Electronic structure and magnetism of $R_2Fe_{14}B$ (R = Y,Nd) compounds

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The linear muffin-tin orbitals (LMTO) method is used to calculate the self-consistent spin-polarized electronic structures of $R_2Fe_{14}B$ (R = Y,Nd) compounds. The present results are compared with those of an earlier non-self-consistent calculation. The calculated results are in good agreement with the experimental data from photoemission, heat-capacity, and magnetic measurements.

INTRODUCTION

It would be an understatement to say that there is considerable current interest in the properties of $R_2T_{14}B$ compounds (R = rare earth; T = Fe, Co, Ni), the latest entry to the permanent-magnet-materials market.[1-3] A good permanent magnet must have large saturation magnetization and coercivity and high Curie temperature. Because of its fundamental role in determining the magnetic properties, a good understanding of the electronic structure of these materials is extremely important. Some empirical[4-6] and non-self-consistent[7] calculations have been reported. Recently we reported the first electronic-structure measurements and self-consistent, spin-polarized band-structure calculations on the $Nd_2Fe_{14}B$ class of permanent-magnet materials.[8] The details of these calculations are presented here and compared with those of the non-self-consistent studies and experimental data.

COMPUTATIONAL PROCEDURE

$R_2T_{14}B$ crystal are tetragonal with 68 atoms per primitive cell and the space-group symmetry $P4_2/mnm$.[1] The atomic-structure information was taken from Ref. 1. The electronic-structure calculations are based on the linear muffin-tin orbitals (LMTO) method in the semirelativistic, local-density, and atomic-sphere approximations.[9] The near-neighbor distances were used to estimate the Wigner-Seitz radii. $4f$ states in rare earths are highly localized and are very difficult to include in a full-fledged band-structure calculation. Fortunately, their photoemission spectra are reasonably well understood with transition-state analysis[10,11] and the renormalized-atom approach.[12] Because of this and the fact that the non-$4f$ parts of the experimental electronic structure are similar, $4f$ states in $Nd_2Fe_{14}B$ were included in the core states.

The core states are the frozen self-consistent atomic states. There are nine valence states per site consisting of s, p and d orbitals. With 68 atoms per unit cell, this leads to 612×612 overlap and Hamiltonian matrices. The self-consistent spin-polarized potential parameters are based on the zero-wave-vector ($k \sim 0$) electronic-structure results. Because of the extremely large size of the unit

cell, this procedure is quite reasonable. The final results are based on the six points in an irreducible part of the Brillouin zone.

RESULTS

Since the results for Y and Nd compounds are similar, the detailed densitities of states (DOS) are given only for $Y_2Fe_{14}B$. The total DOS is in very good agreement with the photoemission data as shown in Ref. 8. The total and partial spin-polarized DOS are plotted in Figs. 1 and 2, respectively. As can be seen in Fig. 2, the Fe d band dominates the spectrum. The average exchange splitting of 2.1 eV is similar to that of pure Fe. B s states give a small peak near -8 eV in good agreement with the experiment. Except for resonance effects due to the Fe d band, Y states give rise to a small background. This is in disagreement with the completely filled and fairly localized Y d band around -5 eV in Ref. 7. The latter situation leads to a charge transfer of about $8e$ to Y, a rather unphysical result. Somehow the same computational procedure does not give rise to a similar unphysical result in $Y_2Co_{14}B$ compound. This may be due to the non-self-consistency of the calculations in Ref. 7. Such calculations do not guarantee the correct relative positions of the bands due to different elements in a compound. This effect is also reflected in the B s peak in Ref. 7 being around -11 eV instead of -8 eV and a large charge transfer of over $2e$ to boron for all the compounds.

The DOS for different Fe sites in $Y_2Fe_{14}B$ are shown in Fig. 3. The results for different sites are qualitatively similar with small variations reflecting the changes in the local site symmetries. Once again, the non-self-consistency leads to much larger variations in Fe-site DOS in Ref. 7.

The results for magnetization and DOS at the Fermi level [$N(E_f)$] for $Y_2Fe_{14}B$ and $Nd_2Fe_{14}B$ are given in Table I. The magnetization per formula unit (f.u.) is in very good agreement with the experimental data. The average Fe DOS at the Fermi level is close to that from the self-consistent spin-polarized calculations for pure Fe (Ref. 13) as expected in Fe-rich compounds. Our calculated value for $N(E_f)$ for $Y_2Fe_{14}B$ and the experimental heat-capacity data[14] give $\lambda_{ep} + \lambda_{sf} = 1.5$, where λ_{ep} and
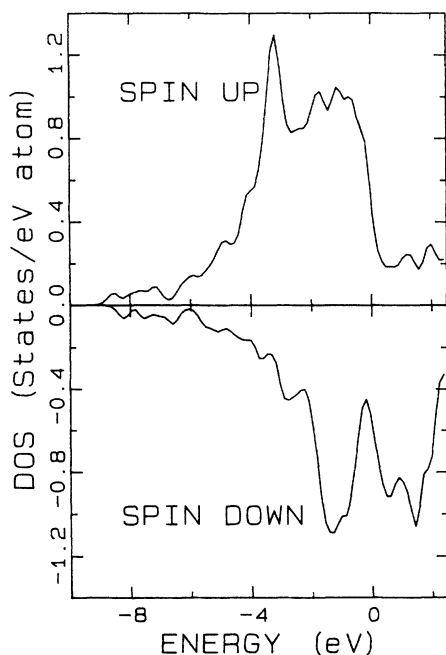
FIG. 1. Total spin-polarized density of states for $Y_2Fe_{14}B$.

λ_{sf} are electron-phonon and spin-fluctuation mass enhancement factors, respectively. This value is comparable to those derived from experimental data in Fe_xZr_{1-x} glasses.[15]

The charge transfers and magnetic moments for different sites in the two compounds are listed in Tables II and III. The charge transfers are from T to R sites and
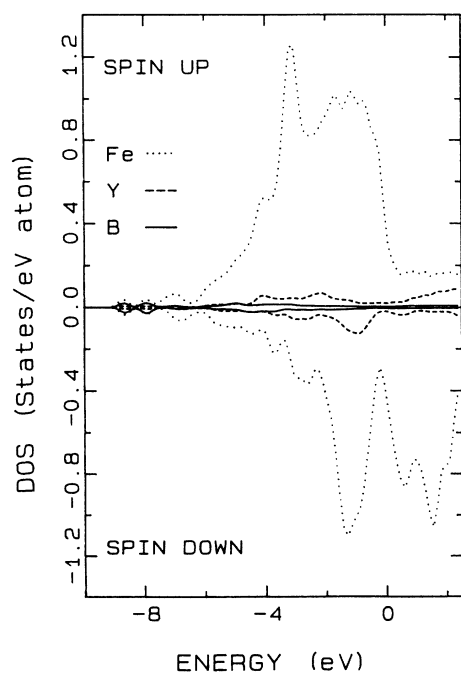

FIG. 2. Partial spin-polarized density of states for Fe, Y, and B in $Y_2Fe_{14}B$.

are small as expected in a metal. Also, these results are quite similar to those for $Y_2Co_{14}B$.[16] The calculated magnetic moments of different Fe sites are in good agreement with the experimental data. The largest moment at the j_2 site is well correlated with the sharpest DOS (Fig. 3) at that site.

One also sees from Table III that non-f R valence electrons give rise to an appreciable magnetic moment opposite to that of Fe. Now non-f R electrons are similar to those of Y, an early transition metal. Thus, our results support the long-standing hypothesis that in a mixture of early and late transition metals (T), the former develop moments opposite to those of the latter[17] It has also been hypothesized that f and non-f R spins (S) align ferromagnetically due to intra-atomic exchange interactions.[17] Hund's rules require that the total angular momentum J for the ground state of the f electrons point opposite to S in early rare earths and along S in late rare earths. This leads to the well-known experimental results of ferromagnetic alignment between the early rare earths and Fe and an antiferromagnetic alignment between the late rare earths and Fe. These results can be pictorially represented as follows:
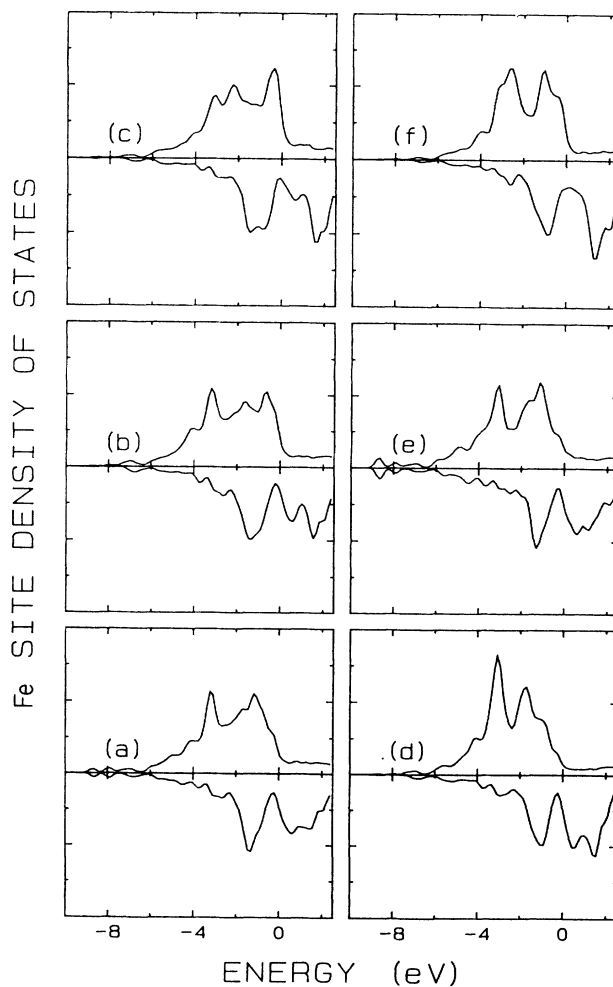

FIG. 3. The spin-polarized density of states for various Fe sites in $Y_2F_{14}B$: (a) k_1 site, (b) k_2 site, (c) j_1 site, (d) j_2 site, (e) e site, and (f) c site.

TABLE I. Magnetization and density of states at the Fermi level $[N(E_f)]$ in $R_2Fe_{14}B$ compounds.

| | Magnetization/f.u. (μ_B) | | | $N(E_f)$ (states/eV atom) | |
	Present calculation	Ref. 7	Expt.[a]	Present calculation	Ref. 7
$Y_2Fe_{14}B$	29.7	32.5	29.5–31.4	0.86	1.88
$Nd_2Fe_{14}B$	37.0[b]	41.45[b]	37.1–37.9	0.81[c]	1.15[c]

[a]Range of the values from Refs. 18, 19, 20 and 21.
[b]Includes the $4f$ contribution of $6.6\mu_B$ per f.u.
[c]Does not include the $4f$ contribution.

TABLE II. Charge transfers (in units of e) for different sites in $Y_2Fe_{14}B$ and $Nd_2Fe_{14}B$.

| | $Y_2Fe_{14}B$ | | $Nd_2Fe_{14}B$ | |
	Present Calculation	Ref. 7	Present Calculation	Ref. 7
Y or Nd (f)	1.54	8.19	1.37	1.06
Y or Nd (g)	1.05	7.82	0.917	1.11
Fe (k_1)	−0.123	−0.50	−0.108	0.61
Fe (k_2)	−0.091	−0.67	−0.0784	0.68
Fe (j_1)	−0.281	−2.32	−0.222	0.54
Fe (j_2)	−0.308	−2.18	−0.277	−1.16
Fe (e)	−0.127	−0.02	−0.096	0.42
Fe (c)	−0.473	−4.66	−0.469	−0.31
B (g)	0.042	2.33	0.020	2.42

TABLE III. Magnetic moments (in μ_B) for different sites in $Y_2Fe_{14}B$ and $Nd_2Fe_{14}B$.

| | $Y_2Fe_{14}B$ | | | $Nd_2Fe_{14}B$ | | |
	Present Calculation	Ref. 7	Expt.[a]	Present Calculation	Ref. 7	Expt.[a]
Y or Nd (f)	−0.64	−0.14		−0.55[b]	0.04[b]	
Y or Nd (g)	−0.60	−0.17		−0.52[b]	0.01[b]	
Fe (k_1)	2.08	2.16	2.07–2.25	2.15	2.15	2.08–2.60
Fe (k_2)	2.15	2.47	2.23–2.32	2.18	2.28	2.16–2.60
Fe (j_1)	2.07	2.50	2.10–2.40	2.12	2.48	2.06–2.30
Fe (j_2)	2.74	3.08	2.43–2.80	2.74	3.40	2.43–2.85
Fe (e)	2.06	1.80	2.03–2.28	2.13	1.99	2.00–2.28
Fe (c)	2.53	1.60	1.24–2.25	2.59	2.97	1.97–2.75
B (g)	−0.19	−0.27		−0.20	0.36	

[a]Range of values from Refs. 22, 23, 24, 25, and 26.
[b]Without the $4f$ electron contributions.

late	early	rare	early
transition	transition	earths	rare
metals	metals		earths
	or rare earths		
↑ Interatomic	↓ Intra−atomic	↓ Hund's	↑
exchange	exchange	rules	
S	*S*	*S*	*J*
s,p,d electrons	*s,p,d* electrons	*f* electrons	*f* electrons

In summary, we have carried out self-consistent, spin-polarized, electronic- structure calculations for $R_2Fe_{14}B$ ($R=Y,Nd$) using the linear muffin-tin orbitals method. The calculated results are in good agreement with the photoemission, heat-capacity, and magnetization data.

ACKNOWLEDGMENTS

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