# Anomalous spin polarization and dualistic electronic nature of CrO$_2$

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Spin-resolved O 1$s$ x-ray absorption measurements on CrO$_2$ reveal that the spin polarization of the states at the Fermi level approaches 100%, providing direct evidence of the half-metallic nature of CrO$_2$. The measurements also show the existence of an atomiclike Cr 3$d$ state not far away from the Fermi level with a spin polarization of only 50%, establishing its Mott-Hubbard character. We conclude that CrO$_2$ has a dualistic electronic nature, in which the states at the Fermi level are bandlike, while those at higher energies are strongly localized of completely different origin and symmetry. The finding of an exceptionally large number of O 2$p$ holes suggests their important role in preventing the strongly correlated CrO$_2$ from being an insulator.

The widely used recording material CrO$_2$ is classified as a half-metallic ferromagnet,[1] based on first-principles calculations using the local-spin-density approximation (LSDA), which elucidate that the majority spin states cross the Fermi level while the minority spin states show a band gap.[2,3] Point contact measurements at superconductor-metal interfaces reveal a larger than 90% spin polarization for the conduction electrons,[4,5] supporting the half-metallic nature predicted by band theory. On the other hand, its magnetic susceptibility in the paramagnetic phase shows a Curie-Weiss-like behavior and indicates the presence of 3$d^2$ local moments,[6] suggesting a mechanism for ferromagnetism beyond the standard band or Stoner-like model.

To reconcile these two apparently contradictory findings, it is essential to address two important questions related to the influence of electron correlation effects on the physical properties of CrO$_2$: why it is metallic despite the presence of strong electron correlation effects and why band structure calculations can explain its half-metallic property but fail completely for the electronic structure of many other 3$d$ transition-metal oxides.

Several recent experiments suggest that electron correlations are essential to account for the underlying physics of CrO$_2$, including photoemission,[7] soft x-ray absorption (XAS),[8] resistivity,[9] and optical[10] measurements. The self-doping concept has been proposed to explain the anomalous properties of CrO$_2$ based on LSDA band structure calculations with on-site Coulomb energy $U$ taken into account (LSDA+U), which indicate that Coulomb interactions indeed play an important role.[11] This picture is also proposed in a recent model that includes orbital correlations.[12] The latest LSDA calculations, however, conclude that there is no need to include strong correlations of the Hubbard type.[13] Moreover, it is even suggested that the inclusion of a Hubbard $U$ leads to unreasonable Kerr spectra.[14]

In this paper, we report on a spin-resolved electron spectroscopic experiment to identify the coexistence of band effects and Mott-Hubbard interactions in the electronic structure of CrO$_2$. We have established that CrO$_2$ is a half-metallic material, and found that it is the very large amount of oxygen holes that prevents CrO$_2$ from being a strongly correlated insulator. With CrO$_2$ being a $p$-type metal,[11,15] we conclude that none of the existing LSDA, LSDA+U, or cluster configuration interaction (CI) models can fully explain the observed spectra. Both band formation and strong correlation effects coexist such that the states at the Fermi level are bandlike while the states at higher energies are localized with different symmetry and origin. We show that it is too naive to expect that either band theory or CI approaches should work well for CrO$_2$. Instead, we find here a fine example for a strongly correlated system in which the high-energy-scale, local-atomic-like properties are renormalized such that new coherent low-energy-scale, bandlike states are formed. This new finding can only be experimentally revealed most clearly by measuring the spin polarization.

The experiments were performed using the elliptically polarized undulator beamline of the National Synchrotron Radiation Research Center in Taiwan.[16,17] Non-spin-resolved XAS spectra were taken in the total electron yield mode by collecting the sample drain current. Spin-resolved XAS spectra were taken in the Auger partial electron yield mode at normal emission from the sample surface using a 25-kV Mott spin polarimeter.[18] The sample was magnetized remanently along the $c$ axis, and the measurements were carried out with the sample kept at 80 K. Epitaxial CrO$_2$ films about 2000 Å thick were grown on TiO$_2$(100) substrates by chemical vapor deposition at 400 °C, using CrO$_3$ as the precursor.[19,20] The film and its epitaxy were fully characterized by x-ray diffraction. The magnetic properties were measured using the magneto-optical Kerr effect, showing that the
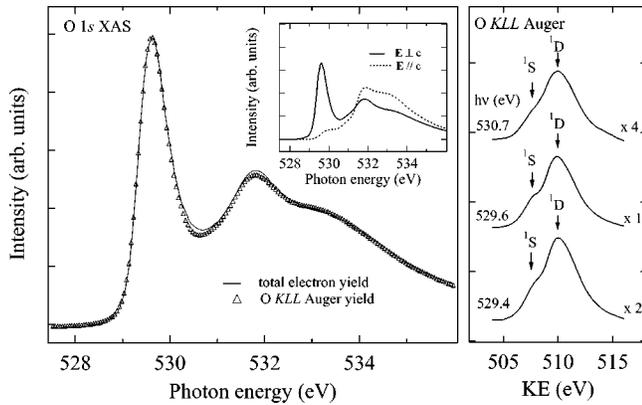
FIG. 1. Left panel: O $1s$ XAS spectra of $CrO_2$ measured in the total electron yield mode (solid line) and in the O $KL_{23}L_{23}$ Auger partial electron yield mode (triangles) with the **E** vector of the light perpendicular to the **c**-axis. The inset displays the spectra with $\mathbf{E}\|c$ (dashed line) and $\mathbf{E}\perp c$ (solid line). Right panel: A selection of the O $KL_{23}L_{23}$ Auger spectra taken with photon energies around the main peak.
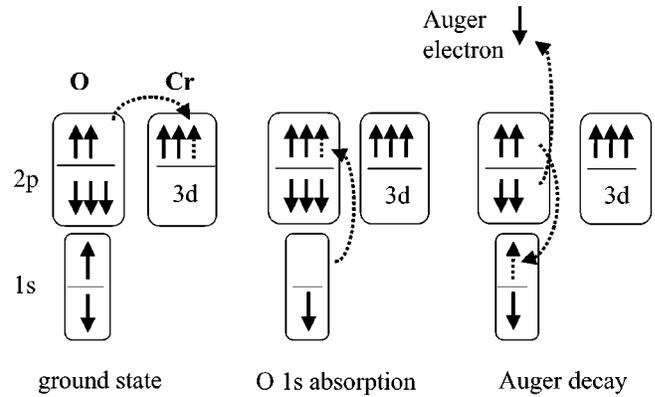


FIG. 2. Schematic illustration of the underlying concept of spin-resolved XAS. Left panel: electronic configuration of $CrO_2$ in the ground state in which the conduction band is composed of mixed Cr $3d$ and O $2p$ states. Middle panel: O $K$-edge absorption process. Right panel: the subsequent O $KL_{23}L_{23}$ Auger decay. The spin of the emitted Auger electron is opposite to that of the O $2p$ holes.

magnetic easy axis is along the [001] direction and that the properties are the same as those of bulk $CrO_2$ and consistent with the results from previous $CrO_2$ thin films.

Figure 1, left panel, displays the O $1s$ XAS spectra of $CrO_2$ measured with a photon energy resolution of 0.2 eV. The spectra recorded in total electron yield mode (solid line) and in the O $KL_{23}L_{23}$ Auger partial electron yield mode (open triangles) are essentially identical, despite the fact that the probing depths of the two techniques are different: namely, 100–200 Å and 15–20 Å, respectively. This clearly demonstrates that our films are of high quality in terms of cleanliness and chemical homogeneity in the sample surface region and that the Auger mode does probe the bulk properties of $CrO_2$ thin films. This fact is important because the Auger signal is later used to obtain the spin-polarized O $1s$ XAS spectrum as explained below. The inset in the left panel of Fig. 1 shows that the main peak at 529.6 eV photon energy exhibits an extremely strong polarization dependence, fully consistent with recent XAS measurements,[8] verifying, again, the good quality of our $CrO_2$ samples.

In order to determine the electronic structure of $CrO_2$ and to verify the predictions made by the various spin-dependent band structure calculations,[2,3,11,13] we have measured the spin polarization of the conduction band using spin polarized O $1s$ XAS.[21,22] The underlying concept of this experiment is shown in Fig. 2. The O $1s$ XAS measures the unoccupied O $2p$ partial density of states of the conduction band which is composed of mixed Cr $3d$ and O $2p$ states (Fig. 2, left panel). If the conduction band is spin polarized, so will be the O $1s$ hole in the XAS state, since the O $1s\rightarrow2p$ transition conserves spin (Fig. 2, middle panel). The subsequent $KL_{23}L_{23}$ Auger decay of the XAS state leads to O $2p^4$-like final states,[23] and the outgoing Auger electron should also be spin-polarized (Fig. 2, right panel). Unique to a $KL_{23}L_{23}$ Auger decay is that the entire two-hole final states are of pure singlet ($^1S$ and $^1D$) symmetry. As indicated in the right

panel of Fig. 1, the O $KLL$ Auger spectra of $CrO_2$ taken at the various photon energies do indeed have the characteristic line shape of a Auger $KLL$ $2p^4$ final state in which only the $^1S$ and $^1D$ states can be reached and in which the $^3P$ are forbidden due to the Auger matrix elements specific for a $KLL$ transition.[21,23,24] This implies that all the O $KL_{23}L_{23}$ Auger electrons have an equally high degree of spin polarization as the O $1s$ hole and the unoccupied O $2p$ partial density of states, but, of course, with an opposite sign because the transition is singlet in character. Thus, the measurement of the spin polarization of the O $KL_{23}L_{23}$ Auger electrons across the O $1s$ edge reflects the spin polarization of the conduction band. This technique is complementary to magnetic circular dichroism in O $K$-edge absorption, which results predominately from the O $2p$-projected orbital magnetization.

Spin-resolved O $1s$ XAS spectra in the vicinity of the main peak taken with $\mathbf{E}\perp c$ and its spin polarization are displayed in the top and the bottom panels of Fig. 3, respectively. The photon energy resolution is set to 0.4 eV. The measurement shows that the states closest to the Fermi level have a spin polarization of $(85 \pm 10)\%$. These states are therefore almost fully spin polarized, consistent with the predictions of band structure calculations[2,3,11,13] and Andreev reflection measurements at the superconductor-metal interfaces.[4]

Strikingly, the spin polarization of the main peak at 529.6 eV is only 50%. This is in strong disagreement with all band structure calculations which predict that the polarization of this feature of the conduction band should have been 100%. In fact, the spin polarization from the LSDA+U (Ref. 11) and also our full-potential linear augmented plane-wave (FLAPW) calculations show a constant spin polarization of 100% for energies from the Fermi level all the way to (and also beyond) the position of the main peak, as shown in Fig. 3. This discrepancy is an indication that strong correlation effects are present in the system, since then it is typical that
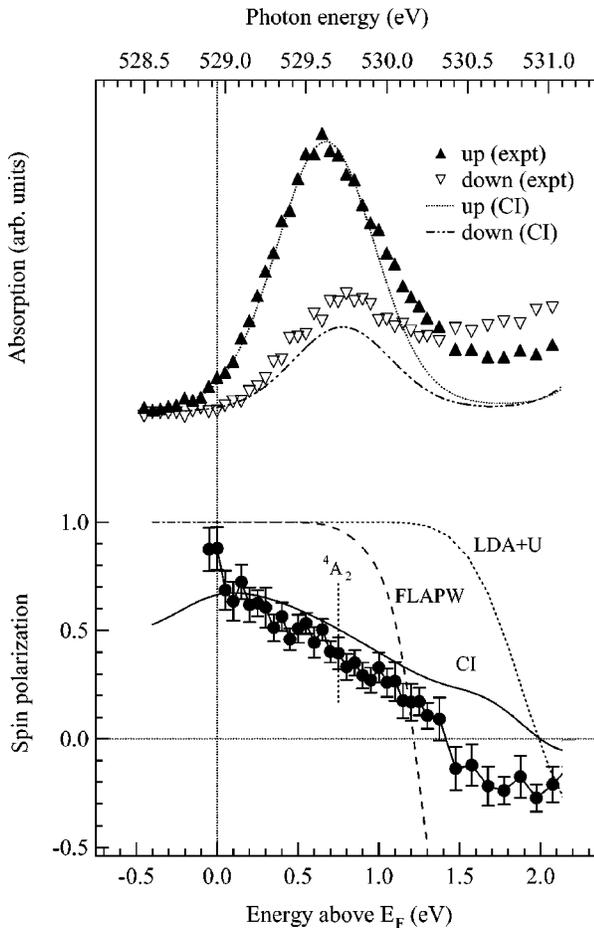
FIG. 3. Upper panel: measured spin-resolved O $1s$ absorption spectra of $CrO_2$ with $\mathbf{E} \perp c$ and calculated spectra obtained by CI calculations in the vicinity of the main peak. Lower panel: spin polarization of the O $1s$ spectrum (solid circles) and calculated spin polarization curves obtained by LSDA+U (dotted line, after (Ref. 11), FLAPW (dashed line), and cluster CI (solid line) calculations.

the concept of density of states, as defined in effective one-particle theories, loses its meaning as a basis for a quantitative understanding of excitation spectra; i.e., density of states are then quite different from spectral weights.[7,25]

If we take correlation effects explicitly into account, at the expense of ignoring the band structure, we can reproduce the 50% spin polarization of the main peak (but not of the states closest to Fermi level). By carrying out CI calculations using a $CrO_6$ cluster, we can identify the main peak as due to a transition from a high-spin, fully magnetized, $3d^2$ initial state to a high-spin $3d^3$ final state with $^4A_2$ symmetry.[26] Based on straightforward fractional parentage arguments, the addition of a spin-up or a spin-down electron to the $3d^2$ state leads to the $3d^3$ $^4A_2$ final state with a probability ratio of $1:\frac{1}{3}$, making the spin polarization of this main peak $(1 - \frac{1}{3})/(1 + \frac{1}{3}) = \frac{1}{2}$, as shown in Fig. 3. Including a molecular field of 0.1 eV for the ferromagnetic state, the CI also reproduces the energy splitting between the spin-up and spin-down peaks as shown in the top panel of Fig. 3. This splitting is the Zeeman splitting between the $m_s = 3/2$ (spin-up) and

$m_s = 1/2$ (spin-down) components of the $^4A_2$ electron addition state. It gives rise to a spin polarization higher (lower) than the average of 50% for the low- (high-) energy side of the main peak (see bottom panel of Fig. 3). The maximum value calculated using this CI model is 68%.

It is remarkable that the spin polarization of the states near the Fermi level can be reproduced by band theory, but not by the CI cluster calculations, while the spin polarization at higher energies can be explained by CI but not by band theory. These spin-resolved data therefore strongly suggest that the electronic structure of $CrO_2$ is dualistic in nature, in the sense that the states at the Fermi level are bandlike while those at higher energies are localized. Before addressing the important issue as to whether the different states have also different origin and symmetry, we will first seek further spectroscopic support for our conclusions.

In particular, to verify further the existence of the atomic-like feature at energies away from the Fermi level in $CrO_2$, we resort to the temperature dependence of the XAS spectra. For a bandlike ferromagnetic material, the exchange splitting between the spin-up and spin-down density of states is expected to decrease and then disappear as the temperature is increased across the Curie temperature $T_C$. An example of such behavior can be found for the itinerant conduction band of ferromagnetic EuO, in which the O $1s$ XAS spectrum changes significantly across $T_C$.[21] In contrast, for an ionic and correlated system, the lineshape of the unpolarized spectra will remain unaltered and only their spin polarization will be reduced. Figure 4 shows the temperature-dependent O $1s$ XAS spectra of $CrO_2$, from well below to above $T_C = 392$ K, and it unambiguously reveals that not much is happening that would otherwise indicate a collapse of the 2 eV exchange splitting in the unoccupied density of states, as calculated from band theory.[2,3,11,13] Instead, the temperature dependence resembles very much that of NiO, which is a local moment insulator. Figure 3 shows that in both cases only the width of the peak increases with temperature, almost linearly, as expected for a localized material due to phonon broadening,[27] which is much larger than the vanishing molecular field splitting. This leads us to conclude that $CrO_2$ exhibits $3d^2$ local moments, consistent with the conclusion of our spin-resolved measurements and the magnetic susceptibility measurements of $CrO_2$ which reveal a clear Curie-Weiss-like behavior in the paramagnetic phase.[6]

These results show that we have indeed identified a very narrow atomiclike state in the conduction band of $CrO_2$, not very far from the Fermi level. This in turn means that, on an energy scale of 1 eV, $CrO_2$ may be regarded as a Mott-Hubbard system, in which the conduction band is given by $3d^2 \rightarrow 3d^3$ transitions and the valence band by $3d^2 \rightarrow 3d^1$, separated in energy by the Hubbard $U$, in accordance with the conclusion reached by Tsujioka and co-workers.[7] A logical consequence would be that this system should have been an insulator. Clearly this is not the case, and some form of band formation or screening must take place in order to form low energy coherent states near the Fermi level out of the incoherent (bare) Mott-Hubbard states,[7,28] such that the ground state is metallic and fully spin polarized.
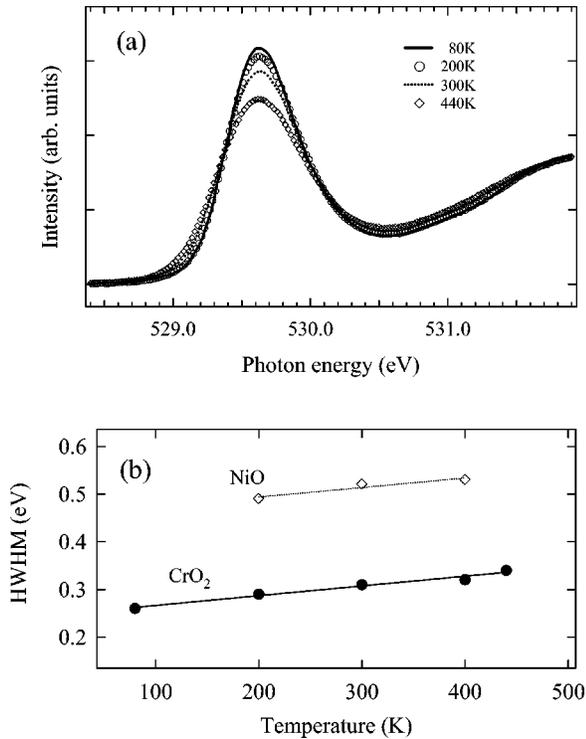
FIG. 4. (a) Temperature-dependent measurements of the main peak in the O $1s$ XAS of $CrO_2$ with $\mathbf{E}\perp c$. The sample was capped with ten monolayers of MgO to avoid any oxygen loss at elevated temperatures. (b) Half width at half maximum (HWHM) of the O $1s$ main peaks of $CrO_2$ and NiO as a function of temperature.



FIG. 5. Isotropic O $1s$ XAS spectra (thick lines) of $CrO_2$ (taken as the 1:2 weighted average of $\mathbf{E}\|c$ and $\mathbf{E}\perp c$ spectra), $V_2O_3$ of paramagnetic metallic and antiferromagnetic insulating phases (Ref. 29) and $LiVO_2$ (Ref. 30).

Spectroscopicly we have found an important indication for such a screening process: while the spin polarization in the main peak is 50%, the one for the states closest to the Fermi level approaches 100%. This observation suggests that the symmetry of the states closest to the Fermi level is completely different from that of the main peak, implying that other types of bands play an important role. We now look in detail into the role of the oxygen $2p$ bands. Figure 5 compares the isotropic O $1s$ spectrum of $CrO_2$ to that of other $3d^2$ oxides: e.g., $V_2O_3$ (Ref. 29) and $LiVO_2$ (Ref. 30). It is clear that the intensity of the main line (at $\approx 529.5$ eV) relative to the higher-lying structures (between 531 and 536 eV) is much higher in $CrO_2$ than in the other compounds. This is apparently not related to the issue whether the compound is metallic, since both metallic and insulating $V_2O_3$, as well as insulating $LiVO_2$, have about the same low main line intensity. Instead, since the line shape of the XAS spectrum is determined by the $3d^{n+1}$ multiplets that can be reached from the $3d^n$ ground-state symmetry via the hybridization with the O $2p$,[26] an anomalously large O $1s$ main line indicates a very small, or even negative, O $2p$ - Cr $3d$ charge-transfer energy, resulting in a Kondo-like energy level diagram, in contrast to $V_2O_3$ and $LiVO_2$, which are known as positive-charge-transfer oxides.[30,31]

Having arrived at the conclusion that $CrO_2$ is essentially a small or a negative-charge-transfer system, we now can understand why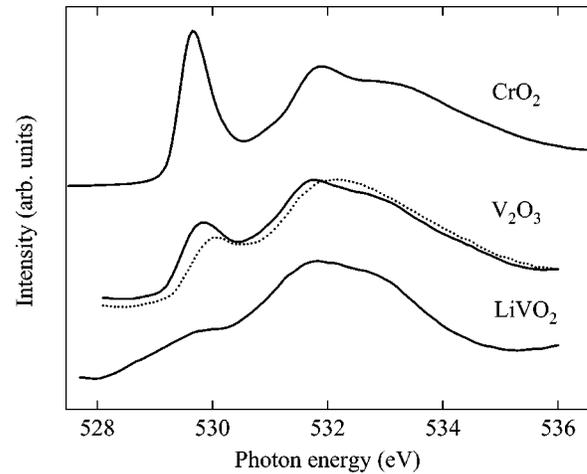 it is not an insulator despite the presence of strong correlations on the Cr $3d$. Within the Zaanen-Sawatzky-Allen phase diagram, $CrO_2$ should be classified as a $p$-type metal.[15] There are a large number of oxygen holes present in the system, even in the hypothetical case in which the hybridization between the Cr $3d$ and the O $2p$ were switched off. This also naturally explains why the symmetry of the states closest to the Fermi level (with almost 100% spin polarization) is completely different from that of the main peak in the conduction band (with 50% polarization); namely, the states closest to the Fermi level are of oxygen $2p$ character, which has hardly any bonding with local Cr $3d$ states. These findings strongly support the LSDA+U results of Korotin *et al.*,[11] from which $CrO_2$ is concluded to be a self-doped system, based on the fact that bands crossing the Fermi level are of almost pure O $2p$ character.

In conclusion, our bulk sensitive spin-resolved O $1s$ XAS data of epitaxial $CrO_2$ thin films show the dualistic electronic character of $CrO_2$, and provide direct spectroscopic evidence for its half-metallic nature. Results in this study reveal the dramatic change in the spin polarization of O $1s$ XAS data for states slightly above the Fermi level, from which the Mott-Hubbard nature of $CrO_2$ is identified. The data show that the presence of a large amount of holes in the oxygen band prevents $CrO_2$ from being an insulator, supporting the notion that $CrO_2$ is a self-doped or $p$-type metal. New theoretical approaches are highly desired,[32] in order to calculate correctly the spectral weights of $CrO_2$, including the spin polarization both at and away from the Fermi level.

[1] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).

[2] K.-H. Schwarz, J. Phys. F: Met. Phys. **16**, L211 (1986).

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

[4] R. J. Soulen, J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, P. R. Broussard, C. T. Tanaka, J. Nowak, J. S. Moodera, A. Barry, and J. M. D. Coey, Science **282**, 85 (1998).

[5] Y. Ji, G. J. Strijkers, F. Y. Yang, C. L. Chien, J. M. Byers, A. Anguelouch, Gang Xiao, and A. Gupta, Phys. Rev. Lett. **86**, 5585 (2001).

[6] B. L. Chamberland, CRC Crit. Rev. Solid State Mater. Sci. **7**, 1 (1977).

[7] T. Tsujioka, T. Mizokawa, J. Okamoto, A. Fujimori, M. Nohara, H. Takagi, K. Yamaura, and M. Takano, Phys. Rev. B **56**, R15 509 (1997).

[8] C. B. Stagarescu, X. Su, D. E. Eastman, K. N. Altmann, F. J. Himpsel, and A. Gupta, Phys. Rev. B **61**, R9233 (2000).

[9] K. Suzuki and P. Tedrow, Phys. Rev. B **58**, 11 597 (1998).

[10] E. J. Singley, C. P. Weber, D. N. Basov, A. Barry, and J. M. D. Coey, Phys. Rev. B **60**, 4126 (1999).

[11] M. A. Korotin, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. Lett. **80**, 4305 (1998).

[12] M. S. Laad, L. Craco, and E. Muller-Hartmann, Phys. Rev. B **64**, 214421 (2001).

[13] I. I. Mazin, D. J. Singh, and C. Ambrosch-Draxl, Phys. Rev. B **59**, 411 (1999).

[14] J. Kunes, P. Novak, P. M. Oppeneer, C. Konig, M. Fraune, U. Rudiger, G. Guntherodt, and C. Ambrosch-Draxl, Phys. Rev. B **65**, 165105 (2002).

[15] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[16] C. S. Hwang and S. Yeh, Nucl. Instrum. Methods Phys. Res. A **420**, 29 (1999).

[17] S.-C. Chung, J. Chen, L.-R. Huang, R. T. Wu, C.-C. Chen, N.-F. Cheng, J. M. Chuang, P.-C. Tseng, D.-J. Huang, C. F. Chang, S.-Y. Perng, C. T. Chen, and K.-L. Tsang, Nucl. Instrum. Methods Phys. Res. A **467-478**, 445 (2001).

[18] D. J. Huang, W. P. Wu, J. Chen, C. F. Chang, S. C. Chung, M. Yuri, H. J. Lin, P. D. Johnson, and C. T. Chen, Rev. Sci. Instrum. **73**, 3778 (2002).

[19] K. Suzuki and P. M. Tedrow, Appl. Phys. Lett. **74**, 428 (1999).

[20] X. W. Li, A. Gupta, and Giang Xiao, Appl. Phys. Lett. **75**, 713 (1999).

[21] P. G. Steeneken, L. H. Tjeng, I. Elfimov, G. A. Sawatzky, G. Ghiringhelli, N. B. Brookes, and D. J. Huang, Phys. Rev. Lett. **88**, 47201 (2002).

[22] D. J. Huang, L. H. Tjeng, J. Chen, C. F. Chang, W. P. Wu, A. D. Rata, T. Hibma, S. C. Chung, S.-G. Shyu, C.-C. Wu, and C. T. Chen, Surf. Rev. Letter **9**, 1007 (2002).

[23] L. H. Tjeng *et al.*, in *Strong Correlation and Superconductivity*, edited by H. Fukuyama, S. Maekawa, and A. P. Malozemoff (Springer-Verlag, Berlin, 1989), p. 33.

[24] G. A. Sawatzky, *Lecture Note on Auger Electron Spectroscopy* (University of Groningen, Groningen, Netherlands).

[25] V. I. Anisimov, in *Spectroscopy of Mott Insulators and Correlated Metals*, edited by A. Fujimori and Y. Tokura (Springer-Verlag, Berlin, 1995), p. 106.

[26] J. van Elp and A. Tanaka, Phys. Rev. B **60**, 5331 (1999).

[27] F. Sette, B. Sinkovic, Y. J. Ma, and C. T. Chen, Phys. Rev. B **39**, 11 125 (1989).

[28] A. Fujimori, I. Hase, H. Namatame, Y. Fujishima, Y. Tokura, H. Eisaki, S. Uchida, K. Takegahara, and F. M. F. de Groot, Phys. Rev. Lett. **69**, 1796 (1992).

[29] J.-H. Park, Ph.D. thesis, University of Michigan, 1994.

[30] H. F. Pen, L. H. Tjeng, E. Pellegrin, F. M. F. de Groot, G. A. Sawatzky, M. A. van Veenendaal, and C. T. Chen, Phys. Rev. B **55**, 15 500 (1997).

[31] A. E. Bocquet, T. Mizokawa, K. Morikawa, A. Fujimori, S. R. Barman, K. B. Maiti, D. D. Sarma, Y. Tokura, and M. Onoda, Phys. Rev. B **53**, 1161 (1996).

[32] K. Held, G. Keller, V. Eyert, D. Vollhardt, and V. I. Anisimov, Phys. Rev. Lett. **86**, 5345 (2001).