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Structure and magnetic properties of $ErFe_{11-x}Ga_xTi$

Y P Shen†‡, X Y Yin‡, N Tang‡, J L Wang‡, D Yang‡, W H Wang‡, G H Wu‡, F M Yang‡ and X P Zhong†

† Institute of Materials Science, Guangxi University, Nanning 530004, People's Republic of China

‡ State Key Laboratory of Magnetism, Institute Of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

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Abstract. $ErFe_{11-x}Ga_xTi$ compounds with $ThMn_{12}$-type structure were synthesized for $x = 0$, 1, 2, 3, 4, 5. The crystalline structure and Ga occupancy in the compounds were analysed in terms of the Rietveld method. With increasing Ga content, the lattice constant and unit-cell volume increase monotonically. Ti atoms are found to occupy 8i sites for all the compounds. Bond length and Ga occupancy factor are given. The Curie temperature increases first, going through a maximum and then decreases with increasing x while saturation magnetization decreases monotonically. Spin re-orientation from the uniaxial to the easy-cone type is detected for all the compounds as the temperature decreases from 300 to 5 K. A tentative spin phase diagram is constructed for the $ErFe_{11-x}Ga_xTi$. In the $ErFe_{11-x}Ga_xTi$ compounds, a magneto-history effect is observed which can be attributed to irreversible movement of narrow domain walls that are easily pinned.

1. Introduction

Since Coey and Sun [1] found that introduction of nitrogen can clearly enhance the magnetic properties of some rare-earth (R) transitional-metal (T) intermetallic compounds, much emphasis has been placed on the interstitial compounds. However, low stability of the interstitial compounds becomes the fatal barrier in application. Research on the parent phase is very important to understand the magnetic properties of the interstitial compounds. Also, many parent phases themselves possess a good possibility to be developed as excellent permanent magnetic materials. Many groups have investigated Ga substitution effects on magnetic properties of R_2Fe_{17} compounds [2, 3], but only a little attention has been placed on the $ThMn_{12}$-type structure [4]. In the compounds with the $ThMn_{12}$ type of structure, there exist three non-equivalent T sites and one rare-earth site. The Mössbauer results of Hu *et al* indicated that in the Fe-based $ThMn_{12}$ type of compounds the atoms of the three different T sites carry different magnetic moments and contribute differently to the magnetocrystalline anisotropy [5]. In the present paper, Ga substitution effects on structure and magnetic properties of the $ErFe_{11}Ti$ compound are reported.

2. Experiment

$ErFe_{11-x}Ga_xTi$ compounds were synthesized by arc melting the constituent elements with purity >99.9%. An additional amount of Er was added to compensate the loss during arc melting. Then the ingots were annealed in Ar atmosphere at 1160–1320 K for 48 hours.

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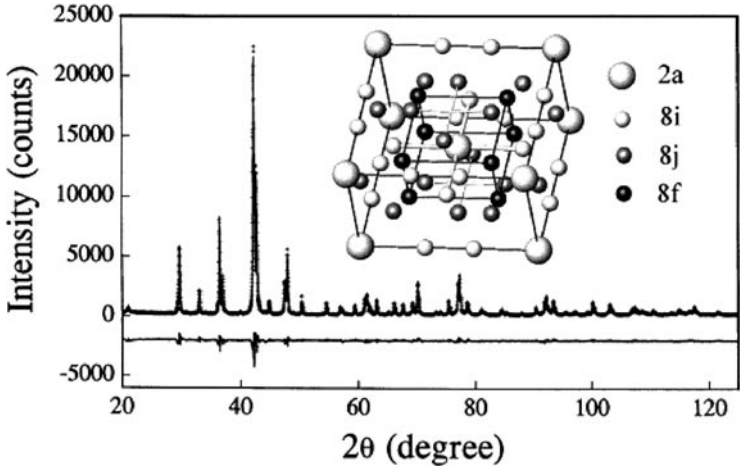

Figure 1. Rietveld analysis of the XRD pattern of the $ErFe_8Ga_3Ti$ compound. The observed data are indicated by crosses and the calculated profile is indicated by the continuous line overlaying them. The lower curve is the difference between the observed and calculated intensity at each step ($0.02^\circ/2$ s). The inset figure is a representation of the $ThMn_{12}$ structure.

Table 1. Atomic position and the lattice parameters of the $ErFe_8Ga_3Ti$ compound obtained from the powder x-ray diffraction pattern refinement according to the $I4/mmm$ space group. $Z = 2$, $a = 8.5788(1)$ Å, $b = 8.5788(1)$ Å, $c = 4.8667(1)$ Å, $R_p = 7.42\%$, $R_{wp} = 9.75\%$, $R_{exp} = 4.53\%$.

Site	Atoms	x/a	y/b	z/c	Ga occupancy factor
2a	Er	0.0000	0.0000	0.0000	0.000
8i	Fe/Ti/Ga	0.3546(2)	0.0000	0.0000	0.168(7)
8j	Fe/Ga	0.2797(2)	0.5000	0.0000	0.367(7)
8f	Fe/Ga	0.2500	0.2500	0.2500	0.215(7)

X-ray diffraction (XRD) patterns and thermomagnetic curves were employed to judge the phase homogeneity. The thermo-magnetic curves were measured by using a SQUID from 4 to 300 K and by a vibrating sample magnetometer (VSM) above 300 K. The values of Curie temperature T_C were derived from the M^2–T curves and by extrapolating M^2 to zero. The isotherms were measured using a SQUID at 5 K in magnetic fields up to 6 T. The saturation magnetizations were derived from M–$(1/H)$ curves and by extrapolating $1/H$ to zero. Magnetically aligned powder samples were prepared at room temperature for magnetic anisotropy measurements. Magnetic anisotropy fields at room temperature were measured by the SPD method [6].

3. Results and discussion

X-ray diffraction pattern and thermomagnetic analyses show that all the compounds investigated are single phase with $ThMn_{12}$-type structure. The crystalline structure and Ga occupation of the compounds were analysed by the Rietveld method [7, 8]. As an example, figure 1 shows the refinement pattern of the $ErFe_8Ga_3Ti$ compound using the refinement program of DBWS-9411 [9]. The analysis results are listed in table 1. The $ErFe_{11-x}Ga_xTi$

Table 2. Lattice parameters, cell volumes, atom positions, Ga occupancy factors and bond lengths of $ErFe_{11-x}Ga_xTi$ compounds. The Ti atom occupies the 8i site in all compounds. The data are calculated from the raw x-ray pattern according to space group $I4/mmm$ by the program DBWS-9411 [9].

		$x = 0$	$x = 1$	$x = 2$	$x = 3$	$x = 4$	$x = 5$
a (Å)		8.5071(28)	8.5323(9)	8.5542(1)	8.5788(1)	8.5990(32)	8.6237(1)
c (Å)		4.7623(28)	4.7970(9)	4.8326(1)	4.8667(1)	4.9076(32)	4.9400(1)
V (Å^3)		344.65(23)	349.22(8)	353.62(1)	358.17(1)	361.65(27)	367.38(1)
x/a	8i	0.3635(7)	0.3606(4)	0.3576(2)	0.3546(2)	0.3513(9)	0.3489(2)
	8j	0.2746(7)	0.2765(4)	0.2781(2)	0.2797(2)	0.2817(9)	0.2833(2)
Ga	8i	—	0.11(4)	0.13(1)	0.17(1)	0.38(4)	0.46(1)
occupancy	8j	—	0.14(4)	0.30(1)	0.37(1)	0.39(4)	0.45(1)
factor	8f	—	0.00(4)	0.07(1)	0.22(1)	0.23(4)	0.34(1)
Bond	8i-8i	2.3229	2.3788	2.4362	2.4947	2.5554	2.6061
length (Å)	8j–8j	2.7123	2.6969	2.6726	2.6727	2.6527	2.6428
	8f–8f	2.3819	2.3989	2.4163	2.4334	2.4538	2.4700
	8i–8j	2.6560	2.6689	2.6807	2.6923	2.7069	2.7204
	8i–8f	2.6222	2.6228	2.6230	2.6240	2.6225	2.6269
	8j–8f	2.4469	2.4576	2.4680	2.4789	2.4888	2.5012
	2a–8i	3.0930	3.0767	3.0590	3.0420	3.0186	3.0088
	2a–8j	3.0581	3.0645	3.0727	3.0811	3.0886	3.0973
	2a–8f	3.2355	3.2463	3.2567	3.2680	3.2763	3.2896
	Error	0.0006	0.0002	0.0001	0.0001	0.0007	0.0001

compounds were judged to be of the $ThMn_{12}$-type structure for $x = 0, 1, 2, 3, 4$ and 5. Table 2 lists the lattice parameters a, c and unit-cell volume V, atom position, Ga occupancy factor and bond length of $ErFe_{11-x}Ga_xTi$ compounds as a function of Ga content. The refinement indicates that Ti atoms occupy 8i sites in all the compounds. Figures 2 and 3 show the concentration dependence of the crystalline parameters a, c, bond lengths between the different sites and Ga occupancy factor at the different sites in the $ErFe_{11-x}Ga_xTi$ compounds, respectively. The lattice constants a, c and the unit-cell volume V increase monotonically with increasing Ga content. This may result from the larger radius of Ga than Fe. In fact, $ThMn_{12}$-type RT_{12} compounds do not exist for any rare earth R. This structure can be stabilized by a third element M. Most of the third elements M (M = Ti, V, Cr, Mo, Si, Ni, Nb) occupy the 8i site except M = Si, and all the compounds $RT_{12-x}M_x$ have a narrow range of x [10]. This implies that the 8i sites of $ThMn_{12}$ type have a significant role in the structure stability in most of this type of compound. In our case, it can be seen from figure 2 that the bond lengths of 8i–8i and 8i–8j increase much faster than those of the others with increasing Ga content x, which implies that the magnetic properties of the compound against the Ga content should be more sensitive to the 8i site compared with the others. It can be seen from figure 3 that the Ga occupancy factor at the 8i site increases slowly until $x = 3$ and then rapidly after $x > 3$. The Ga occupancy factor reaches 0.46 at $x = 5$ and the corresponding Fe occupation factor falls to 0.29.

Magnetic parameters of $ErFe_{11-x}Ga_xTi$ compounds are listed in table 3. The Ga content dependence of Curie temperature is shown in figure 4. It can be seen that the Curie temperature increases at first, going through a maximum at about $x = 2$, and then decreases with further increasing x. It is well known that in the R–T compounds, Curie temperature is mainly determined by the T–T exchange interaction. It is well accepted that, in the $ThMn_{12}$-type R–T compounds, there exist three non-equivalent T sites. The distances between the nearest

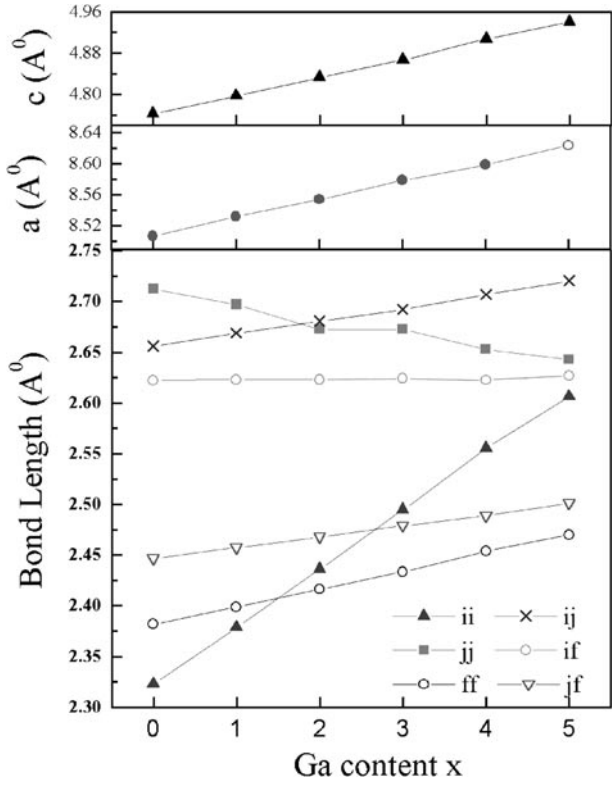

Figure 2. Ga content dependence of cell parameters a, c and bond length between different sites in $ErFe_{11-x}Ga_xTi$ compounds.

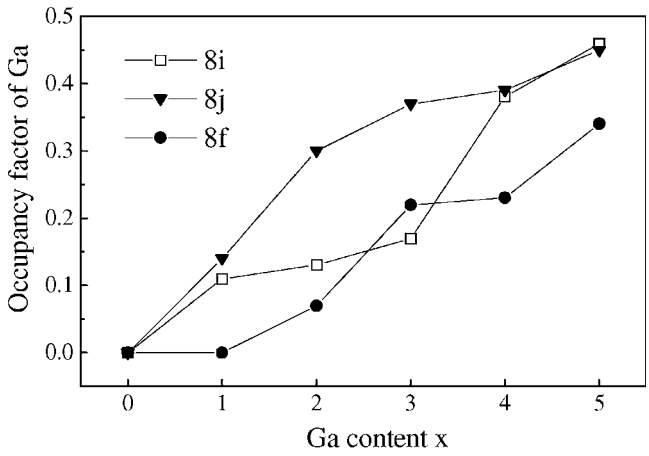

Figure 3. Ga content dependence of Ga occupancy factor at different site in $ErFe_{11-x}Ga_xTi$ compounds.

neighbour Fe atoms at the different sites are different. The previous investigations have shown that the Fe–Fe exchange interaction is sensitive to the Fe–Fe bond length. According to the theory of Givord and Lemaire [11], there are two types of exchange interaction in the R–Fe

Table 3. Magnetic parameters of $ErFe_{11-x}Ga_xTi$ compounds including Curie temperature T_C, spin re-orientation temperature T_{sr}, magnetic anisotropy field B_a, observed saturation magnetization M_s^{Exp} and the calculated saturation magnetization M_s^{Cal} according to a simple dilute model.

				M_s (μ_B fu^{-1})	
x	T_C (K)	T_{sr} (K)	B_a (T) (300 K)	Experiment (5 K)	Calculated (5 K)
0	505	37	2.4	10.92	10.25
1	515	25	2.2	9.75	8.54
2	521	70	2.0	6.39	6.90
3	474	120	2.0	4.81	5.06
4	381	103	2.0	3.78	3.23
5	357	95	—	3.23	1.44

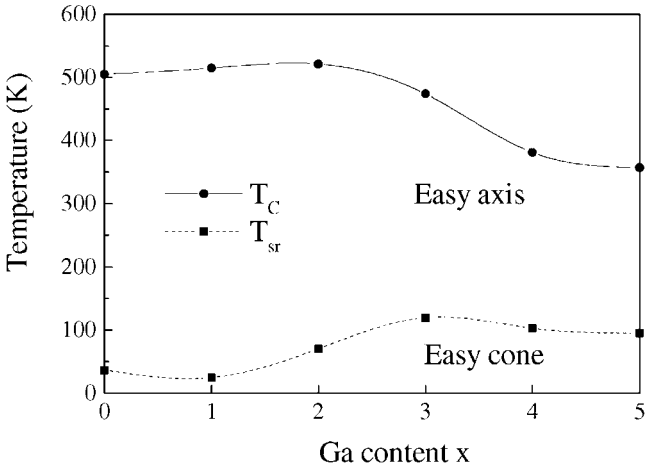

Figure 4. Magnetic phase diagram of $ErFe_{11-x}Ga_xTi$ compounds with x ranging from 0 to 5.

compounds and they have positive and negative sign, respectively. When the distance of the Fe–Fe pair is smaller than a certain value, the electron clouds of Fe atoms overlap too much and the exchange interaction is negative, whereas the interaction is positive for larger Fe–Fe distances [12]. Therefore, the initial increase of T_C may be associated with the elongation of the bond length between the Fe atoms having small distances, which gives rise to an increase of J_{FeFe}. The decrease of T_C with further increasing Ga content may result from the decrease of the number and moment of iron atoms due to the Ga substitution as shown later.

Figure 5 shows the Ga content dependence of saturation magnetization at 5 K. It can be seen that the saturation magnetization M_s decreases monotonically with increasing Ga content. Since the Er and Fe magnetic moments are arranged anti-parallel and one takes the direction of Fe atomic magnetic moments as the positive direction, and using the Ga concentration dependence of Ga occupation factor in the different sites, the total saturation magnetization per formula unit of the $ErFe_{11-x}Ga_xTi$ compound can be written as:

$$\mu_{tot} = 4\mu_{8i}(0.75 - c_{8i}) + 4\mu_{8j}(1 - c_{8j}) + 4\mu_{8f}(1 - c_{8f}) - \mu_{Er} \tag{1}$$

where μ_{8i}, μ_{8j} and μ_{8f} are the iron moments at the 8i, 8j and 8f sites respectively, and c_{8i}, c_{8j} and c_{8f} are the Ga occupation factors in the 8i, 8j, 8f sites, respectively. Taking the value of $\mu_{Er} = 9\mu_B$, the same as for the free Er atom, $\mu_{8i} = 1.95\mu_B$, $\mu_{8j} = 1.52\mu_B$,

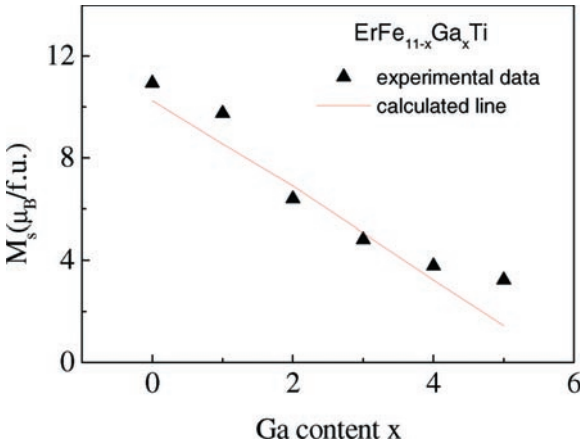

Figure 5. Ga content dependence of saturation magnetization M_s of $ErFe_{11-x}Ga_xTi$ compounds. The dashed line is the trend according to the simple dilute model.

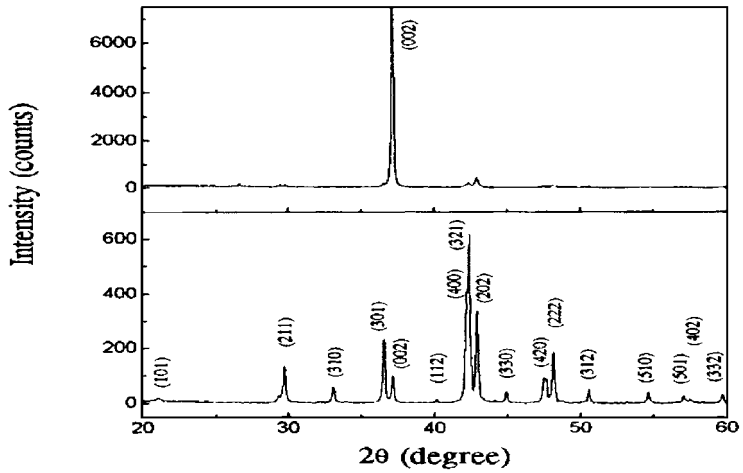

Figure 6. XRD patterns of the magnetically aligned powder (up) and random powder (down) of $ErFe_9Ga_2Ti$ compounds.

$\mu_{8f} = 1.83\mu_B$ [13]. The calculated saturation magnetization as a function of Ga content is shown in figure 5 as a dashed line. The Ga concentration dependence of the calculated saturation magnetization is in agreement with the experimental results. This indicates that the Ga content dependence of the saturation magnetization of $ErFe_{11-x}Ga_xTi$ compounds can be understood by a simple dilution model.

As an example, the XRD patterns of magnetically aligned and random powders of $ErFe_9Ga_2Ti$ compounds at room temperature are shown in figure 6. It has been seen that, compared with the XRD pattern of the random aligned powders, in the XRD pattern of the magnetically aligned powders the (002) peak is enhanced and the other peaks have disappeared. This suggests that the easy magnetization direction of the $ErFe_9Ga_2Ti$ compounds is along the *c* axis. It has been found that the easy magnetization directions of all compounds are along the *c* axis at room temperature and that the magnetocrystalline anisotropy field has a decreasing tendency with increasing Ga content.

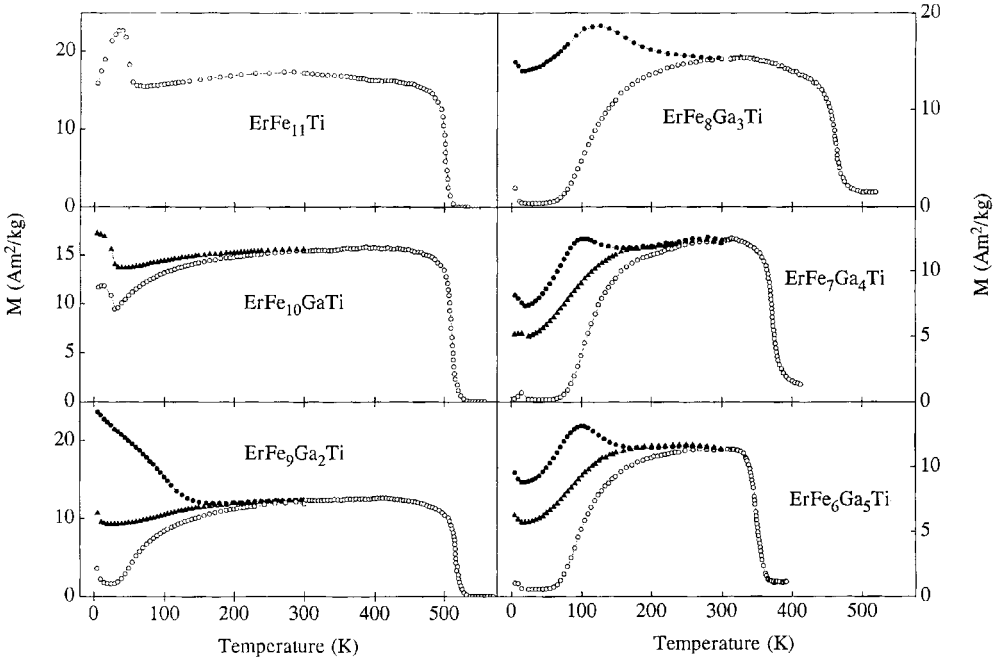

Figure 7. Thermomagnetic curves of $ErFe_{11-x}Ga_xTi$ compounds in the field $B = 0.05$ T for $x = 0, 1, 2, 3, 4, 5$. The open circles present zero field cooling (ZFC) from 300 to 5 K. The solid up triangles present field cooling (FC) with $B = 5$ T from 300 to 5 K. The solid circles present FC with $B = 0.05$ T from 300 to 5 K.

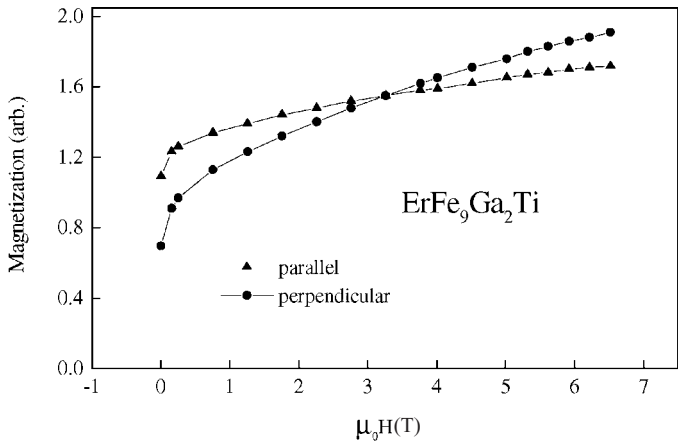

Figure 8. Isotherms of the $ErFe_9Ga_2Ti$ compound at 5 K with field either parallel or perpendicular to the alignment direction.

The thermomagnetic curves measured at $B = 0.05$ T with zero field cooling (ZFC) and field cooling (FC) are shown in figure 7. After the sample was cooled in the field of $B = 5$ T, thermomagnetic curves with $x = 2, 3, 4, 5$ show anomalies at low temperature. These anomalies can be understood as spin reorientation. The corresponding temperatures T_{sr} derived from the peaks in the thermomagnetic curves are listed in table 3 (the values of T_{sr}

of $ErFe_{11}Ti$ and $ErFe_{10}GaTi$ were obtained from the anomalies of the ZFC thermomagnetic curves). In order to make the type of magnetic anisotropy below T_{sr} clear, the magnetization curves of magnetically aligned powder samples were measured at 5 K with the field either parallel or perpendicular to the alignment direction of the powder samples. It has been found that the two curves measured on two samples intersect. As an example, figure 8 shows the magnetization curves of $ErFe_9Ga_2Ti$, which imply that the magnetic anisotropy of the compounds is of an easy-cone type at temperatures below T_{sr}. Therefore, the spin reorientation at low temperature indicates a spin phase transition from uniaxial to cone-type anisotropy with decreasing temperature. By using the values of T_C and T_{sr} a tentative spin phase diagram is constructed for the $ErFe_{11-x}Ga_xTi$ compounds.

It can also be seen from figure 7 that below a certain critical temperature T_f the thermomagnetic curve is irreversible; the ZFC curve deviates strongly from the FC curve. This means that there is a magnetohistory effect [14] in the $ErFe_{11-x}Ga_xTi$ compounds. Christides *et al* [15] considered the magnetohistory effects as resulting from a spin glass. We prefer to propose that magnetohistory effect is attributable to the irreversible movement of narrow domain walls that are easily pinned. The propagation of the narrow Bloch walls needs thermal activation. The energy required for the latter becomes available when the temperature is increased from 5 K to T_f.

4. Conclusion

$ErFe_{11-x}Ga_xTi$ compounds are synthesized and crystallize in $ThMn_{12}$-type structure for $x = 0, 1, 2, 3, 4, 5$. Rietveld method analysis shows that, with increasing Ga content x, the lattice constants and the unit-cell volume V increase linearly. Ti atoms are found to occupy 8i sites in all the compounds investigated. The bond lengths and Ga occupancy factors are given. With increasing Ga content, Curie temperature increases initially, going through a maximum and then decreases, while saturation magnetization decreases, as indicated by a simple dilution model. Magnetic phase transition from easy-axis type to easy-cone type is found for all the compounds investigated with decreasing temperature. A tentative spin phase diagram is constructed for the $ErFe_{11-x}Ga_xTi$ compounds. In the $ErFe_{11-x}Ga_xTi$ compound with $x = 2, 3, 4$ and 5 a magnetohistory effect was observed, which can be attributed to irreversible movement of narrow domain walls that are easily pinned.

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