Ab Initio Calculations of the Curie Temperature of Complex Permanent-Magnet Materials

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The nitrogenation of rare-earth–transition-metal compounds (R_2M_{17}) more than doubles the Curie temperature (T_C) of iron-rich compounds but lowers T_C of cobalt-rich compounds. Self-consistent spin-polarized electronic-structure calculations are carried out to understand this unusual behavior of T_C. T_C is calculated using the Heisenberg model and finite-size scaling in Monte Carlo simulations. The calculated values of T_C are in very good agreement with the experimental data. [S0031-9007(97)03516-3]

A good permanent magnet must have large magnetization (M), high Curie temperature (T_C) and coercivity. Fe and Co satisfy the first two requirements but have low coercivities due to their low magnetic anisotropies. Because of the high anisotropies of the rare earths (R), transition-metal-rich rare-earth compounds have been the prime candidates for permanent-magnet research. Most of the studies in this field deal with light rare earths because of their ferromagnetic coupling with Fe and Co. Unfortunately, rare earths lower T_C of Fe and Co with the larger changes in the Fe-rich compounds. For example, T_C of Sm_2Fe_{17} is about 40% of that of Fe and T_C of Sm_2Co_{17} is about 85% of that of Co. The lowering of T_C also lowers the magnetization at the operating temperature of permanent-magnet applications.

Since the discovery of the supermagnet $Nd_2Fe_{14}B$ in 1984 [1], one of the major challenges in this field has been and still is to find ways to improve the permanent-magnet properties of transition metal-rich rare-earth compounds. It was recently discovered that the addition of about three nitrogen atoms per formula unit to R_2Fe_{17} compounds leads to a considerable improvement of their permanent-magnet properties [2]. On the other hand, the nitrogenation of R_2Co_{17} compounds leads to a moderate lowering of their T_C and magnetization values [3]. An understanding from first principles of T_C and its observed changes in these systems will be very helpful to future advances in the permanent-magnet field. Because of the complicated structure of such systems with a large number of atoms per unit cell, the theoretical understanding of their T_C is in its infancy. We used the spin-fluctuation theory of Mohn and Wohlfarth [4] to explain the large increases in T_C upon nitrogenation of some Fe-rich compounds [5]. However, this theory does not give the absolute value of T_C itself correctly.

We report here *ab initio* calculations of the Curie temperatures of Sm_2Fe_{17} and Sm_2Co_{17} and their nitrides. Such a study requires a model for interatomic exchange interactions. Recent studies of bcc Fe and hcp Co have shown that the Heisenberg model based on electronic structure calculations predicts T_C in good agreement with experimental results [6]. Based on these results, the Heisenberg model is used here to represent the exchange interactions in these compounds. We employ the Monte Carlo method with the Heisenberg Hamiltonian derived from *ab initio* electronic-structure calculations to compute T_C and the results are compared with the available experimental data. The observed changes in T_C upon nitrogenation are related to the magnetovolume effect and changes in hybridization.

The linear-muffin-tin orbitals method (LMTO) in the atomic sphere approximation is used to calculate the electronic structure for $Sm_2M_{17}N_x$ (M = Fe, Co; $x = 0, 3$) [7]. These systems have a fairly complex Th_2Zn_{17} rhombohedral structure with 19 or 22 atoms per unit cell and the four types of M sites ($6c$, $9d$, $18f$, and $18h$; space group number 166). The lattice parameters of $Sm_2M_{17}N_x$ were taken from Ref. [3]. The self-consistent spin-polarized electronic-structure calculations had to be performed at 288 k points in the irreducible part of the Brillouin zone to get stable values of the Heisenberg exchange parameters. Sm $4f$ electrons are treated as spin-polarized core electrons which is a reasonable approximation due to the highly localized nature of the $4f$ electrons.

The densities of states (DOS) of Sm_2Fe_{17} are compared with those of bcc and fcc iron in Fig. 1. It is interesting to note that Fe d bands in Sm_2Fe_{17} are closer to those of fcc Fe than those of bcc Fe. This is due to the fact that the close-packed environment of Fe atoms in 2-17 compounds is similar to that in fcc (or hcp) Fe. Because of the similarity in their electronic structure, the magnetic properties of the 2-17 compounds are closer to those of fcc iron [6]. For example, both R_2Fe_{17} and fcc Fe show strong dependence of the magnetization on the volume. Thus, the rare earths adversely effect T_C of bcc Fe by changing its relatively open structure to a close-packed one. On the other hand, Co d bands in R_2Co_{17} are similar to those of hcp Co because of the close-packed environment of Co in both the systems (Fig. 2). As a result, the rare earths in R_2Co_{17} have a much smaller effect on the magnetic properties of hcp Co.

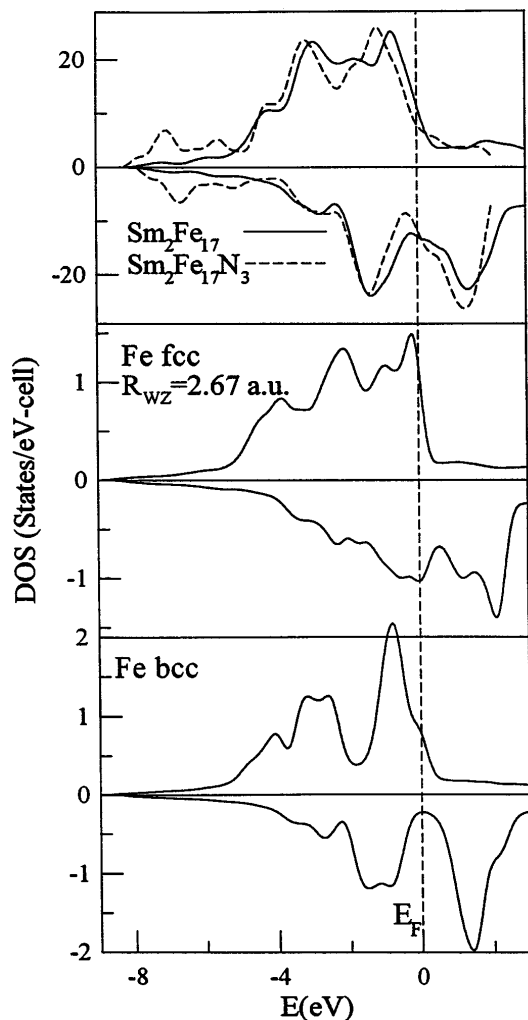The nitrogenation produces a volume expansion of 6.2% in both Sm_2Fe_{17} and SM_2Co_{17} [3]. In addition, the

FIG. 1. Spin-polarized density of states for Sm_2Fe_{17}, $Sm_2Fe_{17}N_3$, and bcc and fcc Fe.

FIG. 2. Spin-polarized density of states for Sm_2Co_{17}, $Sm_2Co_{17}N_3$, and hcp Co.

nitrogen atoms going into the $9e$ sites hybridize predominantly with the transition-metal atoms at the f and h sites. It can be seen from Fig. 1 that the changes in electronic structure due to the addition of nitrogen to Sm_2Fe_{17} correspond essentially to a rigid downward shift of the majority band. Thus the main consequence of nitrogenation of R_2Fe_{17} compounds is the magnetovolume effect. In contrast, Fig. 2 shows no rigid-band shift and hence nitrogen mainly produces small changes in hybridization in R_2Co_{17} compounds.

The Green function formalism to calculate the interatomic exchange parameters from the electronic structure has been developed by Liechtenstein et al. [8] and reviewed recently by Gubanov et al. [9]. The exchange parameters J_{ij} in the Heisenberg Hamiltonian $H_{ex} = -\sum_{ij} J_{ij}\hat{e}_i\hat{e}_j$ ($\hat{e}_i$ is a unit vector in the spin direction at site i) can be derived using spherical charge and spin densities and a local force theorem, and the result is

$$J_{ij} = \frac{1}{4\pi}\sum_{LL'}\mathrm{Im}\int_{-\infty}^{E_F} d\varepsilon \Delta_l^i(\varepsilon)T_{LL'}^{ij\uparrow}(\varepsilon)\Delta_{l'}^j(\varepsilon)T_{LL'}^{ij\downarrow}(\varepsilon). \quad (1)$$
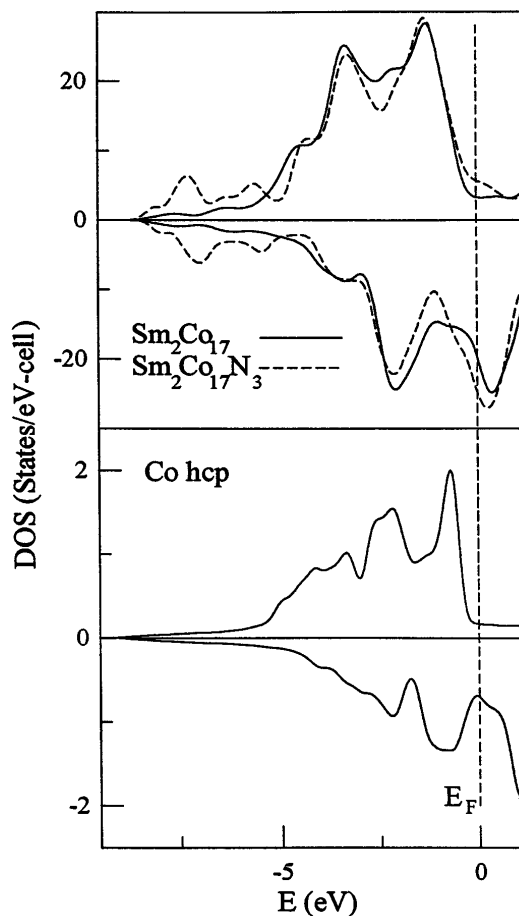
Here $T_{LL'}^{ij\sigma}$ is the scattering matrix in the site (i, j) representation for different spin projections ($\sigma = \uparrow, \downarrow$), $\Delta_l^i(\varepsilon) = t_{li\uparrow}^{-1} - t_{li\downarrow}^{-1}$ is the difference of the inverse single-site scattering matrices, and E_F is the Fermi energy. The total exchange interaction of the given site i with all the other sites j is given by $J_i = \sum_{j\neq i} J_{ij}$. The mean-field estimate of T_C is given by $T_C = 2\langle J_i\rangle/3k$, where k is the Boltzmann constant and $\langle J_i\rangle$ is the weighted average of J_i over the different sites in the unit cell. The rather complicated procedure to calculate $T_{LL'}^{ij\sigma}$ in the LMTO formalism has been developed by Gunnarsson et al. [10].

The exchange parameters (J_{ij}) between M atoms and their neighbors are calculated up to a distance of 6 Å, a distance that includes six neighboring shells in a fcc iron having the same nearest-neighbor distance as that of Fe-Fe in Sm_2Fe_{17}. The exchange interactions decrease and oscillate with the distance, the decrease being more rapid in the Co than in the Fe compounds. The J_{ij} for the first shell are large and positive with the values for the Co compound larger than those of the Fe compound as expected from their T_C values. The second shell parameters are negative for the Fe compound but both positive and negative for the Co compound. J_i for Sm is obtained from self-consistent calculations of $4f$-moment flip energy (which

TABLE I.   Exchange parameters J_i (meV) for different sites, average exchange parameters $\langle J_i \rangle$, and calculated and experimental T_c (K).

	J_c^{Sm}	J_c^{M}	J_d^{M}	J_f^{M}	J_h^{M}	$\langle J_i \rangle$	T_c^{calc}	$T_c^{expt\,a}$
Sm_2Fe_{17}	-44	67	52	49	40	48	287	389
$Sm_2Fe_{17}N_3$	-77	106	128	128	136	123	768	752
Sm_2Co_{17}	-90	228	219	185	192	187	1169	1189
$Sm_2Co_{17}N_3$	-63	171	138	109	141	125	776	783

[a]Reference [3].

is equal to $2J_i$) following a procedure used by Liebs et al. [11]. Because of the highly localized nature of the 4f electrons, the Sm-M antiferromagnetic exchange interactions are considered between Sm and its nearest neighbors only. The J_{ij} for each Sm-M pair is taken to be J_i/N where N is the number of nearest-neighbor M atoms.

The exchange parameters increase in Sm_2Fe_{17} and decrease in Sm_2Co_{17} upon nitrogenation. These changes are reflected in the values for J_i for various sites in Fe and Co compounds as shown in Table I. The average $\langle J_i \rangle$ increases by ~156% for Sm_2Fe_{17} and decreases by ~33% for Sm_2Co_{17} upon nitrogenation, qualitatively reflecting the changes in T_C of the two compounds. The large increase in $\langle J_i \rangle$ for the Fe compound is due to an almost rigid-band downward shift of the majority band with the Fermi energy located along its upper sharp edge (Fig. 1). The physical origin of this change is primarily the magnetovolume effect similar to that in fcc iron [6,12] (not bcc Fe) with the changes in hybridization playing a smaller role. The moderate decrease in $\langle J_i \rangle$ for the Co compound is related to the location of E_F in a valley in the majority DOS (Fig. 2). There is practically no rigid-band shift in this system and the brand-structure changes come primarily from the changes in the hybridization. The nitriding effects can also be understood by examining the values of $\langle J_i(E) \rangle$ near E_F for various compounds (Fig. 3). The $\langle J_i(E) \rangle$ in Fig. 3 is calculated from Eq. (1) by replacing E_F, the upper limit of the integral, by $E[\langle J_i \rangle = \langle J_i(E_F) \rangle]$. The $\langle J_i(E) \rangle$ near E_F for Sm_2Co_{17} has reached a plateau and the nitrogenation lowers its value due to the changes in hybridization. On the other hand, $\langle J_i(E) \rangle$ near E_F for Sm_2Fe_{17} is increasing with a steep slope and the nitrogenation raises its value due to the magnetovolume effect.

Monte Carlo (MC) simulations, based on the Heisenberg Hamiltonian calculated above, are used to find T_C for the various compounds. The Metropolis algorithm [13] is used to find the thermodynamic averages of M^n for $n = 1$ to 4 as functions of temperature for three different cell sizes (2375, 6517, and 9728 sites), where M is the magnetization. The T_C for each cell is calculated from the locations of the extrema of the thermodynamic quantities such as susceptibility and third and fourth order cumulants, following a procedure due to Chen et al. [14]. The extremum values as a function of the cell size N follows the following scaling law:

$$T_C(N) \approx T_C + a_q N^{-1/3\nu}, \qquad (2)$$

where a_q is a thermodynamic quantity-dependent constant and ν is the critical exponent. Thus $T_C(N)$ plotted as a function of $N^{-1/3\nu}$ is a straight line with the intercept as the T_C for the infinite size of the sample. The straight line fits to extrema of susceptibility and third and fourth order cumulants give $\nu = 0.709 \pm 0.006$. The calculated values of T_C for the different compounds are shown in Table I along with the experimental results. The agreement between the calculated results and the experimental data is very good except for Sm_2Fe_{17}. The agreement for Sm_2Fe_{17} is not as good as for other compounds because of a relatively low T_C and its extreme sensitivity to the magnetovolume effect in this system. This can be seen from the small value of $\langle J_i(E) \rangle$ and its variation near E_F plotted in Fig. 3 because T_C is approximately proportional to $\langle J_i(E) \rangle$ at E_F. The curve for Sm_2Fe_{17} has a fairly steep slope at E_F, whereas the curves for the other compounds are quite flat. The steep slope for Sm_2Fe_{17} in Fig. 3 implies a large change in $\langle J_i \rangle$ and hence T_C due to a small change in volume due to the magnetovolume effect discussed before. For example,
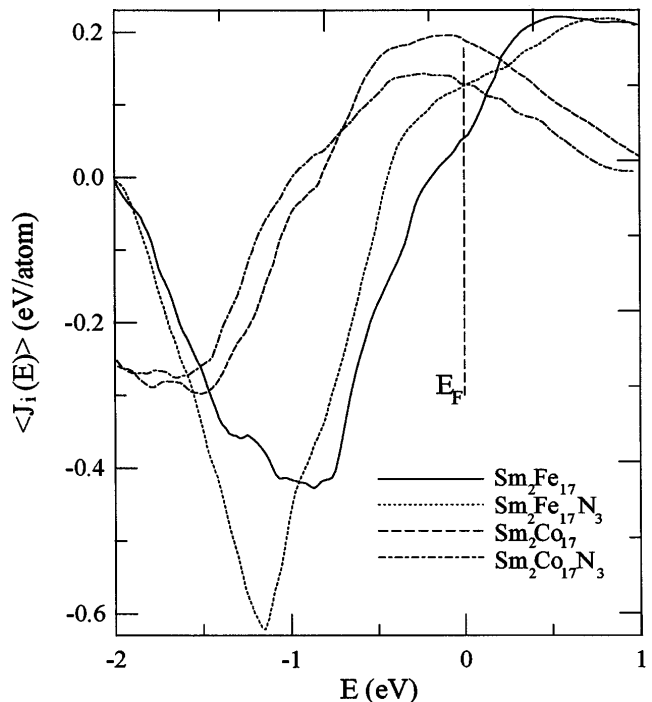

FIG. 3.   The average exchange parameters $\langle J_i(E) \rangle$ as functions of the energy near E_F.

we have estimated that a 0.5% increase in the lattice parameters used in Sm_2Fe_{17} calculations will give a new value of T_C in excellent agreement with the experimental result. The mean-field values of T_C are larger than the Monte Carlo values by a factor of about $5/4$.

In summary, we have shown that first-principle calculations, based on the Heisenberg Hamiltonian and Monte Carlo simulations, are able to predict rather accurately the Curie temperatures of Sm_2Fe_{17}, Sm_2Co_{17}, and their nitrogenated counterparts. Thus, as in the cases of elemental Fe and Co, the Heisenberg model is a good representation of the exchange interactions in these compounds. The substantial increases in T_Cs of Fe compounds and the moderate decreases in T_Cs of Co compounds upon nitrogenation are primarily due to the magnetovolume effect and changes in hybridization, respectively. Having successfully calculated the exchange interactions in these complex materials, we are now in a position to predict by computer simulations the important properties (e.g., T_C and M_s) of proposed new permanent-magnet materials and their modifications by interstitial and substitutional impurities.

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