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Neutron diffraction and magnetic studies of $RFe_{12-x}T_xC_y$ ($R=Y,Er$; $T=V,Ti,Mo$) alloys

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$RFe_{12-x}T_xC_y$ ($R=Y,Er$; $T=V,Ti,Mo$) alloys were prepared by rf induction melting and analyzed using neutron powder diffraction and superconducting quantum interference device (SQUID) measurements. Rietveld analysis of the neutron diffraction data indicates that V, Ti, and Mo atoms all prefer the $8i$ sites. The refined amount of carbon atoms found in the interstitial sites from neutron diffraction data is significantly less than the nominal carbon content. All samples have the easy direction along the c axis. The Er sublattice couples to the Fe sublattice antiferromagnetically. The average Fe site moments range from 1.3 to $2.8 \mu_B$. The anisotropies of the crystal structures are found to relate to both the rare earth atoms and the stabilizing transition metal atoms. The SQUID measurements show that all samples have a Curie temperature near 600 K. © 1996 American Institute of Physics. [S0021-8979(96)32108-5]

INTRODUCTION

It is well accepted that the $RFe_{12-x}T_xC_y$ and $RFe_{12-x}T_xN_y$ (R =rare earths, $T=Ti,V,Mo$) compounds are among the most promising candidates for permanent magnet applications,^{1–8} not only for their excellent magnetic properties, but also for their lower ratio of rare earth to transition metal than those of the 2:17 and 3:29 phases. The nitrogen atoms can only be introduced into the $RFe_{12-x}T_x$ compounds by a gas phase reaction. The carbon atoms can be introduced into the $RFe_{12-x}T_x$ compounds either during melting or by gas phase reaction. Up to the present, better magnetic properties have been observed in nitrides,¹ and thus, the nitrides have attracted much more attention.^{1–8} Because of the technical advantage of the melting method, it is very important to study the carbides prepared by melting. Here we report the results of neutron diffraction and magnetic studies of several carbides ($RFe_{12-x}T_xC_y$ with $R=Y,Er$; $T=V,Ti,Mo$) prepared by rf-induction melting.

EXPERIMENT

Four samples of $RFe_{12-x}T_xC_y$ ($R=Y,Er$; $T=V,Ti,Mo$) were prepared by rf induction melting the constituent elements of purity 99.9%–99.995% in a water-cooled copper boat under flowing argon at the Graduate Center for Materials Research, University of Missouri–Rolla. The ingots were annealed at 980 °C for one week. The ingots were then crushed and ground in an acetone bath. Neutron diffraction data were collected at the University of Missouri Research Reactor using the high resolution linear position sensitive detector diffractometer at room temperature on approximately 2 g samples in about 24 h. The neutron wavelength is 1.4783 Å. The data were measured from 5° to 105° in 2θ . The neutron diffraction powder patterns were analyzed by the Rietveld method using the FULLPROF program for multi-phase refinements including magnetic structure refinements. The superconducting quantum interference device (SQUID) measurements were performed with a Quantum Design MPMS system.

RESULTS AND DISCUSSION

The refinement results of the powder neutron diffraction data are given in Table I. Based on the refinements, all samples were confirmed to have the tetragonal $ThMn_{12}$ -type structure with space group $I4/mmm$. No second phase was recognized for any sample. The two possible sites that can be occupied by interstitial C atoms are the octahedral $2b$ (0 0 1/2) sites, with two rare-earth neighbors and four transition metal neighbors, or the tetrahedral $8h$ ($\sim 1/4 \sim 1/4$ 0) sites, with one rare-earth neighbor and three transition metal neighbors. However, when we refine the C occupancies on those two sites, the C content is found to be much lower than the nominal C content. As shown in Table I, the nominal C content for the Er–V–Fe–C sample is 0.4/formula unit (f.u.), the refined C content on the $2b$ and $8h$ sites is only 0.032/f.u. The nominal C content for the Er–Ti–Fe–C sample is 0.25/f.u., the refined C content on the $2b$ and $8h$ sites is zero. The largest refined C content is obtained for the Y–Mo–Fe–C sample, but the result (0.18/f.u.) is still significantly lower than the nominal value (0.3/f.u.). Because no second phase was observed, this suggests that some or most of the C atoms have possibly been introduced into the structures substitutionally. That is, the C atoms may go into the transition metal sublattice and the doubly substituted compounds form. Because it is not possible to determine the site occupancies of a doubly substituted compound from neutron diffraction data only,⁹ it is difficult to determine which site(s) the C atoms occupy. However, because no second phase was found, we assume that the T/Fe ratio in the samples is the same as nominal (1.5T/10.5Fe). By using this and the assumption that the rare-earth site is fully occupied, it is easy to determine the final net compositions of the samples (see the Appendix), which are given in Table I (where C^s stands for the substitutional carbon and C^i represents the interstitial carbon). They are found to be in good agreement with the nominal compositions. A special case is for the sample with the nominal formula $YFe_{10.5}Mo_{1.5}C_{0.3}$ for which only $8i$ sites were observed to contain substituents. Thus it is clear that

TABLE I. Refinement results for $RFe_{12-x}T_xC_y$ solid solutions.

Parameter	Compound			
	ErFe _{10.5} V _{1.5} C _{0.4} ^a ErFe _{10.17} V _{1.45} C _{0.38} ^b	ErFe ₁₀ TiC _{0.25} ErFe _{10.24} Ti _{1.46} C _{0.30} ^b	YFe _{10.5} V _{1.5} C _{0.4} YFe _{10.33} V _{1.48} C _{0.21} ^b	YFe _{10.5} Mo _{1.5} C _{0.3} YFe _{10.40} Mo _{1.49} C _{0.12} ^b
<i>a</i> (Å)	8.4719(5)	8.5124(7)	8.4948(5)	8.5802(5)
<i>c</i> (Å)	4.7715(3)	4.8028(4)	4.7753(3)	4.8055(3)
<i>c/a</i>	0.5632	0.5642	0.5621	0.5601
<i>V</i> (Å ³)	342.46	348.015	344.59	353.775
<i>x</i> , Fe, 8 <i>i</i>	0.2771(3)	0.2814(4)	0.2756(2)	0.2791(2)
<i>x</i> , Fe, 8 <i>j</i>	0.3564(3)	0.3519(5)	0.3581(3)	0.3585(2)
<i>b</i> _{eff} / <i>b</i> _{Fe} , 8 <i>i</i>	0.61	0.59	0.75	0.89
<i>b</i> _{eff} / <i>b</i> _{Fe} , 8 <i>j</i>	0.88	0.91	0.93	1.00
<i>b</i> _{eff} / <i>b</i> _{Fe} , 8 <i>k</i>	0.90	0.94	0.95	1.00
C%, 2 <i>b</i>	3.2	0.0	4.8	17.6
C%, 8 <i>h</i>	0.0	0.0	0.0	0.0
Interstitial C/f.u.	0.03	0	0.05	0.18
<i>u</i> , R, 2 <i>a</i>	-2.2(2)	-3.4(3)	0	0
<i>u</i> , Fe, 8 <i>i</i>	3.2(2)	1.7(3)	2.8(2)	1.1(2)
<i>u</i> , Fe, 8 <i>j</i>	2.8(2)	1.8(3)	2.3(1)	1.6(1)
<i>u</i> , Fe, 8 <i>k</i>	2.5(1)	1.5(2)	2.2(1)	1.4(1)
<i>R</i> _p (%)	6.18	6.68	5.81	5.59
<i>R</i> _w (%)	8.06	8.98	7.79	7.34
<i>R</i> _m (%)	7.81	9.54	5.62	4.71
χ ²	3.82	5.06	3.09	3.23
<i>T</i> _c (K)	605	590	592	595

^aNominal composition.

^bRefined composition.

any substitutional C atoms in this sample occupy the 8*i* sites as Mo atoms do. For the other three samples, multiple site occupancy by C is possible. In fact, because all samples were prepared in a rare-earth rich environment, it is not unreasonable that C atoms occupy some transition metal sites without affecting the phase mix.

Also given in Table I are the ratios of the effective site scattering length/Fe scattering length (*b*_{eff}/*b*_{Fe}). Fe has the largest scattering length among the elements involved in this study. Thus, the greater the reduction of *b*_{eff}/*b*_{Fe} from 1, the greater the substitution. The biggest reductions of *b*_{eff}/*b*_{Fe} are found for the 8*i* site for all samples, which means the V, Ti, and Mo atoms all show a strong affinity for the 8*i* sites in the transition metal sublattice. This affinity is determined by co-

ordination effects. The 8*i* site has only one rare-earth neighbor and 13 transition metal neighbors, indicating that the substituent atoms V, Ti, and Mo avoid bonding to rare earth atoms. The anisotropy of the crystal structures is found to relate to both the rare-earth atoms and the stabilizing transition metal atoms. The substituted Y-Fe-Mo sample is more anisotropic in crystal structure (*c/a*=0.5601) than the substituted Y-Fe-V sample (*c/a*=0.5621) which is, in turn, more anisotropic than the Er-Fe-V sample (*c/a*=0.5632).

The refinements show that all samples have the easy direction along the *c* axis. The average Fe site moments are 1.36 μ_B for the YFe_{10.5}Mo_{1.5}C_{0.3} sample, 1.67 μ_B for the ErFe₁₁Ti₁C_{0.25} sample, 2.43 μ_B for the YFe_{10.5}V_{1.5}C_{0.4} sample, and 2.83 μ_B for the ErFe_{10.5}V_{1.5}C_{0.3} sample. As expected, the Er sublattice was found to couple to the Fe sublattice antiferromagnetically. The Er site moment is smaller in the Er-V-Fe-C sample than in the Er-Ti-Fe-C sample, indicating the antiferromagnetic interaction between the rare earth sublattice and Fe sublattice is weaker in Er-V-Fe-C than in Er-Ti-Fe-C. The heavy rare-earth-Fe compounds usually have Curie temperatures higher than those of the corresponding light rare-earth-Fe compounds, but the antiferromagnetic exchange between the heavy rare earth sublattice and Fe sublattice is a major deficiency of the heavy rare-earth-Fe compounds. This study suggests that the antiferromagnetic exchange in heavy rare-earth-Fe 1:12 compounds can be reduced by changing the composition of the compound. It is also noted that both V-substituted samples have larger site moments than the Ti and Mo samples do. This suggests that more attention should be paid to V-substituted compounds in the future.

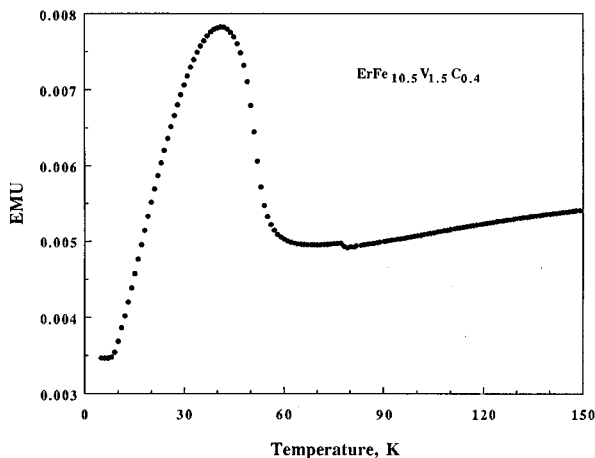


FIG. 1. SQUID magnetization curve for ErFe_{10.5}V_{1.5}C_{0.4}.

It was reported that the easy direction of the $\text{ErFe}_{10}\text{V}_2\text{N}_x$ compound at 10 K is within the ab plane but along the c axis at 300 K.¹ Our SQUID measurement shows that this change of easy direction for $\text{ErFe}_{10.5}\text{V}_{1.5}\text{C}_{0.4}$ happens at around 45 K (Fig. 1). The SQUID measurements also show that all samples have a Curie temperature around 600 K (Table I). The Curie temperatures of the carbides, as expected, are higher than those of the uncarbonated compounds but much lower than those of the corresponding nitrides.¹

CONCLUSIONS

All the V, Ti, and Mo atoms prefer the $8i$ sites. The interstitial carbon atoms were found in the $2b$ sites. However, the refined amount of carbon atoms found in the interstitial sites from neutron diffraction data is significantly less than the nominal carbon content. Calculation of the net scattering amplitudes on each site supports this assumption. All samples have the easy direction along the c axis. The Er sublattice was found to couple to the Fe sublattice antiferromagnetically. The average Fe site moments range from 1.3 to $2.8 \mu_B$. The anisotropy of the crystal structures are found to relate to both the rare-earth atoms and the stabilizing transition metal atoms. All samples have a Curie temperature near 600 K.

APPENDIX: DETERMINATION OF THE SUBSTITUENT CONTENTS IN THE T+C DOUBLE SUBSTITUTED 1:12 PHASE, $\text{RFe}_{12-x-y}\text{T}_x\text{C}_y$

For the T+C doubly substituted 1:12 phase, $\text{RFe}_{12-x-y}\text{T}_x\text{C}_y$, the effective scattering lengths of the three iron sites are

$$b_{\text{eff}1} = x_1 b_{\text{T}} + y_1 b_{\text{C}} + (0.25 - x_1 - y_1) b_{\text{Fe}}, \quad (\text{A1})$$

$$b_{\text{eff}2} = x_2 b_{\text{T}} + y_2 b_{\text{C}} + (0.25 - x_2 - y_2) b_{\text{Fe}}, \quad (\text{A2})$$

$$b_{\text{eff}3} = x_3 b_{\text{T}} + y_3 b_{\text{C}} + (0.25 - x_3 - y_3) b_{\text{Fe}}, \quad (\text{A3})$$

where $b_{\text{eff}1}$, $b_{\text{eff}2}$, and $b_{\text{eff}3}$ are refined effective scattering lengths on the three Fe sites, b_{T} , b_{C} , and b_{Fe} are the scattering lengths of transition metal, carbon, and Fe, respectively,

x_i ($i=1,2,3$) are transition metal site occupancies, and y_i ($i=1,2,3$) are C sites occupancies. Taking Eqs. (A1)+(A2)+(A3) we get

$$b_{\text{eff}} = x b_{\text{T}} + y b_{\text{C}} + (0.75 - x - y), \quad (\text{A4})$$

where b_{eff} is the total effective scattering length of the three Fe sites, x is the total occupancy of transition metal, y is the total occupancy of carbon, and

$$b_{\text{eff}} = b_{\text{eff}1} + b_{\text{eff}2} + b_{\text{eff}3},$$

$$x = x_1 + x_2 + x_3,$$

$$y = y_1 + y_2 + y_3.$$

To determine x and y , we need one more independent equation. Here we assume that the T/Fe ratio in the samples is the nominal one (1.5T/10.5Fe), that is

$$x/(0.75 - x - y) = (W_{\text{T}}/M_{\text{T}})(W_{\text{Fe}}/M_{\text{Fe}}), \quad (\text{A5})$$

where W_{T} and W_{Fe} are the starting weights of transition metals and Fe, M_{T} , and M_{Fe} are the atomic weights of transition metals and Fe, respectively.

By solving the independent Eqs. (A4) and (A5), x and y can be determined.

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