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Neutron diffraction study of $Er_2Fe_{15}Al_2$ and $Er_2Fe_{12}Al_5$

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Abstract The crystallographic and magnetic structures of $Er_2Fe_{15}Al_2$ and $Er_2Fe_{12}Al_5$ have been refined in Gaussian peak-shape by Rietveld analysis of Neutron diffraction data. The refined results indicated that $Er_2Fe_{15}Al_2$ compound has Th_2Ni_{17}-type hexagonal structure (space group: $P6_3/mmc$) and $Er_2Fe_{12}Al_5$ has Th_2Zn_{17}-type rhombohedral structure (space group:$R\,\bar{3}m$). The Al atoms prefer 12j and 12k sites with occupancies 0.21 and 0.13, respectively, in $Er_2Fe_{15}Al_2$ and prefer 18f, 18h and 6c sites with occupancies 0.35, 0.36 and 0.37, respectively, in $Er_2Fe_{12}Al_5$. The magnetic moments of all Fe atoms display ferromagnetically arrangement and the moments of Er atoms couple ferrimagnetically to the moments of the Fe atoms. The moments lie in the plane perpendicular to the six-fold axis and exhibit planar magnetic anisotropy in both samples. The values of Tc were given and the neutron refined results coincide with that of the magnetic measurements. The relation between magnetic properties and structures was discussed.

Keywords Neutron diffraction, Crystallographic structure, Magnetic structure

CLC numbers O571.56, $O766^{+}.4$, O482.5

1 Introduction

In recent years, many studies focus on interstitial $R_2Fe_{17}N_x$ compounds (R=Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu and Y) for improving the magnetic properties.[1] An important common feature by nitrogenation is the increased iron-iron bond length as compared to their parent binary phase material. In the study of the effect of nitrogenation on crystallographic and magnetic structures by neutron diffraction data, Yan *et al*[2,3] reported that the nitrogen atoms occupy 9e, 18g sites of Th_2Zn_{17}-type rhombohedral structure in $Nd_2Fe_{17}N_{4.5}$ and occupy 6h, 12j sites of Th_2Ni_{17}-type hexagonal structure in $Er_2Fe_{17}N_{4.5}$, respectively. However, the interstitial compounds prepared by solid-gas reaction are only stable at temperature below ~600°C. They will decompose into a mixture of Fe and RX above the decomposition temperature. Fortunately, $R_2Fe_{17}C_y$ carbides can be alternatives to 2:17 nitrides because they are stable up to their melting points. Yan *et al.*[4] studied the structure of $R_2Fe_{17-x}Ga_xC_2$. Recently, the substitution of various elements, e.g. Ga, Al, Si and so on, for Fe in rare-earth iron intermetallic

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R_2Fe_{17} compounds has been investigated extensively. Compared with interstitial compounds, substitution compounds may also be prepared for expansion of lattice volume and increase of iron-iron bond length which had been proved by Yelon *et al*[5] in studying neutron diffraction data and Mössbauer effect of $Nd_2Fe_{17-x}Al_x$ series. Therefore, the iron-iron exchange coupling may change significantly with the increase of cell volume because the exchange interaction of Fe-Fe sublattice is sensitive to Fe-Fe interatomic distance. The crystallographic and magnetic structures of $Er_2Fe_{17-x}Al_x$ (x=2 and 5) were studied by Rietveld Method based on neutron diffraction data in this paper. The Curie temperatures Tc of both samples were given, and the relation between magnetic properties and structures was discussed.

2 Experimental details and results

Samples of $Er_2Fe_{17-x}Al_x$ (x=2 and 5) were prepared by arc melting high-purity starting materials Er(99.9%), Fe(99.9%) and Al(99.9%) in an argon arc furnace and were annealed in a quartz tube under an argon atmosphere at 1150°C for 24 h. The X-ray diffraction indicated that the samples were pure Th_2Ni_{17}-type (space group $P6_3/mmc$) and Th_2Zn_{17}-type (space group $R\,\overline{3}\,m$) structure for $Er_2Fe_{15}Al_2$ and $Er_2Fe_{12}Al_5$, respectively.

Powder neutron diffraction was carried out on a neutron triple-axis spectrometer at CIAE. The samples were filled in a vanadium can. The incident neutron wavelength was 0.1541 nm. The neutron diffraction data were collected by step scanning at 0.1° intervals with the range 10~90°. The triple-axis spectrometer was used as a two-axis powder spectrometer to improve the resolution. The neutron diffraction patterns of $Er_2Fe_{17-x}Al_x$ (x= 2 and 5) were analyzed in Gaussian peak-shape by Rietveld structure refinement program FULLPROF and RIETAN for x=2 and x=5 respectively. The parameters of crystallographic structure of Th_2Zn_{17}-type and Th_2Ni_{17}-type compounds were used to start the refinement for $Er_2Fe_{12}Al_5$ and $Er_2Fe_{15}Al_2$. The neutron diffraction data were refined in five steps: (1) Zero point, scale factor and background parameters. (2) Half-width parameters. (3) Cell parameters a, b and c. (4) Atomic coordinates. (5) Other parameters, such as site occupancies, temperature factors and magnetic moments. At the initial stage of refinement, the atomic magnetic moments of Er and Fe were fixed to the value 2.32×10^{-23} A·m^2 and 1.85×10^{-23}A·m^2, respectively. Overall isotropic thermal parameter $Q = 5 \times 10^{-3}\mathrm{nm}^2$, and each atomic isotropic thermal B was given. It was assumed that all Fe atoms have the same thermal parameter and magnetic moment, so that linear constraints were used. After that, all parameters were refined and variable parameters were updated again and again. Finally, a satisfactory result was given.

The crystallographic and magnetic parameters after refinement are listed in Table 1. The rather large value of R_{wp} (10.8% of $x = 2$ and 8.7% of $x = 5$) is caused by the large value of R_{expected} (5.8% of x=2 and 5.3% of x=5). The final observed and calculated diffraction patterns are shown in Fig.1. The values of magnetic order temperature, i.e. Curie temperature Tc, were derived from the temperature dependence of magnetization M-T curves measured by a vibrating sample magnetometer in a low external field of 7.958×10^4A/m, and also listed in Table 1.

Table 1 Crystallographic and magnetic parameters of $Er_2Fe_{15}Al_2$ and $Er_2Fe_{12}Al_5$

$Er_2Fe_{15}Al_2$:		$P6_3/mmc$,	$a=b=0.8520(3)$ nm,		$c=0.8336(2)$ nm,	$T_c=396$ K,
$U=3.0785(deg)^2$,		$V=1.2233(deg)^2$,	$W=0.3229(deg)^2$,		$S=3.063\times10^{-3}$,	$Z=0.0238(deg)$
Atom site	n	x	y	z	$B/10^{-2}$ nm^2	$M/10^{-23}$ A·m^2
Er(2b)	1	0	0	1/4	0.20(5)	-2.51(28)
Er(2d)	1	1/3	2/3	3/4	0.20(5)	-2.51(28)
Fe(12k)	0.87	0.165(1)	0.330(1)	0.983(1)	0.31(4)	1.22(27)
Fe(12j)	0.79	0.330(1)	-0.041(1)	1/4	0.31(4)	1.22(27)
Fe(6g)	1	0.5	0	0	0.31(4)	1.22(27)
Fe(4f)	1	1/3	2/3	0.104(1)	0.31(4)	1.22(27)
Al(12k)	0.13	0.165(1)	0.330(1)	0.983(1)	1.20(8)	0
Al(12j)	0.21	0.330(1)	-0.041(1)	1/4	1.20(8)	0
$Er_2Fe_{12}Al_5$:		$R3m$,	$a=b=0.8645(2)$ nm,		$c=1.2648(3)$nm,	$T_c=338$K
$U=3.1620(deg)^2$,		$V=1.3867(deg)^2$,	$W=0.3496(deg)^2$,		$S=1.843\times10^{-2}$,	$Z=0.1581(deg)$
Atom site	n	x	y	z	$B/10^{-2}$ nm^2	$M/10^{-23}$ A·m^2
Er(6c)	1	0	0	0.340(2)	0.88(7)	-1.99(16)
Fe(9d)	1	1/2	0	1/2	0.39(5)	0.81(21)
Fe(18f)	0.65	0.295(1)	0	0	0.39(5)	0.81(21)
Fe(18h)	0.64	0.502(1)	0.498(1)	0.157(1)	0.39(5)	0.81(21)
Fe(6c)	0.63	0	0	0.097(2)	0.39(5)	0.81(21)
Al(18f)	0.35	0.295(1)	0	0	0.96(6)	0
Al(18h)	0.36	0.502(1)	0.498(1)	0.157(1)	0.96(6)	0
Al(6c)	0.37	0	0	0.097(2)	0.96(6)	0

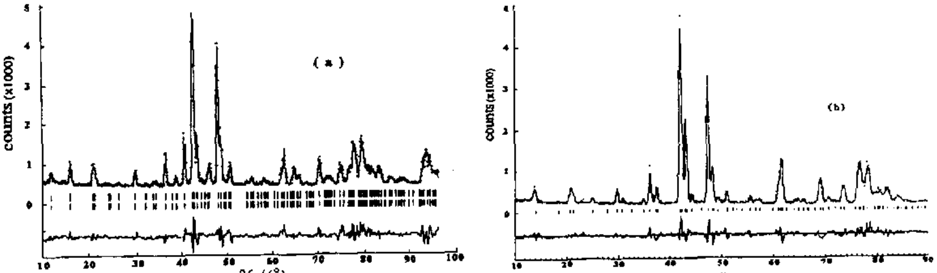

Fig.1 Neutron powder diffraction patterns for (a) $Er_2Fe_{15}Al_2$ and (b) $Er_2Fe_{12}Al_5$

3 Discussion

Neutron and X-ray diffraction measurements show that $Er_2Fe_{15}Al_2$ compound has Th_2Ni_{17}-type hexagonal structure (space group: $P6_3/mmc$) and $Er_2Fe_{12}Al_5$ has Th_2Zn_{17}-type rhombohedral structure (space group: $R\,\bar{3}\,m$), which are shown in Table 1. The lattice parameters and cell volumes obtained by Rietveld method and X-ray diffraction data are also coincident with each other very well. The Al atoms prefer 12j and 12k sites with occupancies 0.21 and 0.13, respectively, in $Er_2Fe_{15}Al_2$, to 6g and 4f dumbbell sites. In $Er_2Fe_{12}Al_5$, Al atoms prefer 18f, 18h and 6c sites with occupancies 0.35, 0.36 and 0.37, respectively. Aluminum shows an almost equal preference for these three sites and do not occupy 9d sites, because of relative small Wegner-Seitz cell volume of 9d sites and the much larger atom metallic radius of Al atom than that of Fe atoms. The result, which is consistent with $Nd_2Fe_{17-x}Al_x$ [5] solid solutions, indicates that the occupancy of Al atoms on the dumbbell site increases from $x=2$ to 5.

Because the magnetic contribution to total neutron diffraction intensity is relative weak compared with nuclear contribution, the magnetic moments of both Er and Fe atoms are refined separately with average moments, which are shown in Table 1. The magnetic moments of all Fe atoms display ferromagnetically arrangement and the moments of Er atoms couple ferrimagnetically to the moments of the Fe atoms. The moments lie in the plane perpendicular to the six-fold axis and exhibit planar magnetic anisotropy in both samples. The neutron diffraction refinements show that at room temperature the iron magnetic moments in the $Er_2Fe_{17-x}Al_x$ compound decrease from 1.22×10^{-23} A·m^2 of x=2 to 0.81×10^{-23} A·m^2 of x=5 with increase of Al concentration. This result is similar to other $R_2Fe_{17-x}Al_x$ solid solutions[6].

In Table 1, the Curie temperatures Tc of $Er_2Fe_{15}Al_2$ and $Er_2Fe_{12}Al_5$ are 396 K and 338 K, respectively. The decrease of Tc is consistent with the decrease of Fe atom magnetic moments. The Tc of Er_2Fe_{17} (297 K) is just below room temperature. It indicated that the Tc can increase about 100 K from x=0 (cell parameters $a = b$=0.8455 nm c=0.8270 nm) to 2, even though, when x=2, the value of Tc is not the highest one of the series. After the critical point of x (about 3), the Tc will decrease gradually. For instance, when x=5, Curie temperature Tc decreases to 338 K. This tendency of the change of Tc with x could be explained by the following reason. Firstly, the Al atom radius is much larger than Fe, then the cell volume can be enlarged by substitution and the distances of Fe-Fe bonds will increase. Hence the exchange interaction of Fe sublattice will increase, leading to increase of Tc. Anyway, the magnetization decreases by magnetic dilution while the substitution continue to increase, therefore the Tc will decrease after the critical value of x (about 3 in this series). This decrease of Tc is due not only to the magnetic dilution but also to the decrease of Fe magnetic moments.

However, the volume effect is apparently not the only reason to determine the Tc. Tc also increase about 60 K from Er_2Fe_{17} to $Er_2Fe_{15}Si_2$, reported by Liang *et al*[7], even though its unit cell contracts because of the relatively smaller metallic radius of Si than that of Fe. The fact can be explained as follows: In certain sense, the expansion of the c-axis can be responsible for the increase of Tc, but it is not the only and main reason to the increase of Tc. It seems that the different mixing degrees of the iron 3 d band with the Al or Si valence band mainly responsible for the values of Tc.

The Er-Er exchange coupling is relative weak compared to Er-Fe and Fe-Fe exchange coupling and its contribution to Tc can be neglected. The mean values of the exchange coupling constant, J_{Fe-Fe} and J_{R-Fe}, have been calculated, and J_{Fe-Fe} is near two times to J_{R-Fe}. $J_{R,R}$ is far smaller than J_{R-Fe}, So Fe-Fe exchange interaction plays the most important role for the value of Tc.

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