Electronic Structure and Magnetism of $Nd_2Fe_{14}B$ and Related Compounds

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(Received 22 February 1988)

The electronic and magnetic structures of $Nd_2Fe_{14}B$ and related compounds have been studied with photoemission spectroscopy and self-consistent spin-polarized electronic structure calculations. The positions of the exchange-split Fe 3*d* bands and the localized 4*f* levels were determined. The densities of states in the ferromagnetic and paramagnetic states are essentially identical which provides strong evidence for considerable magnetic short-range order above T_c, as in the fluctuating-band model of itinerant-electron magnetism.

PACS numbers: 79.60.Cn, 71.20.Cf, 75.30.Cr

The recently discovered $Nd_2Fe_{14}B$ class of permanent-magnet materials has, without doubt, great potential for significant technological applications.[1] However, these compounds have complex tetragonal structures with 68 atoms per unit cell.[2] The important valence electrons which control the properties are certain to possess both itinerant and localized characteristics. As in the case of the new high-temperature superconductors, the complexity of the structure and electronic interactions raises the significant question of the ability of present theoretical methods to handle both the ground- and excited-state properties of the system. The answer to this question will determine whether our understanding and improving of the properties of such materials relies on theory or merely on empirical methods. For example, Mohn and Wohlfarth[3] have argued that a satisfactory theory for understanding the Curie temperature of $Y_2Fe_{14}B$ can be based on the addition of spin-fluctuation effects to the local-spin-density-functional formalism, suitably modified to treat correlation effects. In particular, these authors discussed improving the properties of $Nd_2Fe_{14}B$ (raising T_c) by alloying with Co. This was based on the electronic structure of the impurity atoms and their hybridization with Fe 3*d* states.

In this Letter, we report the first electronic-structure measurements and self-consistent, spin-polarized band calculations on the $Nd_2Fe_{14}B$ class of permanent-magnet materials. In addition to the Nd compound, measurements have been made on Y and Gd compounds to probe the effects of the rare earth on the electronic and magnetic structure.

The experiments consisted of angle-averaged photoemission measurements performed both with He I (21.2 eV) and He II (40.8 eV) radiation and, as a function of photon energy, with synchrotron radiation at the the University of Wisconsin. The helium-discharge ultraviolet photoelectron spectroscopy was performed in a homemade system with a base pressure of $\simeq 3\times 10^{-10}$ Torr and at temperatures ranging from 296 to 623 K. The samples were prepared by arc melting the alloys several times and then homogenizing them with an 8-h anneal at 650°. X-ray diffraction measurements showed that the samples were single phase with the $R_2Fe_{14}B$ structure. After being polished to a highly smooth surface, the samples were cleaned *in situ* by repeated Ar ion bombardment at about 2 keV. The uv photoemission spectroscopy measurements employed a cylindrical mirror energy analyzer with a resolution given by $\Delta E/E \approx 0.015$, where E is the electron kinetic energy. Thus, the He I and He II uv photoemission spectroscopy spectra were obtained with resolutions of about 0.2 and 0.5 eV, respectively. The measurements employing synchrotron radiation ranged in photon energy from 40 to 130 eV. The combined photon-electron resolution varied from about 0.6 eV at 40 eV to 1.3 eV at 120 eV. These experiments were performed without Auger-electron spectroscopy as a test for surface cleanliness, but it was possible for us to follow the surface cleaning adequately by observing the decrease of the oxygen 2*p* line at an energy of about -5.3 eV.

Figure 1 shows the main features of the photoelectron spectroscopy data for 21.2- and 40.8-eV photons. In this and other figures a contribution due to secondary electrons has been removed by a standard empirical procedure. The upper panel, for $h\nu = 21.2$ eV, shows nearly identical spectra including a signal at about -5.2 eV which is explicable by O and/or C contamination of the surface.[4] This signal is estimated from earlier work on pure Fe to correspond to a small fraction of a monolayer.[4] The $h\nu = 40.8$-eV spectra in the lower panel show an additional peak in the Gd spectrum at -8.9 eV and an enhanced peak at -5.4 eV in the Nd spectrum.

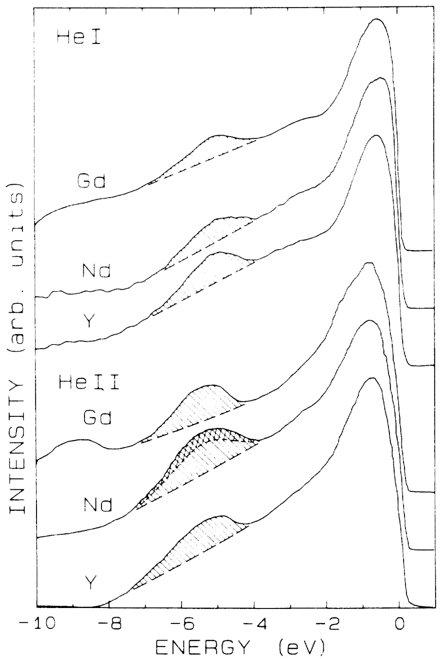

FIG. 1. He I spectra (upper panel) and He II spectra (lower panel) for the $R_2Fe_{14}B$ compounds. The zero of energy is at the Fermi level ($E_F=0$) for this and subsequent spectra. The hatched peaks are surface contaminants (see text) and the cross-hatched area is an approximate contribution from Nd ($4f$) levels.

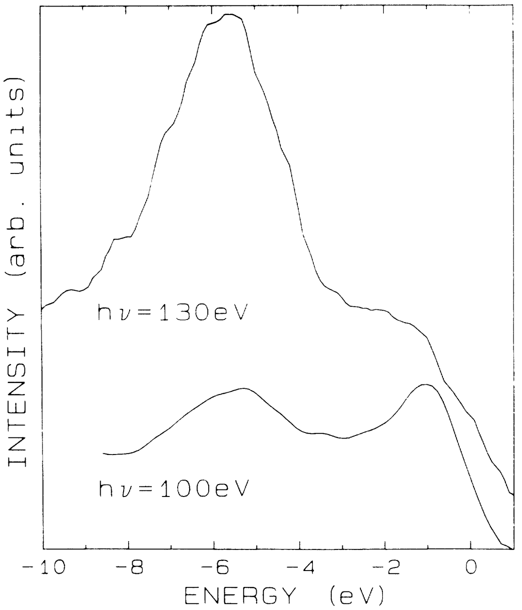

FIG. 2. Photoelectron spectra for $Nd_2Fe_{14}B$ near and off the $4d$-$4f$ resonance of Nd (130 and 100 eV, respectively). The two curves have been normalized to have the same intensity at -1 eV, where the main intensity is from the Fe ($3d$) levels. In these spectra no correction for secondary electrons has been made.

These features are due to Gd and Nd $4f$ levels, respectively, and they appear as a result of considerably larger $4f$ atomic photoionization cross sections for 40.8-eV photons as compared with 21.2-eV photons. A clearer demonstration of the presence of Nd($4f$) levels at about -5.4 eV comes from resonance-enhanced photoemission[5] as seen in Fig. 2. Here, at $h\nu = 130$ eV, close to the $4d$-$4f$ resonance, the peak at -5.4 eV is much larger than that due predominantly to Fe($3d$) levels at about -1 eV. For an off-resonance photon energy (100 eV), the Nd($4f$) photoemission is considerably smaller than that due to the Fe($3d$).

Additional important features of the magnetic and electronic states in $Nd_2Fe_{14}B$ are seen in Fig. 3. First, a 21.2-eV spectrum, taken immediately after sputtering at high temperature (350 °C), where $T > T_c$, shows that the paramagnetic electronic structure is essentially unchanged from that of the ferromagnetic state. In particular, the strong peak at -0.7 eV and the weaker one at -2.9 eV have not shifted from their counterparts in the ferromagnetic state. Second, the O and/or C contamination at $-(5$-$6)$ eV seems to be very nearly eliminated for the $t = 1$-min spectrum suggesting that it could well be due to a C-O reaction to form CO which desorbs from the compound surface at high temperature. It is known that the desorption temperature for CO on Fe is 570 K.[4] However, at elevated temperatures such as 623 K, the O/C surface contamination builds as a function of time as seen in Fig. 3, as well as a large signal at -8.6 eV. The latter is due to the diffusion of B atoms to the surface; these light atoms clearly are essentially completely removed by the sputtering process, as seen in Figs. 1-3, and also as shown by Auger measurements on

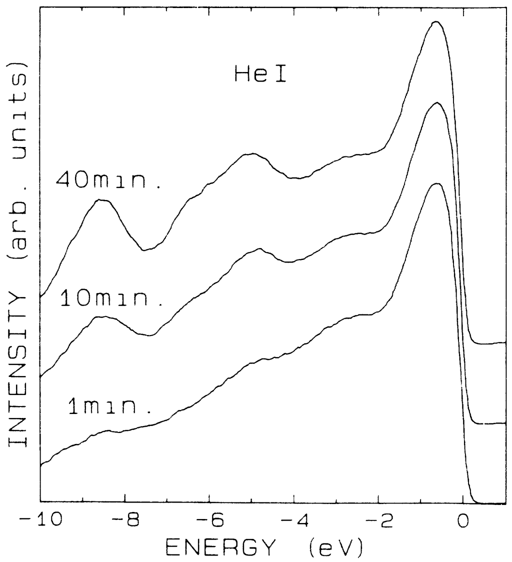

FIG. 3. He I spectra for $Nd_2Fe_{14}B$ in the paramagnetic state ($T > T_c = 585$ K), and as a function of time after surface cleaning by sputtering.

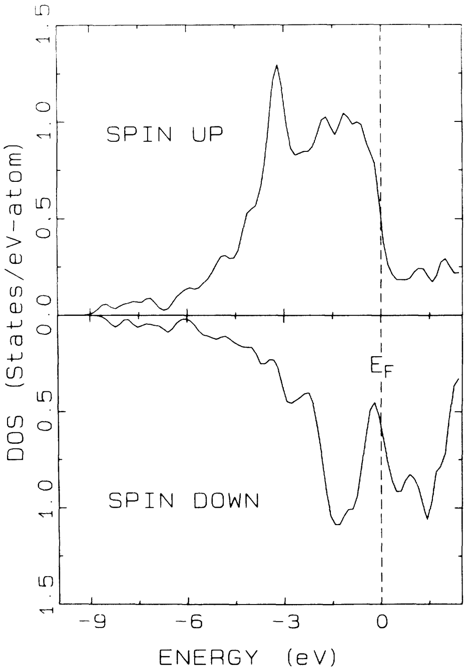

FIG. 4. Spin-polarized densities of states for $Y_2Fe_{14}B$. An average exchange splitting of about 2.1 eV is seen in the Fe (3*d*) bands. The Y-derived states are broadly distributed below E_F and the B(2*s*) levels are at $-(8\text{–}9)$ eV.

these compounds.[6]

In order to understand the above electronic-structure results and to study the site-dependent magnetic moments in these compounds we have performed the first self-consistent spin-polarized calculations for this class of intermetallic compounds. Because of the complexity of the structure and the presence of quasilocalized 4*f* levels, the earlier calculations have been empirical in nature[7] or non-self-consistent.[8] In our determining the specific compound of the $R_sFe_{14}B$ class on which to perform calculations the following points were considered important. First, the experimental results show that the electronic structures of the compounds are similar except for the positions of the rare-earth 4*f* levels. Second, the 4*f* positions as determined in a local-spin-density calculation do not correspond to those measured by photoemission spectroscopy because of many-body screening effects. This has been discussed by several authors, for example, Herbst and Wilkins,[9] who have calculated 4*f* excitation energies for Gd (8.5 eV) and Nd (5.2 eV), in very good agreement with our results discussed above. From these and other studies[10] on rare-earth elements and compounds one is fairly certain where the 4*f* levels will appear in most cases. Clearly, this circumstance arises from the largely localized atomiclike nature of these states in solids. For all of these reasons we have performed our calculations for $Y_2Fe_{14}B$ using the linear-muffin-tin-orbitals method in the local-density and semirelativistic approximations.[11] The spin-polarized densities of states (DOS) are shown in Fig. 4. The structure near the Fermi level is dominated by the Fe *d* states and it, and the exchange splitting of $\simeq 2.1$ eV, are similar to those of pure Fe.[12] The charge transfers for different sites generally are small (<0.4 for Fe sites and <1.5 for Y). These values seem physically more reasonable than those produced by the calculation of Gu and Ching (up to 5 for Fe sites and 8 for Y sites).[8] The calculated magnetic moments for different Fe sites are in good agreement with the neutron-scattering[13] and Mössbauer data[14] as shown in Table I.

TABLE I. Magnetic moments in Bohr magnetons on the Fe sites.

Fe site	Mössbauer[a]	Neutron[b]	Present calculation
k_1	2.1 ± 0.1	2.25 ± 0.03	2.14
k_2	2.23 ± 0.03	2.25 ± 0.03	2.24
j_1	2.31 ± 0.03	2.4 ± 0.4	2.10
j_2	2.4 ± 0.1	2.8 ± 0.4	2.83
c	1.9 ± 0.1	1.95 ± 0.05	2.55
e	2.3 ± 0.1	2.15 ± 0.05	2.20

[a] Reference 14.

[b] Reference 13.

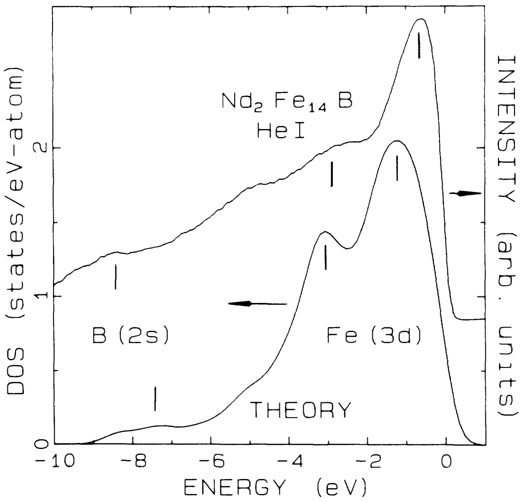

FIG. 5. Comparison of the broadened DOS for $Y_2Fe_{14}B$ with the $Nd_2Fe_{14}B$ spectrum (He I, 623 K). The Nd (4*f*) levels are not seen in the photoelectron spectroscopy spectrum (see text) and the major Fe(3*d*) and B(2*s*) corresponding levels are shown with vertical lines.

In order to compare the theory with the photoemission data, the total (spin summed) DOS was multiplied with the zero-temperature Fermi function, and broadened with a Gaussian of 0.3 eV width. Since the He I spectra are insensitive to the 4*f* levels and, aside from these, all the compounds have similar electronic structures, we compare in Fig. 5 the calculated DOS with the spectrum of $Nd_2Fe_{14}B$ which has the highest resolution and is most representative of this DOS. Aside from small energy shifts in the peak positions, it can be seen that the overall agreement is very good, giving confirmation of the calculated exchange splitting of about 2.1 eV.

In conclusion, our results show that all compounds of the form $R_2Fe_{14}B$ have essentially identical electronic structures except for the $4f$ levels. In addition, we have shown that no significant changes in the electronic structure occur upon going from the ferromagnetic to paramagnetic state. Thus, $Nd_2Fe_{14}B$ appears to be describable as an itinerant-electron magnet with localized Nd $4f$ moments and exchange-split Fe $3d$ bands with magnetic short-range order above T_c, as in the fluctuating-band picture.[15] Finally, this work indicates that the electronic structures of these and other complex magnetic materials can be calculated from first principles; in due course this will be important for tailoring them to enhance their already outstanding properties.

We are grateful to the Department of Energy for financial support under Grant No. DE-FG02-86ER-45262, to J. A. R. Samson, W. Y. Ching, R. D. Kirby, M. Langell, Y. G. Ren, K. Aylesworth, and the staff of the Wisconsin Synchrotron Radiation Center for assistance and helpful discussions, and to the National Science Foundation Supercomputing Facility at Cornell University for a grant of computer time.

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