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Photoemission studies of Co- and Fe-based compounds with the $ThMn_{12}$ structure

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The electronic structures of $NdFe_{11}Ti$, $NdCo_{10}V_2$, and $YCo_{10}Cr_2$ have been studied with photoemission and spin-polarized calculations. The changes in these electronic structures upon nitrogenation have also been investigated. In the Fe compound, the Fe 3*d* states dominate the calculated density of states near the Fermi-edge, and the N(2*p*) peak is evident at around 6.3 eV. There is no shift in Fe 3*d* peaks visible in these compounds upon nitrogenation. Other than small energy shifts in the peak positions, there is an overall agreement between experimental data and the calculated density of states. The calculated density of states in the local-density approximation for $YCo_{10}V_2$ is broadened to account for the well-known many-body effects and compared with the photoemission data.

I. INTRODUCTION

A permanent magnet must have large magnetization and coercivity and high Curie temperature. Fe and Co(*T*) have reasonably high magnetic moments and Curie temperatures and many of the rare earths (R) have large but highly localized magnetic moments and large single-ion anisotropies. The permanent-magnet materials being studied here are R-(Fe,Co) compounds with the body-centered tetragonal $ThMn_{12}$(1:12) structure. The pure 1:12 compounds are normally not stable, but a large number of ternary compounds $R(Fe,Co)_{12-x}M_x$, where *M* is another metal, do exist with the $ThMn_{12}$ structure.[1] Whereas pure 1:12 compounds do not appear promising as permanent-magnet materials, some of them show considerable improvement in their magnetic properties upon nitrogenation.[2]

Since the magnetic properties of a solid are determined by its electronic structure, we report here the photoemission and theoretical studies of the electronic structures of $NdFe_{11}Ti$, $NdCo_{10}V_2$ and $YCo_{10}Cr_2$ before and after nitrogenation.

II. EXPERIMENT

The samples were prepared by arc melting in a water-cooled copper boat in an atmosphere of argon gas. The alloys were melted several times to ensure homogeneity. The samples $RCo_{10}T_2$ and $NdFe_{11}Ti$ were heat-treated in vacuum below 3×10^{-6} Torr at 850 °C for 2 weeks[3] and 4 days,[4] respectively, and afterwards quenched in water. X-ray diffraction measurements showed that the samples were single phase with the $ThMn_{12}$ structure. The buttons were then spark cut into discs approximately 1 cm in diameter and 1 mm thick. The surface was then polished to provide an optically smooth surface. The photoemission spectra were obtained in an ultra-high vacuum chamber with a base pressure of 2×10^{-10} Torr. The samples were cleaned *in situ* with several cycles of 2-keV Ar sputtering and subsequent annealing to 350 °C. Auger-electron spectroscopy (AES) was used to monitor surface cleanliness and to estimate nitrogen concentration. To introduce nitrogen, the cleaned sample surfaces were sputtered with N_2 with a kinetic energy of 2 keV and a current of 6×10^{-6} A for 10 min. The samples were radiantly heated with a tungsten filament to about 350 °C to promote nitrogen diffusion. The nitrogen rich layer was subsequently removed with Ar sputtering to expose the subsurface nitride. The nitrogen concentration *x* measured with AES in $RCo_{10}T_2N_x$ alloys was $\sim0.4\pm0.3$ and in the $NdFe_{11}TiN_x$ compound was $\sim0.7\pm0.4$. The photoelectron spectroscopy measurements were carried out at the Synchrotron Radiation Center in Wisconsin. The total energy resolution is 0.14 eV at a photon energy of 22.5 eV.

III. THEORY

The self-consistent spin-polarized electronic structure calculations are based on the linear-muffin-tin-orbitals method in the local density and scalar-relativistic approximations.[5] To simulate a disordered alloy with the correct stoichiometry, a supercell of four formula units is used for $NdFe_{11}Ti$ and $NdFe_{11}TiN_{0.5}$ calculations. The details of $YCo_{10}V_2$ calculations are published elsewhere.[6] The calculated spin-up and spin-down eigenvalues are truncated at the Fermi energy and broadened with a Gaussian of 0.2 eV to get the total density of states (DOS).

IV. RESULTS AND DISCUSSION

The photoelectron energy distribution curves (EDC) of $NdFe_{11}Ti$ with and without nitrogen at 22.5-eV photon energy are compared with the calculated DOS in Fig. 1. Curves labeled (c) and (d) in Fig. 1 show the calculated DOS of $NdFe_{11}TiN_{0.5}$ and $NdFe_{11}Ti$, respectively. The two peaks near the Fermi level which are separated by ~2.1 eV are due to Fe 3*d* states and are similar to the pure Fe 3*d* states.[7] In curve (c), there is an additional structure around 6.5 eV which is due to the 2*p* states of nitrogen. Except for the small energy shift in the nitrogen 2*p* band, the experimental data are in quite good agreement with the

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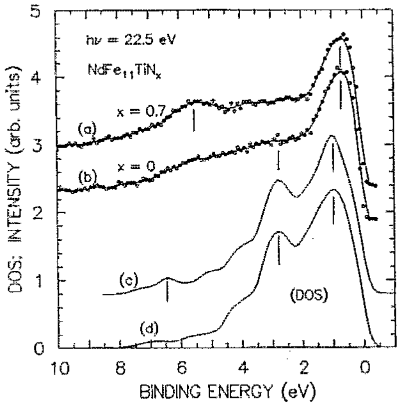

FIG. 1. Calculated DOS and photoelectron spectra ($h\nu = 22.5$ eV) for NdFe$_{11}$Ti at room temperature: (a) Photoemitted EDC of nitrided, (b) non-nitrided NdFe$_{11}$Ti compound, calculated DOS of (c) nitrided and (d) non-nitrided compound. The zero of energy is at the Fermi level ($E_F = 0$).

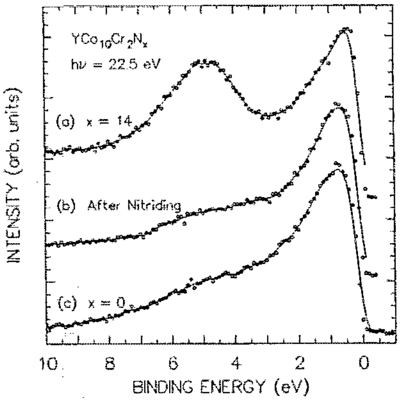

FIG. 3. Photoemitted EDC of nitrided YCo$_{10}$Cr$_2$ with 22.5-eV photon energy: (a) nitrogen-sputtered and heated (350 °C) surface, (b) after removing the nitrogen rich surface layer with Ar sputtering, and (c) non-nitrided YCo$_{10}$Cr$_2$. The zero of energy is at the Fermi level ($E_F = 0$).

calculated DOS. The differences may be due to matrix-element modulation of the calculated DOS and inelastic electron scattering in the experiment.[8,9]

Figure 2 shows the comparison between the experimental data of NdCo$_{10}$V$_2$ and YCo$_{10}$Cr$_2$ compounds and the calculated DOS for YCo$_{10}$V$_2$. The experimental spectra for the two compounds [Fig. 2(a) and (b)] are quite similar because they are dominated by the Co 3*d* band at this photon energy. The principal peak at the Fermi-edge due to the Co 3*d* states agrees with the calculated DOS [Fig. 2(d)]. On the other hand, the second Co 3*d* peak near 2.3 eV in Fig. 2(d) is not noticeable in either of the experimental spectra. The main reason for this difference is due to the importance of many-body effects in Co which are not included in the calculated DOS.[10] After introducing the energy-dependent lifetime broadening (Lorentzian function) in which the full width at half maximum has the form $\alpha(E-E_F)^2$ (Ref. 11), where E_F is the Fermi energy and $\alpha = 0.2$ eV, a good agreement is obtained between the EDC and modified DOS Fig. 2(c). The life-time broadening is not as important in Fe (Ref. 10), and hence it was not applied to NdFe$_{11}$Ti DOS.

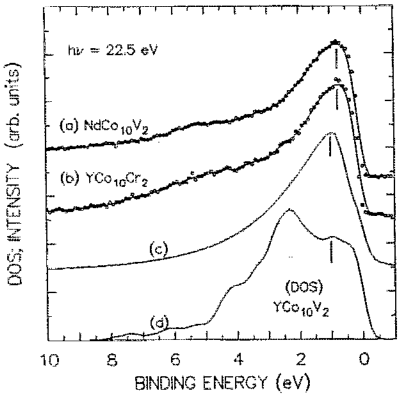

FIG. 2. Total DOS and EDC of 1:12 compounds: (a) photoelectron spectra of NdCo$_{10}$V$_2$, (b) YCo$_{10}$Cr$_2$ compounds, (c) lifetime broadened DOS, and (d) unbroadened DOS of YCo$_{10}$V$_2$. The zero of energy is at the Fermi level ($E_F = 0$).

The experimental data of clean and nitrogenated YCo$_{10}$Cr$_2$ are shown in Fig. 3. The spectrum in Fig. 3(a) was taken after sputtering with N$_2$ and heating the sample to 350 °C for 3 min. AES revealed a large concentration of N on the surface of the sample (about 50 at.% N). The broad peak at 5 eV is due to N(2*p*) electrons. After Ar sputtering the sample, this peak is greatly diminished as seen in Fig. 3(b). The calculated DOS for nitrogenated Co compounds is not available to compare with the experimental data.

V. CONCLUSIONS

There is an overall agreement between experimental data and the calculated DOS for NdFe$_{11}$Ti with and without nitrogen. The electronic structure of this compound is dominated by Fe 3*d* states as in other Fe rich compounds. There is very little change in the calculated and experimental spectra upon nitrogenation. Compared to NdFe$_{11}$Ti, the Co-based compounds absorb a smaller amount of nitrogen. The poor agreement between the experimental spectra and DOS in the local density approximation in Co-based compounds is improved by including life-time broadening effects in the calculated DOS.

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[1] K. H. J. Buschow, J. Appl. Phys. **63**, 3130 (1988).
[2] Y.-C. Yang, X.-D. Zhang, L.-S. Kong, and Q. Pan, Appl. Phys. Lett. **58**, 2042 (1991).
[3] M. Jurczyk, J. Magn. Magn. Mater. **87**, 1 (1990).
[4] B.-P. Hu, H.-S. Li, J. P. Gavigan, and J. M. D. Coey, J. Phys.: Condens. Matter **1**, 755 (1989).
[5] H. L. Skriver, *The LMTO Method*, Vol. 41 of the *Springer Series in Solid State Sciences* (Springer, New York, 1984).
[6] S. S. Jaswal, J. Appl. Phys. **69**, 5703 (1991).
[7] E. Kisker, K. Schroeder, W. Gudat, and M. Campagna, Phys. Rev. B **31**, 329 (1985).
[8] A. M. Turner, A. W. Donoho, and J. L. Erskine, Phys. Rev B **29**, 2986 (1984).
[9] H. Hochst, A. Goldmann, and S. Hufner, Z. Phys. B **24**, 245 (1976).
[10] M. M. Steiner, R. C. Albers, and L. J. Sham, Phys. Rev. B **45**, 13272 (1992).
[11] J. B. Pendry and J. F. L. Hopkinson, J. Phys. F **8**, 1009 (1978).