Half-metallic ferromagnets are materials exhibiting metallic character for the majority-spin electrons but a semiconducting gap for the minority-spin electrons. Correspondingly, one expects complete spin polarization at the Fermi level, making this class of materials ideal for spin-polarized emitters to be used in magnetic tunneling applications such as magnetic random access memory and access memory for spin-polarized emitters to be used in magnetic tunneling devices. 

High-quality, epitaxial thin films of CrO$_2$ have been predicted to be half-metallic. Experimentally, high-quality, epitaxial thin films of CrO$_2$ have been reported recently, providing experimental indication of its half-metallic character. 

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A thick CrO$_2$ film grown on (100) TiO$_2$ substrates. X-ray diffraction indicated that the CrO$_2$ films were single phase and the CrO$_2$ in-plane <100> and <001> (a$_{||}$ and c) axes were aligned with the respective axes of the TiO$_2$ substrate. The third axis, crystallographically equivalent to a$_{||}$ normal to the surface of the films, will be denoted as a$_{\perp}$. The films exhibited a sharp ferromagnetic transition with a Curie temperature of about 393 K and a strong in-plane magnetic anisotropy with c and a$_{||}$ being the easy-axis and hard-axis directions, respectively. Cr$_2$O$_3$ spectra were taken from high-purity pressed-powder samples. Our experiments were performed at the high-resolution Hermon beamline of the University of Wisconsin-Madison Synchrotron Radiation Center. The XAS spectra were taken with a resolution of about 150 meV at 550 eV by measuring the total electron yield. The degree of linear polarization was 85-90%. The XMCD measurements were taken with circularly polarized light (≈ 80%) from CrO$_2$ samples in switching remnant magnetization along the easy-axis which was positioned horizontally and situated at 45° with respect to the direction of the incoming radiation. 

To elucidate the spatial orientation and orbital character of the O 2p unoccupied states we have employed polarization-dependent XAS measurements with linearly polarized light. The results are shown in Fig. 1(a). The CrO$_2$ spectrum displays a sharp peak (1) at ≈ 529.2 eV, followed by two other features (2) and (3) at energies of 2.3 and 3.4 eV higher. The sharp peak (1) exhibits a large intensity variation of ≈ 90%, with a maximum for the geometry with the electric field vector of the light E arranged along a$_{||}$ (normal to the c-axis). As shown further in Fig. 1(b), the φ dependence of (1) follows accurately a cos$^2$(φ) curve. Our fit to the data, together with the degree of linear polarization of 85-90%, gives an orientation of peak (1) perpendicular to the c-axis of more than 95%. The azimuthal dependence of the higher lying features (2) and (3) is considerably smaller exhibiting an excursion of about 28% between the 0° and 90° orientations. At the same time its sign is opposite to that of (1) which indicates a dominant contribution from O 2p states parallel to the c-axis. 

The O K XAS polarization dependence has its origin in the orientation of the O 2p - Cr 3d hybrid states with respect to the crystalline axes. The building blocks of the CrO$_2$'s rutile structure are CrO$_6$ octahedra arranged along and slightly elongated in the direction of the tetragonal c axis. The O 2p - Cr 3d hybridization mechanism can be easily understood in a Goodenough molecular-orbital model electronic structure scheme. The ligand crystal-field splits the Cr 3d manifold into three $t_{2g}$ and two $e_g$ states. Due to the distinction between the $a_{\perp}$($a_{||}$) and c-axes in the tetragonal rutile structure,
Crour samples, we estimated by tunneling measurements the issue of spectral contamination effects of the

dependency splitting into an orbital normal to the trigonal environment forming planar CrO$_3$.

The Cr$_2$O$_3$ K XAS spectrum displays significant intensity only above 532 eV having the highest intensity at about 532.8 eV. Therefore we can conclude that the energy region from 529 to about 532 eV in our CrO$_2$ K XAS does not contain any spectral interference from the surface layer of Cr$_2$O$_3$.

Our CrO$_2$ K XAS spectra (peak (1) at 529.2 eV) have been taken with a resolution of 150 meV and an accuracy of the absolute photon energy scale of about ±100 meV. Previously reported O K absorption energies for peak (1) taken from powder CrO$_2$ are of 527.0 eV, 530.0 eV, and 530.5 eV. Our experience with measuring the Cr$_2$O$_3$ and Cr$_2$O$_3$ absorption spectra suggests that these differences are due to monochromator absolute energy calibration errors rather than to sample differences. The previously reported CrO$_2$ O 1s x-ray photoemission (XPS) binding energy $E_B$ = 529.3 eV, is 0.1 eV above the absorption peak (1). Taking into account the limited accuracies of the two measurements, an energy difference of 0.7±0.3 eV remains between the O 1s XPS binding energy and the measured absorption edge at ≈ 528.6 eV, where we assume a 0.2 eV accuracy of the XPS measured binding energy.

The electron excited in the absorption process interacts with its environment which consists of the other valence electrons (correlation) and the positive charge of the core-hole (additional attractive potential). To understand the effect of these interactions on the absorption spectra we will compare our data with recent CI and band structure calculations. The CI calculations start with a simplified model of a transition metal oxide as a MO$_6$ cluster formed by a transition metal (M, d$^n$) ion situated in the octahedral ligand field of six oxygen ions (O$^{2-}$). Then, the valence electronic structure is described by allowing for $d$–$d$ Hubbard charge transfer ($d^m$ $\to$ $d^{m-1}$+$d^{n+1}$), metal-ligand charge-transfer (e.g. $d^n$ $\to$ $d^{n+1}$+$L$ where $L$= valence oxygen hole), and metal-ligand hybridization which results in a ligand-hole content in the ground-state. The oxygen K absorption spectrum is obtained by calculating the differences in total energy (and the strength of the transitions) between excited-states resulting from annihilation of a valence ligand-hole by addition of one electron to a mixed metal-oxygen state (e.g. $d^{n+1}$+$L$ $\to$ $d^{n+1}$). In Fig. 2 we compare the calculated CI oxygen XAS spectrum with the experimental spectra of two isoelectronic 3d$^2$ oxides, CrO$_2$ (Cr$^{4+}$) and V$_2$O$_3$ ($V^{3+}$). First, there is a good similarity between the O K XAS spectra of the two 3d$^2$ oxides which indicates that, due to strong $p$–$d$ hybridization, the O K edge absorption is mainly determined by the underlying 3d electronic structure. Second, a good correspondence is found between the three strongest CI transitions and the three most prominent experimental absorption features, which validates the choice of parameters used in the calculation.
Finally, two contributions can be proposed as the origin of the small energy difference (≈ 0.4 eV) observed for the CrO$_2$ features (2) and (3) (Fig. 2(a)). First, a more accurate description of CrO$_2$ would have to incorporate the deviation of the ligand-field from octahedral symmetry due to the tetragonal crystal structure distortion. Second, the attractive core-hole potential (not included in the CI calculation) can, in principle, be expected to have a stronger effect (increased downward energy shift) on the narrow, more localized t$_{2g}$ peak (1) than on the broader features (2) and (3).

The two band-structure calculations used in this study are both based on the local-spin-density approximation of the density-functional theory (LSDA). As far as the low-energy excitation spectrum is concerned (e.g. transport properties) both calculations agree in finding CrO$_2$ to be a half-metal with a low density of fully spin-polarized states at $E_F$. However the two calculations differ importantly in the values obtained for the exchange-splitting energy responsible for ferromagnetism ($\Delta_{\text{exch-split}} \approx 3.0$ eV in Ref. 6, $\Delta_{\text{exch-split}} \approx 1.8$ eV in Ref. 7) and in the treatment of the on-site electron-electron correlation. In the LSDA approach of Lewis et al.\textsuperscript{6} the effects of electron-electron correlation are included in an averaged, mean-field way. In contrast, Korotin et al.\textsuperscript{7} use a LSDA scheme modified by the explicit inclusion of a potential correction (U=3 eV) in order to account for the Coulomb interaction between localized d electrons.

We find a good similarity between the O K XAS and the envelope of the O 2$p$ unoccupied DOS obtained by Korotin et al., as can be observed by comparing spectra in panels (a) and (b) of Fig. 3. In particular, the amount of orbital overlap included in the calculation results in a band broadening consistent with the measured width (≈ 0.7 eV) of the O 2$p_y$ - Cr 3$d_{xz-ys}$ t$_{2g}$ peak (1) (Fig. 3(a)). The two other O K XAS features, (2) and (3) at higher energies, correspond to local DOS maxima that have a mixed O 2$p$ - Cr 3$d$ e$_g$ spin-up and O 2$p$ - Cr 3$d$ t$_{2g}$ spin-down character. It becomes clear when looking at the theoretical spin-up/spin-down projected DOS in Fig. 3(c) and 3(d) that the essential parameter controlling the good agreement with the LSDA+U calculation (i.e. the appearance of a broad minimum in the empty DOS at ≈ 1.5 eV above $E_F$ and of significant local maxima (2) and (3) at higher energies, as observed experimentally) is the large upward shift of the spin-down DOS (Δ$_{\text{exch-split}} \approx 3.0$ eV). Our data are not well reproduced by the LSDA calculation which has $\Delta_{\text{exch-split}} \approx 1.8$ eV. This smaller exchange-splitting leads directly to a spin-down DOS filling in the region of the broad experimental minimum (≈ 1.5 eV above $E_F$) and to the presence of the other (higher energy) significant DOS features (mainly due to spin-down t$_{2g}$ states) shifted closer to $E_F$, as seen in Fig. 3(e). An experimental $\Delta_{\text{exch-split}}$ can be determined in a "rigid band" approximation by slightly adjusting the (LSDA+U) exchange-splitting energy shift to fit our data (features (2) and (3)). This "DOS-fit" yields $\Delta_{\text{exch-split}} \approx 3.2$ eV. Given the uncertainties in this fitting and experimental accuracies, we conclude that our data indicate a $\Delta_{\text{exch-split}} \approx 3.1$ eV. This is consistent with the LSDA+U calculation in which a large $\Delta_{\text{exch-split}}$ was obtained as an explicit consequence of including a considerable correlation energy (U=3eV). Thus, our experimental results supports the conclusion of the LSDA+U work\textsuperscript{7} that on-site correlation effects beyond the average LSDA value are present CrO$_2$. Interestingly, we also observe that the correlation energy parameter U is consistent (same origin) for the LSDA+U calculation\textsuperscript{7} (obtained by the local-orbital expansion method described by Pickett et al.\textsuperscript{24} and the CI calculation\textsuperscript{25}).

Finally, as the first empty oxygen states have been experimentally determined to be of O 2$p_y$ origin, a substantial magnetic orbital polarization of these states is expected since their Cr 3$d_{xz-ys}$ t$_{2g}$ counterparts are fully spin-polarized (Fig. 3(d)). Indeed, we have measured a clear O K XMCD signal (not shown here), similar to...
that obtained previously by Attenkofer et al. from polycrystalline CrO$_2$. In conclusion, we used polarization-dependent XAS to determine the orbital character of the unoccupied O 2$p$ states just above $E_F$ in CrO$_2$ which are found to be O 2$p_y$ states hybridized with Cr 3$d_{xz}$-$3d_{yz}$, with a bandwidth of $\approx 0.7$ eV. A large experimental exchange-splitting energy of $\Delta_{exch-split} \approx 3.0$ eV was estimated by comparison between our data and band-structure calculations. Our results support a model of CrO$_2$ as a half-metallic ferromagnet with substantial correlation effects.

The help of X. W. Li in growth of the sample and of M. Bissen and R. Hansen in setting the experiment is gratefully acknowledged. The authors thank M. A. Korotin for communicating his results prior to publication. One of the authors (C. B. S.) thanks G. A. Sawatzky and D. I. Khomskii for useful discussions. This work was supported in part by the DOE under Contract W-31-109-ENG-38. The Synchrotron Radiation Center, UW-Madison, is supported by the NSF under Award No. DMR-9531009.

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