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G. K. Marasinghe

Peter C. Ezekwenna

William Joseph James
Missouri University of Science and Technology

Z. Hu

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/chem_facwork/1612

An analysis of iron-iron interatomic distances in several rare earth transition metal intermetallics

G. K. Marasinghe, Peter C. Ezekwenna, and W. J. James
Department of Physics and the Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri 65401-0249

Z. Hu and W. B. Yelon
University of Missouri Research Reactor, Columbia, Missouri 65211

As a part of a systematic study of the dependence of iron-iron exchange interactions on near neighbor iron-iron distances in rare earth transition metal magnetic materials, we have conducted a statistical analysis of interatomic distances in Nd_2Fe_{17}, $Nd_2Fe_{17}N_3$, and $Nd_2Fe_{14}B$. Results, in general, support the notion that larger near neighbor iron-iron distances promote higher Curie temperatures. In this work, special attention has been paid to the expansion of the Nd_2Fe_{17} lattice due to interstitial nitrogenation and the accompanying increase in the Curie temperature. Within the unit cell, the expansion of the Nd_2Fe_{17} lattice due to nitrogenation is highly nonuniform. When nitrided, the distance between near neighbor 6*c* iron sites in Nd_2Fe_{17} increases only slightly, by 0.021 Å. However, the distances between other near neighbor iron pairs separated by less than 2.45 Å increases by about 0.04 Å. The nitrogenation of Nd_2Fe_{17} effectively reduces the number of near neighbor iron pairs separated by less than 2.45 Å by 92%. However, near neighbor interatomic distances involving the 18*h* sites are the most affected by nitrogenation. Consequently, the 18*h* site may play a major role in the enhancement of the Curie temperature due to nitrogenation. © *1997 American Institute of Physics.* [S0021-8979(97)20308-7]

I. INTRODUCTION

The discovery[1,2] that the addition of interstitial nitrogen dramatically increases the Curie temperature of RE_2Fe_{17} and changes the magnetocrystalline anisotropy from basal in Sm_2Fe_{17} to axial in $Sm_2Fe_{17}N_3$ has led to a renewed interest in the RE_2Fe_{17} compounds. Unfortunately, interstitial $RE_2Fe_{17}N_x$ and $RE_2Fe_{17}C_x$, prepared by gas-solid reactions, are thermally unstable, decomposing at temperatures slightly above their Curie temperatures.[3] Even though $RE_2Fe_{17}N_x$ and $RE_2Fe_{17}C_x$ type materials have not been developed as commercial permanent magnets, their discovery demonstrated the importance of the roles played by iron-iron interatomic distances in determining the magnetic properties of rare earth-iron intermetallics.

Short near neighbor iron-iron distances ($d \lesssim 2.45$ Å) are common in many rare earth iron intermetallics. Iron pairs separated by such short distances are expected to lower the Curie temperatures by promoting negative magnetic exchange interactions within the unit cell.[4] The increase in Curie temperature which accompanies the expansion of the RE_2Fe_{17} unit cell due to nitrogenation suggests that larger neighbor iron-iron distances may lead to higher Curie temperatures.

However, other observations indicate that the relationship between near neighbor iron-iron distances and magnetic properties, especially the Curie temperatures, of rare earth iron type intermetallics is not well understood. As seen in Fig. 1, even though there is a general trend for Nd_2Fe_{17} based solid solutions with larger unit cells to have higher Curie temperatures, the Curie temperature of $Nd_2Fe_{16}TiC_{2.8}$, whose cell volume is larger than that of $Nd_2Fe_{17}N_3$, is lower than the Curie temperature of $Nd_2Fe_{17}N_3$.[5]

Another example which implies a rather complicated relationship between interatomic distances and magnetic properties involves substitution of iron atoms in RE_2Fe_{17} and $RE_2Fe_{14}B$ by silicon or aluminum. As seen in Fig. 2, partially substituting the iron sublattice in RE_2Fe_{17} or $RE_2Re_{14}B$ by silicon causes the unit cell to contract.[6,7] However, this concentration of the lattice is accompanied not by a decrease but by an increase in the Curie temperature of both R_2Fe_{17} and $RE_2Fe_{14}B$ systems. In contrast, partially substituting aluminum for iron expands the R_2Fe_{17} and $RE_2Fe_{14}B$ unit cells but this expansion is accompanied by an increase in the Cu-

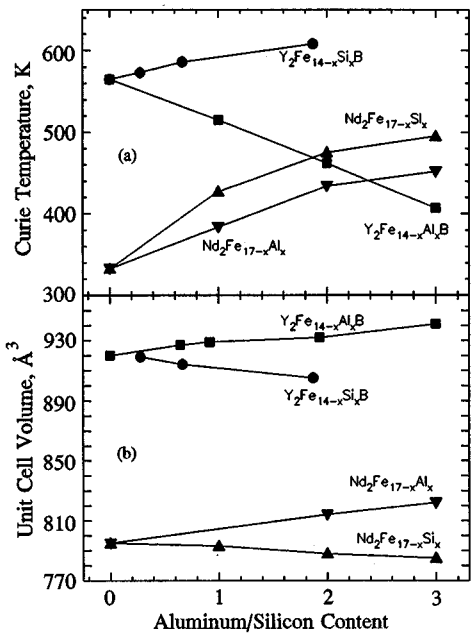

FIG. 1. Curie temperatures and unit cell volumes of several Nd_2Fe_{17} based intermetallics.

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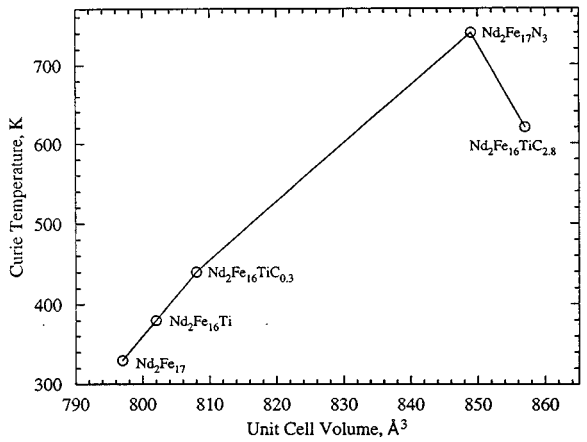

FIG. 2. Dependence of the Curie temperature (a) and unit cell volume (b) on the substituent content in $RE_2Fe_{17-x}(Si/Al)_x$ and $RE_2Fe_{14-x}(Si/Al)_xB$.

rie temperature of RE_2Fe_{17} and a decrease in the Curie temperature of $RE_2Fe_{14}B$.[8,9]

Undoubtedly, interatomic distances in rare earth-iron intermetallics play a major but poorly understood role in determining their magnetic properties. The distance between two near neighbor atoms essentially determines the extent of overlap between their electronic wave functions. Hence, the electronic band structure of rare earth-iron intermetallics is inherently related to the interatomic distances. As a part of a comprehensive study of the relationships between near neighbor iron-iron distances and the magnetic properties of

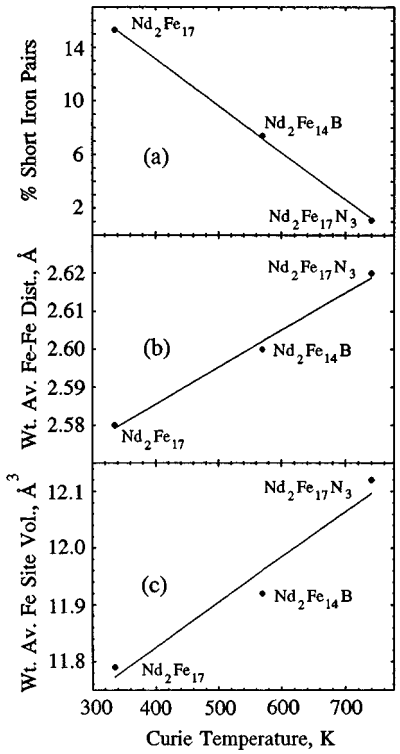

FIG. 3. Dependence of Curie temperature on (a) the percentage of near neighbor iron pairs separated by less than 2.45 Å, (b) weighted average near neighbor iron atom separation, and (c) weighted average iron site volume, in Nd_2Fe_{17}, $Nd_2Fe_{17}N_3$, and $Nd_2Fe_{14}B$.

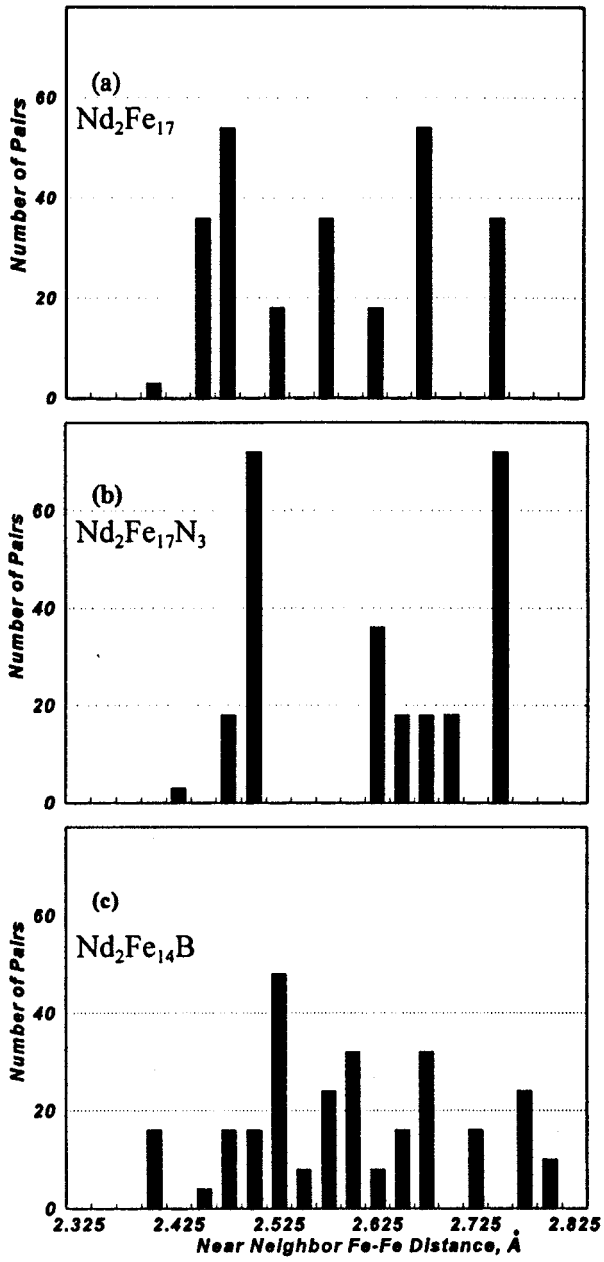

FIG. 4. Distribution of near neighbor iron-iron distances in (a) Nd_2Fe_{17}, (b) $Nd_2Fe_{17}N_3$, and (c) $Nd_2Fe_{14}B$.

rare earth-iron intermetallics, we have analyzed the relationship between the interatomic distances and Curie temperatures of $Nd_2Fe_{14}B$, Nd_2Fe_{17}, and $Nd_2Fe_{17}N_3$.

II. EXPERIMENT

$Nd_2Fe_{14}B$ and Nd_2Fe_{17} samples were prepared from 99.9% pure elements by induction melting followed by annealing at 950 °C for 120 h. $Nd_2Fe_{17}N_3$ was synthesized by gas phase insertion of nitrogen into finely ground Nd_2Fe_{17} at 600 K. The Curie temperatures of the samples were measured by a vibrating sample magnetometer or a superconducting quantum interference device magnetometer. The powder neutron-diffraction patterns obtained at the University of Missouri Research Reactor were refined using the

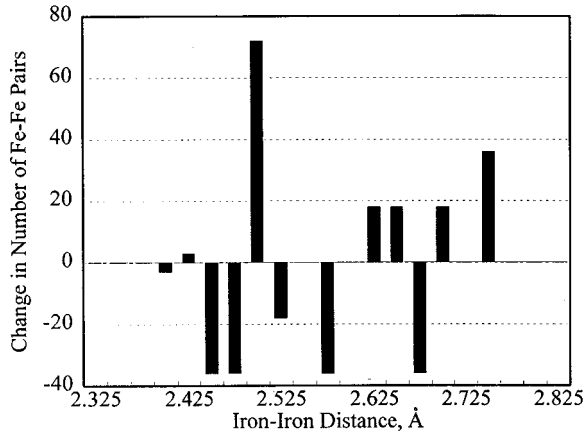

FIG. 5. The change in the distribution of near neighbor iron-iron distances in Nd_2Fe_{17} due to nitrogenation.

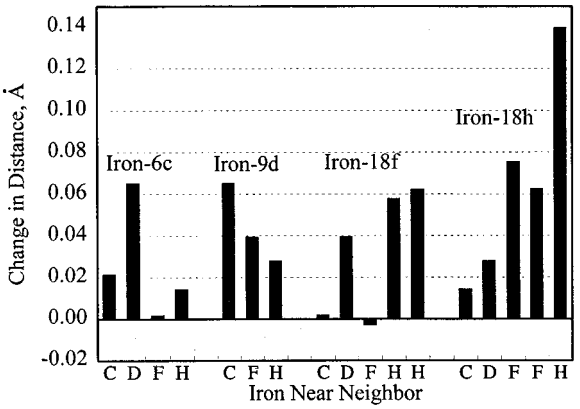

FIG. 6. Change in the near neighbor iron-iron distances for the four iron sites due to nitrogenation of Nd_2Fe_{17}.

FULLPROF code[10] on the basis of the Nd_2Fe_{17} structure.[11] Near neighbor environments and interatomic distances were determined by Wigner–Seitz[12] analysis of the unit cells using atomic positions and lattice parameters obtained by neutron diffraction studies.

III. DISCUSSION

Figure 3 shows how the Curie temperatures of the three samples are related to (a) the percentage of near neighbor iron pairs separated by less than 2.45 Å, (b) the weighted average near neighbor iron atom separation, and (c) the weighted average iron site volume.

Even though these quantities are related to each other, it is important to note that the first two play different roles in determining the Curie temperatures. Because the iron pairs separated by short ($d \lesssim 2.45$ Å) distances are expected to favor negative magnetic exchange interactions, a smaller percentage of such short iron-iron pairs should essentially promote higher Curie temperatures. In contrast, for those interatomic distances for which the magnetic exchange integral is positive, the Bethe–Slater curve suggests that the magnetic exchange interaction between two iron atoms should go through a maximum as the separation between the atoms increases. Consequently, larger weighted average near neighbor iron-iron distances may not necessarily promote higher Curie temperatures, as may be the case for $Nd_2Fe_{15}TiC_{2.8}$, see Fig. 2.

Figure 4 shows the distributions of near neighbor iron-iron distances for Nd_2Fe_{17}, $Nd_2Fe_{17}N_3$, and $Nd_2Fe_{14}B$. Compared to Nd_2Fe_{17} and $Nd_2Fe_{17}N_3$, $Nd_2Fe_{14}B$ structure has a wider, somewhat uniform distribution of near neighbor iron-iron distances. In contrast, the near neighbor iron-iron distances in the $Nd_2Fe_{17}N_3$ structure belong to two well separated groups, one between 2.4 and 2.5 Å and the other between 2.6 and 2.75 Å. It is very likely that the magnetic exchange interactions between iron-iron pairs belonging to the latter group, 2.6 Å$<d<$2.75 Å, are the main contributors to the relatively high Curie temperature in $Nd_2Fe_{17}N_3$.

Figure 5 gives the change in the distribution of near neighbor iron-iron distances which occurs when Nd_2Fe_{17} is nitrogenated. It is evident from Fig. 5 that the expansion of the 2:17 unit cell due to nitrogenation is highly nonuniform. The separation between the shortest near neighbor iron-iron pairs, the 6*c* iron atoms, increases only very slightly, from 2.34 to 2.41 Å. Consequently, it is very likely that the 6*c* $-$6*c* iron pairs make a major contribution towards increasing the Curie temperature by nitrogenation. In sharp contrast, the distances between near neighbor iron pairs involving the 18*h* sites are increased most by nitrogenation, indicating that the 18*h* site may play a major role in the accompanying enhancement of the Curie temperature. (See Fig. 6.)

ACKNOWLEDGMENT

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