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Electronic structure and surface reactivity of $Nd_2Fe_{14}B$ and related compounds

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Electronic structure and surface reactivity of $Nd_2Fe_{14}B$ and related compounds

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Studies of electronic and magnetic structure and surface reactivity are reported for $R_2T_{14}B$ compounds where R = Y, Nd, Gd, and T = Fe, Co. The calculations employed the self-consistent, spin-polarized linear-muffin-tin orbital method. Experiments included ultraviolet, x-ray, and Auger electron spectroscopy. Comparisons are made between the calculated and measured electronic densities of states, and the reactions of the surfaces with O_2, H_2, and CO gases are studied. The effects of heat treatment on surface segregation are also reported.

INTRODUCTION

The discovery of the $Nd_2Fe_{14}B$ class of permanent-magnet materials has stimulated much research on fundamental aspects of electronic and magnetic structures and, of course, methods to predict and improve the properties for applications. Some of the important questions are the relationship between the electronic structure and observable properties such as T_c and site-dependent magnetic moments, and the surface structure, chemical stability, and corrosion behavior of these materials.

Recently we have reported on photoemission studies and electronic structure of $Nd_2Fe_{14}B$ and similar compounds with Y and Gd.[1] First-principles spin-polarized band calculations were performed for $Y_2Fe_{14}B$ and the density of states (DOS) and Fe magnetic moments were found to be in very good agreement with experiment. In this paper we extend this work to $R_2Co_{14}B$ compounds, since Co is an important alloying agent to raise the (somewhat low) Curie point, and also investigate surface cleaning and structure, and reactions of gases such as H_2 and Co with the surface of the Fe-based alloys.

ELECTRONIC STRUCTURE

$R_2T_{14}B$ (R = rare earth, T = Fe, Co, Ni) crystals are tetragonal with 68 atoms per primitive cell and the space group symmetry $P4_2/mnm$.[2] The large number of atoms per unit cell makes electronic calculations quite difficult. Some empirical[3–5] and non-self-consistent calculations[6] have been reported. However, a proper understanding of the electronic structure and magnetic properties of these systems requires spin-polarized self-consistent calculations such as the ones we have reported recently.[1] 4*f* states in rare earths are highly localized and are very difficult to include in a full-fledged band calculation. Their photoemission spectra are reasonably well understood with the transition state analysis[7,8] or renormalized atom approach.[9] Because of this and the fact that the non-4*f* parts of the experimental electronic structure are similar, we have performed calculations on the Y-based compounds.

Our calculations employ the linear-muffin-tin orbitals (LMTO) method in the semirelativistic approximation (spin-orbit interactions are ignored).[10] The Hamiltonian and overlap matrices are 612×612. 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 the irreducible part of the Brillouin zone.

The spin-polarized DOS for $Y_2Co_{14}B$ are shown in Fig. 1. The structure near the Fermi level is primarily due to Co *d* states and is similar to that of pure Co. The average exchange splitting of about[11] 1.3 eV for Co *d* states is similar to the photoemission result (1.1 eV) and a band structure calculation (1.5 eV)[12] in pure Co. The structure around -8 eV is due to B 2*s* states. The density of states at the Fermi level is

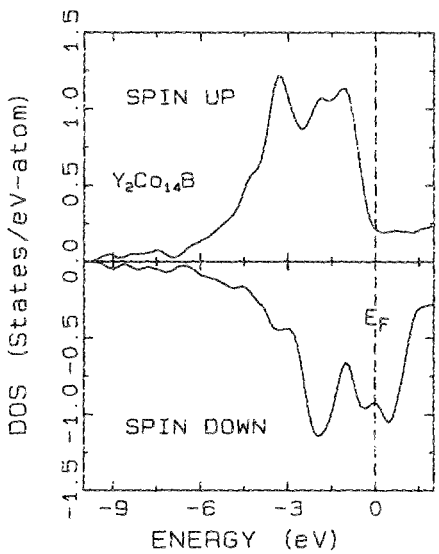

FIG. 1. Spin-polarized densities of states for $Y_2Co_{14}B$. An average exchange splitting of about 1.3 eV is seen in the Co 3*d* bands. The Y-derived states are broadly distributed below $E_F \equiv 0$ and the B 2*s* levels are at $-(8–9)$ eV.

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1.11 states/eV atom and the corresponding value for pure Co is 1.24 states/eV atom.[12] The charge transfers and magnetic moments for different sites are given in Table I. The calculated magnetic moment per formula unit of 18.3 μ_B is in reasonable agreement with the experimental value[13] of 19.4 μ_B. In order to compare the theoretical results with the photoemission data, the total DOS was multiplied with the zero-temperature Fermi function and broadened with a Gaussian of 0.15 eV width. The result is compared with 21.2-eV HeI photoelectron spectrum in Fig. 2, in which vertical lines show the centers of corresponding Co d band features in the experimental and calculated results. The corresponding results for $Y_2Fe_{14}B$ are discussed in Ref. 1.

Finally, we use a theory[14] due to Mohn and Wohlfarth (MW) and our electronic structure results to calculate the Curie temperature T_c for $Y_2Fe_{14}B$. With the average Fe moment of 2.27 μ_B and the spin up and spin down DOS per Fe of 0.42 and 0.56 states/eV atom spin, respectively, the spin-fluctuation temperature $T_{SF} = 3804$ K. Using MW's Stoner temperature $T_C^S = 1508$ K, we get $T_c = 1238$ K. Using the empirical band structure of Ref. 4, MW get $T_{SF} = 674$ K and hence $T_c = 575$ K, which is in very good agreement with experimental T_c of 573 K. Thus, the MW theory seems to be quite sensitive to the electronic structure used.

SURFACE REACTIVITY AND SEGREGATION

The $Y_2Fe_{14}B$, $Nd_2Fe_{14}B$, and $Gd_2Fe_{14}B$ alloys were studied by the UHV surface sensitive techniques of Auger and x-ray photoelectron spectroscopies (XPS) and, as expected, upon introduction to the UHV analysis chamber all three alloy surfaces were highly oxided. Figure 3 shows representative Auger spectra for the $Nd_2Fe_{14}B$ surface and indicates that carbon, nitrogen, and small amounts of sulfur also contaminate the untreated surface. Heating the surface to 350 °C under 5×10^{-7} Torr of either H_2 or CO slowly removes surface oxygen, presumably through the formation and subsequent desorption of H_2O and CO_2, respectively. Heating carbon-contaminated surfaces also results in surface reduction with a concomittant loss of carbon Auger intensity. Again, formation of CO_2 is the suspected mechanism. Initial O/Fe peak to peak Auger intensity ratios of the O 510(KL_2L_2) to Fe 703 ($L_3M_{4,5}M_{4,5}$) transitions are found to be 2–2.5/1 indicating that, with Auger cross sections taken into account[15] the untreated surface is approximately equally populated by oxygen and iron. Boron and rare-earth concentrations are consistent with those expected from bulk alloy values.

TABLE I. Charge transfers (in units of e) and magnetic moments (in Bohr magnetons) for different sites.

Site	Charge transfer	Magnetic moment
Y(f)	1.58	−0.42
Y(g)	1.00	−0.42
Co(k_1)	−0.22	1.21
Co(k_2)	−0.19	1.44
Co(j_1)	−0.18	1.51
Co(j_2)	0.00	1.38
Co(e)	−0.20	1.09
Co(c)	−0.42	1.75
B(g)	0.06	−0.10

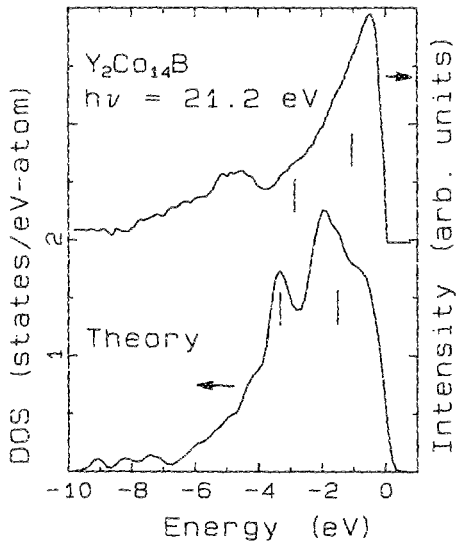

FIG. 2. Comparison of the broadened DOS for $Y_2Co_{14}B$ with the HeI (21.2 eV) spectrum. The peak at about −5 eV is an O($2p$) related feature.

Argon-ion bombardment readily removes carbon, sulfur, and nitrogen contaminants, but also preferentially sputters boron from the alloy surfaces. Subsequent annealing of the sputtered sample to substrate temperatures of 450 °C or greater causes substantial segregation of boron and rare-earth components to the surface, as is evident in Fig. 3(b) for the $Nd_2Fe_{14}B$ alloy treated at 575 °C under UHV for 15 min. This supports the assignment of the −8.6 eV feature in the photoemission spectrum of $Nd_2Fe_{14}B$ in Fig. 3 of Ref. 1 as due to B. The boron concentration of this surface is roughly three times as great as that of iron. Further Ar^+ sputtering at ambient temperature substantially reduces the boron sur-

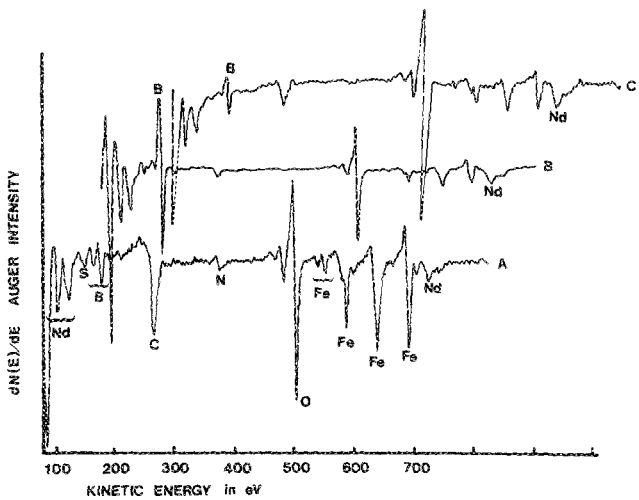

FIG. 3. Auger spectra of $Nd_2Fe_{14}B$ (a) with no pretreatment, (b) after heating under UHV at 575 °C for 15 min, (c) surface B after 15 min of Ar^+ bombardment at 2 keV, 7 μA. Auger spectra were taken at 3 keV with 2-eV modulation and 0.1-s time constant at 5 eV/s sweep rate. Spectra (b) and (c) are offset by 100 and 200 eV, respectively, for clarity.

face concentration but appears to have only a slight effect on that of the rare earth, as is illustrated in Fig. 3(c) for $Nd_2Fe_{14}B$ sputtered for 15 min at 14 μA/cm^2 with 2-keV Ar^+ at 3×10^{-5} Torr.

Oxidation of the rare-earth alloys exposed to ambient atmosphere extends to well into the alloy surface, as is shown by the Auger/Ar^+-ion depth profile for $Y_2Fe_{14}B$. The yttrium and gadolinium alloys appear to be contaminated to greater depths than is the neodymium alloy, even though the initial O/Fe Auger intensities are comparable. After 2×10^{18} Ar^+/cm^2, which is estimated to have sputtered approximately 1500 monolayers into the sample surface,[16] both the gadolinium and yttrium samples have surface oxygen concentrations of $\sim$0.5 O/Fe (Auger ratio of 1/1), whereas this ratio is achieved after only 0.6×10^{18} Ar^+/cm^2 in the case of neodymium. After fluences of 2×10^{18} Ar^+/cm^2, the alloy surfaces were altered by the sputtering process to the extent that no boron and only traces quantities of rare-earth metal were observable with Auger spectroscopy.

XPS results also indicate that some differences exist between the neodymium and other rare-earth alloys. Figure 4 shows the XPS O 1*s* region of untreated $Y_2Fe_{14}B$, Ar^+ bombarded $Y_2Fe_{14}B$, and untreated $Nd_2Fe_{14}B$ surfaces. O 1*s* binding energies of 529.5 eV found for the main oxide peak are comparable to literature values of the O^{2-} lattice oxide species[17] and are indistinguishable among the alloy samples. Untreated gadolinium and yttrium samples show an additional, higher binding energy species that is easily removed by argon-ion bombardment. This surface species, assigned as OH_{ads}, was not detected on the neodymium alloy, either prior or subsequent to any surface treatment performed here.

CONCLUSIONS

Self-consistent LMTO calculations for $Y_2Fe_{14}B$ and $Y_2Co_{14}B$ are, in general, in agreement with the PES data relevant to the transition-metal 3*d* states. The calculated average exchange splitting of 2.1 and 1.3 eV for the Fe and Co compounds, respectively, is supported by the double-peak *d* structure of the PES data. The calculated magnetic moments are in good agreement with experiment.

The surface studies showed a high degree of oxidation after prolonged exposure to the atmosphere. Sputtering produced significant changes of B and rare-earth surface compositions, and heating produced surface segregation of B and rare earths to levels higher than the bulk. Reduction of surface oxides by heating in the presence of H_2 or CO was observed. Further studies of both bulk and surface electronic structure will be reported elsewhere.

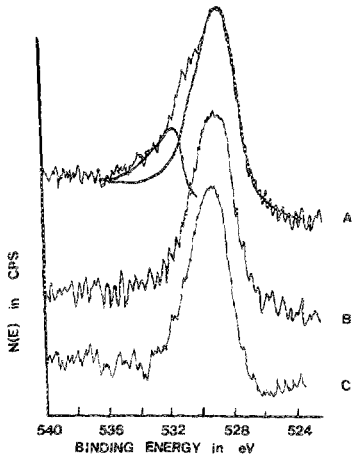

FIG. 4. O 1*s* XPS for (a) $Y_2Fe_{14}B$ with no pretreatment, (b) sample A after 15-min Ar^+ bombardment and, (c) $Nd_2Fe_{14}B$ with no pretreatment. Magnesium anode and 50-eV band pass used.

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