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Structure and magnetic properties of $RFe_{6-x}Ga_{6+x}$ (R =rare earth)

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The crystal structures and magnetic properties of $RFe_{6-x}Ga_{6+x}$ (R =Ce, Pr, Nd, Sm, and Gd) alloys have been investigated by x-ray powder diffraction and magnetic measurement. A ternary intermetallic compound with an orthorhombic $ScFe_6Ga_6$ type structure is found in these alloys. The lattice parameter contraction is observed when the higher atomic number lanthanides are substituted into the intermetallic. In each unit cell, there are six nonequivalent crystal positions, i.e., 2a, 4e, 4f, 4g, 4h, and 8k, which are occupied by 2R, 4Ga^I, 4(Fe^I,Ga), 4Ga^{II}, 4Ga^{III}, and 8Fe^{II}, respectively. The $RFe_{6-x}Ga_{6+x}$ alloys have ferromagnetic ordering but the magnetic transitions have been found in Nd based alloy. The $RFe_{6-x}Ga_{6+x}$ alloys show a soft magnetic behavior but the magnetization hysteresis loops have been observed in the Nd and Sm alloys at 5 K. The saturated magnetic moments per molecule tend to increase from Ce to Nd. However, a drastic decrease of magnetic moment in $GdFe_6Ga_6$ alloy is observed and is likely due to the Gd spin alignment being antiparallel to Fe spin. The saturation magnetic moments of these alloys are calculated and agree with the experimental values. © 2002 American Institute of Physics. [DOI: 10.1063/1.1447507]

In recent years, there has been interest in the RT_6M_6 (R =rare earth; T =Fe; M =Ge,Sn) intermetallic compounds due to their various crystal structures depending on the preparation procedure and R size.^{1,2} Most of these intermetallic compounds exhibit antiferromagnetic behavior but recent studies show that the substitution of Ge by Ga in the RMn_6Ge_6 compound induces the antiferromagnetic-ferromagnetic or antiferromagnetic-ferrimagnetic transition.³ The light rare earth RFe_6Ga_6 (R =Ce,Pr,...Sm) intermetallic compounds do not exist but the rich Ga additions could stabilize the $RFe_{6-x}Ga_{6+x}$ compound with a tetragonal $ThMn_{12}$ type structure in the range of $x=0.2-1.2$.⁴ Here we have successfully synthesized a ternary intermetallic compound with an orthorhombic $ScFe_6Ga_6$ type structure in this system. In this article we will report our study on the crystal structure and magnetic properties of the orthorhombic $RFe_{6-x}Ga_{6+x}$ compounds.

The samples of $RFe_{6-x}Ga_{6+x}$ with the nominal composition $x=0-0.7$ were prepared by arc melting in an atmosphere of argon gas. The purity of the starting metal was better than 99.9%. In order to ensure the homogeneity of the samples, the ingots were melted several times. The weight loss of the samples was less than 1% during arc melting. The crystal structures of these samples were determined by a Rigaku automatic x-ray diffractometer with $Cu K\alpha$ radiation and refined by Rietveld's method.⁵ The magnetization measurements were carried out by a commercial superconducting quantum interference device magnetometer at different temperatures and applied magnetic fields.

The powder x-ray diffraction (XRD) patterns show the $RFe_{6-x}Ga_{6+x}$ alloys crystallize in an orthorhombic

$ScFe_6Ga_6$ type structure. There is a small amount of RGa_2 (R =Ce,Pr) and δ -Fe phases in Ce and Pr based alloys, and the unknown impurity phase coexists with the main phase in Nd, Sm, and Gd based alloys as shown in Fig. 1. The lattice parameters are $a=8.715(7)-8.667(3)$ Å, $b=8.724(1)-8.598(9)$ Å, and $c=5.101(6)-5.066(3)$ Å. The lattice parameters contraction is observed when the higher atomic number lanthanides are substituted into the intermetallic. According to the structural refinement results, the space group is $Immm$ with $z=2$. There are six nonequivalent crystal positions in one unit cell, i.e., 2a: (0,0,0), 4e: (x,0,0), 4f: (x,1/2,0), 4g: (0,y,0), 4h: (0,y,1/2), and 8k: (1/4,1/4,1/4) which are occupied by 2R, 4Ga^I, 4(Fe^I,Ga), 4Ga^{II}, 4Ga^{III}, and 8Fe^{II}, respectively. This orthorhombic structure could be regarded as a structural order from the $ThMn_{12}$ type

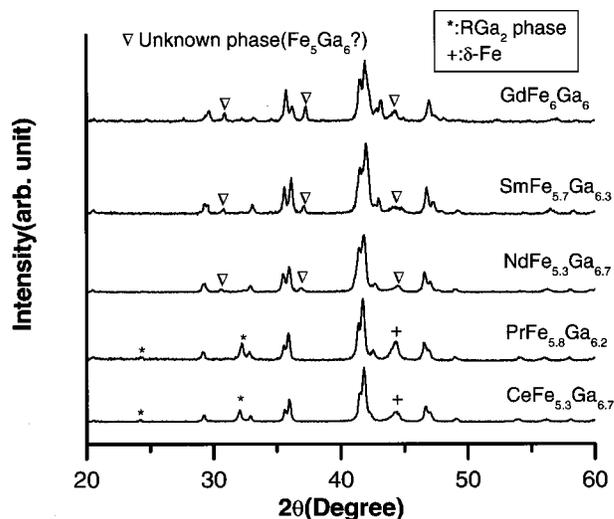
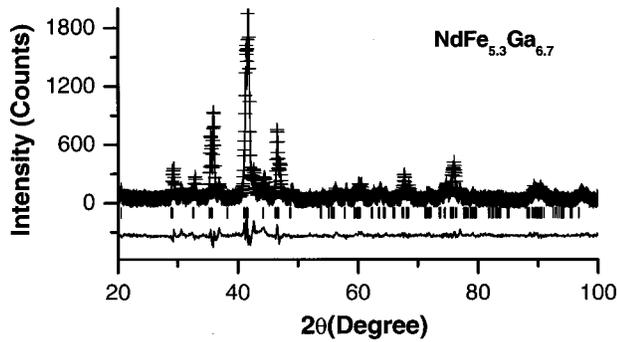


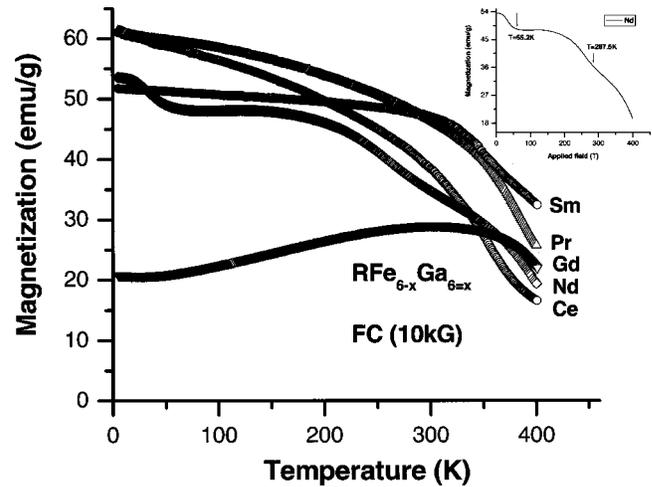
FIG. 1. Powder XRD patterns of $RFe_{6-x}Ga_{6+x}$ alloys.

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FIG. 2. Refined XRD pattern of NdFe_{5.3}Ga_{6.7} alloy.

structure. It can be described as the atomic occupation ordering at 8i and 8j sites in tetragonal ThMn₁₂. The atomic occupation order transfer from 8i and 8j sites in tetragonal structure to (4e,4f) and (4g,4h) sites in the orthorhombic structure, respectively. The refined XRD pattern of NdFe_{5.3}Ga_{6.7} is taken as a typical example, and the experimental and calculated XRD patterns have been compared in Fig. 2, they are marked with “+” points and solid line, respectively. The lowest trace indicates the difference between these two patterns, and the peak positions of the orthorhombic structure is denoted by the middle vertical lines. Table I exhibits the refined structural parameters which include the ionic occupations, coordination number, and the nearest Fe–Fe and R–Fe bond lengths as well as neighbors.

Figure 3 shows the temperature dependent magnetization measured by field cooling in a applied field of 10 kG. The RFe_{6-x}Ga_{6+x} alloys are ferromagnetic, but the exact T_C values are not obtained due to the limitation of the measurement temperature range (5–400 K). Two magnetic transitions have been found in Nd alloys at 55.8 and 288.5 K as shown in the inset plot in Fig. 3. The applied field dependent magnetization is shown in Fig. 4. Some RFe_{6-x}Ga_{6+x} alloys show a

FIG. 3. The temperature dependence of magnetization of RFe_{6-x}Ga_{6+x} alloys with an applied field of 10 kG.

soft magnetic behavior but the magnetization hysteresis loops have been observed in Nd and Sm alloys at 5 K. The inset plot in Fig. 4 shows there are two field dependent magnetic transitions at 0.09 and 0.83 T in Nd based alloy. The saturation magnetization value M_s per molecule are obtained from the magnetic isotherms by extrapolating the $M(1/B)$ curves to $1/B=0$.⁶ The saturated magnetic moment per molecule tends to increase from Ce to Nd. However, a drastic decrease of saturation happens in GdFe₆Ga₆ alloy, which is most likely due to the Gd spin alignment being antiparallel to Fe spin. The average saturation magnetic moment per atom $\langle Z_m \rangle$ has been calculated by the following equation:

$$\langle Z_m \rangle = x_{\text{Fe}} Z_m^{\text{Fe}} + x_{\text{R}} Z_m^{\text{R}} + x_{\text{Ga}} Z_m^{\text{Ga}}, \quad (1)$$

where x_i ($i=\text{Fe}, \text{R}, \text{Ga}$) corresponds to the atomic fraction of Fe, rare earth, and Ga, and Z_m^i ($i=\text{Fe}, \text{R}, \text{Ga}$) is the saturation

TABLE I. List of structural refinement parameters and magnetic properties parameters of the RFe_{6-x}Ga_{6+x} intermetallic compounds.

R	Ce	Pr	Nd	Sm	Gd
x	0.7	0.2	0.7	0.3	0
$a(\text{\AA})$	8.703(6)	8.715(7)	8.698(7)	8.654(6)	8.667(3)
$b(\text{\AA})$	8.708(6)	8.724(1)	8.686(1)	8.639(4)	8.598(9)
$c(\text{\AA})$	5.092(3)	5.101(6)	5.099(1)	5.088(6)	5.066(3)
$v(\text{\AA}^3)$	385.9(7)	387.9(1)	385.2(8)	380.4(5)	377.5(9)
Fe ^I	$x, 0.2910(1)$	0.2905(2)	0.2946(9)	0.2954(8)	0.2722(9)
Ga ^I	$x, 0.3454(1)$	0.3396(1)	0.3423(0)	0.3324(4)	0.3477(7)
Ga ^{II}	$y, 0.3437(8)$	0.3575(3)	0.3444(5)	0.3593(3)	0.3860(6)
Ga ^{III}	$y, 0.7646(4)$	0.7610(1)	0.7615(5)	0.7621(1)	0.7528(0)
R_p (%)	9.9	9.5	8.8	8.7	8.9
R_{wp} (%)	14.6	14.1	11.5	11.4	11.7
s	1.5	1.4	1.2	1.2	1.3
Atom–atom BL (\AA) and NN					
Fe ^I –Fe ^{II} (\AA)	2.547,4	2.556,4	2.543,4	2.541,4	2.503,4
$\langle \text{Fe}^{\text{II}} - (\text{Fe}^{\text{I}}, \text{Fe}^{\text{II}}) \rangle$	2.546,4	2.551,4	2.547,4	2.544,4	2.518,4
$\langle \text{R} - (\text{Fe}^{\text{I}}, \text{Fe}^{\text{II}}) \rangle$	3.230,8	3.226,8	3.231,8	3.205,8	3.258,8
M_s / atom (μ_B)	0.83(1)	1.00(9)	1.00(8)	0.85(3)	0.34(6)
Calculation (μ_B)	0.98	1.14	1.07	0.93	0.38

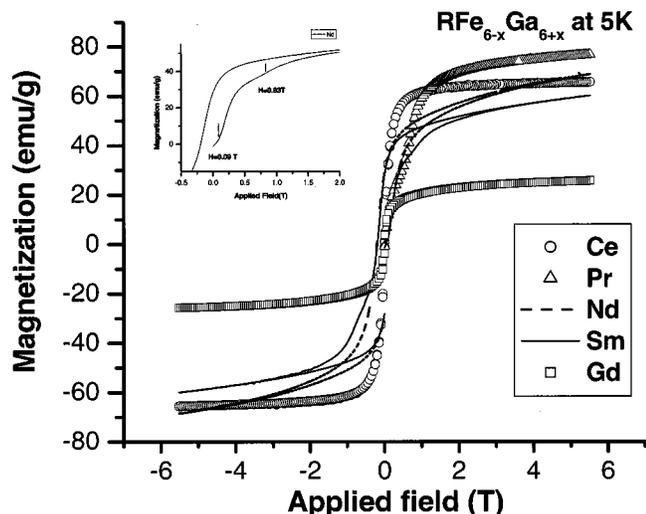


FIG. 4. The applied field dependence of magnetization of $R\text{Fe}_{6-x}\text{Ga}_{6+x}$ alloys at 5 K.

magnetic moment of Fe, R, and Ga. Since Ga is nonmagnetic element, Z_m^{Ga} is zero. Z_m^{R} is calculated by gJ (where J is the total angular momentum and g is Landé factor which corresponds to the spectroscopic state designation).⁷ This value is positive for the rare earth element from Ce to Sm but is negative for Gd due to Gd spin alignment being antiparallel to that of Fe in Gd based alloy. Z_m^{Fe} is defined by magnetic valence model.⁸ $Z_m^{\text{Fe}} = 2N_d\uparrow - Z^{\text{Fe}}$, where Z^{Fe} is electronic valence of Fe constitutions, $N_d\uparrow$ is the number of electrons in the spin-up $3d$ band and is taken to be 5 for the late $3d$ elements (Fe, Co, Ni, Cu, and Zn). Both of the experimental and calculated saturation magnetic moment per atom values are listed in Table I.

In conclusion, a ternary intermetallic compound

$R\text{Fe}_{6-x}\text{Ga}_{6+x}$ with an orthorhombic ScFe_6Ga_6 type structure has been prepared. The lattice parameters and unit cell volumes tend to decrease due to the radii contraction in the lanthanum group. In each unit cell, there are six kinds of nonequivalent crystal positions, i.e., 2a, 4e, 4f, 4g, 4h, and 8k which are occupied by 2R, 4Ga^I, 4(Fe^I,Ga), 4Ga^{II}, 4Ga^{III}, and 8Fe^{II}, respectively. The $R\text{Fe}_{6-x}\text{Ga}_{6+x}$ alloys exhibit ferromagnetic order but the magnetic transitions have been found in Nd and Sm based alloys. These alloys show a soft magnetic behavior but the magnetization hysteresis loops have been observed in the Nd and Sm alloys at 5 K. The saturation magnetic moments per molecule tend to increase from Ce to Sm. However, a drastically decrease of magnetization happens in GdFe_6Ga_6 , which is most likely due to the Gd spin alignment being antiparallel to Fe spin. The calculated saturation magnetic moments of these alloys agree with the experimental values.

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