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Study of Structural and Magnetic Properties of Iron-Rich Mixed Rare-Earth $NdDyFe_{(17-y-x)}Co_xSi_y$ Compounds

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***Abstract*—A series of NdDyFe $_{17-x-y}$Co$_x$Si$_y$ solid solutions with $x = 2$ and 3 and $y = 0.5, 1.0,$ and 1.5 were prepared by induction melting stoichiometric amounts of high-purity elements. The postannealed samples consist of two phases belonging to the space groups R$\bar{3}$ m and P6$_3$/mmc . The lattice parameters and the unit cell volumes were calculated from the refinements of the magnetic and structural unit cells using the FULLPROF version of the Rietveld program. For a fixed content of Co, the maximum Curie temperatures (305 °C to 405 °C) were observed in samples with $y = 1$ and having two phases, a disordered rhombohedral (DR) structure and a disordered hexagonal (DH) structure. An increase in the Curie temperature of 70 °C per atom of cobalt is observed in NdDyFe$_{17-x-y}$Co$_x$Si$_y$ with $y = 1$ and $x \leq 3$, suggesting that with a suitable choice of rare earths this DR phase may be a promising candidate for high-energy product permanent magnets. The magnetization versus temperature (M versus T) plots of the solid solutions, which consist of two phases, exhibit only a single magnetic ordering transition temperature.**

***Index Terms*—Disordered hexagonal (DH), disordered rhombohedral (DR).**

I. Introduction

A RECENT study of a mixed rare-earth–iron–silicon system (SmGd)Fe $_{14}$Si$_3$ revealed the presence of a disordered rhombohedral (DR) structure in the 2 : 17 phase [1]. Subsequently, the same disordered structure was observed for Nd $_{2-x}$Dy$_x$Fe$_{17-y}$Si$_y$ alloys. These systems have the potential of having high Curie temperatures and high remanence and may be suitable candidates for permanent magnets having high-energy products $(BH)_{\max}$.

It was found that the DR phase could be achieved with an appropriate amount of Si content in R$_{2-x}$R$'_x$Fe$_{17-y}$Si$_y$ compounds [2]. The c/a ratio of DR compounds lies between those of the ordered rhombohedral (OR) and the disordered hexagonal (DH) compounds. The choice of rare earths is also crucial to the structure favored by a compound in as much as the light rare earths favor the formation of the OR phase whereas the heavier rare earths favor the DH phase [3]. We studied the effect of partially replacing iron with cobalt in the compounds NdDyFe $_{17-y}$Si$_y$ with $y = 0.5, 1.0,$ and 1.5 to determine if the same structural change can be induced with Co as is observed with Si. Cobalt substitution appeared to be a promising choice because it might favor the formation of the DR phase as does Si, and the magnetic cobalt atoms, unlike Si, may couple with the Fe sublattice, resulting in improved magnetic properties. In this paper, we present and discuss the results of our study of the NdDyFe $_{17-x-y}$Co$_x$Si$_y$ system.

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II. Experimental Method

A series of NdDyFe $_{17-x-y}$Co$_x$Si$_y$ solid solutions with $x = 2$ and 3 and $y = 0.5, 1.0,$ and 1.5 were prepared by induction melting stoichiometric amounts of high-purity elements. The samples were then annealed at 800 °C for a week in an argon atmosphere. The X-ray and neutron diffraction (ND) analysis confirmed that all but one sample NdDyFe $_{13.5}$Co$_2$Si$_{1.5}$ had insignificant amounts of alpha iron. For this particular sample, we achieved good ND refinement by including alpha iron in the refinement.

The ND spectra for samples NdDyFe $_{17-x-y}$Co$_x$Si$_y$ ($x = 2, 3$ and $y = 0.5, 1.0, 1.5$), with the exception of $y = 1$, were fit using two phases R$\bar{3}$ m (the OR phase) and P6$_3$/mmc (the DH phase). The $y = 1$ samples were refined using two phases, the DR and the DH phases. The ND measurements were carried out at room temperature on the high-resolution powder diffractometer at University of Missouri Research Reactor on approximately 1-g samples; the neutron wavelength was 1.293 ± 0.005 Å. The neutron data analysis was done using the FULLPROF version of the Rietveld code [4]. The thermo-magnetic (M-T) behavior was investigated using a vibrating sample magnetometer (VSM) to determine the T_c's for the samples.

III. Results and Discussion

In the ND studies of the 2–17 mixed rare-earth-iron systems (Nd/Dy, Sm/Tb, and Nd/Tb), the existence of a DR phase was established when iron was partially replaced with silicon [5]–[7]. These studies showed that when the c/a ratio had a value of around 1.465 or higher, the system favored the DR phase. A further increase in the silicon content appeared to drive the system toward favoring a two-phase mixture of the OR structure and the DH structure. It has also been observed that in the NdDyFe $_{17-x}$Co$_x$ compounds with $x = 1 - 4$, the favored structure is the OR phase [8]. This clearly shows that Si in these compounds would favor the DR structure.

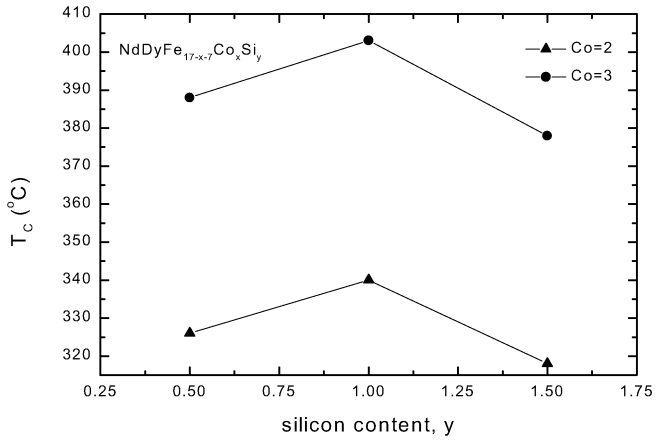

Fig. 1. T_c versus silicon content in the $NdDyFe_{17-x-y}Co_xSi_y$ system.

The study of $NdDyFe_{17-x-y}Co_xSi_y$ solid solutions with $x = 2$ and 3 and $y = 0.5, 1.0,$ and 1.5, in an attempt to realize the DR structure, was motivated by the observed DR structure in the $NdDyFe_{16}Si_1$ compound and the fact that the effect of Si and Co on the lattice parameters of $Nd_2Fe_{(17-x)}T_x$ (T = Si or Co) is similar. Since the DR phase in $NdDyFe_{17-x}Co_x$ compounds with $x = 1 - 4$ remained elusive, it is appropriate to conclude that silicon and cobalt are not similar in their influence on the structure of the compound. By replacing some iron with silicon in the $NdDyFe_{17-x}Co_x$ compounds, we hoped to favor the formation of the DR phase. In as much as cobalt is a magnetic atom, ferromagnetic coupling with iron would improve the saturation magnetization compared to silicon that is nonmagnetic.

Accordingly, Curie temperature T_c data were collected for $NdDyFe_{17-x-y}Co_xSi_y$ solid solutions with $x = 2$ and 3 and $y = 0.5, 1.0,$ and 1.5 and are shown in Fig. 1 as a function of y. T_c is higher for the $y = 1$ samples compared to those of $y = 0.5$ and $y = 1.5$. The highest Curie temperatures are observed for the compounds with $y = 1$, which on the basis of neutron data refinements had the DR and DH structures. The increase in T_c for a particular content of silicon with higher x in the compounds $NdDyFe_{17-x-y}Co_xSi_y$ is expected, as the $R_2Fe_{17-x}Co_x$ compounds are known to possess higher T_c's than the corresponding R_2Fe_{17} compounds. Cobalt at low concentrations avoids the 6c-dumbbell site and prefers the 9d, 18h, and 18f sites in the rhombohedral structure [9]. This preferential site occupancy leads to a contraction in the unit cell volume similar to that seen for Si. The ferromagnetic coupling of Co, being a magnetic atom, with the Fe sublattice contributes further to a higher Curie temperature. The Curie temperature for the $NdDyFe_{16}Si_1$ is 161 °C. For $y = 1$ in the compounds $NdDyFe_{17-x-y}Co_xSi_y$, the T_c's measured are 340 °C and 405 °C for $x = 2$ and 3, respectively. An increase in Curie temperature of about 70 °C per atom is achieved when iron is partially replaced with up to three atoms of Co in the $NdDyFe_{16}Si_1$ compound.

Results of the Rietveld refinement of the atomic and magnetic structures are given in Table I. The samples in which the highest T_c's were observed were refined using two phases: the DR and the DH structures as refinements using the OR and DH phases were not satisfactory. All other samples were refined using two phases, the OR phase and the DH phases. It is observed that the c/a ratios for $y = 1$ samples which were refined using the

TABLE I
LATTICE PARAMETERS, UNIT CELL VOLUMES, MAGNETIC MOMENTS AND RELIABILITY PARAMETERS FOR REFINEMENTS OF THE $NdDyFe_{(17-x-y)}Co_xSi_y$ SYSTEM

NdDy	$Fe_{14.5}Co_2Si_{0.5}$	$Fe_{13.5}Co_3Si_{0.5}$	$Fe_{14}Co_2Si$
Rhomboherdral	OR	OR	DR
weight fraction	15.81	34.76	55.11
a (Å)	5.527	8.519	8.521
c (Å)	12.482	12.495	12.459
c/a	1.463	1.466	1.462
Mag. (μ_B)			
Re (6c)	-2.51	-1.63	-1.70
Fe ($6c_1$)	3.30	3.79	2.14
Fe ($6c_2$)	-	-	2.14
Fe ($6c_3$)	-	-	2.14
Fe (9d,18f,18h)	1.65	2.72	1.76
Hexagonal	DH	DH	DH
weight fraction	82.90	63.82	37.65
a (Å)	8.485	8.482	8.494
c (Å)	8.341	8.337	8.346
1.5*c/a	1.474	1.474	1.473
Mag. (μ_B)			
Re (2d,2b,2c)	-2.51	-1.63	-1.70
Fe (4e,4f)	3.30	3.79	2.14
Fe (6g,12j,12k)	1.65	2.72	1.76
R_p	4.66	5.00	4.44
R_{wp}	5.93	6.57	5.55
R_{exp}	2.03	2.52	3.14
Chi^2	8.57	6.82	3.12
NdDy	$Fe_{13}Co_3Si$	$Fe_{13.5}Co_2Si_{1.5}$	$Fe_{12.5}Co_3Si_{1.5}$
Rhomboherdral	DR	OR	OR
weight fraction	57.23	29.11	57.06
a (Å)	8.504	8.497	8.494
c (Å)	12.471	12.477	12.449
c/a	1.466	1.468	1.465
Mag. (μB)			
Re (6c)	-1.76	-1.84	-1.69
Fe ($6c_1$)	3.34	2.70	3.56
Fe ($6c_2$)	3.34	-	-
Fe ($6c_3$)	3.34	-	-
Fe (9d,18f,18h)	2.69	1.83	2.51
Hexagonal	DH	DH	DH
weight fraction	37.56	51.43	42.94
a (Å)	8.482	8.465	8.463
c (Å)	8.338	8.315	8.314
1.5*c/a	1.474	1.473	1.473
Mag. (μ_B)			
Re (2d,2b,2c)	-1.76	-1.84	-1.69
Fe (4e,4f)	3.34	2.70	3.56
Fe (6g,12j,12k)	2.69	1.83	2.51
R_p	5.00	4.55	4.26
R_{wp}	6.32	5.74	5.45
R_{exp}	2.65	2.85	2.08
Chi^2	5.70	4.06	6.89

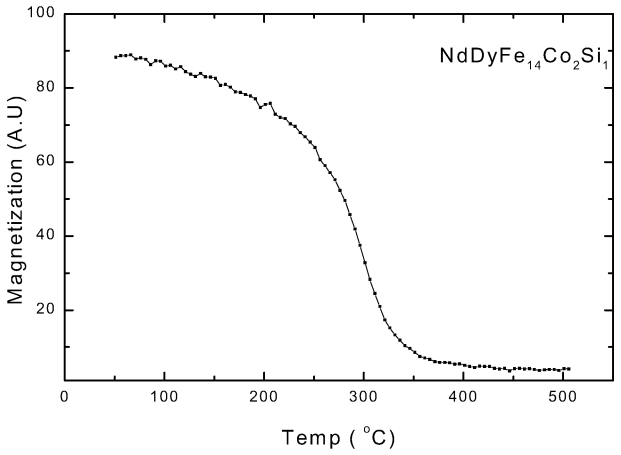

Fig. 2. M versus T for $NdDyFe_{14}Co_2Si$.

DR and DH models are 1.4622 and 1.4665 for Co $= 2$ and 3, respectively, for the DR phase. These values are consistent with the $c/a = 1.465$, the minimum value in the mixed rare-earth system $R_2Fe_{17-x}Si_x$ [2]. For the $y = 1.5$ samples that were refined using the OR and DH models, the (c/a) 's are 1.4683 and 1.4656 for Co $= 2$ and 3, respectively, for the OR phase. These observations suggest that c/a ratio is not a reliable parameter to indicate the presence of the DR structure in these compounds.

The ND refinements clearly indicate that though Si and Co may be treated as similar with regard to site preference and site occupancy, the effect of Co replacing iron is quite different from that of Si. The DR structure coexisting with the DH structure observed for the $NdDyFe_{(17-y-x)}Co_xSi_y$ for $y = 1$ can be expected when compared with the structures associated with $Nd_{(2-z)}Dy_zFe_{17-y-x}Co_xSi_y$ for $x = 2, 3$ and $y = 1$. In these compounds, the light rare-earth-rich compound favors the OR structure, and the heavy rare earth-rich compound favors the two phases of OR and DH. $NdDyFe_{(17-y-x)}Co_xSi_y$ with $y = 1$ can be seen as compounds having the DR phase and the DH phase that bridge the transition from the light rare-earth-rich OR phase to the heavy rare-earth-rich DH phase. The two-phase structure in $NdDyFe_{17-y-x}Co_xSi_y$ for $y = 1.5$ can be attributed to the result of further replacement of iron with silicon compared to the samples with $y = 1$. This influence of silicon on the compound favoring the two-phase structure may be expected from the structures associated with $NdDyFe_{16}Si_1$ (DR) and $NdDyFe_{15}Si_2$ (DR and DH). In the compound having the DR structure, replacing a higher content of Fe with Si favors the two-phase structure of the OR phase and the DH phase. It is seen from the Curie temperature measurements, as shown in Fig. 2, that these samples possess a single magnetic phase transition. A similar result was reported for the $R_{2-x}R'_xCo_{17}$ systems [10]. In studies on the Pr and Nd-substituted 2 : 17 magnets for elevated temperature application, it was observed that the alloys as cast were two-phase but had a unique magnetic transition temperature [11]. The single transition temperature observed in the M versus T plots suggests that the two magnetic phases of OR or DR and DH exist "coherently" as a single magnetic phase. In such an arrangement, there is a possibility for the magnetic unit cell to be comprised of both the rhombohedral and the hexagonal unit cells leading to a single magnetic phase characterized by a unique Curie temperature for the compound.

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