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Intrinsic correlated electronic structure of CrO_2 revealed by hard x-ray photoemission spectroscopy

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Bulk-sensitive hard x-ray photoemission spectroscopy (HAXPES) reveals for as-grown epitaxial films of half-metallic ferromagnetic $CrO_2(100)$ a pronounced screening feature in the Cr $2p_{3/2}$ core level and an asymmetry in the O 1s core level. This gives evidence of a finite, metal-type Fermi edge, which is surprisingly not observed in HAXPES. A spectral weight shift in HAXPES to below the Fermi energy is attributed to single-ion recoil effects due to high-energy photoelectrons. In conjunction with inverse PES the intrinsic correlated Mott-Hubbard-type electronic structure is unraveled, yielding an averaged Coulomb correlation energy $U_{av} \cong 3.2$ eV.

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Transition metal oxides are strongly correlated electron systems, which exhibit a wealth of phenomena and potential, a perspective most challenging to modern solid state physics.[1,2] In the theoretical description of the electronic structure of transition metal oxides seminal progress is owed to dynamical mean-field theory (DMFT).[3,4] This method has called for intrinsic, bulk-sensitive photoemission spectroscopy (PES).[5] The reason is obvious: because electronic states of the clean surface differ from those in the bulk due to the increase in U/t, where U is the on-site electron Coulomb repulsion energy and t is the electron hopping energy between lattice sites. Experimentally a breakthrough toward determining the intrinsic bulk electronic structure occurred due to the development of hard x-ray PES (HAXPES) with a probing depth of 5–10 nm.[6–9] In this context a very controversial and provoking case, overdue for examination, is the half-metallic ferromagnet CrO_2,[10,11] which exhibits a metastable surface, transforming into the stable antiferromagnetic insulator Cr_2O_3.[10] For CrO_2 a discrepancy exists between the correlated Fermi-liquid-type metallic behavior[10,12] and the very small intensity of the sputter-cleaned surface in ultraviolet PES (UPES) near the Fermi energy E_F.[13] The latter was conjectured to be due to surface relaxation of $CrO_2(001)$.[14] The metallicity of $CrO_2(100)$ was even questioned based on UPES measurements.[15] In contrast, an enhanced spectral weight near E_F due to the orbital Kondo effect has been predicted using DMFT.[16] However, the theoretical description of electronic and (magneto-)optical data of CrO_2 has raised doubts about the relevance of strong Hubbard-type correlations.[17–20] This controversy and the surface-related problems described above stress the need to employ HAXPES in addition to and in comparison with soft x-ray PES (SXPES).[8,21,22] Despite the interest in CrO_2 for spintronics applications,[23,24] because of its high spin polarization,[13,17,25–28] the intrinsic correlated electronic structure still remains to be unraveled.[29]

Here we present a bulk-sensitive investigation of valence band states and core levels of CrO_2 by means of HAXPES using photon energies of $h\nu \approx 8$ keV. The photoemission intensity near E_F observed by HAXPES is unexpectedly small, in contrast to the metal-type Fermi edge observed by SXPES. However, with HAXPES we found a strong metallic screening feature in the Cr $2p_{3/2}$ core level and an asymmetry of the O 1s core level, which both imply a finite density of states (DOS) near E_F. This seeming contradiction with the very small photoemission intensity near E_F in HAXPES is resolved by considering single-ion recoil effects in HAXPES. They account for the suppression of the spectral weight near E_F due to its shift to higher binding energy (BE). Using HAXPES, SXPES, and inverse PES (IPES), we identify the salient intrinsic features of the correlated Mott-Hubbard-type electronic structure of CrO_2.

A correlated electronic structure of CrO_2 has been concluded from calculations using the local spin-density approximation LSDA + U.[17] The Cr 3d states split in the octahedral crystal field into a lower and an upper state with t_{2g} and e_g symmetry, respectively. The t_{2g} states split further into a strongly localized $3d(xy)$ orbital near 1 eV BE below E_F and more dispersive $3d(yz \pm zx)$ orbitals. The latter are strongly hybridized with the O 2p states, forming bands which cross E_F and cause a self-doping of CrO_2.[17] The exchange splitting shifts the minority-spin states above E_F, giving rise to a spin gap.

The HAXPES and SXPES experiments were performed at 150 or 20 K at the BL19LXU and BL25SU beamlines of SPring-8,[30] respectively; we used as-grown, otherwise untreated surfaces of $CrO_2(100)$ epitaxial films. The samples were grown by chemical vapor deposition in an oxygen atmosphere on (100)-oriented TiO_2 substrates.[23,28,30] To overcome the low photoionization cross section of the Cr 3d and O 2p valence states for $h\nu > 1000$ eV the PES resolution was set to 250 meV (FWHM), while it was set to 100, 60, and 20 meV, respectively, for $h\nu = 700$, 200, and 11.6 eV. To optimize the photoelectron emission, a so-called p-polarization configuration was employed for HAXPES, whereas fully circularly polarized light was used for SXPES below $h\nu = 2$ keV. The UPES ($h\nu = 11.6$ eV) and IPES measurements were performed in laboratory systems, where both the as-grown and sputter-cleaned surfaces were measured.[30]

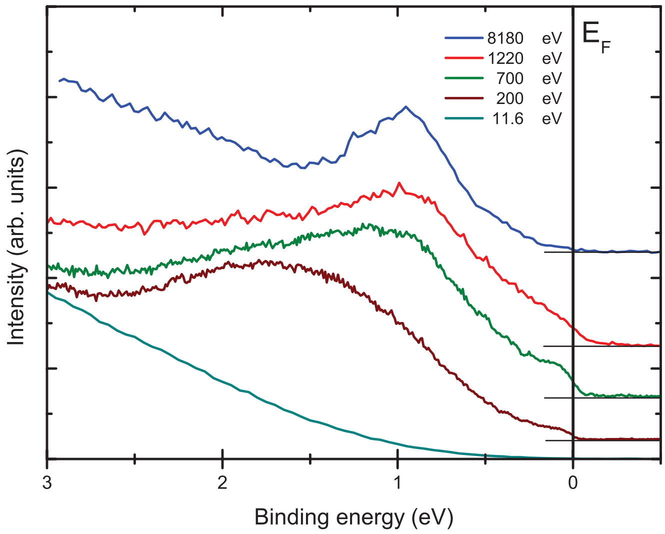

FIG. 1. (Color online) Valence band PES of epitaxial $CrO_2(100)$ films at 20 K for different photon energies in normal emission. The surfaces are as grown, including a nominal Cr_2O_3 surface layer.

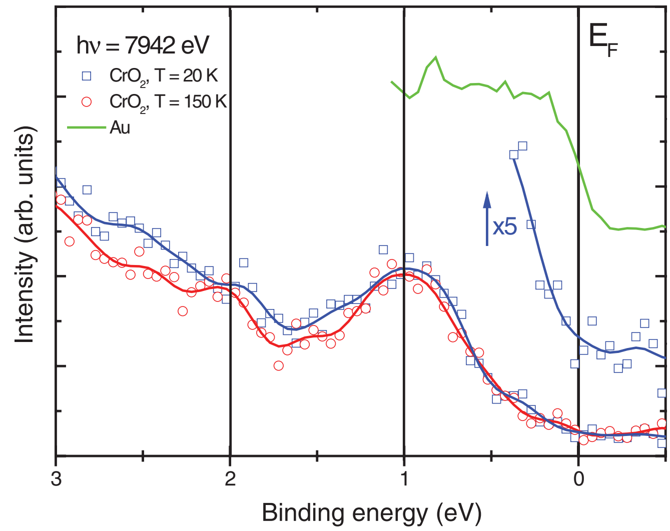

FIG. 2. (Color online) Valence band PES of epitaxial $CrO_2(100)$ films for $h\nu = 7942$ eV in normal emission at 150 and 20 K. The red and blue lines are guides to the eye. Near E_F the CrO_2 spectrum at 20 K (expanded five times) is compared to that of a Au film.

Figure 1 shows valence band PES of as-grown $CrO_2(100)$ in normal emission at different photon energies (and varying probing depth δ),[31] ranging from 11.6 eV ($\delta \leqslant 1$ nm) to 8180 eV ($\delta \approx 10$ nm). Besides a broad peak near 1.75 eV BE for $h\nu = 200$ eV, a peak emerges with increasing photon energy near 1.0 eV BE which becomes enhanced for $h\nu = 8180$ eV. At lower photon energies (<200 eV) the contribution of the insulating surface Cr_2O_3 layer of roughly 2 nm thickness[24] is mostly probed, judging from the low photoemission intensity near E_F (Fig. 1 and Ref. 32). With higher photon energies of 700 eV ($\delta \approx 1.4$ nm) and 1220 eV ($\delta \approx 2.2$ nm) the photoemission spectra show a metal-type Fermi edge. The Fermi edge for $h\nu = 1220$ eV is broader than the one for $h\nu = 700$eV, because of the lower resolution. A metallic Fermi edge was also observed for $h\nu = 385$ eV with 400 meV resolution.[33] However, most unexpectedly we observe no metal-like Fermi edge in HAXPES using $h\nu = 8180$ eV, for which bulk properties are expected. Please note that for $E_F \leqslant E_B \leqslant 0.2$ eV, where E_B is the binding energy, the very weak intensity increases almost linearly with increasing E_B, showing a steeper slope above 0.2 eV BE.

In Fig. 2 we show the valence band spectrum of CrO_2 for $h\nu = 7942$ eV and for $E_F \leqslant E_B \leqslant 3$ eV at 20 and 150 K together with the Fermi edge of Au. Besides the prominent peak at 1.0 eV BE a shoulder near 2.1 eV BE is identified. Please note that there is no significant temperature dependence in the spectra in Fig. 2. The photoemission intensity for 20 K near E_F is expanded by a factor of 5, differing strongly from that of Au. It evidences the absence of a metallic Fermi edge of CrO_2 in HAXPES. The features of Fig. 2 and its overview for $E_F \leqslant E_B \leqslant 14$ eV (Ref. 30) will be discussed below.

The HAXPES core level spectra help to resolve the puzzle about the intrinsic metallicity of CrO_2. The O 1s core level in Fig. 3(a) for $h\nu = 1490$ eV exhibits satellites at 2 and 4 eV BE above its maximum at 528 eV, which are strongly reduced for $h\nu = 7942$ and 8180 eV. These satellites are due to O 2p–O 2p charge transfer and result most likely from a surface-induced chemical shift of the O 1s core level of Cr_2O_3 and from surface-adsorbed oxygen.[30] Most pronounced is the asymmetry in the line shape of the O 1s core level at 528 eV BE in the latter two HAXPES spectra. This asymmetry reflects the intrinsic finite DOS of unoccupied states near E_F,[34,35] implying also a nonzero O 2p and Cr 3d partial DOS of occupied states at E_F. The weak peaks in the HAXPES spectra near 9 and 11 eV BE above the O 1s peak are due to Cr $3d(e_g)$–O 2p charge transfer satellites, analogous to the case of cuprates.[35] The broad feature in Fig. 3(a) near 29 eV BE above the O 1s peak is attributed to plasmon excitations.

Another conclusive feature is found for the Cr $2p_{3/2}$ core level at 576 eV BE in Fig. 3(b). For $h\nu = 1490$ eV the Cr $2p_{3/2}$ level exhibits a weak shoulder near 575 eV BE, which develops for $h\nu \approx 8$ keV into a small but sharp peak. This sharp peak at 575 eV BE is obviously a bulk feature and is attributed to a well-screened satellite.[8,34] The metallic screening of the 2p core-hole potential in the PES final state is due to charge transfer from valence band states at E_F. Such a well-screened satellite was identified by HAXPES for the Mn $2p_{3/2}$ level in the metallic regime of $La_{1-x}Sr_xMnO_3$.[8] This screening due to hybridized Mn 3d and doping-induced states near E_F of metallic $La_{1-x}Sr_xMnO_3$ has to be replaced in the case of CrO_2 by the $2p-3d$ hybridized states near E_F. The latter states account for the well-screened feature of the $2p_{3/2}$ level of CrO_2, supporting its intrinsic metallicity for one spin channel. The Cr $2p_{1/2}$ level positioned at 586 eV BE does not exhibit such a satellite, most likely due to multiple configurational interactions and lifetime effects.[30]

In order to reconcile the discrepancy in HAXPES between the well-screened $2p_{3/2}$ core level evidencing metallicity and the very small photoemission intensity near E_F, we attribute the latter observation to recoil effects,[36] i.e., to a shift of orbital-dependent spectral weight to a BE higher than E_F. These recoil effects induced by the emission of high-energy photoelectrons in HAXPES are relevant upon photoexciting not only core levels but also valence band states of light

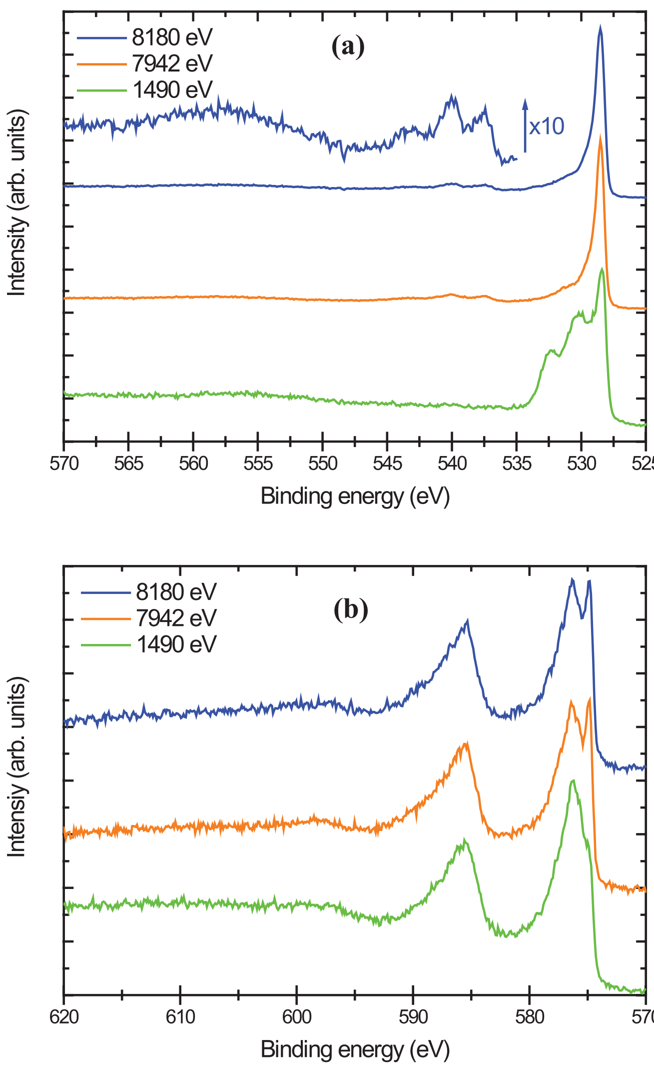

FIG. 3. (Color online) PES of epitaxial $CrO_2(100)$ films at 20 K for different photon energies. (a) O 1s core level PES; expanded ten times for $h\nu = 8180$ eV. (b) Cr 2p core level PES; the Cr $2p_{3/2}$ state near 576 eV BE exhibits a well-screened feature near 575 eV.

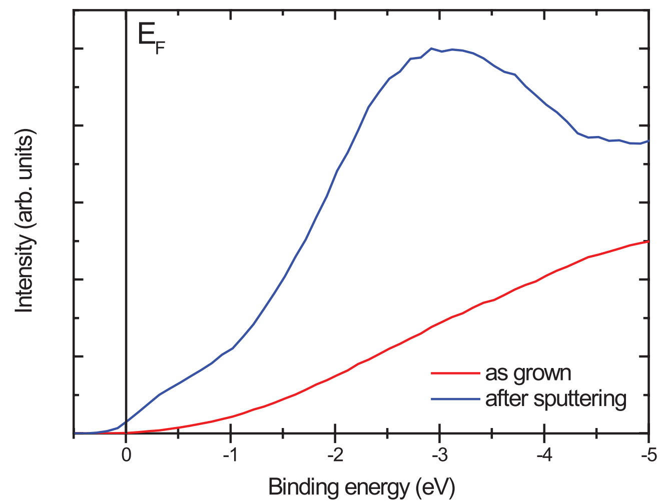

FIG. 4. (Color online) IPES spectra at room temperature on as-grown and sputter-cleaned [using Ne^+ ions (Ref. 30)] epitaxial $CrO_2(100)$ films.

elements.[37] Instead of the whole crystal, the single ion is found to accept the photoelectron momentum. The single-ion recoil shift is given by $E_R \sim E_K(m/M) \sim (h\nu - E_B)(m/M)$, where E_K is the photoelectron kinetic energy, m the electron mass, and M the nuclear mass. Estimates of the single-ion recoil shifts show that, e.g., the O 1s core level of CrO_2 near 528 eV BE is shifted towards larger BE with respect to E_F by $E_R^H \approx 260$ meV in HAXPES ($h\nu = 8180$ eV) compared to $E_R^S \approx 24$ meV in SXPES ($h\nu = 1220$ eV). The difference between the two types of spectra amounts to $E_R^{H-S}(\text{O } 1s) = 236$ meV. For the Cr $2p_{3/2}$ core level near 576 eV BE the recoil shift is estimated as $E_R^H \approx 81$ meV compared to $E_R^S \approx 7$ meV, thus yielding $E_R^{H-S}(\text{Cr } 2p_{3/2}) = 74$ meV. Consequently, the splitting between O 1s and Cr $2p_{3/2}$ states is estimated as $E_R^{H-S}(\text{O } 1s) - E_R^{H-S}(\text{Cr } 2p_{3/2}) = 236\text{ meV} - 74\text{ meV} = 162$ meV smaller in HAXPES compared to SXPES. In our experiment, the O 1s and Cr $2p_{3/2}$ core levels measured each for $h\nu = 7942$ eV with reference to $h\nu = 1490$ eV (see the Supplemental Material[30] Fig. 4) show (H-S) shifts of 180 and 70 meV, respectively, which compare reasonably well with the corresponding estimates of 219 and 68 meV. Hence, the experimental splitting of $E_R^{H-S}(\text{O } 1s) - E_R^{H-S}(\text{Cr } 2p_{3/2}) = 180 - 70 = 110$ meV is in fair agreement with the estimate of $219 - 68 = 151$ meV, given the crude single-ion recoil approximation. On the other hand, concerning the 2p-3d hybridized valence band states of CrO_2, which show experimentally a wide spread in energy and no specific line shape, the recoil shifts cannot be determined straightforwardly. Hence an upper estimate of the recoil shifts between HAXPES ($h\nu = 8180$ eV) and SXPES ($h\nu = 1220$ eV) of the O 2p and Cr 3d states is obtained by comparison with the above O 1s and Cr 2p states, amounting at most to $E_R^{H-S}(\text{O } 2p) - E_R^{H-S}(\text{Cr } 3d) \approx 162$ meV. Because of the experimental resolution, only a p vs d states weighted average of the two recoil shifts can be observed, which is estimated by these numbers to be at least 135 meV.[30] This shift value agrees roughly with the energy range $E_F \leqslant E_B \leqslant 0.2$ eV in the HAXPES spectrum ($h\nu = 8180$ eV, Fig. 1) over which the intensity is increasingly suppressed toward smaller BE. This gradual suppression toward E_F instead of a rigid shift is attributed to nonideal single-nucleus recoil due to slight collisions with neighboring atoms. Please note that despite the 250 meV HAXPES resolution, a recoil shift of, e.g., 100 meV can still be resolved.[30] Moreover, the strongly suppressed intensity of the p-d hybridized states for $E_F \leqslant E_B \leqslant 0.2$ eV in HAXPES compared to SXPES (Fig. 1) is not due to a more strongly decreasing photoionization cross section of the O 2p atomic subshell with increasing $h\nu$ compared to the Cr 3d subshell.[30]

We now discuss the electronic structure of CrO_2 in terms of the Mott-Hubbard model.[3,4,29,34] Based on the above discussion we attribute the peak in Fig. 2 near 1 eV BE below E_F to the (coherent) quasiparticle peak of p-d hybridized states and the weak (incoherent) peak near 2.1 eV to the lower Hubbard band (LHB). The latter feature appeared similarly in UPES after prolonged surface sputtering.[28] The weak intensity near 2.1 eV in Fig. 2 is most likely due to the strong p-d

hybridization. A similarly weak photoemission intensity has been found for the LHB of strongly correlated Sr_2RuO_4.[38] On the other hand, the upper Hubbard band (UHB) is identified by IPES.[39] In this experiment, the emitted photon energy is 9.9 eV and the overall energy resolution is 350 meV.[40] After sputtering the as-grown film surface, the structureless background intensity in Fig. 4 changes into a broad maximum around about -2.8 eV BE above E_F, which we attribute to the UHB. A small but finite intensity appears near E_F, consistent with UPES ($h\nu = 11.6$ eV) after identical sputtering (see the Supplemental Material[30] Fig. 1). A peak near -3.6 eV BE above E_F has been found in bremsstrahlung isochromat spectroscopy.[41] The measurements, however, were carried out on compressed CrO_2 powder samples, which were scraped *in situ*. By the energy difference between the LHB near 2.1 eV and the UHB at $|-2.8$ eV$|$ we obtain an estimate of the local (intraorbital) Coulomb repulsion U of about 4.9 ± 0.2 eV. From this value we have to subtract the *d-d* exchange splitting of 1.7 eV obtained from the LSDA calculation,[25] which neglects correlation effects. Hence, we obtain for the averaged *d-d* Coulomb interaction[5] $U_{\mathrm{av}} \cong 4.9 - 1.7 \cong 3.2$ eV. A value of the *d-d* Coulomb interaction $U = 3.0$ eV has been used in electronic structure calculations due to the constrained screening method.[17]

In analogy to the screening of the Cr $2p_{3/2}$ core level it may be suggestive to consider the Kondo screening of a localized d moment by the Cr $3d$–O $2p$ hybridized states. Craco *et al.*[16] tested the scenario of an orbital Kondo effect within LDA + U and DMFT calculations. As impurity solver the iterated perturbation theory (IPT) approximation was used. A pronounced quasicoherent spectral weight is predicted at E_F. It disagrees, however, with the experimentally observed photoemission intensity near E_F for photon energies ranging from 11.6 to 8180 eV and for temperatures between 300 and 20 K (Figs. 1 and 2 here and Figs. 1 and 2 in the Supplemental Material[30]).

In conclusion, the comparison of core level and valence state shifts of CrO_2 in HAXPES and SXPES reveals the crucial role of single-ion recoil effects in HAXPES. They result for the *p-d* hybridized valence band states in a significant shift (>100 meV) of spectral weight toward higher BE below E_F. CrO_2 appears as a favorable recoil-effect case because of its less dense, open rutile structure, where about 66% of the unit cell volume lies outside the atomic spheres.[25] Despite the small HAXPES intensity near E_F, the asymmetry of the O 1*s* core level and the bulk-type screening feature in the Cr $2p_{3/2}$ level corroborate the metallicity of CrO_2 and its intrinsic nonvanishing, finite DOS near E_F. This is also supported by our IPES (Fig. 4) and UPES (Fig. 1 in the Supplemental Material[30]) measurements for the sputter-cleaned samples. Along this line we do not find evidence for an anomaly near E_F due to a predicted orbital Kondo effect. By employing HAXPES and IPES, the intrinsic correlated Mott-Hubbard-type electronic structure is identified unambiguously. For this there remains still room for a deeper understanding by applying the DMFT approach.[29]

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