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Hubbard splitting and electron correlation in the ferromagnetic metal CrO_2

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We have studied the electronic structure of CrO_2 by photoemission spectroscopy and specific heat measurements. The Cr $3d$ band shows a splitting into the upper and lower Hubbard bands with a small but finite density of states at the Fermi level, consistent with its metallic behavior. The small renormalization factor ($z\sim 0.1 \ll 1$) signifies strong electron correlation, but is still large compared with many $3d$ transition-metal oxides. [S0163-1829(97)51248-3]

CrO_2 is a ferromagnetic metal with the Curie temperature of $T_c \sim 390$ K.[1] The electrical resistivity has metallic temperature dependence (although it is rather high: $\sim 2.5\times 10^{-4}$ Ωcm at 300 K) and shows an anomaly at T_c,[2] indicating scattering of conduction electrons by fluctuating magnetic moments at finite temperatures. In spite of its great technological importance as magnetic recording media, relatively little is known about the electronic structure. A band-structure calculation was first performed by Schwarz[3] using the local-spin-density approximation (LSDA). The result predicts a ''half-metallic'' behavior, in which only the Cr $3d$ ($t_{2g\uparrow}$) band accommodates conduction electrons (two per Cr) and crosses the Fermi level (E_F), resulting in the 100% spin polarization at E_F. This is consistent with the saturation magnetization of $2.00\mu_B$/Cr.[4] The half-metallic behavior has also been obtained by subsequent calculations.[5] The half metal is predicted to show strong coercive force and magneto-optical effects.[6] Photoemission experiment was made by Kämper *et al.*[7] for a thin film sample cleaned by ion-sputtering, but the spectra show no spectral weight at E_F, inconsistent with its metallic behavior.[2] Very recently, Korotin *et al.*[8] have performed a band-structure calculation using the LSDA+U method, in which not only the spin polarization but also the orbital polarization is allowed by incorporating the nonlocal exchange interaction on the level of the Hartree-Fock approximation. The orbital polarization has led to a substantial increase in the splitting of the Cr $t_{2g\uparrow}$ band into the almost occupied and empty bands of different orbital characters, corresponding to the lower and upper Hubbard bands. Accordingly, the density of states (DOS) at E_F is reduced compared to the LSDA result (although it still remains substantial). According to Korotin *et al.*, the double exchange mechanism due to the coexistence of localized Cr $3d$ orbitals and strongly hybridized Cr $3d$-oxygen $2p$ orbitals is the driving force for the ferromagnetism.

In this work, we have performed photoemission and inverse-photoemission experiments as well as specific heat measurements on bulk polycrystals of CrO_2. The spectra exhibit a weak but clear Fermi edge characteristic of a metal. Most of the spectral weight of the Cr d band is distributed in broad peaks well above and below E_F, reminiscent of the upper and lower Hubbard bands, respectively, consistent with the LSDA+U results. A combined analysis of the spectroscopic and thermodynamic data has revealed a small renormalization factor z, implying strong correlation effects,

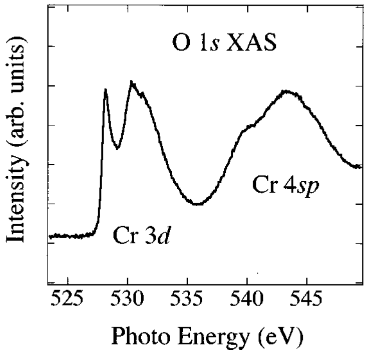

FIG. 1. O 1*s* core-level XPS spectrum of CrO_2.

namely, effects of fluctuations around the mean-field LSDA $+U$ ground state.

Polycrystalline samples of CrO_2 were prepared as follows: Crystals of Cr_2O_3 were resolved into CrO_2 powders at 420 °C under a 100 atm partial pressure of oxygen. Then the obtained powders were sintered to polycrystals at 800 °C under a pressure of 6 GPa so as to prevent the reduction to Cr_2O_3. The sintered pellets were confirmed to be single-phase by x-ray diffraction. X-ray photoemission (XPS) measurements were made using a Mg $K\alpha$ source. Ultraviolet photoemission (UPS) measurements were made using a He discharge lamp and using synchrotron radiation at beamline BL-28A at the photon factory (PF). The resolution varied from ~25 meV to ~0.2 eV depending on experimental conditions. X-ray absorption (XAS) spectra were taken in the total electron-yield mode at beamline BL-2B of PF. The energy resolution was ~0.2 eV. X-ray inverse-photoemission spectroscopy or bremsstrahlung isochromat spectroscopy (BIS) measurements were made with the resolution of ~0.8 eV. Clean sample surfaces were obtained by frequently scraping *in situ* with a diamond file at measurement temperature. The UPS measurements were made at ~25 K and the BIS measurements at ~80 K. The XAS measurements were performed at room temperature. Specific heat measurements were performed by the relaxation method. The O 1*s* XPS spectrum showed a single peak, indicating a rather high quality of the sample and the surfaces.

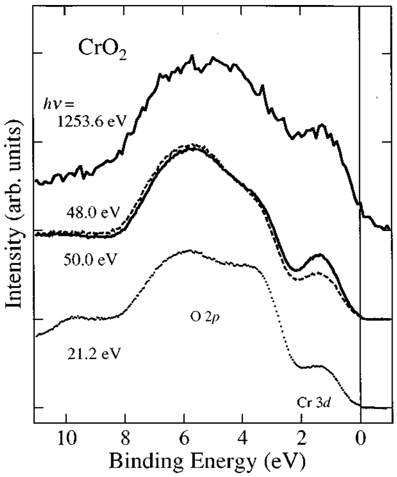

FIG. 2. Valence-band photoemission spectra of CrO_2 taken with various photon energies.

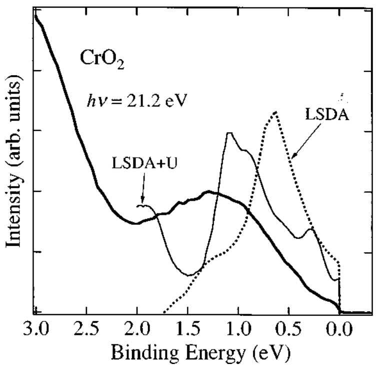

FIG. 3. High-resolution UPS ($h\nu=21.2$ eV, $\Delta E \simeq 25$ meV) spectrum of CrO_2 compared with the LSDA (Ref. 3) and LSDA $+U$ (Ref. 8) band-structure calculations. The experimental and calculated spectra have been normalized to the integrated Cr 3*d* band intensity.

Figure 1 shows the XAS spectrum in the O 1*s* core region. The structures above and below ~535 eV arise from transitions into the Cr 4*sp* and Cr 3*d* bands, respectively. The first peak (~527 eV) is attributed to the unoccupied part of the Cr 3*d* $t_{2g\uparrow}$ band and the second, more prominent peak (~531 eV) to the remaining unoccupied Cr 3*d* ($t_{2g\downarrow}$, $e_{g\uparrow}$, and $e_{g\downarrow}$) bands. This assignment is consistent with the orbital degeneracy of each component, considering the empirical fact that each of the empty e_g and t_{2g} states has nearly the same intensity in the O 1*s* XAS spectra of transition-metal oxides.[9] The present XAS spectrum is in good agreement with bulk-sensitive electron energy-loss spectra taken in the transmission mode,[10] meaning that the present XAS data indeed represent the bulk electronic structure of CrO_2.

Valence-band photoemission spectra are shown in Fig. 2. Because the relative photoionization cross section of the Cr 3*d* to O 2*p* orbitals increases with photon energy,[11] we conclude that the bands at ~1.3 eV and 3–7 eV are mainly derived from the Cr 3*d* and O 2*p* atomic orbitals, respectively. The spectra for $h\nu=50$ and 48 eV are on- and off-resonance photoemission spectra, respectively, in the Cr $3p \rightarrow 3d$ core absorption region. The ~1.3 eV peak is enhanced in the on-resonance spectrum, indicating that this structure is mainly derived from the Cr 3*d* states.

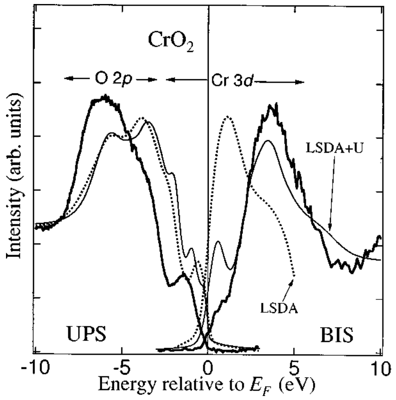

FIG. 4. UPS ($h\nu=40.8$ eV) and BIS ($h\nu=1486.6$ eV) spectra (solid curves) compared with theoretical spectra deduced from the LSDA (Ref. 3) and LSDA$+U$ (Ref. 8) calculations (dashed curves).

UPS spectra shown in Figs. 2 and 3 exhibit a weak but finite intensity at E_F, consistent with the metallic behavior of CrO_2. A weak Fermi edge intensity as well as a peak at a binding energy of ~ 1.5 eV have been observed in the metallic oxides of early transition metals such as $Ca_{1-x}Sr_xVO_3$,[13,14] $La_{1-x}Sr_xTiO_3$, and $Y_{1-x}Ca_xTiO_3$.[15] In these compounds, emission from E_F to a few tenths of an eV below it has been assigned to the coherent part or the quasi-particle (QP) band and the peak at ~ 1.5 eV to the incoherent part of the spectral function or the remnant of the lower Hubbard band. The photoemission line shape of CrO_2 is similar to those of the V and Ti oxides and may be interpreted in the same way. The present spectral line shape is quite different from that reported by Kämper *et al.*[7] The position of the Cr $3d$ band is much shallower than the previous one (~ 2.5 eV) and the intensity at E_F is much higher. It is likely that the sputtering and annealing changed the stoichiometry of the sample surfaces in their measurement. The presence of a weak feature at ~ 9 eV in the 21.2 eV spectrum, however, indicates that a small amount of contamination/degradation could not be removed even with the above experimental precautions.

Figure 4 shows a combined plot of UPS and BIS spectra, compared with theoretical spectra deduced from the LSDA and LSDA$+U$ band-structure calculations.[3,8] Here, the theoretical curves have been obtained from the calculated Cr $3d$ and O $2p$ partial DOS and the atomic photoionization cross-sections:[11] A Gaussian and a Lorentzian broadening, which represent the instrumental resolution and the lifetime broadening, respectively, has been made and backgrounds due to secondary electrons have been superimposed.[12] The most remarkable difference between the LSDA and LSDA $+U$ calculations is the position of the main Cr $3d$ peak above E_F. The experimental BIS spectrum is in better agreement with the LSDA$+U$ result. Feature ~ 0.8 eV above E_F in the BIS spectrum appears at the same energy as the Cr $t_{2g\uparrow}$ peak in the LSDA$+U$ calculation. The prominent structure at ~ 4 eV is attributed to the rest of the unoccupied d band. The observed ~ 0.8 eV peak is weak and broad compared to the LSDA$+U$ result probably due to spectral weight transfer away from E_F induced by electron correlation. The much sharper $t_{2g\uparrow}$ peak in O $1s$ XAS than in BIS is most likely due to the effect of the core-hole potential in XAS. The positions of the Cr $3d$ peaks are also different between the LDSA and LSDA$+U$ calculations. The large (~ 5 eV) splitting between the prominent Cr $3d$ peaks in the combined UPS-BIS spectra is thus closer to the value (~ 4.5 eV) deduced from the LSDA$+U$ calculation than that (~ 1.6 eV) deduced from the LSDA calculation. The underestimate of the splitting in the LSDA calculation is due to the neglect of the Hubbard splitting of the d band by $\sim U$. Thus we estimate $U \sim 5-1.6=3.4$ eV. In fact, the U value employed in the LSDA$+U$ calculation was taken at 3 eV.[8] (In the LSDA$+U$ calculation, an insulating gap opens only for $U>6$ eV.[8])

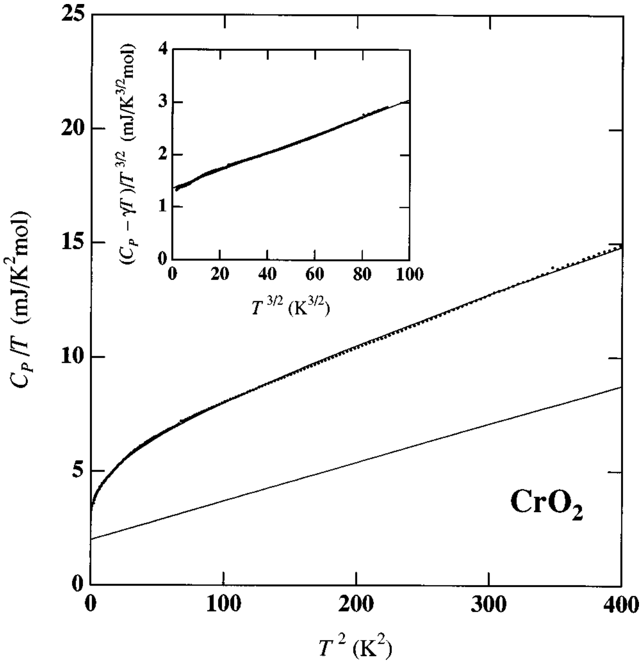

FIG. 5. Low-temperature specific heat of CrO_2 (dots) fitted to $c(T)=\gamma T+\beta T^3+\alpha T^{3/2}$ (solid curve). The solid line shows the γT contribution. The inset shows the $(c-\gamma T)/T^{3/2}$ vs $T^{3/2}$ plot.

Although the observed ''coherent'' and ''incoherent'' parts of the photoemission spectra appear to be those of typical Mott-Hubbard compounds, CrO_2 is different from the paramagnetic metallic Ti and V oxides in that the experimentally observed Hubbard splitting can be explained within the mean-field (LSDA$+U$) level because the Cr d band is spin and orbital polarized. The relative spectral weight of the coherent part, which is equal to z, is too weak in CrO_2 to be accurately determined from the spectral line shape. Alternatively, one can estimate z using the relationship $z=\rho(0)/N^*(0)$, where $\rho(0)=0.14$ states/eV Cr is the DOS at E_F [i.e., the spectral intensity at E_F deduced under the assumption that the integrated spectral weight of the Cr $3d$ band is 2 states/Cr (Ref. 16)] and $N^*(0)$ is the density of QP's at E_F deduced from the specific heats. Therefore we have made low-temperature specific-heat measurements as shown in Fig. 5, where the experimental data $c(T)$ is analyzed using the formula

$$c(T)=\gamma T+\beta T^3+\alpha T^{3/2}. \tag{1}$$

Here, the $T^{3/2}$ term is magnon contributions. Thus we obtain $\gamma=2.5\pm0.5$ mJ/K ^{2} mol, $\alpha=1.36$ mJ/K$^{5/2}$ mol and $\beta=0.0169$ mJ/K ^{2} mol and hence $N^*(0)=3\gamma/\pi k_B^2$ $=1.06\pm0.21$ states/eV Cr. The spin-wave dispersion constant $D_s=1.1\times10^{-29}$ erg cm^2 deduced from α well agrees with the value ($D_s=1.9\times10^{-29}$ erg cm^2) deduced from the temperature dependence of magnetization $M(T)/M(0)$ $=1-aT^{3/2}$. Thus there is no indication of ''orbital-wave'' contributions to $c(T)$, which does not contradict with the existence of the orbital polarization because the orbital wave is predicted to have a large excitation gap.[17]

Thus we obtain $z=\rho(0)/N^*(0)=0.13\pm0.03 \ll 1$, signaling a strong mass renormalization as in other transition-metal oxides. However, this z value is substantially larger than those for $CaVO_3$, $La_{1-x}Sr_xTiO_3$ ($z\sim0.05$), and $Y_{1-x}Ca_xTiO_3$ ($z\sim0.01$) and is comparable to $SrVO_3$ ($z\sim0.16$), a typical itinerant Pauli-paramagnetic metal.[13–15]

The deduced z value may be consistent with the small Drude weight of ~0.1 electrons/Cr integrated up to $h\nu \sim 1.5$ eV.[18] The mass enhancement factor $m^*/m_b = N^*(0)/N_b(0)$, where $N_b(0)$ and m_b are the DOS and the effective mass derived from the band-structure calculation, cannot be uniquely determined because $N_b(0)$ depends on U in the LSDA+U calculation. For $U=3$ eV, $N_b(0) \simeq 0.42$ states/eV and therefore $m^*/m_b \simeq 2.5$. The **k**-mass m_k/m_b $[=zm^*/m_b = \rho(0)/N_b(0)]$ then becomes ~0.3. For larger U, m^*/m_b and hence m_k becomes larger.

If the Cr $3d$ band is fully spin polarized in CrO_2, there is no spin fluctuations in the ground state and the electron correlation effects are attributed to fluctuations of the charge and/or orbital degrees of freedom. The double exchange mechanism for CrO_2 proposed by Korotin *et al.*[8] implies a similarity with the giant-magnetoresistive manganites. Indeed, the manganites show a small Drude weight,[19] small electronic specific heats,[20] and low photoemission intensity at E_F.[21] These results may be understood if $La_{1-x}Sr_xMnO_3$ has ‘‘small Fermi surfaces.’’ Its small Hall coefficient implies a large hole number ~1 hole per Mn atom if analyzed using the one-band model,[22] but may also be due to a semimetallic electronic structure. The Hall coefficient of CrO_2 yields ~0.5 electron per Cr atom,[6] probably indicating semimetallic small Fermi surfaces. As for the QP weight, the photoemission[21] and specific heat[20] data of $La_{1-x}Sr_xMnO_3$ yield $z \lesssim 0.05$, a value smaller than CrO_2.

In conclusion, the photoemission spectra of CrO_2 are found to have a finite intensity at E_F, consistent with the metallic behavior. The spectral function consists of the upper and lower Hubbard bands and the coherent part in between. Comparison of the photoemission spectra and the electronic specific heat has revealed substantial renormalization, $z \ll 1$. Nevertheless, this z value is relatively large among metallic $3d$ transition-metal oxides, implying that the mean-field, i.e., LSDA+U, band description is a rather good starting point to understand the electronic structure of CrO_2.

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[1] J. S. Kouvel and D. S. Rodbell, J. Appl. Phys. **38**, 979 (1967).

[2] D. S. Rodbell, J. M. Lommel, and R. C. DeVries, J. Phys. Soc. Jpn. **21**, 2430 (1966).

[3] K. Schwarz, J. Phys. F **16**, L211 (1986).

[4] B. L. Chamberland, in *CRC Critical Reviews in Solid State and Materials Sciences*, edited by D. E. Schuele and R. W. Hoffman (CRC Press, Boca Raton, FL, 1977), p. 1.

[5] S. P. Lewis, P. B. Allen, and T. Sasaki, Phys. Rev. B **55**, 10 253 (1997), and references therein.

[6] H. Brändle *et al.*, Phys. Rev. B **46**, 13 889 (1992).

[7] K. P. Kämper *et al.*, Phys. Rev. Lett. **59**, 2788 (1987).

[8] M. A. Korotin, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky (unpublished).

[9] F. M. F. de Groot *et al.*, Phys. Rev. B **40**, 5715 (1989).

[10] S. Suzuki, M. Tomita, S. Okada, and H. Arai, J. Phys. Chem. Solids **57**, 1851 (1996).

[11] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[12] The Gaussian FWHM was taken to be 0.2 eV for PES and 0.8 eV for BIS. The Lorentzian FWHM to be energy dependent: $0.2|E-E_F|$.

[13] K. Morikawa *et al.*, Phys. Rev. B **52**, 13 711 (1995).

[14] I. H. Inoue *et al.*, Phys. Rev. Lett. **74**, 2539 (1995).

[15] K. Morikawa *et al.*, Phys. Rev. B **54**, 8446 (1996).

[16] In transition-metal oxides, the DOS at E_F, $\rho(0)$, is known to be reduced by degradation of surfaces, and therefore the observed $\rho(0)$ may be better taken as the upper bound for the intrinsic $\rho(0)$. The data shown in Figs. 1 and 2 indicate a rather high quality of the sample surfaces and the reduction in $\rho(0)$ would not be very strong. If $\rho(0)$ has been underestimated due to contamination, actual z should be larger, strengthening the present conclusion that z is relatively large among the metallic oxides.

[17] S. Ishihara, J. Inoue, and S. Maekawa, Physica C **263**, 130 (1996).

[18] L. L. Chase, Phys. Rev. B **10**, 2226 (1974).

[19] Y. Okimoto *et al.*, Phys. Rev. Lett. **75**, 109 (1995).

[20] J. M. D. Coey, M. Viret, L. Ranno, and K. Ounadjeda, Phys. Rev. Lett. **75**, 3910 (1995).

[21] D. D. Sarma *et al.*, Phys. Rev. B **53**, 6873 (1996).

[22] P. Matl, Y. F. Fan, N. P. Ong, Y. Q. Li, D. Studebaker, T. Baum, and G. Doubibia (unpublished).