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Peter C. Ezekwenna

G. K. Marasinghe

William Joseph James
Missouri University of Science and Technology

Oran Allan Pringle
Missouri University of Science and Technology, pringle@mst.edu

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/chem_facwork/913

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Magnetic and structural properties of $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions

P. C. Ezekwenna, G. K. Marasinghe, W. J. James, O. A. Pringle,
and Gary J. Long

Departments of Physics and Chemistry and the Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri 65409-0010

H. Luo, Z. Hu, and W. B. Yelon

University of Missouri Research Reactor, Columbia, Missouri 65211

Ph. l'Héritier

Laboratoire des Matériaux et du Génie Physique, UMR 5628 CNRS, ENSPG, F-38402 Grenoble, France

A series of $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions with x values between 0 and 6 were prepared and analyzed using magnetic measurements, neutron diffraction, and Mössbauer spectroscopy. All of the $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ samples crystallized in the $\text{Th}_2\text{Zn}_{17-x}$ -type rhombohedral structure. The lattice parameters and unit cell volumes decrease with increasing manganese content up to x equal to 2, and then increase for higher manganese content. The magnetizations of $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ decrease with increasing manganese content and $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ is paramagnetic at room temperature for x greater than 3. The Curie temperature in $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions is maximum for x equal to 0.5 and decreases at a rate of $\sim 10^\circ$ per substituted manganese up to x equal to 3, after which it drops sharply. These results are discussed in terms of the manganese site occupancies in $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$. © 1997 American Institute of Physics. [S0021-8979(97)42608-7]

I. INTRODUCTION

The Curie temperatures of $\text{R}_2\text{Fe}_{17}(\text{N/C})_x$ interstitial permanent magnetic materials¹ exceed those of $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based permanent magnets, the strongest of the commercially available iron-based permanent magnets. However, certain properties of these interstitially substituted compounds must be improved appreciably if they are to be developed as commercial magnets. It has been observed that the magnetic properties of R_2Fe_{17} -based solid solutions can be modified by partially substituting the iron sublattice with certain other elements, such as aluminum,^{2,3} gallium,^{4,5} or silicon.⁶ As a part of a study of substituted R_2Fe_{17} compounds, we have synthesized and characterized several $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions with $0 \leq x \leq 6$, by neutron diffraction, magnetic and thermomagnetic measurements, and Mössbauer spectral studies.

II. EXPERIMENT

The $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ samples were prepared by induction melting stoichiometric amounts of high purity elements, 99.9% or better, in a purified argon atmosphere. Approximately 3 wt % excess manganese was added to allow for possible manganese loss by evaporation during melting. The ingots were annealed at 1240 K for 6 days under argon. Powder neutron diffraction data were collected on a linear position sensitive diffractometer and by neutrons with a wavelength of 1.4783 Å. The lattice parameters, site occupancies, and magnetic moments were obtained by refining the neutron diffraction data using the FULLPROF⁷ computer code. Because of the different signs of the scattering lengths of iron and manganese, the scattering for the Fe/Mn $6c$ site was virtually zero and it was not possible to refine its z positional parameter for x equal to 6. As a consequence, this parameter was constrained to the value given in Table I. The Curie temperatures were obtained by vibrating sample mag-

netometry, thermogravimetric analysis, and superconducting quantum interference device (SQUID) measurements.

III. RESULTS AND DISCUSSION

A refinement of powder neutron diffraction data indicated that all of the $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions crystallized in the $\text{Th}_2\text{Zn}_{17}$ -type rhombohedral structure. The resulting structural parameters are given in Table I and the composition dependence of the lattice parameters is shown in Fig. 1. The presence of manganese in the samples and the elemental compositions were confirmed by energy dispersive spectroscopy. The lattice parameters and unit cell volumes decrease with increasing manganese content up to $x=2$, and then increase at higher manganese content, whereas the c/a ratio is approximately constant for x up to 2 and then decreases slightly. The contractions are rather surprising because manganese, with a 12-coordinate metallic radius of 1.35 Å, is larger than iron, with a metallic radius of 1.26 Å. However, the contraction may well be associated with specific details of the bonding within the solid solutions, as will be discussed. It should be noted, however, that all the unit cell positional parameters remain virtually constant with increasing x except for the Fe/Mn, $18f$, x positional parameter, which decreases almost linearly from 0.2882(1) to 0.2833(7) between $x=0$ and 6. In contrast the Fe/Mn, $6c$, z parameter is virtually constant and, as a consequence, the $6c-6c$ "dumbbell" bond distance varies only between 2.38 and 2.40 Å in the series of solid solutions.

The percentage of manganese found on each of the transition metal sites in $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$, as obtained from the neutron diffraction refinements, is given in Table I and shown in Fig. 2. In Fig. 2 it can be seen that manganese completely avoids the $9d$ site at low x values, whereas manganese favors the $6c$ site and occupies the $18f$ and $18h$ sites almost randomly. The occupancy pattern, which is rather similar to that observed for related solid solutions,³⁻⁵ is to a

TABLE I. Neutron diffraction refinements and Curie temperatures for $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions.

x , nominal	0 ^a	0.5	1.0	1.5	2.0	4.0	6.0
x , refined	0	0.52	1.08	1.48	1.88	4.04	5.86
a , Å	8.6002(1)	8.5955(3)	8.5920(3)	8.5918(3)	8.5876(4)	8.6198(3)	8.6457(11)
c , Å	12.4835(2)	12.4849(4)	12.4788(4)	12.4761(4)	12.4628(5)	12.4902(5)	12.5162(16)
c/a	1.4515(4)	1.4525(1)	1.4524(1)	1.4521(1)	1.4513(1)	1.4490(1)	1.4477(3)
V , Å ³	799.60(3)	798.81(8)	797.77(8)	797.56(8)	795.91(1)	803.68(9)	810.2(2)
%Mn, $6c$	0	7.8(5)	17.4(5)	25.8(5)	33.6(5)	58.0(5)	71.3(6)
%Mn, $9d$	0	0.0	0.0	0.0	0.0	4.8(1)	10.8(1)
%Mn, $18f$	0	3.8(4)	6.6(4)	9.2(4)	10.6(4)	22.6(1)	33.4(2)
%Mn, $18h$	0	2.2(4)	5.6(4)	6.8(6)	9.6(4)	22.8(1)	35.2(2)
Nd, $6c, z$	0.3426(3)	0.3436(3)	0.3440(3)	0.3437(4)	0.3443(4)	0.3434(5)	0.3434(7)
Fe/Mn, $6c, z$	0.0957(2)	0.0959(2)	0.0958(3)	0.0961(3)	0.0956(5)	0.0961(16)	0.0961 ^b
Fe/Mn, $18f, x$	0.2882(1)	0.2879(2)	0.2876(2)	0.2872(2)	0.2868(2)	0.2851(3)	0.2833(7)
Fe/Mn, $18h, x$	0.1687(1)	0.1685(1)	0.1687(1)	0.1692(1)	0.1689(2)	0.1696(2)	0.1688(5)
Fe/Mn, $18h, z$	0.4893(1)	0.4895(1)	0.4894(1)	0.4894(2)	0.4889(2)	0.4884(3)	0.4896(5)
μ , Nd, $6c, \mu_B$	2.1(2)	1.2(3)	1.1(3)	1.7(2)	0.3(6)	0	0
μ , Fe/Mn, $6c, \mu_B$	2.5(2)	1.3(3)	1.0(4)	1.5(4)	0.0(6)	0	0
μ , Fe/Mn, $9d, \mu_B$	1.7(2)	1.0(3)	0.9(3)	1.9(3)	0.8(6)	0	0
μ , Fe/Mn, $18f, \mu_B$	2.4(2)	2.2(3)	2.1(3)	2.1(3)	0.9(6)	0	0
μ , Fe/Mn, $18h, \mu_B$	1.7(2)	1.4(2)	1.4(2)	2.4(2)	1.0(6)	0	0
T_c , K	330	345	320	315	310	180	...
R_p	5.48	4.09	3.94	4.41	4.43	5.18	6.01
χ^2	3.11	1.35	1.31	1.54	1.65	1.60	2.24

^aData obtained from Ref. 3.

^bParameter not refined.

large extent clearly determined by the relative site volumes. In $\text{Nd}_2\text{Fe}_{17}$ the Wigner–Seitz cell volumes⁸ are 12.33, 11.99, 11.70, and 11.23 Å for the $6c$, $18h$, $18f$, and $9d$ sites, respectively, values that correlate almost perfectly with the preference of the larger sized manganese for substitution. In this regard it should be noted that, whereas the Fe/Mn $6c$ site has six Fe/Mn $18f$ near neighbors, it has only one Fe/Mn $6c$

neighbor and three each of $9d$ and $18h$ near neighbors.⁸ Thus it would seem that the Fe/Mn $6c$ site, which is preferentially occupied by the larger manganese, has the most influence on the position of the atoms on the $18f$ site. The decrease in the Fe/Mn, $18f, x$ positional parameter with increasing manganese content, as noted above, corresponds to a decrease in the $18f$ to ‘‘dumbbell pair’’ distance, a decrease that must correspond to an increased covalency of the iron–manganese bonds relative to the iron–iron bonds. This increased covalency is also observed in the Mössbauer spectral isomer shifts, see below.

The magnetic moments, as determined by neutron diffraction, decrease as the manganese content increases. As is shown in Fig. 3, the room temperature saturation magnetiza-

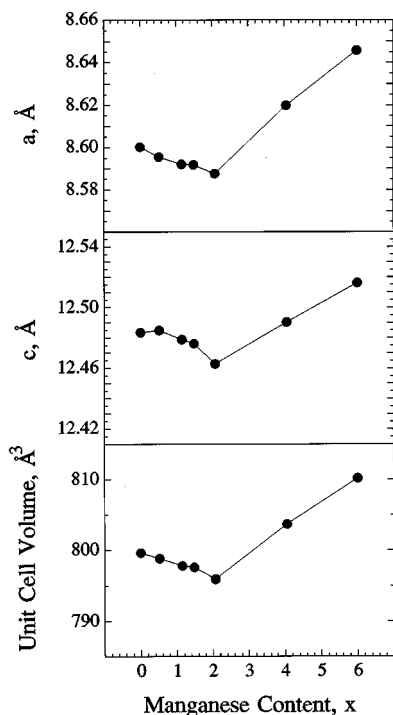


FIG. 1. The compositional dependence of the 295 K unit cell parameters in $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions.

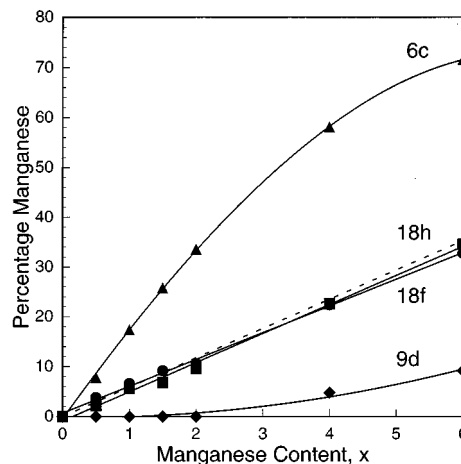


FIG. 2. The compositional dependence of the manganese site occupancy in $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions. The dashed line corresponds to random occupancy.

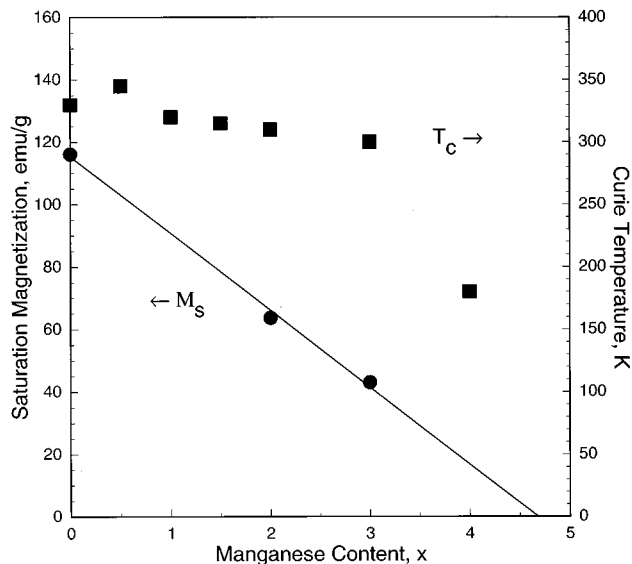


FIG. 3. The compositional dependence of the room temperature saturation magnetization and Curie temperature in $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions.

tion decreases virtually linearly with manganese content and is zero above $x=4$. In contrast, the Curie temperature remains virtually constant at $\sim 320\text{--}300$ K between $x=0$ and 3 and then decreases rapidly. These results should be compared to those found for $\text{R}_2\text{Fe}_{14-x}\text{Mn}_x\text{B}$ solid solutions, in which the substitution of iron by manganese rapidly decreases both the Curie temperature and the saturation magnetization.⁹ More specifically, the Curie temperature decreases at the rate of $\sim 100^\circ$ per manganese, a decrease which indicates a weakening of the iron–iron magnetic exchange interactions.¹⁰ This decrease in Curie temperature is in contrast to the significant increase¹¹ of $\sim 80^\circ$ per cobalt atom in $\text{R}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$. As a result of the antiparallel coupling between the manganese magnetic moments and the moments of the other $3d$ metals, there is also a rapid decrease in the Curie temperature^{12,13} in the $\text{R}_6\text{Fe}_{23-x}\text{Mn}_x$ and $\text{R}_2\text{Co}_{17-x}\text{Mn}_x$ solid solutions. In contrast, the $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions show quite a different and unusual magnetic behavior. The preferential substitution of manganese on the Fe $6c$ site may account for the initial small increase in the Curie temperature of $\text{Nd}_2\text{Fe}_{16.5}\text{Mn}_{0.5}$. Yelon *et al.*¹⁴ have suggested that, because most manganese atoms occupy the $6c$ site, the site that has the largest Wigner–Seitz cell volume and the longest average site bond length in $\text{Nd}_2\text{Fe}_{17}$, the $6c$ manganese atoms may weakly couple ferromagnetically to their nearest-neighbor iron atoms. However, it should also be noted that the presence of manganese strongly reduces the Curie temperature of $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$ solid solutions. For in-

stance, the T_c of $\text{Nd}_2\text{Fe}_{13}\text{Al}_4$ is ~ 450 K as compared to 180 K in $\text{Nd}_2\text{Fe}_{13}\text{Mn}_4$. This would indicate that, at least at higher contents, the manganese produces an antiferromagnetic exchange that is not present with aluminum.

A Mössbauer spectral study of $\text{Nd}_2\text{Fe}_{13}\text{Mn}_4$ reveals that it is paramagnetic at 295 and 225 K and magnetically ordered at 155 and 85 K with average hyperfine fields of ~ 41 and 100 kOe, respectively, results that agree with the T_c value of 180 K reported in Table I and Fig. 3. The weighted average isomer shift decreases linearly with temperature with a slope of $\sim -5.9 \times 10^{-4}$ (mm/s)/K and a corresponding average effective recoil mass of ~ 70 g/mol. It should be noted that the weighted average isomer shifts in $\text{Nd}_2\text{Fe}_{13}\text{Mn}_4$ are substantially lower³ than those of $\text{Nd}_2\text{Fe}_{13}\text{Al}_4$, a decrease that corresponds to a higher s electron density at the iron sites in the former compound, and an increase that is consistent with the higher covalency in these compounds, as was noted above.

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