Calculations of the band structure and Curie temperature for Y_2Fe_{17} and $Y_2Fe_{17}N_3$

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Abstract. The very large enhancement of the Curie temperature in the novel ferromagnetic nitride $Y_2Fe_{17}N_3$ results from the obvious change of the electronic structure compared with that of its paternal compound Y_2Fe_{17}. Their electronic structures in both spin-polarized and non-spin-polarized states are calculated in the local spin-density functional approximation. From the band structure obtained by us, the Curie temperature of these compounds is calculated by including the effects of both the Stoner excitation and the spin fluctuation on the basis of the theory of Mohn and Wohlfarth without any adjustable parameters. The calculated enhancement of the Curie temperature for the nitride $Y_2Fe_{17}N_3$ is in good agreement with the measurement. Our results concerning the enhancement of the Curie temperature T_C for this ferromagnet upon nitrogenation suggest that the spin fluctuation is an important factor for this class of compounds, while the Stoner excitation must be involved in the calculation as well.

1. Introduction

The tremendous success of the permanent magnetic materials $Nd_2Fe_{14}B$ has led to the search for the next generation of hard magnetic materials [1].

A good permanent magnet material must have a large saturation magnetization, high Curie temperature, and large magnetic anisotropy for high coercivity. Among all of the binary rare-earth–iron compounds, R_2Fe_{17} is the richest in iron content, and thus has a very large saturation magnetization. However, the low Curie temperature T_C of R_2Fe_{17} is a serious drawback for any practical applications. In 1990, a new series of interstitial ternary nitrides $R_2Fe_{17}N_\delta$ (δ is the concentration of nitrogen) have been prepared where R represents Y (yttrium) and all of the rare-earth elements except La [2]. The large enhancement of the Curie temperature T_C for all of these ternary rare-earth–iron nitrides has attracted wide attention. Meanwhile, the magnetizations of Fe atoms in nitrides are increased by about 5%. The enhancement of T_C induced by nitrogenation has also been observed in two other kinds of rare-earth–iron compound, RFe_{12} and R_2Fe_{14}, surprisingly.

It is important to understand the underlying mechanism of T_C-enhancement upon nitrogenation. According to the theory of Mohn and Wohlfarth [3], the Curie temperature T_C is closely related to the electronic band structure of materials, and in the calculation of the Curie temperature at least two types of elementary excitation should be involved: single-particle (Stoner) excitations, and spin fluctuations. The characteristic parameters T_C^S (the Stoner temperature) and T_{SF} (the spin-fluctuation temperature) have been used to describe the above two elementary excitations, respectively.

Calculations of the electronic band structure for Y_2Fe_{17} and the related nitride $Y_2Fe_{17}N_3$ have been reported by Jaswal *et al* [4]; they used the first-principles LMTO (linear muffin-tin orbital) method. Their calculations of the electronic structure give excellent results

Table 1. Magnetic moments (in μ_B) for different sites, the average moment M_0 of iron atoms in the unit cell, and the total moments M per formula unit for the ferromagnetic phase of Y_2Fe_{17}.

	Fe(4f)	Fe(6g)	Fe(12j)	Fe(12k)	Y(2b)	Y(2d)	M_0	M
This work	2.55	1.63	2.16	2.27	−0.48	−0.41	2.15	35.67
Experiment[a]	2.5(0.2)	1.1(0.2)	1.83(0.05)	2.3(0.1)	−0.4	−0.4	1.9 ± 0.1	32.3
Experiment[b]	2.5	1.9	2.2	2.0			1.98	32.8
Reference [4]	2.53	1.92	2.25	2.00	−0.47	−0.45	2.11	35.40
Reference [9]	2.41	1.91	2.35	2.12	−0.41	−0.41	2.20	36.56
Reference [10]	2.45	2.15	2.09	2.10	−0.43	−0.43	2.15	35.63
Reference [11]	2.959	1.775	2.230	2.141	−0.247	−0.228	2.20	37.0

[a] Reference [8].
[b] Reference [6].

for site-dependent Fe-atom moments and, with spin-fluctuation theory, explain the large change in the Curie temperature on nitrogenation qualitatively. However, due to the lack of calculations for paramagnetic states of the above compounds, they neglected the Stoner excitation and considered only part of the spin fluctuation. Recently, the investigation by Ching and Huang [5] has shown that for R_2Fe_{17}-based intermetallic compounds the use of the spin-fluctuation temperature T_{SF} as an estimate for T_C may not be justified. They calculated the Curie temperatures of Nd_2Fe_{17} and $Nd_2Fe_{17}N_3$ with rhombohedral structure ($R3m$, 19 atoms per unit cell) using the first-principles orthogonalized linear combinations of atomic orbitals (OLCAO) method. According to their results, the Stoner temperature T_C^S and spin-fluctuation temperature T_{SF} are both important for the calculation of T_C.

The electronic structures of the R_2Fe_{17} and $R_2Fe_{17}N_\delta$ compounds were investigated by focusing on Y_2Fe_{17} and $Y_2Fe_{17}N_\delta$ mostly. In this compound and nitride, the replacement of the rare-earth element with Y avoids the difficulty of handing the 4f states without any loss of understanding of the electronic and magnetic structure of the Fe magnetic subnetwork, and therefore the main features of the magnetization and Curie temperature of these compounds.

In this paper, we present a calculation of the electronic band structure (both the paramagnetic and ferromagnetic states) of the novel ferromagnet Y_2Fe_{17} and its nitride $Y_2Fe_{17}N_3$ with the hexagonal structure by using the first-principles LMTO method in the local spin-density functional approximation. From the band structure obtained by us, the Curie temperature—including the effects of both Stoner excitation and spin fluctuation—is calculated self-consistently without any adjustable parameters. Our results show that the significant increase in T_C on nitrogenation is due to the large change of the density of states near the Fermi level and the increase of magnetization.

2. Electronic structure

Both Y_2Fe_{17} and $Y_2Fe_{17}N_3$ have the hexagonal Th_2Ni_{17}-type structure (space group D_{6h}^4) and their respective crystal lattice constants are [6] $a = 8.48$ Å, $c = 8.26$ Å for Y_2Fe_{17} and $a = 8.65$ Å, $c = 8.44$ Å for $Y_2Fe_{17}N_3$, respectively. The complicated hexagonal unit cell of Y_2Fe_{17} contains 34 Fe atoms on four distinct sites labelled 4f, 6g, 12j, and 12k, and four Y atoms on two distinct sites labelled 2b and 2d. In the case of $Y_2Fe_{17}N_3$, the additional six N atoms are assumed to occupy site 6h.

The linear muffin-tin orbital method in the atomic-sphere approximation (LMTO-ASA) is used in our calculation without involving empty spheres. In the LMTO-ASA band calculation, the atomic radius of each atom should be chosen so as to satisfy

$V = (4\pi/3) \sum_i S_i^3 Q_i$, where V is the volume of a primitive cell, and S_i is the atomic radius of the equivalent Q_i-atoms in the cell. In our calculations the ratios of the atomic radii for the different atoms are $S_Y : S_{Fe} = 1.33:1.00$ for Y_2Fe_{17}, and $S_Y : S_{Fe} : S_N = 1.33:1.00:0.75$ for $Y_2Fe_{17}N_3$. The atomic-sphere radii utilized are $S_Y = 3.55460$ au and $S_{Fe} = 2.67263$ au for Y and Fe atoms in Y_2Fe_{17}. For $Y_2Fe_{17}N_3$, $S_Y = 3.56003$ au, $S_{Fe} = 2.67671$ au, and $S_N = 2.00754$ au for Y, Fe, and N atoms, respectively. Self-consistent charge densities are obtained by using three special k-points [7] for the irreducible Brillouin zone (IBZ). The densities of states (DOS) are obtained by using twelve special k-points inside an IBZ. Because the unit cell is large and, thus, the Brillouin zone is small, a relatively small number of sampling k-points appears to be adequate.

Table 2. Magnetic moments (in μ_B) for different sites, the average moment M_0 of iron atoms in the unit cell, and the total moments M per formula unit for the ferromagnetic phase of $Y_2Fe_{17}N_3$.

	Fe(4f)	Fe(6g)	Fe(12j)	Fe(12k)	Y(2b)	Y(2d)	N(6h)	M_0	M
This work	2.69	2.52	2.05	2.47	−0.35	−0.33	0.06	2.36	39.56
Experiment[a]								2.29	38.1
Reference [4]	2.65	2.53	2.01	2.57	−0.20	−0.45	−0.04	2.34	39.60
Reference [11]	3.446	3.112	1.688	2.223	−0.055	−0.085	−0.118	2.33	39.2

[a] Reference [6].

2.1. Spin-polarized (ferromagnetic) states

The magnetic moments for different atomic sites, the average moment M_0 of iron atoms in the unit cell, and the total moments M per formula unit in the two compounds Y_2Fe_{17} and $Y_2Fe_{17}N_3$ are given in table 1 and table 2, respectively. For comparison, the values from other calculations and experiments are also listed in the tables. The calculated results are in good agreement with experiments.

For Y_2Fe_{17}, among the four kinds of Fe, the Fe(4f) has the largest magnetic moment ($2.55\mu_B$), while the Fe(6g) has the smallest ($1.63\mu_B$), which is consistent with other calculations and experiments. The total moment per formula unit is $35.67\mu_B$, which agrees with the calculation of Jaswal *et al* [4] and the magnetization measurement [6, 8]. It should be noted that the magnetic order obtained by us is $m_{12k} > m_{12j}$, consistent with experiment [8].

Up to now there have only been few calculations of the electronic structure of the nitride $Y_2Fe_{17}N_3$. For the hexagonal Th_2Ni_{17}-type structure, Jaswal *et al* [4] completed a self-consistent calculation using LMTO, Li *et al* [11] performed a non-self-consistent LCAO calculation, and Fähnle and Beuerle [12] presented the density of states. For the rhombohedral Th_2Zn_{17}-type structure, Ching *et al* [13] gave their results using the self-consistent OLCAO method. In our calculations, the magnetic moments of the four kinds of Fe atom are 2.69, 2.52, 2.05, and $2.47\mu_B$, respectively, which are consistent with the results of Jaswal *et al* [4]. For Y_2Fe_{17} and $Y_2Fe_{17}N_3$, the maximum magnetic moments of atoms are all at the Fe 4f site, and are equal to $2.55\mu_B$ and $2.69\mu_B$, respectively. After the introduction of nitrogen, the average iron moment is changed from 2.15 to $2.36\mu_B$—increased by about 9.8%—which is in good agreement with experiments. The moments at 4f and 12k sites increase by 5.5% and 8.8%, respectively. The magnetic moment at the 6g site has a very large enhancement from $1.63\mu_B$ in Y_2Fe_{17} to $2.52\mu_B$ in $Y_2Fe_{17}N_3$. But the moment at the 12j site is reduced from $2.16\mu_B$ to $2.05\mu_B$, because these Fe atoms are

the nearest neighbours of N atoms. These variational trends of the magnetic moments at different neighbouring sites are the same as those for other Fe–N compounds.

The spherical potentials and ASA spheres should influence the assignment of a magnetic moment to a site. However, this influence was restricted to within ten per cent for such simple metals as Fe, Co, Ni and alloys as Fe_4N, $Fe_{16}N_2$, and so on, but no comparison for complex compounds is given now.
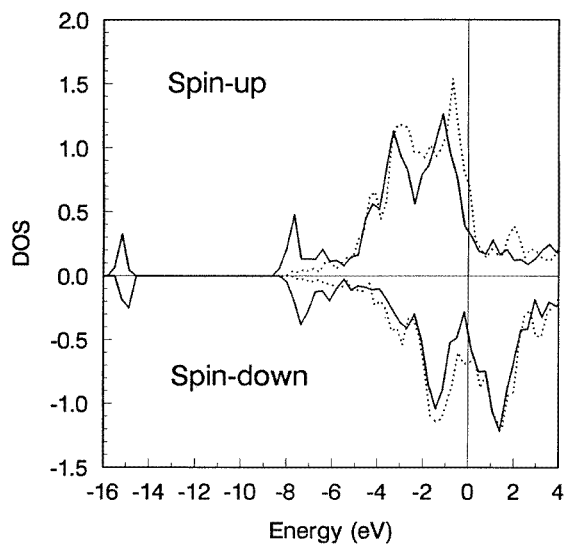

Figure 1. The total density of states (DOS) for Y_2Fe_{17} (dotted line) and $Y_2Fe_{17}N_3$ (solid line) in the ferromagnetic phase. The values of the DOS are in units of states eV^{-1}/(atom spin). We have set the Fermi energy E_F equal to zero.

In figure 1 we present the total density of states (DOS) for Y_2Fe_{17} (dotted line) and $Y_2Fe_{17}N_3$ (solid line) in the ferromagnetic phase. The DOS near E_F is determined by the d band of the Fe atoms. The DOS of $Y_2Fe_{17}N_3$ is shifted to higher binding energy due to the reduction of overlap upon nitrogenation. This leads to a decrease in both the spin-up and spin-down DOS values at the Fermi level. The DOS values above -5 eV are dominated by the Fe 3d bands. The peaks at around -8 eV and -15 eV in $Y_2Fe_{17}N_3$ are due to the N 2p states and 2s states, respectively.

The partial density of states (not shown) for different sites of Y_2Fe_{17} and $Y_2Fe_{17}N_3$ show that there are obvious hybridizations between the valence bands of N, Fe, and Y except for Fe(4f) and Fe(6g) which are far away from the N site.

2.2. Non-spin-polarized (paramagnetic) states

The paramagnetic state of ferromagnetic metals is a complex and challenging problem. More recent work indicated that the correct description is provided by disordered local moments in such simple magnetic metals as bcc Fe [14]. However, the materials currently considered by us possess very complex crystalline structures with such large units as 44 atoms per unit cell. For technical reasons, it is a realistic approach to simply treat the non-spin-polarized LDA state as the paramagnetic phase, which appears to be based upon the work of Gunnarsson [15].
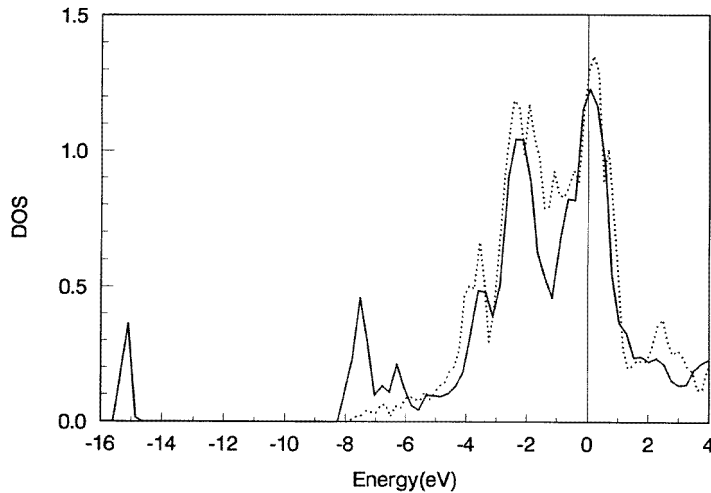
Figure 2. The total density of states (DOS) for Y_2Fe_{17} (dotted line) and $Y_2Fe_{17}N_3$ (solid line) in the paramagnetic phase. The other details are the same as for figure 1.

In figure 2 we present the total density of states for Y_2Fe_{17} (dotted line) and $Y_2Fe_{17}N_3$ (solid line) in the paramagnetic phase (PM). Although their band structures are different, their densities of states at E_F are very large, suggesting that ferromagnetic instability could occur.

The calculated total energy differences for the unit cell between the paramagnetic and the ferromagnetic states are 6.62 eV and 10.25 eV for Y_2Fe_{17} and $Y_2Fe_{17}N_3$, respectively, which are in good agreement with reference [9]. This result means that the ferromagnetic phases of the two compounds are stable. The partial density of states for four types of Fe atom in Y_2Fe_{17} and $Y_2Fe_{17}N_3$ are given in figure 3. The situation is similar to that in the ferromagnetic phase: there are strong hybridizations between the N atom and its nearest-neighbour Fe atoms—for example, Fe(12j) and Fe(12k). Among the Fe atoms of $Y_2Fe_{17}N_3$, the Fe(4f) atoms have the highest local density of states at E_F and the Fe(12j) atoms have the lowest, which is consistent with their magnetic moments.

3. The calculation of the Curie temperature

Mohn and Wohlfarth [3] have pointed out that in the calculation of the Curie temperature of the ferromagnetic 3d metals and their compounds, at least two types of elementary excitation are involved: namely single-particle (Stoner) excitation, and spin fluctuations. On the basis of the theory of the renormalization of Landau coefficients, they developed an approach for relating the Curie temperature to the electronic structure of the compounds. The Curie temperature T_C of the system can be determined from the following formula:

$$\left(\frac{T_C}{T_C^S}\right)^2 + \frac{T_C}{T_{SF}} - 1 = 0 \qquad (1)$$

where the first term describes the contribution from single-particle excitation, and the characteristic parameter T_C^S is the Stoner temperature. According to the theory of
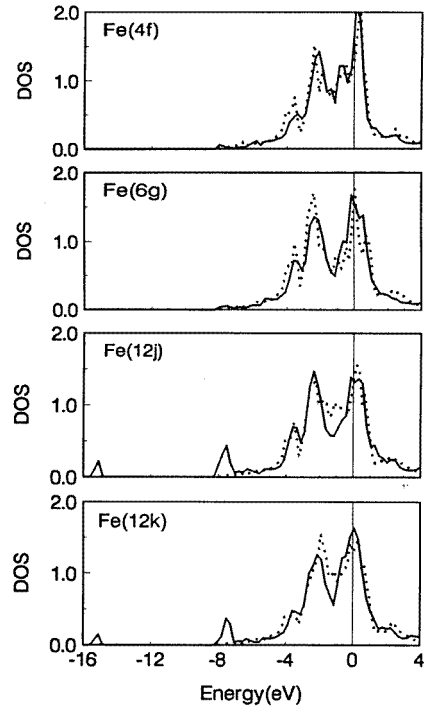
Figure 3. The partial density of states (DOS) for four inequivalent iron sites of Y_2Fe_{17} in the paramagnetic phase. The other details are the same as for figure 1.

Gunnarsson [15], the Stoner temperature is identified as the solution of the equation

$$I \int_{-\infty}^{\infty} \frac{\partial f(E, T)}{\partial E} N(E) \, dE + 1 = 0 \tag{2}$$

where I is the Stoner parameter generally given by $I = \Delta E / M_0$, $N(E)$ is the density of states per atom per spin in the paramagnetic state, and $f(E, T)$ is the Fermi distribution function. ΔE is the exchange splitting energy, and M_0 is the equilibrum magnetic moment at $T = 0$. The second term in equation (1) describes the effect of spin fluctuations, and the characteristic parameter T_{SF} is named the spin-fluctuation temperature, and is given by

$$T_{SF} = M_0^2 \chi_0^{-1} / 10 \kappa_B. \tag{3}$$

Here κ_B is Boltzmann's constant, and the susceptibility χ_0 is given by

$$\chi_0^{-1} = (4\mu_B^2)^{-1} (N^+(E_F)^{-1} + N^-(E_F)^{-1}) - I / 2\mu_B^2 \tag{4}$$

where $N^+(E_F)$ and $N^-(E_F)$ are the DOS of spin-up and spin-down bands at the Fermi level E_F, respectively. I is the Stoner parameter and μ_B is the Bohr magneton.

On the basis of the above equations, T_C^S and T_{SF} can be calculated directly from the band structure of the compounds. From our spin-polarized band calculations, the average exchange-splitting energies ΔE of iron atoms are obtained as 1.98 eV for Y_2Fe_{17}, and 2.25 eV for $Y_2Fe_{17}N_3$, respectively. So the value of I is found to be 0.92 (for Y_2Fe_{17}) and 0.95 (for $Y_2Fe_{17}N_3$). From our non-spin-polarized band structure, we completed the

integral

$$I(T) = \left(- \int_{-\infty}^{\infty} \frac{\partial f(E, T)}{\partial E} N(E) \, dE \right)^{-1}$$

as a function of the temperature. The solution of equation (2) gives the Stoner temperatures T_C^S of Y_2Fe_{17} and $Y_2Fe_{17}N_3$ as 4350 K and 5750 K, respectively, which is consistent with the result of Gunnarsson [15] for the metal Fe. The enhancement of T_C^S for the nitride $Y_2Fe_{17}N_3$ is due to the increasing of the DOS near the Fermi level. According to equations (3) and (4), T_{SF} can be derived from our spin-polarized band structure.

Table 3. The calculated DOS at E_F for both paramagnetic (PM) and ferromagnetic (FM) states, average magnetic moment, Stoner parameter I, and characteristic and Curie temperatures T_C^S, T_{SF} and T_C.

	DOS at E_F (states eV^{-1}/(Fe-atom spin))			Magnetic moment M_0	Stoner parameter	Temperatures (K)		
	PM	FM		(μ_B/Fe-atom)	I	T_C^S	T_{SF}	T_C
		Spin-up	Spin-down					
Y_2Fe_{17}	1.385	0.678	0.725	2.15	0.92	4350	1359	1247
$Y_2Fe_{17}N_3$	1.531	0.395	0.553	2.36	0.95	5750	3939	2922

The calculated band-structure parameters (DOS), the Stoner parameter I, and two characteristic temperatures T_C^S and T_{SF} are listed in table 3. From these results the first-principles calculations of the Curie temperature for Y_2Fe_{17} and the nitride $Y_2Fe_{17}N_3$ can be completed according to equation (1), which includes both the Stoner excitation and the spin fluctuation. The calculated Curie temperatures T_C are also listed in table 3.

For Y_2Fe_{17} compounds, the calculated value of T_C^S is about three times that of T_{SF}. This means that the smaller T_{SF} is dominant in determining the value of the Curie temperature T_C. Ignoring the single-particle (Stoner) excitation in the calculation of T_C will not introduce much error. However, the situation for the nitride $Y_2Fe_{17}N_3$ is different. Due to the increase in magnetization and obvious decrease in $N^+(E_F)$ and $N^-(E_F)$, the spin-fluctuation temperature T_{SF} has a much larger enhancement, from 1359 K for Y_2Fe_{17} to 3939 K for $Y_2Fe_{17}N_3$, but T_C^S only increases by 30% from 4350 K (for Y_2Fe_{17}) to 5750 K (for $Y_2Fe_{17}N_3$). T_C^S is only 1.46 times T_{SF}. Then for $Y_2Fe_{17}N_3$, both T_{SF} and T_C^S must be included on an equal footing in the determination of the Curie temperature from equation (1).

Even though the calculated Curie temperatures T_C for both Y_2Fe_{17} and $Y_2Fe_{17}N_3$ are systematically much larger than the experimental ones due to the substantial overestimate of the parameters calculated from band theory in the local density approximation, the calculated ratio $R \equiv T_C(Y_2Fe_{17}N_3)/T_C(Y_2Fe_{17}) = 2.34$ is in good agreement with the experimental data for the nitrogen concentration $\delta = 2.6$; it is given by $R = 694/325 = 2.14$. The good qualitative agreement between experiment and theory concerning the increase of T_C indicates that the spin-fluctuation excitation is an important factor for the magnetism of this class of compounds, while the Stoner excitation must also be involved in the calculation.

In summary, on the basis of first-principles electronic band-structure calculations without any adjustable parameters, the Stoner, spin-fluctuation, and Curie temperatures T_C^S, T_{SF}, and T_C have been calculated in a united scheme for the novel permanent magnet Y_2Fe_{17} and related nitride $Y_2Fe_{17}N_3$. The calculations concerning the enhancement of the Curie temperature T_C for this ferromagnet upon nitrogenation suggest that the spin fluctuation

is an important factor for this class of compounds, while the Stoner excitation must be involved in the calculation as well. The significant increase in T_C on nitrogenation is due to the increase of magnetization and decrease of both spin-up and spin-down DOS at the Fermi level. In addition, the increase in M_0 upon nitrogenation was demonstrated firstly by experiment, while a substantial decrease in $N(E_F)$ was predicted earlier by Jaswal *et al* [4], and then proved to occur by an x-ray photoemission spectrum experiment [16].

Acknowledgments

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