CrO_2— A New Half-Metallic Ferromagnet?

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Spin-resolved photoemission from polycrystalline CrO_2 films shows a spin polarization (P) of nearly +100% for binding energies near 2 eV below the Fermi level (E_F). Despite the metallic resistivity behavior, extremely low intensity is observed in the photoemission spectra near E_F. Our findings are in contrast to recent band-structure calculations, predicting CrO_2 to be a half-metallic ferromagnet with $P=+100\%$ at E_F.

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The ferromagnet CrO_2 is one of the technologically most important transition-metal oxides. But surprisingly enough, its electronic structure is up to now an open question. A first qualitative model was proposed by Goodenough[1] in 1971, but the first self-consistent band-structure calculation was not published until 1986 by Schwarz.[2] This theoretical study yields the interesting result that CrO_2 is a "half-metallic" ferromagnet, i.e., that it is a metal for majority (spin-up) electrons, but exhibits a semiconductor-type gap for the minority (spin-down) electrons. This type of band structure should yield interesting magneto-optical properties. Moreover, the theoretically predicted 100% spin polarization of the electrons at the Fermi level would make a new type of spin-polarized electron source feasible, applicable to such fascinating ideas such as spin-polarized scanning tunneling microscopy.

In this Letter we report on the first study of the electronic structure of CrO_2 by spin- and energy-resolved photoemission spectroscopy. We found nearly +100% spin polarization for electrons with binding energies in the range of 2 eV below the Fermi energy (E_F). In contrast to the prediction of the band-structure calculation, we observed only negligible photoemission intensity near E_F, despite the metallic resistivity behavior.[3-5]

The CrO_2 films were obtained by chemical vapor deposition, i.e., by decomposition of CrO_3 in a closed reactor onto heated substrates of RuO_2, TiO_2, or Al_2O_3. The films were introduced into the UHV chamber and the surfaces cleaned by very soft sputter cycles of 30 s, with a defocused 500-eV Ne ion beam under almost grazing incidence. We used this gentle cleaning method in order not to destroy the structural and chemical order at the surface, since especially the magnetic order reacts very sensitively to any changes at the surface. The usual method to heal the structural defects by annealing was not applicable since the surface of CrO_2 transforms into Cr_2O_3 at temperatures above 200 °C (see below and Dissanayake and Chase[6]).

The photoemission spectra were measured with a He I gas discharge lamp with a photon energy of $h\nu=21.2$ eV. The photoelectrons were detected normal to the film plane by means of a 180° spherical energy analyzer with an energy and angle resolution of 100 meV and ±3°, respectively. The apparatus used for this work is described in detail elsewhere.[7] In the context of the present work the angle resolution is of no relevance, since, for the polycrystalline samples, practically the whole Brillouin zone is sampled. No significant change of the photoemission spectrum was found for films on c-axis-oriented sapphire, which showed a preferred orientation of their rutile-structure c axis along the growth direction perpendicular to the substrate. After each 30 s of sputtering, a photoemission spectrum was recorded. The spin analysis of the photoelectrons was performed by means of a Mott detector. For that purpose the films were magnetized in the film plane with use of a coil with a field pulse of about 500 Oe. This field strength is sufficient to yield a remanent magnetization of the film according to hysteresis-loop measurements by means of a vibrating-sample magnetometer.[5]

Figure 1 shows several energy distribution curves (EDC) of the photoelectrons for different times (t_{sp}) of the sputter cleaning. The EDC before any sputtering ($t_{sp}=0$ s) is shown in the bottom curve, which starts near a binding energy (E_b) of 1 eV below the Fermi energy because of the negligibly small photoemission intensity between E_F and $E_b=1$ eV. The EDC increases gradually toward 6 eV binding energy. After four cycles of sputter etching ($t_{sp}=120$ s) a shoulder develops near $E_b\approx2.7$ eV. Upon further sputtering, this shoulder grows into a peak at this energy as shown for $t_{sp}=335$ s. The upper inset of Fig. 1 shows the EDC for $t_{sp}=335$ s on a larger binding-energy scale. Besides the peak near 2.7 eV, a broad maximum is found near 5.5 eV. The lower inset shows this EDC in the vicinity of the Fermi

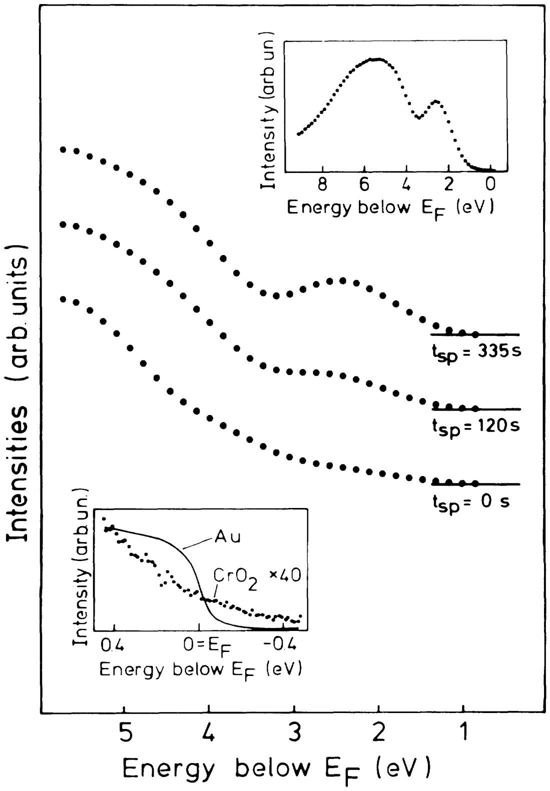

FIG. 1. Photoemission energy distributions curves (EDC) of polycrystalline CrO_2 films at 300 K for $h\nu = 21.2$ eV and for different times (t_{sp}) of sputter cleaning. Upper inset: EDC for $t_{sp} = 335$ s on an expanded binding-energy scale; lower inset: EDC in the vicinity of the Fermi energy of CrO_2 (expanded by a factor of 40) as compared to the EDC of a polycrystalline Au foil.

energy together with the EDC of a polycrystalline Au foil. The latter shows a well-defined Fermi edge, whereas CrO_2 does not exhibit any edgelike structure even on an intensity scale expanded by a factor of 40.

After 120 s of sputter cleaning, we find the maximum spin polarization of $P \approx +95\%$ near $E_b = 2$ eV and a gradual decrease toward $E_b = 5$ eV, as shown in Fig. 2. In the energy range between $E_b \approx 2$ eV and E_F the intensity is too low to give reasonable statistics for the spin-polarization measurements. Thus the measured maximum spin polarization is close to the predicted $P(T=0) = 100\%$, but in contrast to the ground-state band-structure calculation only negligible emission intensity is found near the Fermi level. The observed nearly $+100\%$ spin polarization near 2 eV binding energy coincides with the center of gravity of the shoulder in the EDC for $t_{sp} = 120$ s in Fig. 1. On further sputtering, this shoulder in the EDC grows into a peak (see, e.g., the EDC for $t_{sp} = 335$ s), but the spin polarization decreases and eventually disappears completely for $t_{sp} > 210$ s.

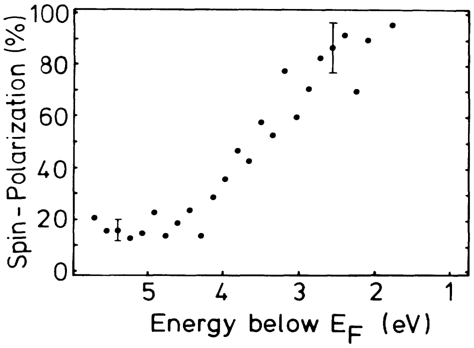

FIG. 2. Spin-polarization spectrum of a polycrystalline CrO_2 film at 300 K after 120 s of sputter cleaning.

This effect is probably due to increasing destruction of the surface order, i.e., sputtering produces a more or less amorphous nonmagnetic layer[8] of CrO_2 at the surface. This is qualitatively corroborated by the lack of any significant changes in the Auger-electron spectra. The binding energies seem to be quite insensitive to this kind of structural disorder at the surface, whereas the spin polarization responds most dramatically. The decrease in spin polarization may be caused by destruction of the magnetic order at the surface or depolarization by scattering of the photoelectrons in the disturbed surface layer.

We tried to anneal the surface *in situ* by heating the sample ($t_{sp} \geq 335$ s) for 12 h at 200 °C. The spectra recorded directly after heating (top curve in Fig. 3) show an EDC similar to the EDC before heating, but shifted rigidly by about 0.9 eV toward E_F. The EDC measured after heating compares well with that of Cr_2O_3.[9] This is possible because bulk CrO_2 decomposes into Cr_2O_3 at temperatures above 280 °C,[4] whereas at the surface this may occur at lower temperatures. After some additional sputtering ($t_{sp} = 30$ s) we recovered the original peak po-

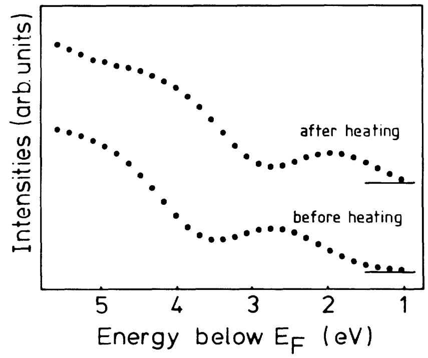

FIG. 3. Energy distribution curves (EDC) of a polycrystalline CrO_2 film at 300 K. Bottom curve: EDC after 335 s of sputter cleaning (before heating); top curve: same EDC after heating at 200 °C for 12 h.

sitions of the EDC before heating and the high spin polarization ($P \approx +100\%$) was observed again. Hence we conclude that the heating has produced a layer of Cr_2O_3 at the very surface, but at the same time has healed the subsurface layers from the defects produced by sputter cleaning.

Transition-metal oxides exhibit a great variety in their electronic structure. We find insulators with strongly localized d electrons like TiO_2, semiconductors like CuO, and typical metals with delocalized d electrons like RuO_2. A similar diversity is also given for the different oxidation stages of the chromium oxides: Cr_2O_3 is an insulator, while CrO_2 is a metallic conductor (although with a quite high room-temperature resistivity[3-5]). In Cr_2O_3 the Cr^{3+} ion has three well-localized $3d$ electrons which form a spin-$\frac{3}{2}$ antiferromagnet below 308 K. CrO_2 orders ferromagnetically below 392 K with a magnetic moment of $2\mu_B$ per Cr atom. The question about the degree of localization of the d electrons in CrO_2, i.e., also about the type of magnetism in CrO_2, is still open and it is one of the goals of this work to gain new insights to answer this question.

Since the magnetism in transition metals and their oxides is always carried by the $3d$ electrons, it seems plausible that the peak in the EDC at 2.7 eV below E_F, where we find the nearly +100% spin polarization, is due to emission from d states. From the width of this peak we can estimate the d-band width w to be about 1.6 eV. Hence we conclude that in CrO_2 the d band does not cut the Fermi level. This has severe consequences on the type of magnetism in CrO_2: The magnetism cannot be of the Slater-Stoner-Wohlfarth band type, but instead there have to be localized magnetic moments which must be aligned by some kind of interatomic exchange interaction. One may think of superexchange via the oxygen orbitals. The 100% spin polarization of the d peak is equivalent to 100% alignment of the spins of the d electrons at the Cr sites. In contrast to the theoretical prediction,[2] we thus cannot exclude a Cr^{4+} configuration with two d electrons remaining at the Cr site, which are completely aligned and yield a magnetic moment of $2\mu_B$. However, because of the approximately octahedral coordination of the oxygen atoms about the Cr atom, its $3d$ states are split into low-lying t_{2g} states with three electrons per spin direction, and higher e_g states containing two electrons per spin direction. In the calculation of Ref. 2, the Fermi level falls into a dip of the t_{2g}-derived spin-up density of states. In order to accomodate two electrons in the Cr $3d$ states either the sequence of the t_{2g}-e_g splitting has to be inverted, or more likely, the dip near E_F in the t_{2g}-derived spin-up density of states has to open up into a gap.

A similar discrepancy between ground-state band-structure calculations and photoemission and inverse photoemission is found in NiO. The small d-d gap ($E_g \approx 0.6$ eV) in the calculated band structure is suggested to be increased to $E_g \approx 4.6$ eV in the photoemission and inverse photoemission process because of the slow ionic-motion–based (polaronic) screening.[10] An opposing point of view has been taken in a localized, ionic-configuration–based approach in the framework of the Anderson impurity model.[11] The energy-level scheme deduced in this model compares directly with the experimental excitation spectra. The two approaches differ in the effective d-d Coulomb interaction (U), i.e., small U (≈ 0) for the effective one-particle potential used in the band-structure calculation and large U ($\approx E_g$) for the ionic-level model.

In the case of CrO_2, it would therefore be desirable to determine the Coulomb interaction U. Under the assumption of a Cr^{4+} configuration, the difference in binding energies of the d-derived peaks in the photoemission spectra of CrO_2 and Cr_2O_3 can be used to estimate the Coulomb interaction $U \approx 0.9$ eV. This estimate has to be taken with caution because of the different chemical environments of Cr^{3+} and Cr^{4+} and because we note that in Fig. 3 the whole spectrum of Cr_2O_3 is shifted rigidly, including a major portion of the oxygen-derived peak. In any case, because of the virtue of spin-resolved photoemission we can identify a d-d gap of CrO_2 of $E_g \gtrsim 2$ eV which implies within the ionic-configuration–based approach a small U ($\lesssim 2$ eV). It remains to be shown whether this U is sufficient to give rise to discrepancy between the ground-state band-structure calculation and the photoemission spectra. A rather analogous discussion concerns present photoemission investigations of the novel oxide-based high-T_c superconductors.[12] The apparent discrepancy between the metallic resistivity behavior of CrO_2 (Refs. 3–5) and the very low density of states observed in the photoemission near E_F may imply that there are low-energy excitations of polaronic nature which are too slow to be observable in the photoemission process. Specific-heat measurements, presently being carried out, should help to clarify this point.

In conclusion, we would like to emphasize that we have observed for the first time in any of the half-metallic ferromagnets a spin polarization of nearly +100%. Previous spin-resolved photoyield measurements[13] of Fe_3O_4 showed spin-polarization values down to $P \approx -65\%$ near photothreshold, contrary to the expected $P(T=0) = -100\%$.[14] Measurements[15] by the same technique of NiMnSb gave $P \approx +50\%$ instead of the theoretically predicted $P(T=0) = +100\%$.[16] The reason for these discrepancies may lie in the difficult surface preparation. On the other hand, our results point to the observation of intrinsic properties of CrO_2.

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