Considering that the target atomic numbers are not quite the same, the fit is very good above $\theta \simeq 45°$. Hence single-atom scattering effects can be prominent in this region.

In conclusion, our measurements show that for relatively large angles of incidence the polarizations from W(001) are not very large (maximum 27%). While the match with the theoretical LEED intensity profile is good, the fit with the theoretical polarization is not satisfactory. The reasons for this are not yet established but one factor to be taken into account is that theoretical polarization curves are sometimes much more sensitive than LEED curves to the precise dilation or contraction that has been assumed. LEED, however, appears to be more sensitive to surface temperature than polarization.

The authors are grateful to Dr. R. Feder for communicating the results of his calculations and to Dr. N. Avery for providing the W(001) specimen. This work was supported by the Australian Research Grants Committee.

---

[1] M. R. O'Neill, M. Kalisvaart, F. B. Dunning, and G. K. Walters, Phys. Rev. Lett. 34, 1167 (1975).

[2] J. Van Klinken, Nucl. Phys. 75, 161 (1966).

[3] R. Loth, Z. Phys. 203, 66 (1967).

[4] R. Feder, private communication.

[5] R. Feder, Phys. Rev. Lett. 36, 598 (1976).

[6] P. S. P. Wei, J. Chem. Phys. 53, 2939 (1970).

[7] J. Kessler, Rev. Mod. Phys. 41, 3 (1969).

[8] R. Feder, N. Müller, and D. Wolf, in Proceedings of the Third International Conference on Surface Science, Vienna, 1977 (to be published).

[9] D. C. Gregory and M. Fink, Electronics Research Center, The University of Texas, Technical Report No. 160, 1974 (unpublished).

Width of the *d*-Level Final-State Structure Observed in the Photoemission Spectra of Fe_xO

P. S. Bagus, C. R. Brundle, T. J. Chuang, and K. Wandelt[a]
IBM Research Laboratory, San Jose, California 95193

(Received 13 June 1977)

X-ray photoemission (XPS) measurements of wustite, Fe_xO ($x = 0.90-0.95$), show that the Fe (3*d*) valence-band final states spread ~10 eV below E_F. This is much broader than previous claims based on the analysis of lower-energy (5–90 eV) photoemission spectra. Crystal-field–theory results, based on *ab initio* calculations, are consistent with the broader spectrum. Configuration interaction is found to have important consequences for the position and intensity of the XPS peaks.

Crystal-field–theory (CFT) analyses have been made for the *d*-level final states of Fe_xO by Eastman and Freeouf[1] and by Alvarado, Erbudak, and Munz.[2] The parameters[3] were estimated empirically to obtain agreement with *d*-level structure deduced from UPS (ultraviolet photoelectron spectroscopy) spectra[1,2] In these spectra, metal *d* and ligand *p* levels have comparable intensities making it necessary to deconvolute the spectra.[1,2,4] This led to estimated *d*-level widths of ~5.5 eV[1] and ~6.5 eV.[2] The reported theoretical CFT widths are ~4.5 eV[1] and ~5.5 eV.[2] In XPS (x-ray photoemission spectroscopy), the ligand intensity is reduced and the *d* levels can be observed directly.[5-7] We report the XPS spectrum for Fe_xO. Structure extends ~10 eV below E_F. We have obtained *ab initio* self-consistent-field (SCF) and configuration-interaction (CI) wave functions for an FeO_6 cluster simulating bulk FeO. From these wave functions we have deduced values, appropriate for the photoemission final states, of B and C to represent interactions among the *d* electrons[3] and of $10Dq$ to represent the crystal-field splitting of the +2 and *e* levels.[3] A CFT analysis was then performed where CI wave functions which mix one-electron allowed final states with one-electron forbidden final states are used for the first time. Mixing leads to additional intensity at higher binding energy and to an uncertainty in the relative intensities for some of the states.[8,9]

Previous analysis of Fe_xO involved a separation of the O 2*p* and metal 3*d* contributions utilizing cross-section changes as function of $h\nu$.[1] This yielded an Fe 3*d* final structure spread between E_F and about 5 eV, and an O 2*p* structure centered at ~5.5 eV [Fig. 1(b)]. A subsequent analysis[2] places the O 2*p*-band center at 7.3 eV, and gives slightly broader 3*d* final states [Fig. 1(c)]. This analysis relies on electron-spin-polarization (ESP) measurements on Fe_3O_4 (*not* Fe_xO for determination of the onset of the O 2*p* band. Essentially the argument is that the spin polarization of the photoelectrons, as a function of $h\nu$, will

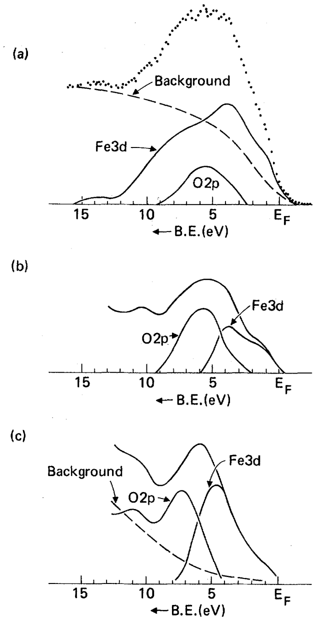

FIG. 1. Valence band of Fe_xO showing experimental spectra, estimated scattered-electron background, and estimated O $2p$ and Fe $3d$ structures. (a) Present XPS spectrum; (b) Ref. 1, $h\nu = 30$ eV; and (c) Ref. 2, $h\nu = 20$ eV.

only drop below 25% for Fe_3O_4 once the O $2p$ threshold is reached.[2] The ESP analysis[2] assumes that $3d$ ionization cross sections are independent of $h\nu$ though $h\nu$ is near threshold. If the d and p states overlap, the analysis will also fail to yield the $2p$ onset position.

Our XPS valence-band structure, taken using an HP 5095A spectrometer ($h\nu = 1486.6$ eV) is shown in Fig. 1(a). To ensure that the surface is representative of the bulk material, we used an Fe_xO single crystal crushed under argon and checked the surface using core-level spectra.[10]

The estimated O $2p$ and Fe $3d$ contributions are also shown in Fig. 1(a). The O $2p$ area is taken as 0.14 times that of the total signal after background subtraction. This ratio is estimated from atomic cross sections[11] for Fe $3d$, O $2p$, and O $2s$, adjusting for electron occupancies and stoichiometry. The chosen position and width of the O $2p$ peak are consistent with the Eastman and Freeouf analysis.[1] Our choices are based on XPS and UPS studies of the oxidation of Fe, of the other bulk Fe oxides, and of FeOOH.[10,12] However, the precise position and area of O $2p$ are not critical to our resultant Fe $3d$ width because of the low XPS ligand intensity. Disagreement with both previous analyses[1,2] concerns the width of the $3d$ structure. Their claims that it is completed by ~5.5 eV[1] or 6.5 eV[2] are based on the assumption that all the intensity observed above these values is O $2p$ and background. This is not supported by the present XPS data.

The XPS results demonstrate that Fe $3d$-derived structure spreads some 10 eV below E_F, completely over-lapping the O $2p$ band. This has to be rationalized in terms of electronic structure and nature of the photoemission process. Our theoretical treatment is based on the assumption that the metal atom can be treated as an ion in a crystal field. The initial state is $Fe^{2+}(3d^6)$ and the final states are multiplet and crystal-field-split levels[3] of $Fe^{3+}(3d^5)$. The initial state is the high-spin ${}^5T_{2g}$ configuration, $t_{2g}{}^4 e_g{}^2$. The photoemission selection rules[8,9] determine that the allowed final states have total symmetry ${}^6A_{1g}$, ${}^4A_{1g}$, ${}^4E_g$, ${}^4T_{1g}$, and ${}^4T_{2g}$. The crystal-field-split configurations of these symmetries are listed in Table I. For each of ${}^4E_g$, ${}^4T_{1g}$, and ${}^4T_{2g}$, one of the configurations is a forbidden final state which involves ionization of one d electron plus rearrangement (excitation) of another d electron. However, the final-state wave functions, Ψ_K, are mixtures of the allowed and forbidden configurations Φ_j (Table I). For ${}^4T_{1g}$ symmetry, the Ψ_K are given by

$$\Psi_K = \sum_{j=1}^{3} C_{K,j}\Phi_j, \quad K = 1, 2, 3. \tag{1}$$

The $C_{K,j}$ are obtained as solutions of a many-

TABLE I. Configurations for final d^5 states of allowed total symmetry.

Total symmetry	Allowed configurations	Forbidden configurations
${}^6A_{1g}$	${}^6A_{1g}(1) \equiv t_{2g}{}^3({}^4A_{2g})e_g{}^2({}^3A_{2g})$	...
${}^4A_{1g}$	${}^6A_{1g}(1) \equiv t_{2g}{}^3({}^4A_{2g})e_g{}^2({}^3A_{2g})$	...
${}^4E_g$	${}^4E_g(1) \equiv t_{2g}{}^3({}^2E_g)e_g{}^2({}^3A_{2g})$	${}^4E_g(2) \equiv t_{2g}{}^3({}^4A_{2g})e_g{}^2({}^1E_g)$
${}^4T_{1g}$	${}^4T_{1g}(1) \equiv t_{2g}{}^3({}^2T_{2g})e^2({}^3A_{2g})$, ${}^4T_{2g}(2) \equiv t_{2g}{}^4({}^3T_{1g})e_g{}^1({}^2E_g)$	${}^4T_{1g}(3) \equiv t_{2g}{}^2({}^3T_{1g})e_g{}^3({}^2E_g)$
${}^4T_{2g}$	${}^4T_{2g}(1) \equiv t_{2g}{}^3({}^2T_{1g})e_g{}^2({}^3A_{2g})$, ${}^4T_{1g}(2) \equiv t_{2g}{}^4({}^3T_{1g})e_g{}^1({}^2E_g)$	${}^4T_{2g}(3) \equiv t_{2g}{}^2({}^3T_{1g})e_g{}^3({}^2E_g)$

electron Hamiltonian matrix, H, connecting the three states. In CFT, H is expressed[3] in terms of B, C, and $10Dq$.

Our treatment involves SCF wave functions (using an extended basis set of contracted Gaussian functions) for the initial state of an octahedral FeO_6^{10-} cluster and for several of the allowed final states of FeO_6^{9-}. The Fe-O distance is 2.16 Å. The cluster is surrounded by point charges fitted to the Madelung potential. All electrons are explicitly included. The initial- and final-state wave functions show little covalency—less than 7% ligand character for the d-shell orbitals of any state.

To calculate the positions of the final-state d levels from CFT, it is necessary to obtain B, C, and $10Dq$ values. B and C have been computed from the differences in the SCF energies of the ${}^6A_{1g}$, ${}^4A_{1g}$, and ${}^4E_g$ (allowed) final-state configurations of the cluster as $B = 1190$ and $C = 4560\ \mathrm{cm}^{-1}$. These are ~10% lower than values that we have obtained in a like manner for the free Fe^{3+} ion. The experimental free-ion values are available and it is known[13] that they differ significantly from calculated SCF values. We regard a 10% reduction of the *experimental* Fe^{3+} free-ion values[3b] as a reliable estimate; values are $B = 913.5$ and $C = 4320\ \mathrm{cm}^{-1}$.

$10Dq$ for the final state is calculated from the SCF energy differences between the ${}^6A_{1g}$, and ${}^4T_{1g}$ and ${}^4T_{2g}$ $(t_{2g}{}^4e_g{}^1)$ states as 1.1 eV. The value for the initial state, obtained from the ${}^5T_{2g}$ and ${}^5E_g$ separation in FeO_6^{10-} is 0.81 eV. Although $10Dq$ for FeO is not known experimentally, it is 1.3 eV for Fe^{2+} in aqueous solution,[14] i.e., 62% higher than our calculated value. We pick 1.7 eV as an appropriate value for the final state. Support for this estimate comes from cluster SCF calculations for Ni in $KNiF_3$[15] and in NiO.[16] Here, the experimental $10Dq$'s are ~55% larger than the calculated values.

TABLE II. CFT results for the energies and intensities of the CI final states for FeO. $B = 913.5\ \mathrm{cm}^{-1}$, $C = 4320\ \mathrm{cm}^{-1}$, and $10Dq = 1.7$ eV.

	E_{rel} (eV)	$I_{\mathrm{rel}}^{\mathrm{out}}$	I_{rel}^{r}	$I_{\mathrm{rel}}^{\mathrm{in}}$
${}^6A_{1g}$	0	···	1.20	···
${}^4T_{1g}(1)$	2.52	0.74	0.98	1.22
${}^4T_{2g}(1)$	3.17	0.33	0.93	1.53
${}^4A_{1g}, {}^4E_g(1)$	3.81	···	0.51[a]	···
${}^4T_{2g}(2)$	4.26	0.37	1.00	1.63
${}^4E_g(2)$	4.60	···	0.29	···
${}^4T_{1g}(2)$	5.49	0.56	0.57	0.58
${}^4T_{1g}(3)$	6.59	0.22	0.45	0.68
${}^4T_{2g}(3)$	7.23	0.04	0.07	0.10

[a] Intensity is the sum for ${}^4A_{1g}$ and ${}^4E_g$ (1) which are exactly degenerate.

We then performed CFT calculations to determine the relative energies of the ten final ionic states of allowed total symmetry. For all but A_{1g} symmetry, the wave functions for these states are CI mixtures of allowed and forbidden configurations. Using considerations of angular momentum coupling, it is possible to determine the relative photoionization cross sections, I_{rel}, to the allowed configurations.[8,9] However, these considerations do not yield information about the relative phases of the transition integrals. When there is more than one allowed final configuration, this information is required to determine the intensity for the CI wave functions, Ψ_K; cf., Eq. (1). For either ${}^4T_{1g}$ or ${}^4T_{2g}$, we have

$$I_{\mathrm{rel}}(\Psi_K) = |C_{K,1}[I_{\mathrm{rel}}(\Phi_1)]^{1/2}\exp(i\varphi_1) + C_{K,2}[I_{\mathrm{rel}}(\Phi_2)]^{1/2}\exp(i\varphi_2)|^2, \tag{2}$$

where the $I_{\mathrm{rel}}(\Phi_i)$ are the relative intensities to each configurations[9]; and the $\exp(i\varphi_i)$ are the (unknown) relative phases. We can estimate I_{rel} in three extreme cases: out of phase, $I_{\mathrm{rel}}^{\mathrm{out}}$; in phase, $I_{\mathrm{rel}}^{\mathrm{in}}$; and random phase, I_{rel}^{r}. The differences among these three estimates are a clear measure of the importance of the configuration mixing in Ψ_K.

In Table II, we present our results for E_{rel} and I_{rel}. The third ${}^4T_{1g}$ state $[{}^4T_{1g}(3)]$ has significant intensity, increasing the width of the d levels by ~1 eV. Further, the configuration mixing is sufficiently important that, except for ${}^4T_{1g}(2)$ and ${}^4T_{2g}(3)$, it is not possible to obtain a good estimate of the relative intensities of the ${}^4T$ states.

In Fig. 2, we have plotted relative intensities and positions with the XPS d-level intensity. The major discrepancy between experiment and theory is that the calculated intensity is too low near 9 eV below E_F. This could be accounted for by intensity from shakeup peaks as found in NiO[1,5,7] and CoO.[7]

When CFT is applied correctly using the parameters of Refs. 1 and 2, the results (Fig. 2) are substantially closer to our results.[17]

In summary, our XPS results clearly show that the d-level structure spreads to ~10 eV below E_F.

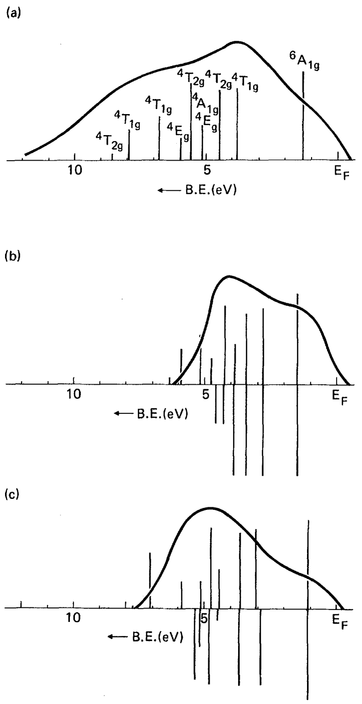

FIG. 2. (a) XPS Fe $3d$ structure [from Fig. 1(a)]. Vertical lines are the theoretical final-state positions and intensities ($\Gamma_{\text{rel}}{}^r$) from Table II. (b) and (c) UPS Fe $3d$ structure, as given in Refs. 1 and 2. Lines above axis are our recalculated final-state positions and intensities ($\Gamma_{\text{rel}}{}^r$) for the CPT parameters of Refs. 1 and 2. Lines below axis are the values as given in Refs. 1 and 2.

This casts doubt on the reliability of the analysis of variable-energy UPS[1,2] and ESP[2] results to determine the d-level features. A CFT is in agreement with the XPS experimental results, confirming that an ionic model is appropriate. CI effects are important both for the energy spread of the final states and for the assignment of intensities.

We thank H. C. Siegmann for stimulating discussions and J. L. Freeouf for the Fe_xO crystal.

(a) Present address: Institut für Physikalische Chemie, Universität München, München, Germany.

[1] D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 34, 395 (1975).

[2] S. F. Alvarado, M. Erbudak, and P. Munz, Phys. Rev. B 14, 2740 (1976).

[3a] Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. 9, 753 (1954).

[3b] Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. 9, 766 (1954).

[4] T. Ishii, S. Kono, S. Suzuki, I. Nagakura, T. Sagawa, R. Kato, M. Watanabe, and S. Sato, Phys. Rev. B 12, 4320 (1975).

[5] G. K. Wertheim and S. Hüfner, Phys. Rev. Lett. 28, 1028 (1972).

[6] G. K. Wertheim, H. J. Guggenheim, and S. Hüfner, Phys. Rev. Lett. 30, 1050 (1973).

[7] K. S. Kim, Chem. Phys. Lett. 26, 234 (1974), and Phys. Rev. B 11, 2177 (1975).

[8] P. A. Cox, S. Evans, and A. F. Orchard, Chem. Phys. Lett. 13, 386 (1972).

[9] P. S. Bagus, J. L. Freeouf, and D. E. Eastman, Phys. Rev. B 15, 3661 (1977).

[10] C. R. Brundle, T. J. Chuang, and K. Wandelt, to be published.

[11] J. H. Scofield, J. Electron Spectrosc. 8, 129 (1976).

[12] C. R. Brundle, to be published.

[13] R. E. Watson, Phys. Rev. 118, 1036 (1960).

[14] L. E. Orgel, *An Introduction to Transition Metal Chemistry: Ligand Field Theory* (Methuen, London, 1966).

[15] H. M. Gladney and A. Veillard, Phys. Rev. 180, 385 (1969).

[16] P. S. Bagus and U. Wahlgren, Mol. Phys. 33, 641 (1977).

[17] In addition to the neglect of CI effects, Refs. 1 and 2 also give an incorrect E_{rel} for $^4T_{1g}(2)$ because of an error in Fig. 9 of Ref. 3b.