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Electronic structure and magnetic properties of Fe-rich ternary compounds: YFe$_{10}$V$_2$ and YFe$_{10}$Cr$_2$

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These compounds are prototypes of the Fe-rich ternary systems of ThMn$_{12}$ structure which are of considerable current interest as permanent magnet materials. The electronic structure of YFe$_{10}$V$_2$ and YFe$_{10}$Cr$_2$ have been studied with photoemission and spin-polarized calculations. The Fe d states dominate the calculated density of states (DOS) near the Fermi energy and there is a good correspondence between the DOS and the experimental spectra. The calculated magnetization is in very good agreement with the experimental data. The calculations give a magnetic moment of $\sim 1\,\mu_B$ at the V or Cr site antiferromagnetically coupled to the Fe moments. This leads to a significant reduction in the average moment per Fe atom in these systems. The charge transfers are, in general, small and are mostly from V or Cr to Y atoms. These charges are used to show that the point-charge model alone cannot explain the crystal-field data.

I. INTRODUCTION

There is considerable current interest in iron-rich compounds as possible permanent magnet materials. One of the structures being actively explored is that of tetragonal ThMn$_{12}$. A binary compound in which Fe replaces Mn in this structure does not exist. However, a fairly large class of ternary compounds RFe$_{12-x}$T$_x$ in the ThMn$_{12}$ structure exists, where R and T are rare-earth and transition-metal elements, respectively.[1] x is close to 2 for T = V, Cr, or Mo and 1.2 for T = Ti or W. Structural and magnetic properties of many of these compounds have been studied recently.[2-5] A key to the understanding of the magnetic properties of a material is its electronic structure.

We report here the electronic structure studies of the prototypes YFe$_{10}$V$_2$ and YFe$_{10}$Cr$_2$ by photoemission and spin-polarized band-structure calculations. These compounds were chosen because they permit the study of the main features of the electronic structure of these systems without the theoretical complications of the rare-earth $4f$ electrons.[6] This is possible because the highly localized $4f$ electrons do not hybridize with the other valence electrons. The calculated densities of state (DOS) are compared with the photoemission data. The self-consistent spin-polarized calculations also give the magnetization which is compared with the experimental data available in the literature.[4] Finally, the calculated charge transfers are used to find the crystal-field parameters in the point-charge-model approximation.

II. ELECTRONIC STRUCTURE

The samples were prepared by arc melting and were checked with x-ray diffraction for the correct crystalline structure. The angle-averaged photoemission experiments were performed in a homemade system with a base pressure of $\sim 3 \times 10^{-10}$ Torr using HeI (21.2 eV) radiation and at temperatures below and above the Curie temperature. The samples were cleaned *in situ* by 3-keV argon ion bombard-

ment. The resolution of the measurement is about 0.2 eV at the HeI line.

The self-consistent spin-polarized electronic structure calculations are based on the linear-muffin-tin-orbitals (LMTO) method in the semirelativistic approximation.[7] The lattice parameters for the tetragonal structure are taken from Ref. 2 (YFe$_{10}$V$_2$: $a = 0.8501$ nm, $c = 0.4775$ nm; YFe$_{20}$Cr$_2$: $a = 0.8463$ nm, $c = 0.4775$ nm). Neutron scattering data show that V atoms prefer to substitute for Fe on the i sites.[3] We place V atoms at the ($\pm x$,0,0) i sites. Since there is no experimental information on the Cr sites, we use the same sites for Cr as for V. The core states for the constituent atoms were frozen to be the same as the atomic states found self-consistently. The Hedin–von Barth form[8] of the local spin-density approximation to the exchange-correlation potential with Janak parameters[9] was used. The s, p, and d basis functions were used for the valence states of each atom.

III. RESULTS AND DISCUSSION

The calculated spin-polarized DOS for YFe$_{10}$V$_2$ and YFe$_{10}$Cr$_2$ are shown in Figs. 1 and 2, respectively. The two results are quite similar with the main peaks being due to Fe d states. The contribution due to V and Cr are relatively small. These results are similar to other Fe-rich compounds such as Y$_2$Fe$_{14}$B with an average exchange splitting of about 2 eV.[6] In order to compare theory with the photoemission data, the total DOS is multiplied with the zero-temperature Fermi function, and broadened with a Gaussian of 0.25 eV width. The results for the two systems are compared in Figs. 3 and 4. The experimental data are below and above the Curie temperatures (T_c for YFe$_{10}$V$_2$ and YFe$_{10}$Cr$_2$ are 540 and 510 K, respectively[2]). First of all, the paramagnetic electronic structure is essentially unchanged from that of the ferromagnetic state in both systems. The O and/or C contamination peak at ~ -6 eV in YFe$_{10}$Cr$_2$ is very nearly gone at high temperature due to desorption. The desorption of
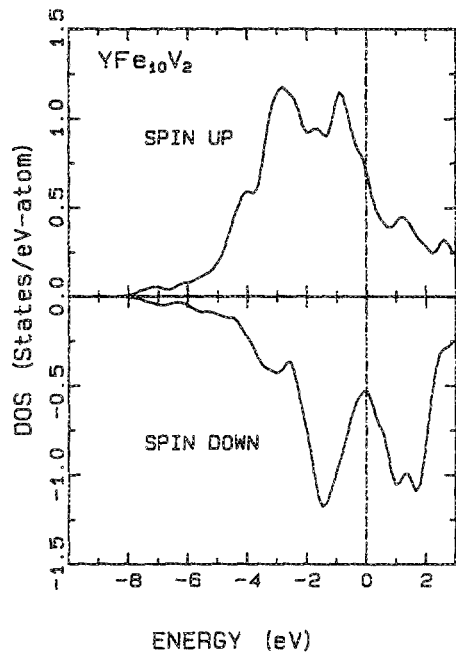
FIG. 1. Spin-polarized densities of states of $YFe_{10}V_2$. The zero on the energy axis corresponds to the Fermi energy.

FIG. 3. Comparison of the broadened total density of states (multiplied with the zero-temperature Fermi function) with the photoemission data below and above the Curie temperature for $YFe_{10}V_2$. The zero on the energy axis refers to the Fermi energy.

contaminants at high temperature also appears to enhance the intensity of the exchange-split Fe d peak near -3 eV in both compounds. The similarity of the paramagnetic to the ferromagnetic spectrum in iron is well known and is due to the short-range magnetic order.[10] Secondly, the calculated DOS are in good overall agreement with the experimental data. While making this comparison, one must keep in mind
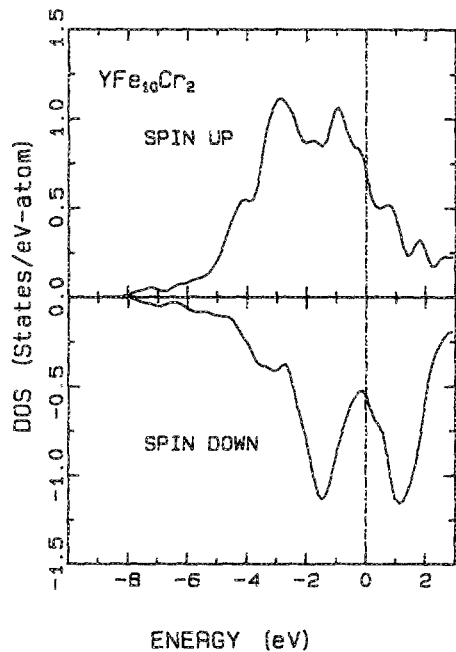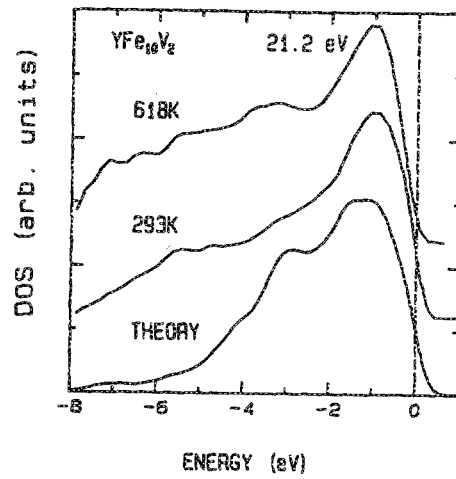
that the calculated DOS does not include the dipole-matrix-element effects present in the photoemission data. The small relative shift (~ 0.3 eV) of the Fe d band in the photoemission spectra of the two compounds is not supported by the DOS calculations based on the same crystal structure. This may be related to the difference in the hypothetical structure of $YFe_{10}Cr_2$ used in the present calculations and its real structure.

The calculated magnetic moments per formula unit are 16.8 and 17.2 μ_B for $YFe_{10}V_2$ and $YFe_{10}Cr_2$, respectively. These are in very good agreement with the corresponding experimental values of 16.2 and 16.7 μ_B.[4] Finally, the calculated charge transfers and magnetic moments at various sites are listed in Table I. The table also includes the results of

FIG. 2. Spin-polarized densities of states of $YFe_{10}Cr_2$. The zero on the energy axis corresponds to the Fermi energy.
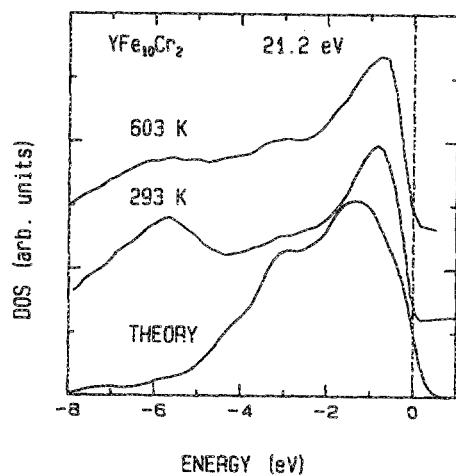

FIG. 4. Comparison of the broadened total density of states (multiplied with the zero-temperature Fermi function) with the photoemission data below and above the Curie temperature for $YFe_{10}Cr_2$. The zero on the energy scale corresponds to the Fermi energy.

TABLE I. Charge transfers (in units of e) and magnetic moments (in Bohr magnetrons) for different sites in YFe$_{10}$V$_2$ and YFe$_{10}$Cr$_2$.

			Y	Fe(8f)	Fe(8i)	Cr or V(8i)	Fe(8j)
Charge transfer	YFe$_{10}$V$_2$		0.37	0.0175	0.1	− 0.24	− 0.04
	YFe$_{10}$Cr$_2$		0.35	0.003	0.093	− 0.17	− 0.052
Magnetic moments	YFe$_{10}$V$_2$	Calc.	− 0.35	1.68	2.1	− 0.87	1.99
		Expt.[a]	0.00	1.83	1.95	0.00	1.52
	YFe$_{10}$Cr$_2$	Calc.	− 0.33	1.77	2.23	− 1.18	2.08

[a] Reference 3.

neutron scattering data for YFe$_{10}$V$_2$ when fitted with the Fe moments only. Our calculation gives sizable moments at Y and V (or Cr) sites which couple antiferromagnetically to the Fe moments. Since the calculated electronic structure is in very good agreement with the photoemission data and the observed total magnetization, it is reasonable to expect the individual moments to be reliable. The present results for V and Cr moments are consistent with the reduction in the average moment per Fe atom as a function of V and Cr concentration in V-Fe and Cr-Fe alloys.[11] Thus, we suggest that the neutron scattering data should be fitted with non-zero moments on all sites.

As expected in metals, the charge transfers listed in Table I are quite small. We expect the charges to be qualitatively similar when Y is replaced with a rare earth. Using these charges we have calculated the crystal-field parameter A_2^0 for the Y site in the point-charge-model (PCM) approximation using the expression

$$A_2^0 = -\frac{e}{4} \sum_i Z_i \frac{3z_i^2 - r_i^2}{r_i^5}, \tag{1}$$

where Z_i is the charge at site i, r_i is the distance of site i, and z_i is the component of r_i in the c direction. The calculated values of A_2^0 are 1623 and 1577 (K/a_0^2) for YFe$_{10}$V$_2$ and YFe$_{10}$Cr$_2$, respectively, where a_0 is the Bohr radius. The corresponding experimental value for GdFe$_{10}$V$_2$ is $-140(K/a_0^2)$.[1] This comparison clearly points out the inadequacy of the PCM in crystal-field calculations. As shown recently by Zhong and Ching for Nd$_2$Fe$_{14}$B, the crystal-field effects in the Wigner–Seitz cell of the site itself are very important.[12] It is worth emphasizing the PCM should give a realistic value for the contribution of the rest of the lattice to A_2^0 provided the charges Z_i used in Eq. (1) are obtained through a self-consistent calculation.

IV. CONCLUSIONS

We have obtained a reasonable model of the electronic and magnetic structure of YFe$_{10}$V$_2$ and YFe$_{10}$Cr$_2$ by photoemission and self-consistent calculations. As in other Fe-rich compounds, the electronic structure is dominated by the Fe d states. However, the stabilizing transition metal in this system couples antiferromagnetically to Fe giving it a much smaller average moment per atoms than that in Y$_2$Fe$_{14}$B. It is shown that the point-charge model by itself is totally inadequate to describe the crystal-field effects in such systems.

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