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The atomic and magnetic structure of $NdMn_{(6-x)}Fe_xGe_6$ solid solutions

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The magnetic and crystallographic properties of induction-melted $NdMn_{(6-x)}Fe_xGe_6$ intermetallics ($x=0$, 1.0, and 1.5) in the temperature range of 30–475 K have been studied by x-ray and neutron diffraction techniques and SQUID measurements. All of the samples crystallized in the YCo_6Ge_6-type structure ($P6/mmm$). A small amount (<5 mol%) of $Nd(MnFe)_2Ge_2$ is present as an impurity. As expected, iron replaces manganese at the $3g$ site. The unit cell volume decreases slightly with increasing iron content at an average rate of 1.3% per substituted atom. Lattice parameters a and c contract at a rate of 0.6% and 0.2% per substitution atom, respectively. The net magnetization of these samples decreases rapidly with increasing iron content. According to neutron diffraction data, the magnetic moment of the iron sublattice couples negatively with ferromagnetically coupled manganese and neodymium moments. Addition of iron suppresses the spin reorientation processes observed in $NdMn_6Ge_6$. Whereas the net moment in $NdMn_5Fe_1Ge_6$ slowly cants away from the c-axis with increasing temperature, the easy direction of $NdMn_{4.5}Fe_{1.5}Ge_6$ is approximately parallel to the c-axis in the temperature range mentioned above.
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INTRODUCTION

RMn_6Ge_6 intermetallics (R=rare earth) belong to the $P6/mmm$ space group and are isostructural with YCo_6Ge_6[1] (R=Nd, Sm) or $HfFe_6Ge_6$[2] (R=Sc, Y, Gd-Lu). Of these intermetallics, only $NdMn_6Ge_6$ and $SmMn_6Ge_6$ display ferromagnetic ordering within and between rare earth and Mn sublattices. The Curie temperatures of $NdMn_6Ge_6$ and $SmMn_6Ge_6$ are 417 and 441 K, respectively.[3] In the present study, we have used x-ray and neutron diffraction and SQUID measurements to investigate the crystallographic and magnetic structure of $NdMn_{6-x}Fe_xGe_6$ ($x=0$, 1.0, and 1.5) intermetallics.

EXPERIMENT

$NdMn_{6-x}Fe_xGe_6$ samples were prepared from elements of purity 99.99% or better by induction melting in a cold copper crucible followed by annealing at 750 °C for two weeks. The phase purity of the samples was checked by x-ray diffraction utilizing Cu K_α radiation. The bulk magnetic properties were measured at the Southern Illinois University–Carbondale (SIUC) on a Quantum Design SQUID magnetometer.

The powder neutron diffraction data were obtained at the University of Missouri Research Reactor for samples placed in thin-walled vanadium containers utilizing neutrons of wavelength 1.4875 Å. Neutron diffraction data were collected at 30 and 295 K for each sample. Crystallographic and magnetic structural parameters were refined by fitting the neutron diffraction data using the FULLPROF technique.[4]

Additional information about the easy direction of magnetization was obtained from x-ray diffraction studies of samples which were magnetically aligned in-plane. The applied magnetic field forces those crystallographic planes perpendicular to the easy direction of magnetization to preferentially orient themselves perpendicular to the sample surface. Similarly, crystallographic planes which are parallel to the easy direction of magnetization will preferentially orient themselves, even though to a lesser degree, parallel to the sample surface. Consequently, the relative intensities of reflections in the x-ray diffraction pattern of the oriented samples will differ from those of the random powder sample.

RESULTS AND DISCUSSIONS

The thermomagnetic data for $NdMn_6Ge_6$, see Fig. 1 are in good agreement with the work of Chafik El Idrissi[3] *et al.* and show a sharp transition at approximately 40 K and a hump with its leading and trailing edges in the vicinity of 275 and 400 K, respectively. Whereas the trailing edge of the hump represents the Curie point, see Table I, the transitions at 40 and 275 K have been assigned[3] to spin reorientation processes as described below. Even though the M vs T plot for $NdMn_5Fe_1Ge_6$ contains a hump similar to that observed for $NdMn_6Ge_6$, the sharp low temperature transition is clearly absent in this case. In contrast, none of the above mentioned magnetic transitions are evident in the M vs T plot for $NdMn_5Fe_{1.5}Ge_6$. A less obvious magnetic transition occurring around 175 K is visible in the thermomagnetic data for the two samples containing iron. Even though we are unable to rule out the major phase, $NdMn_{6-x}Fe_xGe_6$ as the source of this weak transition, the likely candidate is the

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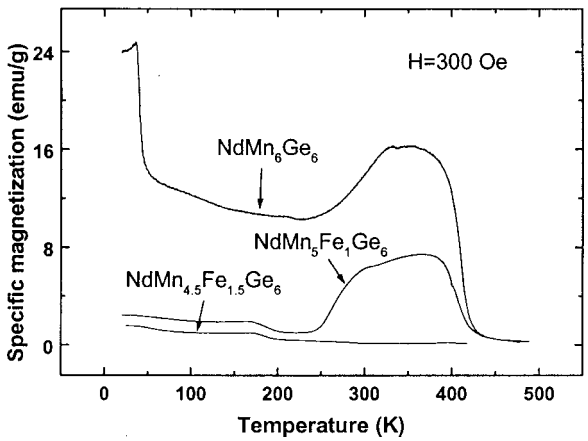

FIG. 1. Specific magnetization vs temperature data for $NdMn_{6-x}Fe_xGe_6$ at an applied field of 300 Oe.

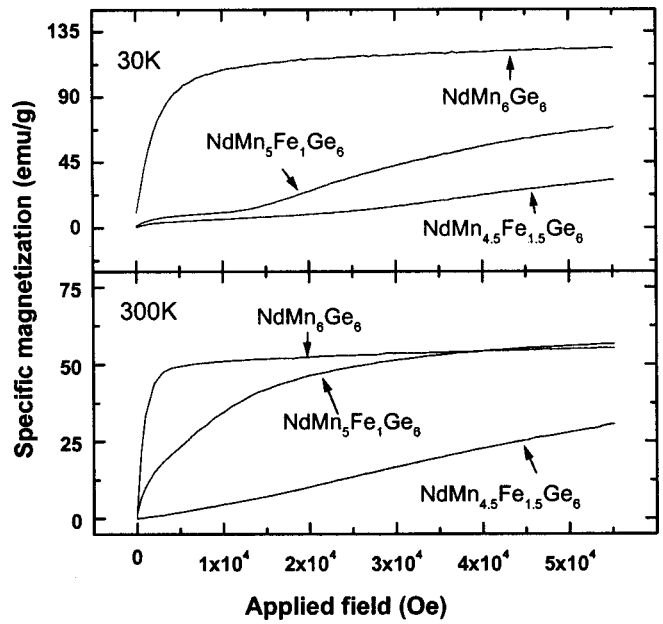

FIG. 2. Specific magnetization of $NdMn_{6-x}Fe_xGe_6$ vs applied field at 30, 150, and 300 K.

impurity $NdMn_2Ge_2$, whose manganese sublattice could be partially substituted by iron atoms. The main magnetic transition of $Nd(MnFe)_2Ge_2$ intermetallics occurs in the 100–200 K range.[5]

As seen in Fig. 2, the net magnetization of $NdMn_{6-x}Fe_xGe_6$ decreases rapidly with increasing iron content, most likely due to negative coupling between the magnetic moments of iron and manganese-neodymium sublattices. The effects of iron substitution on the net magnetization are most prominent at 30 K. At 150 and 300 K, the magnetization of $NdMn_5Fe_1Ge_6$ approaches that of $NdMn_6Ge_6$ as the applied field exceeds 5.5 and 3.5 T, respectively. The magnetization of $NdMn_{4.5}Fe_{1.5}Ge_6$, however, does not show signs of saturation and remains much smaller than that of the other two samples at the applied field strengths used herein, i.e., up to 5.5 T.

The neutron diffraction data were refined based on a YCo_6Ge_6-type crystal structure.[1] A small amount (<5 mol%) of $Nd(MnFe)_2Ge_2$, most likely with manganese partially substituted by iron, is present as an impurity. Refined lattice parameters are given in Table I. The unit cell contracts slightly with increasing iron content at an average rate of 1.3% per substituted atom. Lattice parameters *a* and *c* contract at a rate of 0.6% and 0.2% per substitution atom, respectively, indicating that the contraction of the unit cell is anisotropic. As expected, iron atoms occupy only the 3*g* transition metal sites because of the similar size of manganese and iron atoms.

The refinement of the magnetic structure of $NdMn_{6-x}Fe_xGe_6$ samples was based on the collinear magnetic structure proposed by Chafik El Idrissi[3] *et al.* for $NdMn_6Ge_6$. According to this model, neodymium and manganese magnetic moments are ferromagnetically coupled at temperatures between 2 K and the Curie temperature. The easy direction of magnetization, however, changes sharply from basal to a direction that makes an angle of about 30° with the *c*-axis around 30 K and cants back slightly toward the *c*-axis as the sample temperature increases beyond 250 K.[3] Within this collinear magnetic structure, the best fits were obtained for a model in which the magnetic moments of iron atoms couple negatively with those of neodymium and manganese atoms at all three temperatures (30, 150, and 300 K) investigated.

Refined magnetic parameters are listed in Table II. Note that the directions of magnetization of manganese, iron, and neodymium have been refined independently. Even though our results for $NdMn_6Ge_6$ are in general agreement with those previously published, the easy direction we obtained at 150 and 300 K is closer to the *c*-axis by ~20° compared with Chafik's work.[3] In contrast to $NdMn_6Ge_6$, for which the easy direction of magnetization at 30 K is at an angle of 42° from the *c*-axis, that for $NdMn_5Fe_1Ge_6$ is only 13°. This difference is expected because the spin reorientation observed in $NdMn_6Ge_6$ at ~30 K is absent in $NdMn_5Fe_1Ge_6$, see Fig. 1. Whereas the easy direction in $NdMn_5Fe_1Ge_6$ does not change appreciably between 30 and 150 K, it moves to ~30° at 300 K. This spin reorientation is the most likely source of the leading edge of the hump in the thermomagnetic data de-

TABLE I. Lattice parameters and Curie temperature for $NdMn_{6-x}Fe_xGe_6$ intermetallics.

		a (Å)			*c* (Å)		
Sample	T_c (K)	30 K	150 K	300 K	30 K	150 K	300 K
$NdMn_6Ge_6$	418	5.232(1)	5.233(1)	5.260(1)	4.091(1)	4.098(1)	4.113(1)
$NdMn_{5.0}Fe_{1.0}Ge_6$	416	5.197(1)	5.205(1)	5.229(1)	4.086(1)	4.090(1)	4.105(1)
$NdMn_{4.5}Fe_{1.5}Ge_6$		5.191(1)	5.204(1)	5.215(1)	4.084(1)	4.088(1)	4.103(1)

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TABLE II. Refined magnetic properties for $NdMn_{6-x}Fe_xGe_6$ at 30, 150, and 300 K. Parameters for which a zero uncertainty is listed were fixed during refinement.

	$NdMn_6Ge_6$			$NdMn_{5.02}Fe_{0.98}Ge_6$			$NdMn_{4.46}Fe_{1.54}Ge_6$		
	30 K	150 K	300 K	30 K	150 K	300 K	30 K	150 K	300 K
μ_{Nd} (μ_B)	3.1(1)	2.9(2)	2.2(2)	2.9(2)	2.7(2)	2.6(2)	2.6(2)	2.2(2)	2.1(2)
μ_{Mn} (μ_B)	2.7(1)	2.3(1)	2.1(1)	2.4(1)	2.2(1)	2.1(1)	2.3(1)	2.0(1)	1.9(1)
μ_{Fe} (μ_B)	⋯	⋯	⋯	1.7(0)	1.5(0)	1.0(0)	1.5(0)	1.0(0)	1.0(0)
$\Phi_{Nd}(°)$[a]	42(2)	0(1)	20(3)	13(1)	15(2)	31(3)	2(2)	7(2)	6(2)
$\Phi_{Mn}(°)$[a]	42(2)	0(1)	20(3)	14(1)	14(2)	30(3)	3(2)	3(2)	3(2)
$\Phi_{Fe}(°)$[a]	⋯	⋯	⋯	193(0)	195(0)	216(0)	180(0)	180(0)	180(0)

[a]Angle between the direction of the magnetic moment and the *c*-axis.

scribed above. In the case of $NdMn_{4.5}Fe_{1.5}Ge_6$, however, the easy direction of magnetization is virtually along the *c*-axis at all temperatures. It appears that the reorientation processes observed in $NdMn_6Ge_6$ are suppressed by the partial substitution of manganese by iron.

The difference between the orientation of the easy axes of $NdMn_5Fe_1Ge_6$ and $NdMn_{4.5}Fe_{1.5}Ge_6$ is confirmed by x-ray diffraction data for magnetically aligned powders, see Fig. 3. The relative intensity of the (111) reflection for the aligned $NdMn_5Fe_1Ge_6$ sample is considerably less than that for the nonaligned sample. This indicates that the net magnetic moment of the $NdMn_5Fe_1Ge_6$ unit cell is close to being perpendicular to the (111) plane, quite in-step with the refined ϕ of ~30°, see Table II. In the case of $NdMn_{4.5}Fe_{1.5}Ge_6$, however, the most noticeable change in the x-ray diffraction pattern upon alignment is the growth of the (110) reflection. This indicates that the net magnetic moment of $NdMn_{4.5}Fe_{1.5}Ge_6$ is, at least, close to being parallel to the (110) plane instead of being perpendicular to the (111) plane as is the case for $NdMn_5Fe_1Ge_6$.

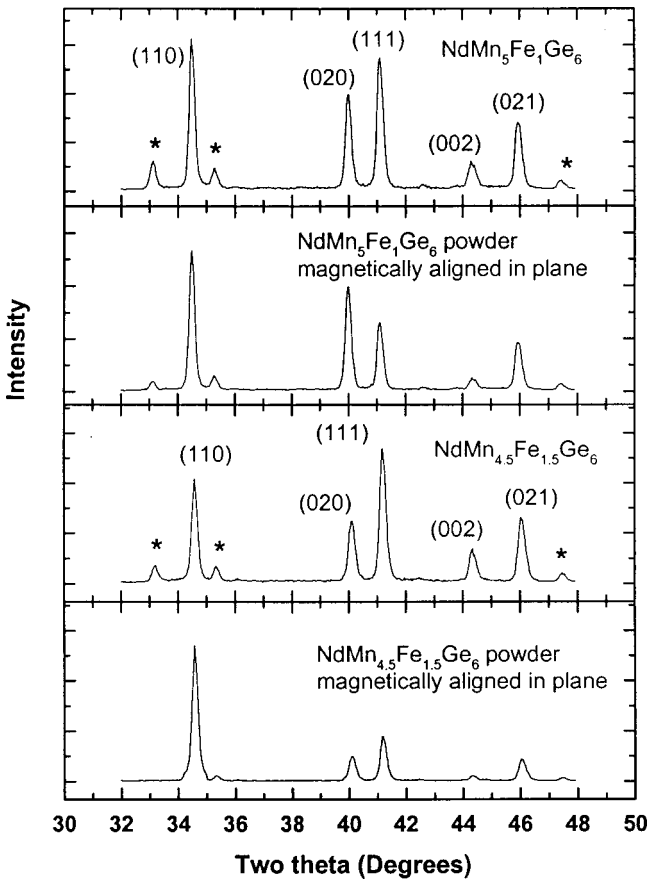

FIG. 3. X-ray diffraction data measured at 300 K for random and magnetically aligned powders of $NdMn_5Fe_1Ge_6$ and $NdMn_{4.5}Fe_{1.5}Ge_6$. Diffraction lines denoted by a* belong to the impurity phase.

CONCLUSIONS

Up to 1.5 manganese atoms per formula unit of $NdMn_6Ge_6$ can be replaced by iron atoms before a significant amount of impurities occur. The unit cell volume decreases anisotropically with increasing iron content at an average rate of 1.3% per substituted atom. The net magnetization decreases rapidly with increasing iron content. The magnetic moment of the iron sublattice couples negatively with the ferromagnetically coupled magnetic moments of manganese and neodymium atoms. Addition of iron suppresses the spin reorientation processes observed in $NdMn_6Ge_6$. Whereas the net moment in $NdMn_5Fe_1Ge_6$ slowly cants away from the *c*-axis with increasing temperature, the easy direction $NdMn_{4.5}Fe_{1.5}Ge_6$ is approximately parallel to the *c*-axis in the temperature range investigated.

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