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The relationship between magnetic interactions and near neighbor interatomic distances in the transition metal sublattice of $R(Mn/Fe)_6A_6$ (R=Nd or Sm, A=Ge or Sn)

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The magnetic and crystallographic structures of $R(Fe/Mn)_6A_6$ (R=Nd or Sm and A=Ge or Sn) intermetallics have been investigated using x-ray and neutron diffraction techniques and superconducting quantum interference device magnetic measurements. For both stannides (A=Sn) and germanides (A=Ge), the lattice contracts with increasing iron content. In the case of the stannides, substitution of manganese by iron enhances the saturation magnetization and Curie temperature at low iron concentrations ($x \leqslant 2$) suggesting the presence of an extremely rare occurrence, positive coupling between iron and manganese magnetic moments. In contrast, the magnetic properties of the germanides deteriorate rapidly as manganese is replaced by iron. This difference in the dependence of magnetic properties on the iron content between the germanides and stannides is explained using the Bethe–Slater relationship between near neighbor exchange interactions and interatomic distances. Based on the observations described in this article, it is concluded that the critical near neighbor interatomic distance above which manganese/iron moments couple positively in these intermetallics is ~2.614 Å. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1451305]

INTRODUCTION

Even though manganese atoms have the potential to possess the largest magnetic moment[1] among 3*d* metals, the majority of manganese containing intermetallics cannot be considered for development as permanent magnets because they possess antiferromagnetic or ferrimagnetic magnetic structures.[2,3] On the other hand, even though some of the most widely used permanent magnetic materials are iron containing intermetallics, partial substitution of the iron sublattice of these intermetallics by manganese, even at very low concentrations,[4] results in marked deterioration of their magnetic properties. Investigating how the partial substitution of the manganese sublattice of manganese containing ferromagnetic materials by iron affects their magnetic and crystallographic properties can lead to a better understanding of the magnetic interactions of these intermetallics.

Depending on whether the exchange integral[5] (J_{ex}) for a pair of near neighbor magnetic atoms is positive or negative, the mutual alignment of the two magnetic moments will be either parallel or antiparallel, respectively. As depicted by the Bethe-Slater curve,[5] J_{ex} for a given pair of near neighbor atoms changes from negative to positive as the distance between the two atoms is increased. Consequently, if by some means, the distance between a pair of magnetic atoms having a negative J_{ex} is increased such that J_{ex} becomes positive, the mutual alignment of the magnetic moments should cross over from antiferromagnetic to ferromagnetic and vice versa.

The interatomic distance dependence of J_{ex} is often used to explain why neither manganese nor the majority of maganese containing intermetallics display ferromagnetism. The near neighbor Mn–Mn distances in metallic manganese and the majority of manganese containing intermetallics are in that region for which J_{ex} is negative. On the other hand, the near neighbor Mn–Mn distances in the few manganese containing ferromagnetic intermetallics such as the Heusler alloys[5] and MnBi are in that range for which J_{ex} is positive. Investigating the crystallographic and magnetic properties of other manganese containing ferromagnetic intermetallics may lead to a better understanding of magnetic interactions of this rare family of materials. Herein, we present an investigation of the relationship between the near neighbor transition metal–transition metal distances (d_{TT}) and the magnetic coupling within the transition metal sublattice of several $RMn_{6-x}Fe_xA_6$ intermetallics, where R is Nd or Sm and A is Ge or Sn. $NdMn_6A_6$ and $SmMn_6A_6$ belong to that rare category of intermetallics in which the magnetic moments of near neighbor manganese atoms are ferromagnetically coupled. RMn_6A_6 and $RMn_{6-x}Fe_xA_6$ intermetallics crystallize in one of four highly correlated crystal structures, $HfFe_6Ge_6$,[6] YCo_6Ge_6,[7] $HoFe_6Sn_6$,[8] or $TbFe_6Sn_6$[8] type belonging to the space groups $P6/mmm$, $P\bar{6}/mmm$, $Immm$, and $Cmcm$, respectively.

EXPERIMENTAL AND CALCULATION METHODS

$NdMn_{6-x}Fe_xA_6$ and $SmMn_{6-x}Fe_xA_6$ were prepared from elements of purity 99.99% or better by induction melting in a cold copper crucible followed by annealing at 1043

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TABLE I. Structure types of the RMn_6Ge_6 intermetallic compounds.

Sample	Structure type
$NdMn_6Sn_6$	$HoFe_6Sn_6$
$NdMn_{5.5}Fe_{0.5}Sn_6$	$TbFe_6Sn_6$
$NdMn_5FeSn_6$	$TbFe_6Sn_6$
$NdMn_{4.5}Fe_{1.5}Sn_6$	$TbFe_6Sn_6$
$NdMn_4Fe_2Sn_6$	$TbFe_6Sn_6$
$SmMn_6Sn_6$	$HoFe_6Sn_6$
$SmMn_{5.5}Fe_{0.5}Sn_6$	$TbFe_6Sn_6$
$SmMn_5FeSn_6$	$TbFe_6Sn_6$
$SmMn_{4.5}Fe_{1.5}Sn_6$	$TbFe_6Sn_6$
$SmMn_4Fe_2Sn_6$	$TbFe_6Sn_6$
$NdMn_6Ge_6$	YCo_6Ge_6
$NdMn_5FeGe_6$	YCo_6Ge_6
$SmMn_6Ge_6$	YCo_6Ge_6
$SmMn_{5.5}Fe_{0.5}Ge_6$	YCo_6Ge_6
$SmMn_5FeGe_6$	YCo_6Ge_6
$SmMn_{4.5}Fe_{1.5}Ge_6$	YCo_6Ge_6
$DyMn_6Ge_6$[a]	$HfFe_6Ge_6$
$HoMn_6Ge_6$[b]	$HfFe_6Ge_6$
$ErMn_6Ge_6$[c]	$HfFe_6Ge_6$

[a]See Ref. 16.
[b]See Ref. 17.
[c]See Ref. 18.

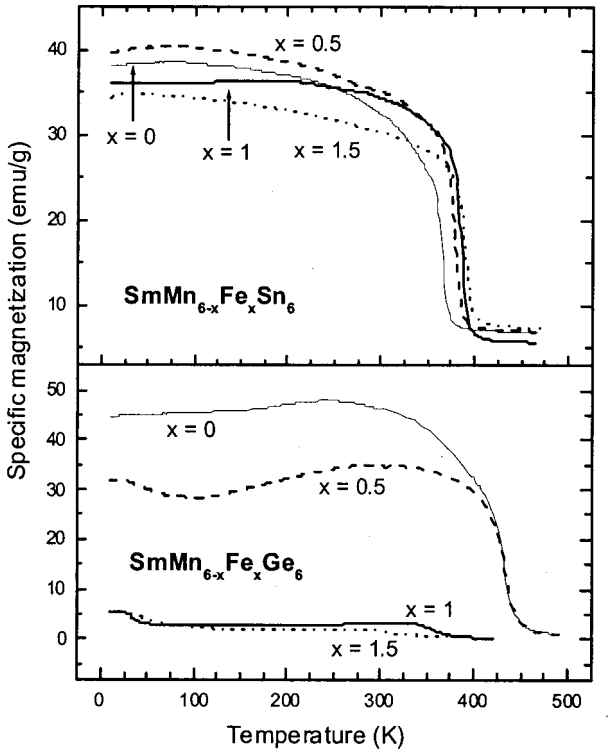

FIG. 1. Temperature dependence of the magnetization for $SmMn_{6-x}Fe_xGe_6$ and $SmMn_{6-x}Fe_xSn_6$ measured at an applied field of 0.2 T.

K for 2 weeks. The phase purity of the samples was checked by x-ray diffraction utilizing Cu K_α radiation. The bulk magnetic properties were measured on a superconducting quantum interference device (SQUID) magnetometer. Powder neutron diffraction data were measured on samples placed in thin-walled vanadium containers with neutrons of wavelength 1.4875 Å.

For $SmMn_{6-x}Fe_xA_6$ samples, the lattice parameters were obtained by Rietveld[9] analysis of x-ray diffraction data. The lattice parameters and atomic positions for $NdMn_{6-x}Fe_xA_6$ were obtained from either FULLPROF[10] or Rietveld refinement of neutron diffraction data. The interatomic distances, coordination environments, and the dimensions of Wigner–Seitz cells were calculated using the BLOKJE[11] code. This article reports on the average d_{TT} values obtained from BLOKJE calculations. Details of these calculations will be published elsewhere.

RESULTS AND DISCUSSION

Table I gives the structure types of the samples investigated. Attempts to substitute more than two manganese atoms per formula unit by iron atoms resulted in samples which were dominated by impurity phases. Note that previously published data for $DyMn_6Ge_6$,[12] $HoMn_6Ge_6$,[13] and $ErMn_6Ge_6$,[14] will be used for comparison. The unit cell volumes of stannides and germanides decrease almost linearly at rates of 1.7% and 2.3%, respectively, per substituted atom with increasing iron content. This contraction may be attributed to the relatively smaller size of iron as compared to manganese.[4]

Magnetization versus temperature ($M-T$) and magnetization versus applied field ($M-H$) data clearly show the difference in the way magnetic properties of stannides and germanides respond to partial substitution of the manganese sublattice by iron. Within the compositions investigated herein, the addition of iron to the stannides does not deteriorate their magnetic properties. In fact, partial replacement of the manganese sublattice of $Nd/SmMn_{6-x}Fe_xSn_6$ by iron results in increases in the Curie temperature and saturation magnetization (see Figs. 1 and 2).[15,16] These observations indicate that the addition of iron strengthens the magnetic exchange interactions within the lattice. Hence, one can infer that iron and manganese magnetic moments interact ferromagnetically in the stannides.

The affects of substituting iron for manganese in germanides are markedly different from those for the stannides. As seen in Figs. 1 and 2, the magnetic properties of $SmMn_{6-x}Fe_xGe_6$ deteriorate rapidly when the iron content exceeds $x=0.5$.[15] In the case of $NdMn_{6-x}Fe_xGe_6$, the same level of deterioration in magnetic properties appears to start at a slightly higher iron content, near $x=1$.[16] Consequently, substituting iron for manganese in $Nd/SmMn_{6-x}Fe_xGe_6$ seems to break down the ferromagnetic coupling within the transition sublattice. To that effect, $SmMn_{6-x}Fe_xGe_6$ appears to be more sensitive to iron substitution than $NdMn_{6-x}Fe_xGe_6$. As suggested below, the average d_{TT} values of these intermetallics may play a considerable role in determining their above described magnetic properties.

Table II gives the near neighbor weighted average d_{TT} values, calculated using the BLOKJE code. Table II also gives the general magnetic state of the transition metal sublattice of the samples. The magnetic states noted in Table II have been assigned based on the $M-T$ and $M-H$ data mentioned above and the magnetic structures determined from neutron diffraction measurements.[15,16]

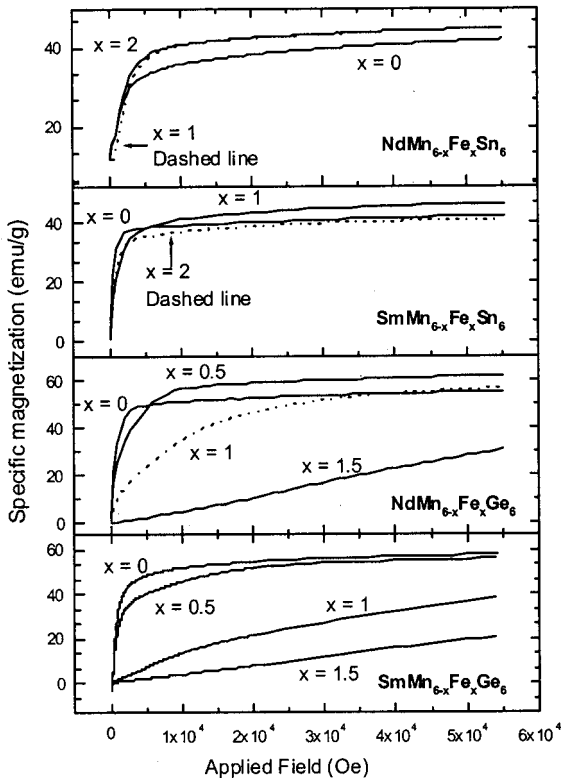

FIG. 2. *M* vs *H* plots measured at 300 K.

Note that data in Table II are arranged such that the d_{TT} values decreases from top to bottom. This ordering of data allows one to clearly see the transition from positive coupling to negative coupling when the average near neighbor transition metal–transition metal distance, d_{TT}, decreases below a certain value. In the case of the $RMn_{6-x}Fe_xA_6$ intermetallics investigated herein, that critical value for d_{TT} appears to be about 2.614 Å.

TABLE II. Weighted averaged near neighbor $T-T$ distances (d_{TT}) and the general magnetic state of the transition metal sublattice. A magnetic state denoted by *F* suggests positive (ferromagnetic) coupling withing the Mn/Fe sublattice. AFR suggests negative coupling (antiferro- or ferri-) withing the Mn/Fe sublattice.

Sample	d_{TT} (Å)	Magnetic state
$NdMn_6Sn_6$	2.7813	*F*
$SmMn_6Sn_6$	2.7777	*F*
$NdMn_{5.5}Fe_{0.5}Sn_6$	2.7772	*F*
$NdMn_5FeSn_6$	2.7685	*F*
$SmMn_{5.5}Fe_{0.5}Sn_6$	2.7669	*F*
$NdMn_{4.5}Fe_{1.5}Sn_6$	2.7617	*F*
$SmMn_5FeSn_6$	2.7561	*F*
$NdMn_4Fe_2Sn_6$	2.7556	*F*
$SmMn_{4.5}Fe_{1.5}Sn_6$	2.7521	*F*
$SmMn_4Fe_2Sn_6$	2.7465	*F*
$SmMn_6Ge_6$	2.6375	*F*
$NdMn_6Ge_6$	2.6300	*F*
$SmMn_{5.5}Fe_{0.5}Ge_6$	2.6215	*F*
$NdMn_5FeGe_6$	2.6145	*F*
$DyMn_6Ge_6$[a]	2.6111	AFR
$HoMn_6Ge_6$[b]	2.6103	AFR
$ErMn_6Ge_6$[c]	2.6102	AFR
$SmMn_5FeGe_6$	2.6085	AFR
$NdMn_{4.5}Fe_{1.5}Ge_6$	2.6077	AFR
$SmMn_{4.5}Fe_{1.5}Ge_6$	2.5935	AFR

[a]See Ref. 16.
[b]See Ref. 17.
[c]See Ref. 18.

Even though the transition metal sublattice of these intermetallics contains both manganese and iron, the low iron concentration allows for the manganese moments to dominate the magnetic exchange interactions. Furthermore, as shown in Table I, the samples investigated belong to four different, yet related, crystal structures. Consequently, it is prudent to conclude that the average critical distance at which the exchange integral J_{ex} for near neighbor manganese atom pairs changes sign in most $RMn_6Fe_xA_6$ based intermetallics is ~2.614 Å. However, because iron substitution cannot be used to decrease d_{TT} of stannides below the critical distance, it remains to be seen if the manganese sublattice of the stannides indeed will become antiferro/ferrimagnetic if d_{TT} is reduced below that value by some other means such as external pressure. In any case, whenever the structure and the composition of these intermetallics permit larger near neighbor transition metal–transition metal distances, the possibility exists for their magnetic properties to be appreciably improved by the partial substitution of the manganese sublattice by iron.

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