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15 Apr 1996

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### Recommended Citation

Z. Hu et al., "Neutron Diffraction Studies of  $\text{Nd}_n\text{Fe}_{m-x-y}\text{V}_x\text{Al}_y$  [(n,m)=(1,12), (2,17), (3,29)]," *Journal of Applied Physics*, vol. 79, no. 8, pp. 6315-6317, American Institute of Physics (AIP), Apr 1996. The definitive version is available at <https://doi.org/10.1063/1.362704>

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# Neutron diffraction studies of $\text{Nd}_n\text{Fe}_{m-x-y}\text{V}_x\text{Al}_y$ [( $n,m$ ) = (1,12), (2,17), (3,29)]

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Several  $\text{Nd}_n\text{Fe}_{m-x-y}\text{V}_x\text{Al}_y$  [( $n,m$ ) = (1,12), (2,17), (3,29)] samples were prepared and analyzed using neutron powder diffraction. Rietveld analysis of the neutron diffraction data indicates that the V and Al substituents take those sites with similar environments in all three phases, as observed in our previous study of Ti-substituted compounds. It was confirmed that the diffraction data of the 3:29 compound can be better refined using the  $A2/m$  space group than using the  $P2_1/c$  space group. The SQUID measurements show that all samples have Curie temperatures well above room temperature. The neutron diffraction results show that the easy direction is along the  $a$  axis for the 3:29 compounds, along the  $c$  axis for the 1:12 compounds and in the  $a$ - $b$  plane for 2:17 compounds, respectively. The average site magnetic moments, the metal-metal bond lengths and the unit cell parameters of these compounds are compared with those of the Ti-substituted compounds. © 1996 American Institute of Physics. [S0021-8979(96)34508-4]

## I. INTRODUCTION

Because the number of known rare-earth-iron phases with high iron/rare-earth ratios is very limited, improving the magnetic properties of the known phases, especially the 2:17, 1:12 and the newly discovered 3:29 phases, to make them practically useful is a focus for research. Addition of some other elements into these phases, such as the interstitial atoms (C or N)<sup>1-5</sup> or substitutional atoms (Al,Ga,Si),<sup>6-14</sup> results in a dramatic enhancement in magnetic properties.

The unit cell of the rare-earth-iron compounds can expand upon the addition of substitutional atoms (Ga,Al)<sup>6-8</sup> or contract upon the addition of Si.<sup>9-14</sup> In both cases the magnetic properties can be enhanced significantly. It is believed that in the expansion case, like the Al-substituted 2:17 compounds, the lattice expansion is sufficient to decrease the antiferromagnetic exchange and to enhance the ferromagnetic exchange.<sup>7</sup> In the contraction case, the enhancement of magnetic properties with Si substitution may be related to the expansion of the bond lengths around the  $6c$  and  $18f$  sites.<sup>14</sup> However, it appears that the increase in the iron-iron bond lengths is not the only mechanism to improve the magnetic properties of these compounds.<sup>15</sup>

Our previous studies showed that Al and Si have similar site affinities at low Al or Si content and it was found that a combined substitution of Fe by Si and Al (both are nontransition metal atoms), at the appropriate levels, could lead to greater enhancement of the magnetic properties than the singly substituted compounds.<sup>16</sup> It is obviously interesting to study doubly substituted compounds using two substituents of different site affinities. Our previous studies showed that while Al prefers the  $18h$  site at low Al contents in 2:17 compounds,<sup>6,7</sup> V atoms strongly prefer the  $6c$  sites.<sup>17</sup> Here we report studies of Al+V (a nontransition atom plus a transition atom of different site affinity) substitution compounds,  $\text{Nd}_n\text{Fe}_{m-x-y}\text{V}_x\text{Al}_y$  [( $n,m$ ) = (1,12), (2,17), (3,29)].

## II. EXPERIMENT

Samples used in this research were synthesized by rf induction melting of the constituent elements (purity 99.9% or better) in a water-cooled copper boat under a flowing argon atmosphere at the Graduate Center for Materials Research of the University of Missouri-Rolla. The ingots were annealed under vacuum at temperatures of 980 °C for one week. The annealed ingots were then crushed and ground in an acetone bath for neutron diffraction and other studies. Neutron diffraction data were collected using the position sensitive detector (PSD) diffractometer at the University of Missouri Research Reactor. Data collection times for each sample were typically 24 h on about 2 g of the powdered samples in a 3-mm-diam vanadium can at a wavelength of 1.4783 Å.

Neutron diffraction data were analyzed using the program FULLPROF, a program for Rietveld analysis of neutron (nuclear and magnetic scattering) or x-ray powder diffraction data collected at constant steps in the scattering angle  $2\theta$  on a conventional instrument. The Curie temperatures  $T_c$  were measured using a Quantum Design MPMS system.

## III. RESULTS AND DISCUSSION

It was suggested<sup>18</sup> recently that the structure of the 3:29 phase can be described more accurately by using the space group  $A2/m$ , a minimal nonisomorphic supergroup of type II of  $P2_1/c$  space group which was initially used for solving the structure of this phase.<sup>19-21</sup> Thus, the neutron diffraction data of the 3:29 compounds were refined in both space groups ( $P2_1/c$  and  $A2/m$ ). It was found that the fitting factors were only slightly better when the space group  $P2_1/c$  was used, in which as many as 91 parameters were refined, compared to 57 parameters refined for the space group  $A2/m$ . The  $R$ -factor ratio<sup>22</sup> test leads to the conclusion that the model based on the space group  $A2/m$  is more reliable, which confirms the conclusion of Kalogirou *et al.*<sup>18</sup>

Samples with V and Al content ratio changing in a limited range were prepared but only one of each type with the

TABLE I. Refinement results for NdFe<sub>10.05</sub>V<sub>1.38</sub>Al<sub>0.57</sub>.

Space group: <i>I4/mmm</i>		Unit cell volume=351.443 Å <sup>3</sup>				
Atom and site	<i>x</i>	<i>y</i>	<i>z</i>	V (%)	Al (%)	<i>m</i>
Nd, <i>2a</i>	0	0	0			1.8(2)
Fe, <i>8i</i>	0.2704(3)	0.5	0	34.8		2.2(2)
Fe, <i>8j</i>	0.3586(3)	0	0		14.4	2.4(3)
Fe, <i>8k</i>	0.25	0.25	0.25			2.0(1)
Lattice parameters: <i>a</i> = 8.5691(3) <i>c</i> = 4.7861(2)						
Fitting factors: <i>R<sub>p</sub></i> = 5.80 <i>R<sub>wp</sub></i> = 7.06 <i>R<sub>mag</sub></i> = 3.29 $\chi^2$ = 1.44						

best phase purity are reported in this paper and the refinement results are given in Tables I, II, and III. Previous work shows that Al and V atoms introduced into Nd<sub>2</sub>Fe<sub>17</sub> compounds will expand the cell of the compounds by 1.44 Å<sup>3</sup>/V atom<sup>17</sup> and 8.49 Å<sup>3</sup>/Al atom.<sup>7</sup> The lattice parameters of the V+Al double substituted 2:17 compound are linear combinations of the corresponding singly substituted compounds (Table II). For 1:12 and 3:29 compounds, no data for Al or V single-substitution compounds are available and thus no comparison can be made.

It is not possible to determine the site distributions of the substituents in doubly substituted compounds directly from the neutron diffraction techniques. We use some assumptions based on our previous work to determine the locations of the substituents, as was done for Nd<sub>2</sub>Fe<sub>17-x-y</sub>Al<sub>x</sub>Si<sub>y</sub>.<sup>16</sup> It is found that the V atoms will mostly occupy the 6*c* sites, which have the fewest rare-earth neighbors and the most transition metal neighbors in Nd<sub>2</sub>Fe<sub>17-x</sub>V<sub>x</sub>,<sup>17</sup> and it is assumed that the V atoms will occupy the same sites in the Nd<sub>2</sub>Fe<sub>17-x-y</sub>V<sub>x</sub>Al<sub>y</sub> compound. It was also found that the Ti atoms will occupy sites with similar environments in all 1:12, 2:17, and 3:29 phases.<sup>21</sup> In fact, because the structures of all three compounds are derived from the same parent structure of *RT*<sub>5</sub> with differing degrees of Fe–Fe dumbbell replacement for the rare-earth atoms, it is assumed that a given substituent will occupy those sites with similar environments in all 1:12, 2:17, and 3:29 compounds. Thus, we assume that the V atoms will occupy those sites with the fewest rare-earth neighbors and most transition metal neighbors, while Al atoms will prefer those sites with the most rare-earth neighbors and the fewest transition metal neighbors in all V+Al double-substituted 1:12, 2:17, and 3:29 compounds. Thus, the V atoms occupy the three dumbbell sites in the 3:29 phase, the 6*c* sites in the 2:17 and the 8*i* sites in the 1:12 phase, while the substituents found in any other sites are Al atoms. In fact, the neutron data show a

strong decrease of the effective scattering length in those sites with the fewest rare-earth neighbors, which indicates substitution of V atoms at those sites because V has a very small scattering length. By using these assumptions, the site occupancies of V and Al in Tables I, II, and III are obtained.

The refined site magnetic moments are also given in Tables I, II, and III. The easy direction is found along the *a* axis for the 3:29 compounds, along the *c* axis for the 1:12 compounds and in the *a*-*b* plane for the 2:17 compounds, respectively. The 1:12 compound has the biggest site moments whereas the 3:29 compound has the smallest site moments. The average Fe site moments are 2.2, 1.81, and 1.5 μ<sub>B</sub> for the 1:12, 2:17, and 3:29 compounds, respectively. Compared to the average site moment of Nd<sub>2</sub>Fe<sub>16.03</sub>Ti<sub>0.97</sub>, 1.95 μ<sub>B</sub>,<sup>21</sup> the average site moment of Nd<sub>2</sub>Fe<sub>15.66</sub>V<sub>1.06</sub>Al<sub>0.28</sub> is a little lower, very possibly due to the higher substituent content in the V+Al double-substituted compound. Similarly, the average site moment of NdFe<sub>10.05</sub>V<sub>1.38</sub>Al<sub>0.57</sub>, 2.2 μ<sub>B</sub>, is lower than that of the Nd<sub>2</sub>Fe<sub>10.9</sub>Ti<sub>1.1</sub> compound, 2.36 μ<sub>B</sub>.<sup>21</sup> For the 3:29 compounds, the refined average site moment of Nd<sub>3</sub>Fe<sub>26.97</sub>V<sub>1.83</sub>Al<sub>0.20</sub>, 1.11 μ<sub>B</sub>, is a little higher than that of the Nd<sub>3</sub>Fe<sub>27.76</sub>Ti<sub>1.24</sub> compound (1.05 μ<sub>B</sub>) in spite of the higher substituent content in Nd<sub>3</sub>Fe<sub>26.97</sub>V<sub>1.83</sub>Al<sub>0.20</sub>. The SQUID measurements give Curie temperatures of 600, 395, and 385 K for the 1:12, 2:17, and 3:29 compounds, respectively. Because the Curie temperatures of the corresponding Al or V single-substitution compounds are not available at present, no comparison between single- and double-substituted compounds can be made. The high *T<sub>c</sub>* and large site magnetic moment of the 1:12 compound suggests that it can be of economic interest even without nitriding or carbiding. Since the substituents and their content ratio can be adjusted in a wide range for doubly substituted compounds, it will not be surprising if doubly substituted compounds with even better properties are discovered.

TABLE II. Refinement results for Nd<sub>2</sub>Fe<sub>15.66</sub>V<sub>1.06</sub>Al<sub>0.28</sub>.

Space group: <i>R-3m</i>		Unit cell volume=813.306 Å <sup>3</sup>				
Atom and site	<i>x</i>	<i>y</i>	<i>z</i>	V (%)	Al (%)	<i>m</i>
Nd, <i>6c</i>	0	0	0.3439(3)			2.8(2)
Fe/V, <i>6c</i>	0	0	0.0949(4)	37.7		1.6(4)
Fe, <i>9d</i>	0.5	0	0.5			1.4(2)
Fe/V, <i>18f</i>	0.2902(2)	0	0	5.0		2.1(2)
Fe/Al, <i>18h</i>	0.1691(1)	-0.1691(1)	0.4907(2)		4.6	1.8(2)
Lattice parameters: <i>a</i> = 8.6428(3) <i>c</i> = 12.5722(4)						
Fitting factors: <i>R<sub>p</sub></i> = 4.16 <i>R<sub>wp</sub></i> = 5.20 <i>R<sub>mag</sub></i> = 5.18 $\chi^2$ = 1.54						

TABLE III. Refinement results for Nd<sub>3</sub>Fe<sub>26.97</sub>V<sub>1.83</sub>Al<sub>0.20</sub>.

Space group: <i>A2/m</i>	Unit cell volume=886.210 Å <sup>3</sup>			V (%)	Al (%)	<i>m</i>
Atom and site	<i>x</i>	<i>y</i>	<i>z</i>			
Nd1, <i>2a</i>	0	0	0			1.5(2)
Nd2, <i>4i</i>	0.5982(16)	0	0.1864(17)			1.5(2)
Fe1, <i>2c</i>	0.5	0	0.5			1.5(2)
Fe2, <i>4e</i>	0	0.25	0.25			1.5(2)
(Fe/V)3, <i>4e</i>	0	0.3578(20)	0	16.4		1.5(2)
Fe4, <i>4i</i>	0.1138(15)	0	0.7103(16)			1.5(2)
(Fe/Al)5, <i>4i</i>	0.3055(18)	0	0.0891(20)		3.6	1.5(2)
(Fe/V)6, <i>4i</i>	0.2312(24)	0	0.5019(23)	37.4		1.5(2)
(Fe/V)7, <i>4i</i>	0.1327(23)	0	0.2901(22)	37.6		1.5(2)
Fe8, <i>8j</i>	0.6232(9)	0.1440(13)	0.6804(12)			1.5(2)
Fe9, <i>8j</i>	0.8102(10)	0.2188(8)	0.1003(11)			1.5(2)
(Fe/Al)10, <i>8j</i>	0.4059(9)	0.2486(14)	0.0688(8)		3.2	1.5(2)
Fe11, <i>8j</i>	0.1998(9)	0.2545(16)	0.1577(12)			1.5(2)
Lattice parameters: <i>a</i> = 10.6576(14) <i>b</i> = 8.5937(7) <i>c</i> = 9.7508(15) <i>b</i> = 96.978(11)						
Fitting factors: <i>R<sub>p</sub></i> = 5.77 <i>R<sub>wp</sub></i> = 7.01 <i>R<sub>mag</sub></i> = 7.06 $\chi^2$ = 3.35						

## IV. CONCLUSIONS

It was confirmed that the diffraction data of the 3:29 compound can be better refined using the *A2/m* space group than using the *P2<sub>1</sub>/c* space group. All samples have Curie temperatures well above room temperature. The easy direction is along the *a* axis for the 3:29 compounds, along the *c* axis for the 1:12 compounds and in the *a-b* plane for the 2:17 compounds. The average site magnetic moments are similar to those of the Ti-substituted compounds.

## ACKNOWLEDGMENT

This work is supported by the Division of Materials Research of the National Science Foundation (Grant No. DMR-9305782) and the Missouri University Research Board.

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