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Conduction-electron screening in metallic oxides: IrO_2

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Valence-band spectra from single crystals of IrO_2 reproduce the general features of a recent band-structure calculation. Good agreement with the unusual asymmetric core-electron line shapes is obtained by a perturbation-theory treatment of the d-electron many-body screening response.

It is now well established that the effects of conduction-electron screening manifest themselves quantitatively in core-electron photoemission line shapes of simple metals.[1] Although a theoretical line shape valid over an extended range is not available in closed form, the asymptotic solution has proved amazingly successful in representing experimental data from a variety of metals over a range of a few eV.[2,3] Only in metals with highly structured densities of states does one find significant deviations, which can, however, be related to the density of states through a simple formalism.[4]

As a subject of investigation we selected the metallic rutile structure oxide IrO_2 because band-structure calculations[5] show a strongly modulated density of states and the core-level spectra are known to be very asymmetrical.[6] Single crystals of IrO_2 were grown by chemical vapor transport using an NiO catalyst. The crystals grow as faceted prisms. Oriented growth on a TiO_2 substrate crystal was also demonstrated. The best results were obtained using the following conditions: Iridium metal was reacted with 1 atm of flowing dry O_2 at 1150 °C in a quartz tube. The resultant IrO_3 was allowed to pass over NiO at 1150 °C and then into a lower-temperature region. IrO_2 was found to crystallize at 900–950 °C. Experiments without the NiO catalyst produced excessive intergrowth due to extraneous nucleation.

Prismatic crystals with a needlelike morphology oriented along the [111] axis and dimensions typically $1\times2\times10$ mm^3 were used in the experiments. Attempts to vacuum-cleave these crystals along the natural-growth faces were not successful. Data were obtained after two types of surface preparation: (1) heating in 10^{-9}-Torr vacuum to a temperature just short of decomposition[7,8] and (2) abrasion with a diamond file. A modified HP 5950A ESCA spectrometer was used.

VALENCE-BAND SPECTRUM

A comparison of the XPS (x-ray photoemission spectroscopy) valence-band spectrum from a natural (110) growth face of IrO_2 with the total density of states (DOS) calculated by Mattheiss[5] is given in Fig. 1. Heating in vacuum up to the point of decomposition did not alter the experimental result in any significant detail. Similar spectra have also been obtained from surfaces abraded in vacuum, from powders obtained by the reaction of the chloride with oxygens,[6] and from thermally oxidized Ir metals.[9]

The experimental spectrum and the total DOS are, of course, not strictly comparable because the photoelectric cross sections[10] for O $2p$ electrons are much smaller than those for Ir $5d$. The experimental results, therefore, largely represent the $5d$ component of the DOS. By comparison with the partial DOS for the closely related compound RuO_2 (Ref. 5), it appears that there is a significant $5d$ component in all parts of the $2p$ band except for the peak at 3.9 eV. Bearing this in mind one finds a close correspondence between the general features of the theory and the experiment. The major differences lie in a 0.5 to 1.0 eV shift toward greater binding energy in the experiment and the loss of detail, i.e. the DOS is ~10% wider and the individual bands somewhat broader than indicated by the theory. The loss of resolution is due only in small part to the 0.6-eV experimental resolution which is confirmed by the cutoff at the Fermi energy. Based on the known resolution function, the gap between the O $2p$ and Ir t_{2g} bands should be resolved in the data. It is therefore clear that the experimental data are affected by another mechanism, namely, lifetime broadening. The lifetime of holes in the valence band should decrease rapidly with increasing binding energy, leading to progressive broadening of the deeper states in accord with the experimental observations.

CORE-LEVEL SPECTRA

Both Ir $4f$ and O $1s$ core-level spectra exhibit strongly asymmetric lines, but the shape is not compatible with the asymptotic Mahan, Nozières and De Dominicis (MND) theory.[11,12] This is not

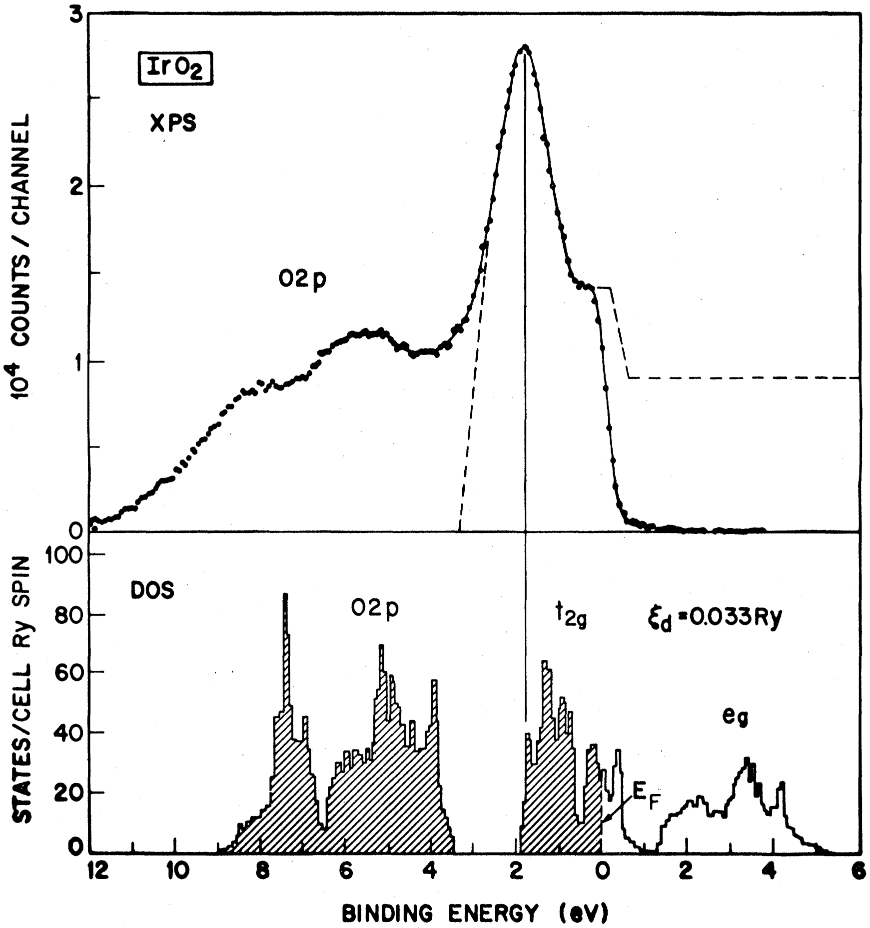

FIG. 1. Comparison of the XPS valence-band spectrum of IrO_2 with the density of states due to Mattheiss, Ref. 5. The dashed line in the upper half is the model density of states used in the calculation of the core-electron line shape.

a novel observation; see for example, the work on $NbSe_2$,[13] Na_xWO_3,[14] and Pt (Ref. 4) in which such line shapes are attributed to the final-state screening response. Strange line shapes could also arise simply from the presence of inequivalent atoms in the initial state. Such initial-state effects due to deviations from stoichiometry in the bulk or surface are ruled out because the spectrum is not sensitive to the method of sample preparation. No change is found on heating, even close to the temperature at which metallic Ir appears, ruling out other oxides as a source of the tailing. (It is known independently that IrO_2 is the only stable oxide at room temperature.[8]) Final-state effects require more detailed consideration.

The connection between the core-level line shape and the valence-band structure is made[4] through a perturbation-theory model due to Hopfield.[15] One first calculates the joint density of states for electron-hole pair excitations N_{eh} numerically from the one-electron DOS, assuming a constant excitation matrix element. The equation for the line shape

$$I(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} dt \exp\left(\int_0^{E_c} \frac{\alpha(\epsilon)}{\epsilon} (e^{-i\epsilon t} - 1) d\epsilon\right), \quad (1)$$

where

$$\alpha(\epsilon) = N_{eh}/\epsilon \quad (2)$$

can then be integrated numerically. For $\alpha(\epsilon) = \alpha$ (a constant), this formalism reproduces the asymptotic solution of Nozières and DeDominicis,[12] namely, a line shape of the form $(\omega - \omega_0)^{\alpha-1}$. This line shape (convoluted with a lifetime-width Lorentzian and the instrumental resolution function) does not give a satisfactory fit to the data for any set of parameters. This is in accord with expectations because a constant $\alpha(\epsilon)$ is hardly appropriate for IrO_2 with its narrow, high-density-of-states d bands. The details of the conduction band should enter explicitly into the calculation of the core-electron line shape.

In order to carry out this program we need both the occupied and the empty parts of the density of states. An initial calculation using the theoretical DOS gave generally discouraging results. Failure was traced to the gap in the DOS between 1.9 and 3.5 eV. Since the valence-band data show that the peak of the t_{2g} DOS actually lies at 1.9 eV, this comes as no surprise. We then decided to construct a model DOS from the experimental valence-band spectrum for use in the line-shape calculations. No attempt was made to reproduce the details of the theoretical DOS since these are lost in the calculation of $\alpha(\epsilon)$, which is in effect an averaging about E_F with increasing window. The resulting DOS, shown by the dashed lines in the upper part of Fig. 1, is an attempt to represent both the filled and empty 5d bands. Since the asymmetric tail of the core spectra (see Figs. 2 and 3) extends out ~3 eV from the peak, we require a reasonable representation of the DOS within ±3 eV of E_F. In view of the 0.6-eV full width at half maximum (FWHM) of the resolution function and the ~0.2-eV lifetime width of the Ir 4f level, structure on a scale finer than 0.7 eV is not required. The major adjustable parameter, the level of the plateau representing the e_g band, was determined empirically. It was found that inclusion of the O 2p band gave unrealistic line shapes.

The optimum fit obtained by this procedure is shown in Fig. 2. The two spin-orbit components were constrained to have the same shape and the theoretical 3:4 intensity ratio. (The anomalously large peak height of the $4f_{5/2}$ component is the result of the long tail of the $4f_{7/2}$ line.) The spin-orbit splitting was found to be 3.00 ± 0.05 eV.

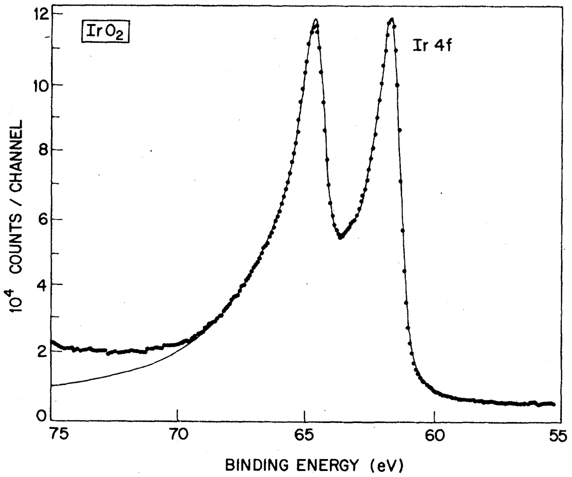

FIG. 2. Ir 4f core-electron spectrum of IrO_2. The solid line is the result of integrating Eq. (1) with an $\alpha(\epsilon)$ obtained from the model density of states in Fig. 1.

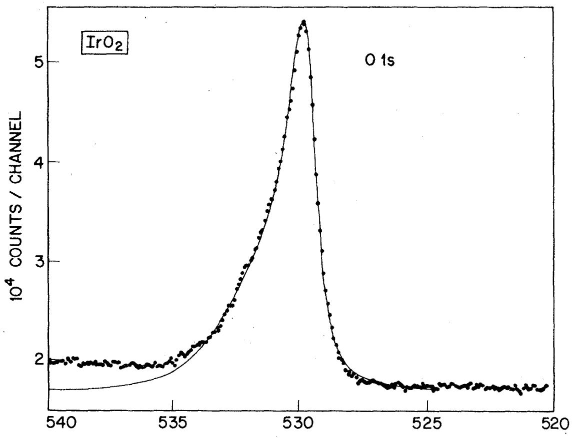

FIG. 3. O 1s line of IrO_2, fitted as in Fig. 2.

In order to test the sensitivity of this procedure to the details of the DOS we studied the effect of moving the Fermi level from the experimentally determined position. It was found that the fit deteriorated significantly, even for shifts as small as 0.1 eV. This was traced to the fact that the calculated line shape is extremely sensitive to the location of the high-density t_{2g} peak relative to E_F. This shows that the tail represents d-band excitations and is dominated by those from the high DOS region of the occupied t_{2g} band to the states just above E_F, with an energy of ~2 eV.

The effective singularity index is large, 0.34, reflecting the high DOS at E_F. However, the line shape cuts off much more strongly than the corresponding Doniach-Sunjic[16] function. This is a result of the nature of the model DOS which terminates 3.3 eV below E_F.

The Ir 4f spectrum is thus compatible with the assumption that its unusual shape derives from the screening response of the 5d conduction electrons. The model DOS should strictly be associated with the *local final-state DOS* in the vicinity of a core-ionized Ir atom. It could, in principle, differ significantly from the initial-state DOS. However, the final-state DOS is not determined with sufficient precision to consider possible differences. Past experience in the analysis of the line shapes of a variety of metals suggests that this difference is generally not significant in the region near E_F which determines the line shape. The major exception is the semimetal graphite.[17]

The other possibility that should be considered is that the core hole splits off a state from the bottom of the 5d band. This would produce a satellite corresponding to the empty state lying at an energy greater than that of the main line by binding energy of the split-off state. Such a state would be greatly lifetime broadened and would fall into the gap between the O $2p$ and Ir $5d$ bands, giving it a binding energy greater than ~3 eV. Since such a satellite is not resolved in the data of Fig. 2, we consider this model inappropriate.

A further argument against it comes from the line shape of the O $1s$ line. The salient observation is that O $1s$ line, Fig. 3, has a shape not unlike that of the Ir $4f$'s. This is a reasonable result for a simple screening model since the same conduction-electron states screen both Ir $4f$ and O $1s$ holes. The Friedel state would be split off by an Ir $4f$ hole, but not by an O $1s$ hole requiring quite different line shapes for the two constituents. The present case is then quite different from that encountered in the Na_xWO_3, where the predictions of the Friedel model are more nearly realized.[14]

In summary, we have found that the unusual asymmetric core-electron line shapes in the metallic oxide IrO_2 can be understood in terms of many-body screening response of the $5d$ conduction electrons.

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