PHYSICAL REVIEW B VOLUME 44, NUMBER 19 15 NOVEMBER 1991-I

Empty electron states in Fe_2O_3 by ultraviolet inverse-photoemission spectroscopy

F. Ciccacci, L. Braicovich, E. Puppin, and E. Vescovo
Istituto di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy

(Received 25 April 1991)

We present a set of angle-integrated inverse-photoemission data on Fe_2O_3 taken in the ultraviolet region (12.1–24.2 eV) in the isochromat mode. The photon-energy dependence of the spectra gives direct insight into the orbital origin of the empty electron states in the oxide. The results are discussed in terms of the available theories based on a cluster model with configuration interaction, which reproduce quite well the direct-photoemission results. It is shown that these calculations are less satisfactory in fitting the electron-addition spectroscopy of empty states. We suggest that this might be due to an overestimation of U, the on-site d-d Coulomb correlation energy.

I. INTRODUCTION

In the physics of correlated systems the electron states of transition-metal compounds have great relevance. Considerable effort is currently devoted to the understanding of the role of multielectron correlation effects versus bandlike behavior, anion to cation charge transfer, insulating versus metallic character. A general approach for $3d$ transition-metal compounds which allows one to classify them into several groups, including the charge-transfer and the Mott-Hubbard regime, has been developed by Zaanen, Sawatzky, and Allen.[1] In this connection Fe oxides are very interesting and their spectroscopy attracted much attention. Extensive results on the electron states as measured by direct photoemission are presently available for several stoichiometries (Fe_xO, Fe_2O_3, and Fe_3O_4).[2-7] In particular, accurate studies with synchrotron radiation at different photon energies, including the Fe $3p$-$3d$ excitation threshold, have been reported for Fe_2O_3 and Fe_xO by Fujimori and co-workers,[5,6] and for all stoichiometries by Lan and Henrich.[7] The discussion in these cases has been done in the framework of a cluster model with configuration interaction (CI) developed by Fujimori and co-workers on Fe_2O_3.[5] Such an approach has been selected in order to account for the localization of the d states and for the electron-subtraction effects in the final photoemission state.[8] These results have contributed to the picture of Fe oxides as charge-transfer insulators in which the top of the photoemission spectrum has $d^n\underline{L}$ character ($\underline{L}$ indicates a ligand hole) and not d^{n-1} character as assumed in previous photoemission works.[2-4] A similar picture had already emerged for NiO:[9-11] in this case the available results on the empty electron states as measured by inverse photoemission (IP) have been included in the scheme.[10,11]

On the other hand, IP studies on Fe oxides are still at the beginning:[12] this is a severe limitation since a broader experimental basis is interesting per se and can be very useful for a more accurate tuning of the model parameters. Thus it seemed timely to perform IP measurements on Fe_2O_3, i.e., the only iron oxide, to our knowledge, in which calculations are available for the ground state, for the (N-1)-electron subtraction and for the ($N+1$)-electron addition systems.

Here we report IP results on Fe_2O_3 taken in the isochromat mode in the ultraviolet (uv) region (12.1–24.2 eV), i.e., in a region where the spectra, due to cross-section reasons, are dominated by d-related states.

The data are discussed in connection with the cluster calculation of Ref. 5. The problems raised by the comparison of the existing theory with our experimental results are indicated. It is also qualitatively shown that the present calculations are likely to overestimate the on-site d-d Coulomb correlation energy U. We hope that our experimental results could stimulate future theoretical researches, which are definitely beyond the purpose of the present work.

II. EXPERIMENT

The data have been acquired with an IP spectrograph described in detail elsewhere.[13] It is based on an uv grating which disperses photons with energy $h\nu$ in the 10–25-eV range on a flat field where a position-sensitive detector is located. The spectra are taken in the multichannel isochromat mode by scanning the energy of the electrons emitted by a thoriated tungsten filament close to the sample and by keeping constant the photon energy of each channel: 12 isochromat spectra corresponding to different $h\nu$'s can be measured simultaneously. The total resolution amounts to a full width at half maximum of 0.55 eV at $h\nu=17$ eV. The electron current impinging onto the sample is continuously monitored for normalization purposes. All spectra reported here are angle integrated.

Natural mineral Fe_2O_3 (hematite) was cleaned in ultrahigh vacuum ($p \approx 1\times10^{-10}$ Torr) by scraping with a diamond file. In order to avoid sample contamination or damage, a very low current density ($\approx 0.5\ \mu A/mm^2$) has been used. We did not observe any variation in the spectra on the time scale needed for the data acquisition. However, for the sake of safety, acquisition times larger than 1 h were avoided. Measurements were repeated several times always starting from a freshly prepared surface: excellent reproducibility was found. Moreover, no charging effect (either rigid spectra displacement or line-shape distortion) was detected while varying the impinging current over a considerably wide range (0.1 to 5 $\mu A/mm^2$).

For comparison, we also performed measurements in the same conditions on polycrystalline Fe, cleaned by scraping in vacuum. The spectra on clean iron were taken just before and then repeated just after the measurements on hematite, with perfectly reproducible results. In particular, the energy scale was the same, this fact indicating that the electron-emitting filament work function, and in turn the position of the Fermi level of the spectrograph, did not change during the data acquisition. This procedure ensures the strict comparability between the hematite and the iron spectra, an important point for the discussion given below.

III. RESULTS AND DISCUSSION

Inverse-photoemission spectra from Fe_2O_3 and Fe, taken at $h\nu=15$ eV and normalized to the impinging current, are shown in Fig. 1. The energy is referenced to the Fermi level E_F of our spectrometer, whose position is indicated by the dashed line. As clearly seen in the more expanded scale of the inset, in Fe_2O_3 the onset occurs at energies larger if compared to the pure metal. This fact reflects the insulating nature of hematite in which the Fermi level lies in the bulk band gap: in this case the onset corresponds to the conduction-band edge. We find it around 1 eV above the onset observed in metallic Fe, in agreement with the 2–2.5 estimated value of the band gap.[14] The same shift is observed in the spectra corresponding to other photon energies in the investigated range (12.1–24.2 eV).

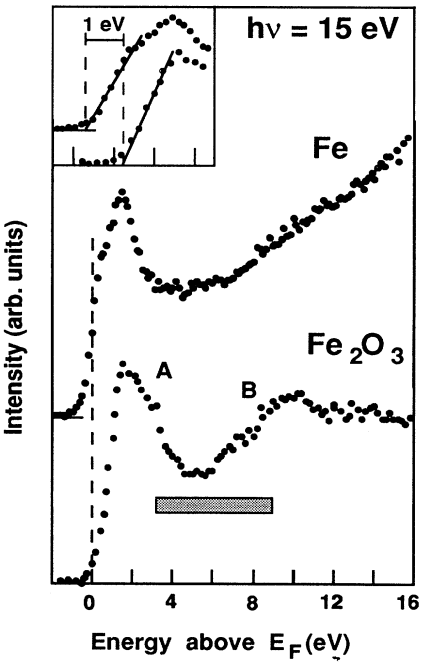

FIG. 1. Inverse-photoemission spectra from Fe_2O_3 and Fe taken in the isochromat mode at $h\nu=15$ eV. The spectra have been normalized to the same height of the main peak (the peak intensities roughly scale as the Fe content in the solid; see also the inset of Fig. 3). The horizontal shaded bar indicates the position of the onset of the 3*d* signal as predicted in Ref. 5. The inset is a blowup of the region near the Fermi level in which the extrapolated onsets of the spectra are indicated.

In clean iron, the spectra are dominated by the 3*d* empty states as already seen with IP in the x-ray regime:[15] in particular also the details of the empty density of state, such as the shoulder just above E_F, are clearly observed.

In Fe_2O_3 a similar narrow peak (*A*) and a broad structure (*B*), located, respectively, at 2 and $\approx 8-12$ eV above E_F, are observed. Similar features in the empty density of states of several transition-metal oxides have been recently reported in an x-ray-absorption experiment above the oxygen 1*s* edge.[16] In this work the authors assume that the empty states with O 2*p* character are distributed up to about 15 eV above E_F. Moreover, they attribute the observed features to the O 2*p* component in states with predominant transition-metal 3*d* and 4*sp* character (which correspond in our spectra to structures *A* and *B*, respectively).

On the other hand, in the CI cluster model of Fujimori *et al.*,[5] Fe 4*s* character is attributed to the lowest empty states, while the 3*d*-derived features in the IP spectra are expected at higher energies. The onset of such 3*d* features was predicted to occur in a region corresponding to the shaded horizontal bar of Fig. 1 (for more details see below). In the following we present an accurate analysis of the orbital origin of the spectral features by examining their $h\nu$ dependence. We concentrate mainly on the first structure (*A*), which is the most critical in order to test the CI predictions. Then we discuss feature *B* by considering the different contributions which could in principle be present in that region.

A. Low-energy region

A selection of IP spectra from Fe_2O_3 taken at different $h\nu$'s in a wide energy range above E_F is presented in Fig. 2, where the spectra have been normalized to the same height of the peak (for the sake of clarity, in Fig. 2 we only present spectra taken at four different $h\nu$'s, while spectra have been collected also at several other photon energies). The intensity of each peak depends on several factors such as the efficiency of the grating and the yield of the photon detector, both of which strongly depend on the photon energy. For this reason the absolute intensities of the spectra taken at different photon energies cannot be compared. However, it is possible to compare the intensities of spectra taken from different samples at the same photon energy: for this reason we also collected a series of isochromat spectra from pure Fe in order to compare the relative intensity of the spectral features closer to the Fermi level versus $h\nu$. The result of this comparison is shown in Fig. 3 where the relative intensity of peak *A* in Fe_2O_3 with respect to the 3*d* peak observed

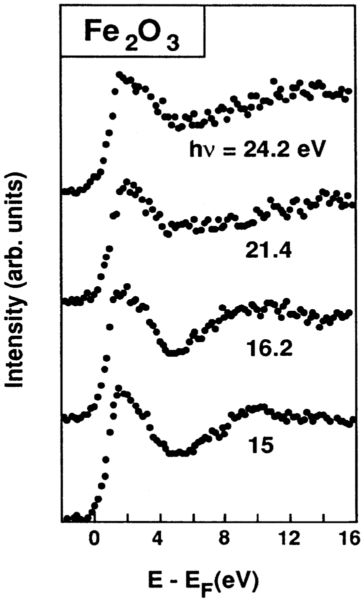

FIG. 2. Inverse-photoemission spectra from Fe_2O_3 at different $h\nu$'s in a wide energy range above E_F. The spectra have been normalized to the same height of the main peak.

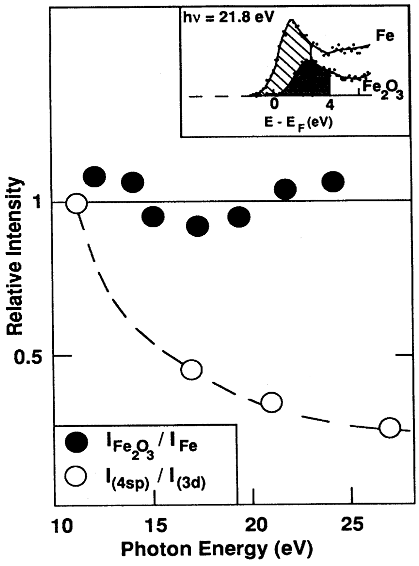

FIG. 3. Photon-energy dependence of the relative intensity of the near-edge peak in Fe_2O_3 and in Fe (solid dots). The peak intensity is defined as the area below the curve in the first 4 eV above threshold, as shown in the inset for $h\nu = 21.8$ eV (here the curves are normalized only to the impinging current). For comparison also shown is the relative intensity between the 4*sp* and 3*d* signals as measured in direct photoemission (Ref. 18) in the same range (open dots, dashed line). For the sake of clarity, the two relative intensities have been set equal to one at the low-energy side.

in pure Fe is presented as a function of the photon energy (solid dots). The intensity of each peak is defined as the area under the spectrum in a 4-eV-wide window above threshold,[17] as shown in the inset for $h\nu = 21.8$ eV. Clearly, in the explored range the relative intensity does not present considerable variations. This is a strong indication of the 3*d* orbital character of the states which give rise to feature *A*. If other significant contributions were present, the $h\nu$ dependence would be quite different. In fact, in the same range the relative 4*sp* to 3*d* cross-section changes remarkably as demonstrated by direct photoemission (the 4*sp* over 3*d* cross-section ratio decreases by a factor of 4 in Cu).[18] The same trend is expected to be followed in inverse photoemission since the excitation processes in these two spectroscopies are related to each other by a time-reversal relation. Regarding the O 2*p* states, even though the atomic dipole cross section for each electron is comparable with the 3*d* one, their contribution is certainly negligible due to the low number of available empty states (on the order of a few tenths in front of more than five empty 3*d* states).

On the basis of the above assignment one can compare our results with the calculations by Fujimori *et al.*[5] on a $(FeO_6)^{9-}$ cluster, which give an excellent fitting for the occupied states spectroscopy. CI has been introduced in order to account for the noninteger *d* occupancy, which is greater than the purely ionic value of 5 (i.e., in order to account for the covalent contribution to the chemical bond). The energy differences between the various configurations were treated as adjustable parameters so that they are lower than a free ion because of the polarization of the solid, including the charge transfer between O 2*p* and Fe orbitals. For the ground state the single d^5 and the two d^6 configurations ($t_{2g}{}^3 e_g{}^3 \underline{L}$ and $t_{2g}{}^4 e_g{}^2 \underline{L}$), both with a ligand hole but with a different (*pd*) transfer integral, were considered. In the direct- and inverse-photoemission theoretical spectra the corresponding $(N-1)$ and $(N+1)$ configurations were included. With this approach Fujimori *et al.*[5] produced an excellent fitting of the experimental direct-photoemission *d* features, which were found to spread over ≈ 15 eV in the valence band by means of resonant photoemission at the crossing of the Fe 3*p* threshold. Moreover, the shape of the resonance suggested the charge-transfer nature of hematite; afterwards this general scheme has been confirmed by very detailed experiments by Lad and Henrich.[7]

In order to discuss the present IP data one can use the results of Ref. 5, although they are presented in a less detailed way if compared to direct photoemission. Fujimori *et al.*[5] evaluate a very important parameter typical of the IP spectrum, i.e., the *minimum energy* at which the *d* signal is expected. In the electron-addition spectrum this is the lowest term of the d^6 configuration. According to Ref. 5 and using the same notation,[19] it is approximately given by $E_6 - \Delta E_6{}^M = E_5 + \varepsilon_d + U - \Delta E_6{}^M$, where E_6 and E_5 are the centers of gravity of the d^6 and d^5 configurations, $\Delta E_6{}^M$ is the maximum lowering due to multiplet splitting, *U* is the on-site *d*-*d* Coulomb correlation energy, and ε_d is the energy required to add an electron to the d^4 configuration. Using the values of the parameters which produce a good fit of the occupied states spectroscopy, the estimated value of the 3*d* onset lies 8 ± 2 eV above E_F, with a possible reduction to 6 ± 3 eV above E_F, allowing for relaxation. This last interval is shown in Fig. 1 by a shaded horizontal bar. Note that this represents a theoretical estimate of the 3*d* *onset.* Clearly, the center of gravity will be centered at higher energy. Even by considering the above uncertainties, it seems difficult to reconcile theory and experiment: 2 eV would be necessary to fit the experimental results with the most favorable estimate on the onset.

This is the main direct result of the comparison between theory and experiment and raises the question of the possibility of fitting both direct and inverse photoemission without losing the excellent results reported in Refs. 5 and 7 for direct photoemission. A definite assessment of this point calls for a new calculations: however, it is already possible to anticipate some qualitative arguments. The following considerations can be made.

(i) The multiplet splitting $\Delta E_6{}^M$ cannot be substantially increased beyond the values given in Ref. 5 since it would expand the total width of the region having *d* nature too much. In the calculations $\Delta E_6{}^M$ is 3.7 eV, which means a total *d* width of about 7 eV, already too large if compared to the observed value.

(ii) A very direct way of shifting down the d^6 configuration would be the reduction of the Coulomb term U from 8 to about 6 eV. In this case there is in principle some possibility of preserving a good fitting of the direct-photoemission data. In fact, the most important terms in the theoretical direct-photoemission spectrum come from the $d^5\underline{L}$ and d^4 configurations (in order of increasing binding energy) with a mutual distance which is on the order of $\varepsilon_d-\varepsilon_L$ ($-\varepsilon_L$ is the ligand hole energy). Formally, one could say that the valence photoemission fitting is sensitive to ε_d and not to U. On the contrary, U directly enters into the IP spectrum which should be really used to determine the Coulomb term. However, ε_d is also physically due to the Coulomb interaction and therefore ε_d and U cannot be changed in a totally independent way (see also Ref. 5).

We conclude that the present CI calculations are a useful first-order approximation, but that a further improvement, i.e., a better fitting of both direct and inverse photoemission, is not a trivial extension of the works already published. In fact, most probably the value of U must be substantially decreased and the value of ε_d readjusted; furthermore, the role played by hybridization and polarization must be reassessed. The solution of this discrepancy could help in clarifying the nature of the lowest empty states. In fact, Fujimori *et al.*,[5] owing to the high energy of the d^6 configuration, attribute an exclusively 4*s* nature to these states. In consideration of our results, instead, the onset of the *d* character is found at the bottom of the conduction band.

B. High-energy region

In the region above 5 eV two types of contributions are expected. The first one is due to the empty 4*s* and 4*p* Fe states as pointed out by oxygen *K*-edge absorption[16] and, according to Ref. 16, it is to be expected at 8–10 eV above the 3*d*-like peak. The second one is due to the final-state features originating from the $d^7\underline{L}$ configuration in electron-addition spectroscopy. Indeed, satellitelike emission corresponding to the $d^{n+2}\underline{L}$ configuration lying well above E_F has been experimentally identified in IP for NiO.[10,11] A similar structure is predicted in the CI calculations for Fe_2O_3 at about $\varepsilon_d-\varepsilon_L+2U=11$ eV above the d^6 states. With our suggested reduction of U this feature should be found around 7–8 eV above the peak *A*, i.e., almost in the same position as the Fe 4*sp* contribution. Therefore both these terms could be present in structure *B* and a clear distinction between them is not straightforward. Here too, however, exploiting the $h\nu$ dependence of the cross sections shines new light onto the problem. Even without performing a detailed analysis, from Fig. 2 a definite trend towards reduction of feature *B* at high $h\nu$ (eventually disappearing in the background) is clearly evident. This is an indication of the dominant 4*sp* nature of such a structure: it is well known from direct photoemission that the 4*sp* peak is strongly reduced with respect to the 3*d* one when increasing $h\nu$ in this range.[18] Therefore we can conclude that structure *B* mostly originates from Fe 4*sp* states, while the $d^7\underline{L}$ satellitelike emission, which bears a considerable *d* character, is not evident in our spectra. This fact also suggests that in Fe_2O_3 the (*pd*) transfer integral for the $d^{n+2}\underline{L}$ configuration is lower if compared to NiO, which such a feature has instead been observed.[10,11]

IV. CONCLUSIONS

We have presented ultraviolet inverse-photoemission spectra ($h\nu=12.1-24.2$ eV) from hematite. The mail results are along two directions.

The first one, which is interesting per se, is the detection of spectral features directly related to the ground-state density of states. By exploiting the photon-energy dependence of the isochromat spectra in the uv, such states are unambiguously identified as Fe 3*d*- and 4*sp*-derived states.

The second one deals with the comparison with available CI calculations. In particular, we have shown that even though such calculations reproduce very well the electron-subtraction spectra, they are less satisfactory in fitting the result of electron-addition spectroscopy.

Our results suggest some reduction on the on-site *d*-*d* Coulomb correlation energy U. Moreover, satellitelike emission, corresponding to the $(N+1)$-final-state-electron system with a ligand hold, is not identified in the spectra: this finding puts an upper limit to the transfer integrals in future theoretical works.

ACKNOWLEDGMENTS

This work has been supported by the Ministero della Pubblica Istruzione, the GNSM of the Consiglio Nazionale delle Ricerche, and the Consorzio INFM.

[1] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 606 (1985).

[2] D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. **34**, 395 (1977).

[3] S. F. Alvarado, M. Erbudak, and P. Munz, Phys. Rev. B **14**, 2740 (1986).

[4] P. S. Bagus, C. R. Brundle, T. J. Chuang, and K. Wandeldt, Phys. Rev. Lett. **39**, 1229 (1977).

[5] A. Fujimori, M. Saeki, N. Kimizuka, M. Taniguchi, and S. Suga, Phys. Rev. B **34**, 7318 (1986).

[6] A. Fujimori, N. Kimizuka, M. Taniguchi, and S. Suga, Phys. Rev. B **36**, 6691 (1987).

[7] R. J. Lad and V. E. Henrich, Phys. Rev. B **39**, 13 478 (1989).

[8] The usefulness of such an approach is also pointed out by the well-known difficulties in treating most of the transition-metal oxides with conventional band models [for the difficulties in local-spin-density calculation in FeO see A. Svane and O. Gunnarsson, Phys. Rev. Lett. **34**, 1148 (1990)].

[9] A. Fujimori, F. Minami, and S. Sugano, Phys. Rev. B **29**, 5225 (1984); **30**, 957 (1984).

[10] S. Hüfner, J. Osterwalder, T. Riesterer, and F. Hullinger, Solid State Commun. **52**, 793 (1984).

[11] G. A. Sawatzky and J. W. Allen, Phys. Rev. Lett. **53**, 2339 (1984).

[12] Concerning bulk oxides only one study has been recently performed on magnetite [M. Sancrotti, F. Ciccacci, M. Finazzi, E. Vescovo, and S. F. Alvarado, Z. Phys. B **84**, 243 (1991)]. Limited isochromat data at 9.7 eV, not usable for comparison with ours, are available on iron oxidation [Bong-soo Kim, S. Hong, and D. W. Lynch, Phys. Rev. B **41**, 12 227 (1990)].

[13] M. Sancrotti, L. Braicovich, C. Chemelli, F. Ciccacci, E. Puppin, G. Trezzi, and E. Vescovo, Rev. Sci. Instrum. **62**, 639 (1991).

[14] R. H. Chang and J. B. Wagner, Jr., J. Am. Cer. Soc. **55**, 211 (1972); S. Mochizuki, Phys. Status Solidi A **41**, 591 (1977).

[15] W. Speier, J. C. Fuggle, R. Zeller, B. Ackermann, K. Szot, F. Hillebrecht, and M. Campagna, Phys. Rev. B **30**, 6921 (1984).

[16] F. M. F. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky, and H. Petersen, Phys. Rev. B **40**, 5715 (1989).

[17] Using other definitions for the peak intensity (i.e., using a different energy range) does not cause variations in the reported behavior of the relative intensities.

[18] D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. **24**, 310 (1970); D. E. Eastman, in *Techniques of Metal Research,* edited by E. Passaglia (Interscience, New York, 1972), Vol. 6, p. 412.

[19] For the sake of comparison, in the present work we use the symbols as in Ref. 5; it is to be noted that such symbols, although analogous, are different with respect to those of other papers (for instance, Ref. 1). Here for a system with $5d$ electrons ε_d is defined as the energy required to add one electron to the d^4 configuration, while in Ref. 1 it would refer to the d^5 configuration.