{111}$  is determined by the anisotropy of the rare earth ion, thus  $\text{PrFe}_2$  should have a larger  $\lambda_{111}$  than  $\text{DyFe}_2$ . The  $\lambda_{111}$  of  $\text{DyFe}_2$  is 1260 ppm as extrapolated by Clark *et al.* from  $\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$  compounds.<sup>15</sup> Attention should be paid to the  $\text{Tb}_{0.2}\text{Dy}_{0.4}\text{Pr}_{0.4}(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloy that has a large magnetostriction ( $\lambda_{111} \approx 1200$  ppm) and a low anisotropy because it is very near the composition compensating point in the  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  series. Furthermore, the Laves phase is essentially single phase in the alloy containing 40 at. % light rare earth Pr, which is cheaper than the heavy rare earth Dy or Tb.

In conclusion, the composition anisotropy compensation in  $\text{Dy}_{1-x}\text{Pr}_x\text{Fe}_2$  systems is first proved phenomenologically by a single-ion approach and then realized experimentally by synthesizing the multicomponent compounds

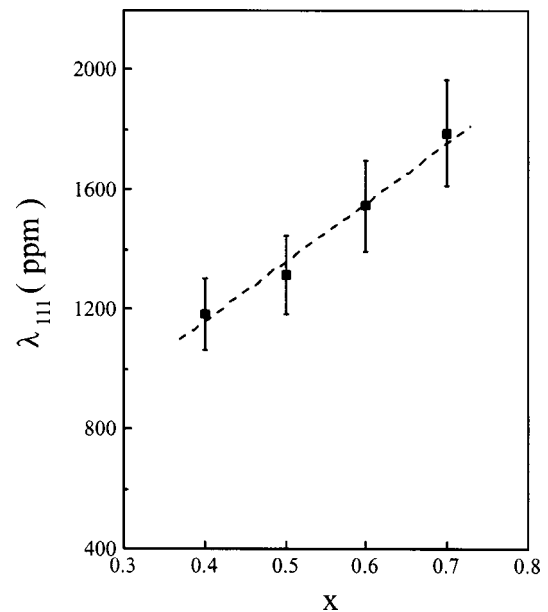


FIG. 4. Concentration dependence of the magnetostriction coefficient  $\lambda_{111}$  of the Laves phases in  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys.

$\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$ . The single  $\text{Tb}_{0.2}\text{Dy}_{0.4}\text{Pr}_{0.4} \times (\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  Laves phase synthesized by melting and consequently annealing has large magnetostriction and low anisotropy. It may be a good practical magnetostriction material also because a large amount of cheap Pr can be used for replacement of expensive Dy or Tb. It has been predicted from the results of  $\text{Tb}_{0.2}\text{Dy}_{0.8-x}\text{Pr}_x(\text{Fe}_{0.9}\text{B}_{0.1})_{1.93}$  alloys that  $\lambda_{111}$  of  $\text{PrFe}_2$  should be larger than that of  $\text{DyFe}_2$ .

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- <sup>1</sup>A. E. Clark, AIP Conf. Proc. **10**, 1015 (1974).
- <sup>2</sup>A. E. Clark, H. Belson, and N. Tamagawa, Phys. Lett. A **42**, 160 (1972).
- <sup>3</sup>A. E. Clark, R. Abbundi, O. McMasters, and H. Savage, Physica B **86-88**, 73 (1977).
- <sup>4</sup>U. Atzmony, M. P. Dariel, E. R. Bauminger, D. Lebenbaum, I. Nowik, and S. Ofer, Phys. Rev. B **7**, 4220 (1973).
- <sup>5</sup>M. Shimotomai, H. Miyake, and M. Doyama, J. Phys. F: Met. Phys. **10**, 707 (1980).
- <sup>6</sup>U. Atzmony and M. P. Dariel, Phys. Rev. B **13**, 4006 (1976).
- <sup>7</sup>G. Bertotti, *Hysteresis in Magnetism*, (Academic, London, 1998), Chap. 5, p. 129.
- <sup>8</sup>M. Shimotomai, H. Miyake, and M. Doyama, J. Phys. F: Met. Phys. **10**, 707 (1980).
- <sup>9</sup>Z. J. Guo, B. W. Wang, Z. D. Zhang, X. G. Zhao, X. M. Jin, W. Liu, and Q. F. Xiao, Appl. Phys. Lett. **71**, 2836 (1997).
- <sup>10</sup>W. J. Ren, Z. D. Zhang, X. G. Zhao, C. Y. You, and D. Y. Geng, J. Alloys Compd. (in press).
- <sup>11</sup>W. J. Ren, Z. D. Zhang, A. S. Markosyan, X. G. Zhao, X. P. Song, and X. M. Jin, J. Phys. D **34**, 3024 (2001).
- <sup>12</sup>A. Dwight and C. Kimball, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **30**, 2791 (1974).
- <sup>13</sup>A. E. Clark, J. R. Cullen, and K. Sato, AIP Conf. Proc. **24**, 670 (1975).
- <sup>14</sup>E. Gratz, A. Lindbaum, A. S. Markosyan, H. Mueller, and A. Yu Sokolov, J. Phys.: Condens. Matter **4**, 6699 (1994).
- <sup>15</sup>A. E. Clark, in *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1980), Vol. 1, p. 531.