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Studies of V, Nb, Cr, and Zr substituted 2:17 compounds and their carbides using neutron diffraction

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Samples of $\text{Nd}_2\text{Fe}_{17-x}\text{T}_x\text{C}_y$, with $T=\text{V, Nb, Cr, and Zr}$ were prepared by melting of the constituent elements including C and studied by neutron diffraction. Comparing with their uncarbided counterparts, we found that the substituents transfer, more or less, from the $6c$ site to the $18f$ and $18h$ sites with the introduction of C atoms. This behavior appears to relate to the electronegativities between the C atoms and the early transition series elements because the $18f$ and $18h$ sites are near neighbors of the interstitial C site. However, the C effects in the V, Nb, Cr, and Zr samples are not as strong as those in Ti samples. SQUID measurements show that the Curie temperatures of these samples depend on both the interstitial C atoms and the substituents. © 1997 American Institute of Physics. [S0021-8979(97)55108-5]

I. INTRODUCTION

The intrinsic magnetic properties of the rare-earth iron based hard magnetic compounds are controlled predominantly by the Fe-Fe exchange of the Fe sublattices and it is believed that different Fe sites have different contributions. At the same time, different substituent elements for Fe have different site preferences. For low substituent content, the metalloids (Al, Ga, and Si, etc.) strongly prefer the Fe $18h$ site, which has the most rare-earth neighbors.¹⁻⁵ The situation for transition metal substituents is somewhat more complicated⁶—Ti, V, and Cr prefer the Fe $6c$ site, which has the biggest Wigner-Seitz site volume;² Nb and Zr are found on the Fe $6c$ and $18f$ sites; Cu is the only element found to substitute at a significant level on the smallest Fe $9d$ site. This diversity in site preference of the substituents can give different modifications of the Fe-Fe exchange of the four Fe sites and lead to different changes in the magnetic properties of the compounds.

The incorporation of C and N into the rare-earth transition metal compounds leads to a big improvement in their magnetic properties.⁷⁻⁹ This is thought to be a result of lattice expansion which in turn enhances the Fe-Fe positive exchange. The introduction of C atoms from the melt does not induce a change in the site preference of the metalloid substituents.^{10,11} However, an interesting change was observed in the $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x\text{C}_y$,¹² in which case, the site preference of the Ti atoms changes from the Fe $6c$ site to the $18f$ and $18h$ sites after the incorporation of C from the melt. It is necessary to investigate other early transition metal substituted compounds to see the effect of C insertion on the site preference of the substituents and on the magnetic properties. In this paper, we report neutron diffraction structural analysis results of $\text{Nd}_2\text{Fe}_{17-x}\text{T}_x\text{C}_y$ (where $T=\text{V, Nb, Cr, and Zr}$) alloys with comparisons to their uncarbided counterparts. The data for the uncarbided V, Nb, and Zr samples are from Ref. 6.

II. EXPERIMENT

Five of the six $\text{Nd}_2\text{Fe}_{17-x}\text{T}_x\text{C}_y$ samples ($T=\text{V, Nb, Zr}$) were prepared by radio frequency (rf) induction melting of the constituent elements of purity 99.9%~99.95% at the Materials Research Center at the University of Missouri-Rolla. The melted samples were wrapped in tantalum foil and annealed in an argon atmosphere at 950 °C for one week. The carbided and uncarbided Cr samples were synthesized by arc melting in a high purity argon atmosphere at the National Chung Cheng University in Taiwan. They were then homogenized at 1100 °C for 24 h. Neutron diffraction data were collected on approximately 1 g samples at the University of Missouri Research Reactor using the high resolution position-sensitive detector (PSD) diffractometer. The samples were contained in thin wall V cans and were measured at room temperature. The neutron wavelength used was 1.4807 Å. The data were accumulated in five settings of the detector in 24 hours with 2θ values ranging from 5° to 105° in 0.05° steps. The neutron diffraction powder patterns were analyzed by the Rietveld method¹³ using the FULLPROF program for multiphase refinement, including magnetic structure refinement. The Curie temperatures for all samples were measured with a SQUID magnetometer using a QUANTUM DESIGN MPMS system.

III. RESULTS AND DISCUSSION

All samples were confirmed to have the $\text{Th}_2\text{Zn}_{17}$ -type rhombohedral structure (space group $R\bar{3}M$). The refined cell parameters, substituent occupancies and the measured Curie temperatures for these samples are listed in Table I. Some α -Fe was found in all carbided samples which indicates some difficulties in making these samples. In the Nd-Fe-Nb-C and Nd-Fe-Zr-C samples, some NbC and ZrC was also found in the compounds with relatively less α -Fe.

The $\text{Nd}_2\text{Fe}_{17}$ parent compound has a unit cell volume of 799.7 Å³. Comparing this with the refined data in Table I, we notice that for the uncarbided samples the volume effect of

TABLE I. Lattice parameters, site occupancies of the substituents and the Curie temperatures in the 2:17 compounds.

Refined compositions	Lattice parameter				Substituent occupancies (%)				χ^2	T_c (K)
	a , Å	c , Å	c/a	V , Å ³	$6c$	$9d$	$18f$	$18h$		
Nd ₂ Fe _{16.03} V _{0.97}	8.5993(2)	12.5109(4)	1.4549	801.211	38.9	0.0	3.2	0.0	1.69	365
Nd ₂ Fe _{15.82} V _{1.18} C _{0.46}	8.6198(3)	12.4736(5)	1.4471	802.636	22.2	0.0	7.8	4.4	1.89	460
Nd ₂ Fe _{15.99} Nb _{1.01}	8.5971(2)	12.4912(3)	1.4530	799.527	16.2	0.0	7.0	4.4	1.54	370
Nd ₂ Fe _{16.11} Nb _{0.89} C _{0.11}	8.5868(2)	12.4677(3)	1.4520	796.117	10.0	0.0	11.6	0.0	2.20	376
Nd ₂ Fe _{16.05} Nb _{0.95} C _{0.34}	8.6256(2)	12.4722(4)	1.4460	803.628	5.4	0.0	6.0	8.0	3.34	^a
Nd ₂ Fe _{14.95} Cr _{2.05}	8.5648(2)	12.4754(3)	1.4566	792.531	53.3	0.0	12.6	3.8	2.87	384
Nd ₂ Fe _{14.87} Cr _{2.13} C _{0.71}	8.6452(2)	12.4837(4)	1.4440	808.042	31.0	0.0	20.2	11.0	1.50	407
Nd ₂ Fe _{16.12} Zr _{0.88}	8.5903(3)	12.4730(5)	1.4520	797.100	7.8	0.0	12.0	0.0	2.24	375
Nd ₂ Fe _{16.28} Zr _{0.72} C _{0.13}	8.5868(2)	12.4635(3)	1.4515	795.846	4.2	0.0	7.6	3.0	3.98	^a
Nd ₂ Fe _{16.11} Zr _{0.89} C _{0.41}	8.6270(2)	12.4722(4)	1.4457	803.889	4.2	0.0	6.0	7.4	2.45	^a

^aCurie temperature not yet measured.

the transition metal substituents is weaker than that of the metalloid substituents^{2,3,6} even though some of their metallic radii are larger than those of the metalloids and are all larger than that of Fe. This suggests a stronger bond between the transition metal substituents and the Fe or Nd atoms. All compounds show some expansion except the Cr sample whose unit cell volume is 792.531 Å³ with 2.05 substituted Cr atoms per formula unit (f.u.) which corresponds to a contraction of 3.6 Å³ per Cr atom. This is surprising considering that the metallic radius of Cr is 1.18 Å which is slightly larger than that of Fe (1.17 Å). Similar behavior is observed in Cr substituted 3:29 compounds¹⁴ in which case the cell volume also contracts.

The results become even more complex with the introduction of C into the samples. Even though the substituent contents are somewhat different between samples with and without C, the differences are small enough that comparisons can be made between these two types of samples. In the Nd–Fe–V–C sample, the expansion in the unit cell volume is small with C insertion (about 3 Å³ per C atom), whereas in the Ga and Al carbided samples^{10,11,15} one inserted C atom per formula unit can lead to an expansion of about 14 Å³. There are two samples each for the Nd–Fe–Nb–C and Nd–Fe–Zr–C series synthesized with nominal contents of C of 1.0 and 1.5. There is very little C (~0.1 atom/f.u.) in the compounds with starting C content of 1.0 while a somewhat higher amount of C (>0.3 atom/f.u.) is found in the compounds with nominal C content of 1.5. The unit cell volume of Nd₂Fe_{16.11}Nb_{0.89}C_{0.11} contracts (796.117 Å³) with a small C content in the compound even though the cell volume for Nd₂Fe_{15.99}Nb_{1.01} is almost the same as that of Nd₂Fe₁₇. The sample with higher C content has a larger (803.628 Å³) cell volume. The results for the Nd–Fe–Zr–C samples are almost the same as those of the Nb sample. The cell volume of the Nd–Fe–Cr–C sample (0.71 C atom/f.u.) is, however, much larger (~15.5 Å³) than that of its uncarbided counterpart. The above results indicate that the volume effects of the substituted transition metal atoms and the interstitial C atoms are not simply additive. It is also interesting to notice that the c/a ratios of these carbided samples are lower than those of their uncarbided counterparts—the more C found in the in-

terstitial 9e site, the smaller the c/a ratios. This indicates a larger expansion in the basal plane with C insertion, as is also the case for the metalloid carbided samples.^{10,11,16} The C atoms are only found in the interstitial 9e site. The refined contents of C in these samples are lower than the nominal content (1.0 or 1.5 C atom/f.u.) as can be seen in Table I. The loss of the C atoms inside the 2:17 cells may occur during the annealing treatment, that is, the C atoms can escape more easily under certain annealing atmospheres. This may explain why the Nd–Fe–Cr–C sample retained more C with a shorter postmelting treatment time. The low C content may also result from the formation of transition metal carbides (which was observed for Nd–Fe–Nb–C and Nd–Fe–Zr–C) and/or rare earth carbides (which have not been detected in our measurements) in the grain boundaries. One remaining possibility is that some C atoms could occupy transition metal sites as well as the interstitial sites, which means they enter the compounds substitutionally. This assumption was first proposed in the study of RFe_{12-x}T_xC_y (R=Y, Er; T=V, Ti, Mo)¹⁷ but it cannot be confirmed solely by neutron diffraction in this study.

There is a trend for the substituents to occupy the Fe 18f and 18h sites with introduction of the C atoms (see Table I) compared with the site occupancies of the uncarbided samples. These C effects in V, Nb, Cr, and Zr samples are not as strong as in the Nd–Fe–Ti–C sample¹² but they are obvious. With the introduction of C from the melt, the site occupancies of the transition metal substituents in the Fe 6c site decrease, with a drop of 40%–67%. On the other hand, more substituents are found in the Fe 18f and 18h sites. In the V and Cr samples, more V or Cr is found in the 18f site, which is the nearest site to the interstitial 9e site. However, in the Nb and Zr sample, more Nb or Zr is found in the 18h site for those samples with higher C contents. The change is large if you consider the 18-fold degeneracy of these two sites. Even though very little C was detected in the Nd–Fe–Nb–C and Nd–Fe–Zr–C samples, the site occupations of the substituents, namely the Nb and Zr atoms, do change. This strongly suggests that the C atoms were present during the phase formation and later lost during annealing. This behavior appears to relate to the electronegativities of the early

TABLE II. Bond lengths (Å) between the interstitial 9e site and the Fe 18f/18h sites in carbided samples.

Bonds	Nd-Fe-C (C=2.94)	Nd-Fe-Ti-C (C=0.29)	Nd-Fe-Nb-C (C=0.11)	Nd-Fe-Nb-C (C=0.34)	Nd-Fe-Zr-C (C=0.13)	Nd-Fe-Zr-C (C=0.41)	Nd-Fe-V-C (C=0.46)	Nd-Fe-Cr-C (C=0.17)
9e-18f	1.9079	1.8118	1.8152	1.8355	1.8195	1.8364	1.8248	1.8613
9e-18h	1.9159	1.9477	...	1.9485	1.9511	1.9447	1.9471	1.9301

transition series elements, as it is well known that their carbides are highly stable compounds. Having high affinity for the C atoms, more transition metal substituents were attracted to the near neighbors of the interstitial 9e site, namely the 18f and 18h sites, during the melting. Even though the C atoms in the 9e site were lost in some ways later, the substituents have already occupied these two sites.

Table II shows the bond lengths between the 9e interstitial site and the Fe 18f and 18h sites in these samples. The data for Nd₂Fe₁₇C_{2.94}¹⁶ and Nd-Fe-Ti-C are also included. As compared with the data for Nd₂Fe₁₇C_{2.94} in which the C was introduced from gas phase, the bond lengths between the 9e and 18f for all samples are much shorter, ranging from 1.8118 to 1.8364 Å except in the Cr sample. This again indicates the strong bonding between the C atoms and the transition metal substituents. For the Nd-Fe-Cr-C sample, the 9e-18f bond length is 1.8613 Å, comparable to that in the Si, Al, and Ga carbided samples but is still smaller than 1.9097 Å in Nd₂Fe₁₇C_{2.94}.

The measured Curie temperatures (T_c) are higher than that of Nd₂Fe₁₇ (330 K). The T_c of the Nd-Fe-V-C sample is 460 K which is almost 100 K higher than that of the Nd-Fe-V sample even though its unit cell volume is only 1.4 Å³ larger. The T_c for the Nd-Fe-Cr-C sample (407 K) is only 23 K higher than that of the Nd-Fe-Cr despite its much larger unit cell as mentioned above. The T_c for the Nd-Fe-Nb-C (C=0.11) is a little higher than that of the Nd-Fe-Nb even though its cell volume is smaller. All this suggests that some effects other than that of lattice expansion, such as electron transfer, can also affect the T_c .

IV. CONCLUSIONS

The site preference of the substituted V, Nb, Cr, and Zr changes with the introduction of C into the compounds from the melt. Both the substituents and the C atoms have affected

the unit cell volume and the T_c of the studied compounds. A study of C content with annealing conditions is being carried out and will complement this work.

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