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Auger and autoionization features of clean and oxygen-exposed iron

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Studies have been made of the $M_{2,3}VV$ Auger transition and the $3p$-core loss feature for the Fe(110) surface, both for the clean surface and after various dosages of oxygen. The peaks within the Auger feature are shown to be directly related to the oxygen-induced changes in the d band observed in ultraviolet photoemission spectroscopy studies. Changes in intensity and position of the anomalous peak above the $M_{2,3}VV$ Auger threshold and the feature past the $3p$-core loss threshold after oxygen exposure suggest a correlation between the two features. The major core loss feature is interpreted as a resonant excitation of $3p$ electrons to a localized state above the Fermi level, with the decay of this state by direct recombination, resulting in an autoionization peak above the Auger threshold. Although changes in autoionization features are rare as they are quasiatomic and hence less likely to be affected by chemical environment, we interpret our results to be due to changes in the excited state from $3d$ for the clean surface to a $4s$ state, localized by the presence of the $3p$ hole, in the oxide.

INTRODUCTION

Recently there has been a considerable amount of interest shown in processes involving excitation of the $3p$ level, in the first transition-metal series, to localized excited states and their subsequent deexcitation. Such resonant behavior was first observed for the noble gases,[1] and subsequently invoked for a solid by Dufour and Bonnelle,[2] who related the "giant resonances" in x-ray absorption and electron-loss spectra to the anomalous feature above the Auger transition in Gd. Since then numerous studies of the lanthanides and actinides have shown autoionization features involving excitations to highly localized f states.

In the first transition-metal series the unfilled $3d$ levels are intrinsically less localized than the f levels of the higher transition-metal series. However, autoionization has been used to explain the line shape in the $3p$ x-ray absorption spectra of the first transition-metal series, which Dietz *et al.*[3] and Davis and Feldkamp[4] have shown to be due to a Fano-type interference between the $3p^63d^n \rightarrow 3p^53d^{n+1}$ and the $3p^63d^n \rightarrow 3p^63d^{n-1}+\epsilon f$ transitions, because the $3p^53d^{n+1}$ state autoionizes to $3p^63d^{n-1}+\epsilon f$. Following the resonant photoemission study of Ni by Guillot *et al.*,[5] autoionization processes in the first transition-metal series have attracted considerable interest. Recently Bertel *et al.*,[6] studying Ti, and Bader *et al.*,[7] studying V and Cr, have identified features due to the excitation $3p^63d^n \rightarrow 3p^53d^nd^*$ and subsequent emission $3p^53d^nd^* \rightarrow 3p^63d^{n-1}+\epsilon l$ of autoionization levels in the $3p$ loss and $M_{2,3}VV$ Auger features, respectively. For these metals at the low-Z end of the series, the energy separation between the normal and autoionization features is large and this makes for ease in identification. In the case of Fe there is a small energy separation between the features which has led to a degree of uncertainty as to the nature of the $M_{2,3}VV$ Auger transition. This problem is exacerbated on oxidation, as the autoionization peak grows to rival the normal Auger features in intensity.

Our results confirm the presence of autoionization features in the electron spectrum of Fe and show them undergoing changes in both energy and intensity on oxygen absorption. Such changes are unexpected, since the process is quasiatomic, requiring a high degree of localization of the excited state, making them reasonably independent of the chemical environment. We interpret our results in terms of a change in the excited state from a localized $3d$ state for the clean surface to a $4s$ state on oxide formation.

EXPERIMENTAL

The experiments were performed in an ultrahigh vacuum system with a base pressure in the 10^{-10}-torr range. The spectra were recorded in first- and second-differential mode using a Varian cylindrical mirror analyzer with coaxial electron gun. Resolution of 1% was obtained with a 1.0-V peak-to-peak modulation potential on the external cylinder.

The iron single crystal was oriented by Laue back-reflection x-ray analysis and was subsequently mechanically polished to produce a surface within $\frac{1}{4}°$ of the (110) orientation. The specimen was mounted on tungsten wires attached to a Varian crystal manipulator. Cleaning of the surface was carried out by cycles of argon-ion bombardment (400 eV, 2 μA cm^{-2} for 20 min) and resistive heating. This procedure was found to remove the nitrogen, sulfur, and oxygen contamination from the surface and near-surface region but left a very small, though detectable trace of carbon.

High-purity (99.998%) oxygen was introduced into the system via a high-precision variable leak valve. For oxygen exposures in the range 10^{-7} to 10^{-1} torr sec, oxygen pressures were increased correspondingly over the range 10^{-8} to 5×10^{-5} torr and the time chosen appropriately. During oxygen exposure the electron gun was switched off. However, the nude ionization gauge located in a short side tube in close proximity to the crystal surface must be considered to produce excited oxygen.[8,9]

RESULTS

The super-Coster-Kronig $M_{2,3}VV$ Auger feature, in first-differential mode, is shown in Fig. 1. This result for the clean surface is similar to previously published results[10–14] and shows a large asymmetric peak with a negative excursion at 47 eV followed by an anomalous step at 51 eV. Adsorption of oxygen results in a general decrease in the intensity and energy of the Auger feature while the high-energy peak becomes more prominent with no significant energy shift. Even though the $dN(E)/dE$ mode gives a qualitative "fingerprint" of the surface, the spectra in $-d^2N(E)/dE^2$ mode, Fig. 2, give a more quantitative result as peaks here correspond to peaks in $N(E)$ mode without the problem of a steeply sloping background. In second-differential mode, the asymmetry of the main feature in first differential mode is seen to be due to two peaks centered at 40.0 and 44.4 eV. As the surface is exposed to oxygen the 40-eV peak remains effectively unchanged in intensity and energy while the major clean peak at 44.4 eV steadily decreases in intensity. At a 10-L oxygen exposure the anomolous high-energy peak begins to become prominent and steadily increases in intensity until it rivals the other Auger peaks in intensity at saturation coverage of oxygen.

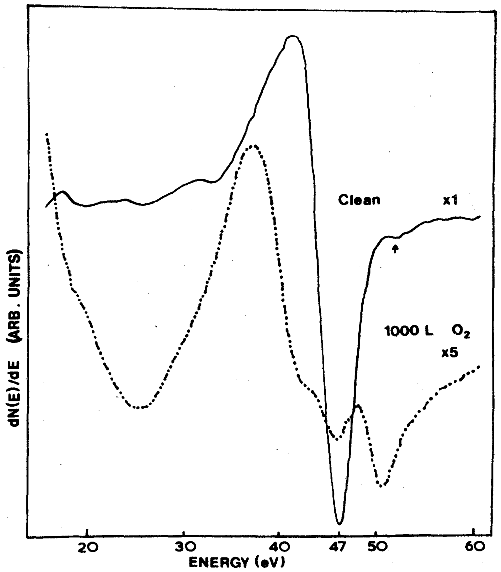

FIG. 1. $M_{2,3}VV$ Auger feature for clean and oxygen-saturated Fe(110) surfaces [$dN(E)/dE$ mode]. Primary beam energy, 400 eV. [1 langmuir (L)$\equiv 10^{-6}$ Torr sec.]

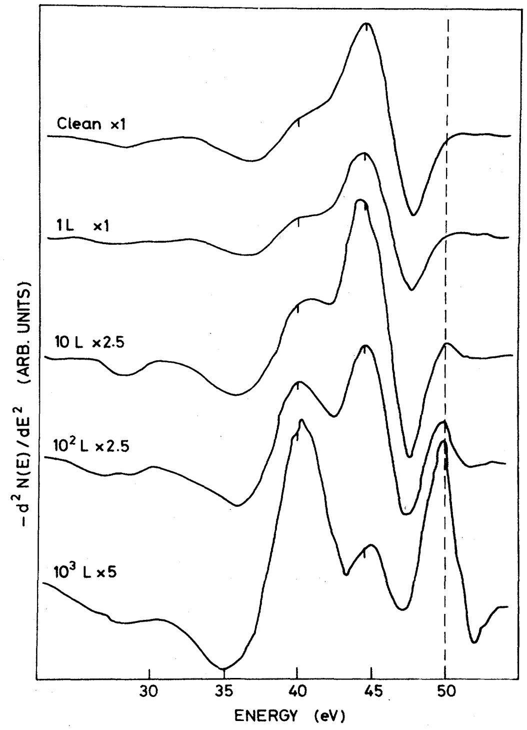

FIG. 2. Series of $M_{2,3}VV$ Auger spectra for clean and oxygen-exposed Fe(110) surfaces [$-d^2N(E)/dE^2$ mode]. Primary beam energy, 400 eV.

The L_2, L_3, M_1, and $M_{2,3}$ core losses have been observed for various primary beam energies and doses of oxygen. The L_2, L_3, and M_1 levels were found to by symmetric and their core-loss energy coincided with their accepted binding energy. On oxygen exposure no changes in their intensity or loss energy were observed. The $M_{2,3}$ level, on the other hand, is an asymmetric feature which undergoes both changes in intensity and loss energy on absorption of oxygen (Fig. 3). The $M_{2,3}$ core loss feature for increasing oxygen exposure is shown, in second-differential mode, in Fig. 4. The clean $M_{2,3}$-core loss consists of two peaks E and F with loss energies of 53.2 and 55.2 eV, respectively. The first observable changes in the feature occurs at 10-L exposure; as the oxygen exposure is increased, peak F undergoes an increase in loss energy and a dramatic increase in intensity, while peak E decreases in energy slightly. At saturation coverage of ox-

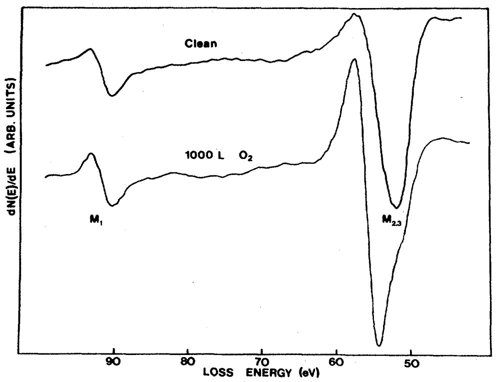

FIG. 3. M_1 and $M_{2,3}$ core loss spectra for clean and oxygen-saturated Fe(110) surfaces. Primary beam energy, 300 eV.

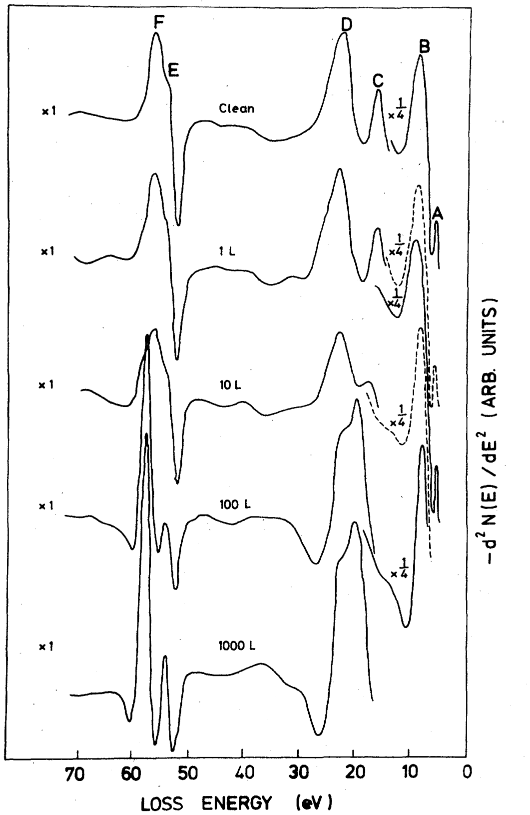

FIG. 4. Electron-energy-loss spectra for clean and oxygen-exposed Fe(110) surfaces. Primary beam energy, 150 eV.

ygen, the $M_{2,3}$-core loss feature consists of two distinct peaks at 53.0 and 56.7 eV.

DISCUSSION

A summary of the major peak positions in the Auger and $3p$-core loss results together with our calculations for these peaks are shown in Table I. The Auger energies were calculated using the expression employed in a number of recent studies.[15,17] Using ultraviolet photoemission spectroscopy (UPS) and x-ray photoemission spectroscopy (XPS) values for the binding energies and the U_{eff} calculated by Yin *et al.*[17] (see data in Table I and references therein) from the $L_3M_{4,5}M_{4,5}$ clean-iron Auger transition, we calculate that peaks in the $M_{2,3}VV$ transition should occur at 40.2 and 44.4 eV, in excellent agreement with the experimental result. In previous Auger studies the small feature at 50 eV has generally been accepted as being part of the normal $M_{2,3}VV$ Auger transition.[10–14,18] The accepted value of the $3p$ binding energy has decreased significantly since these studies were made and it is now clear that this feature cannot be considered to be part of the normal $M_{2,3}VV$ Auger transition since it lies above the $M_{2,3}VV$ threshold. As will be shown below, this feature can be explained in terms of an autoionization process.

TABLE I. Comparison between observed and calculated major peak positions (in eV) in the Auger and $3p$-core loss spectra from the Fe(110) surface. AES represents Auger electron spectroscopy and BE represents binding energy. E_{3p}: BE of $3p$ level from XPS (Ref. 15); E_{3d}: BE of valence-band peaks in UPS data (Refs. 15 and 16); ϕ: work function (4.8 eV) (Ref. 16); U_{eff}: valence-band hole-hole Coulomb interaction (2.6 eV) (Ref. 17); $(E_{\text{exc}})_{3p}$: $3p$ resonant excitation energy from core loss results (clean: 55.2 eV; Fe plus O: 56.7 eV).

Clean Fe(110)				
$M_{2,3}VV$ AES	(expt)	40.0	44.2	50
$M_{2,3}VV$	(calc)[a]	40.2	44.2	
Autoionization	(calc)[b]			49.8
$3p$-core loss	(expt)	53.2	55.2	
$3p$ BE	(XPS)[c]	52.0	53.0	
$3d$ BE	(UPS)[d]	0.6	2.7	
Fe(110) plus oxygen				
$M_{2,3}VV$ AES	(expt)	40.0	44.4	49.8
$M_{2,3}VV$	(calc)[a]	39.6	44.6	
Autoionization	(calc)[b]			49.2
$3p$-core loss	(expt)	53.0	56.7	

[a] $E_{\text{AES}}=E_{3p}-2E_{3d}-\phi-U_{\text{eff}}$.

[b] $E'=(E_{\text{exc}})_{3p}-E_{3d}-\phi$.

[c] Reference 15.

[d] References 15 and 16.

On exposure to oxygen a general decrease in the size of the $M_{2,3}VV$ Auger peak is observed and at saturation oxygen coverage, the peak positions were found to be at 40.0, 44.6, and 49.8 eV, in agreement with past Auger studies of the Fe-O system.[10–14,18] The speculation in the literature regarding these features has been mainly concerned with the major feature at 40 eV. Explanations for this peak are as follows:

(i) cross transitions of the type Fe($3p$)O($2p$)O($2p$),[11,12]

(ii) a simple chemical shift,[10,13]

(iii) an interfacial peak of the type Fe($3p$)Fe($3d$)O($2p$),[14] and

(iv) changes in the valence-band structure at the surface.[18]

(i) and (ii) can be shown to be ruled out on energetic grounds since there is no evidence of any significant chemical shift in the $M_{2,3}$ level (if there was a chemical shift in the $M_{2,3}$ core then a similar shift would be expected in the core loss results for the other core levels, and no such shifts are observed) and the position of the O($2p$) level at 5.3 eV below E_F would give rise to a peak at least 4 eV below the energy observed.

An explanation of the 40.0-eV peak in terms of the interfacial transition Fe($M_{2,3}$)Fe($M_{4,5}$)O($L_{2,3}$) would seem feasible on energetic grounds given the UPS binding-energy values of 5.3 eV for O($L_{2,3}$) and 2.7 eV for Fe($M_{4,5}$). If this was the correct assignment the growth in the 40-eV Auger peak would be expected to occur in the (1—10)-L oxygen exposure range in which the O($L_{2,3}$), observed in UPS studies, undergoes its major growth.[16,19,20] However, for the results shown here, the 40-eV peak does not grow larger for oxygen exposures less than 10 L. Indeed any explanation involving the O(2*p*) electrons seems unlikely given the general decline in the intensity of the Auger feature with increasing oxygen exposure. Furthermore, the intensities of the iron core loss features do not decrease with oxygen. "Shadowing" of the iron by oxygen is ruled out (cf. intensity of Auger and core loss features). The decrease in the Auger feature must be due to the bonding of the iron with the oxygen decreasing the number of *d*-band electrons available to take part in the Auger transition. We therefore favor an explanation based purely on the observed changes in the Fe *d* band. The clean Fe(110) UPS spectra show a major and minor peak in the band at binding energies of approximately 0.6 and 2.7 eV, respectively.[15,16,19,20] As oxygen is adsorbed the UPS difference curves (16) show a decrease in the intensity of the 0.6-eV peak while the 2.7-eV peak does not appreciably alter in intensity until, at high exposures, the 2.7-eV peak becomes the dominant *d*-band feature. Given these binding energies and relative sizes we calculate the energy of the major normal oxygen exposed Auger feature to be 40.2 eV and a minor peak at 44.4 eV in excellent agreement with the observed values (40.0 and 44.6 eV).

For the clean surface spectra, the higher energy Auger feature cannot be explained in terms of the normal Auger processes. Dietz[3] and Davis and Feldkamp[4] have shown that the 3*p*-core excitation line shape, in the first transition-metal series, is a consequence of the $3p^5 3d^n d^*$ excited state decaying to $3p^6 3d^{n-1} + \epsilon f$ in an autoionization process. The electron (ϵf) emitted to the continuum, in analogy to the results obtained for the rare earths, gives rise to the feature above the $M_{2,3}VV$ threshold with an energy equal to the 3*p* excitation energy less the sum of the binding energy of the 3*d* electron and work function. An energy-level schematic representation of the 3*p*-core loss results is shown in Fig. 5. For the clean surface the first peak *E* has an energy equal to the 3*p* binding energy and is due to raising 3*p* electrons to the first available empty *d* states just above E_F. The second peak *F* is due to raising electrons to a maxima in the density of empty *d* states 2.2 eV above E_F. This is in qualitative agreement with the paramagnetic calculations of Moruzzi *et al.*,[21] which show the maxima in empty *d* states to be 1.75 eV above E_F, and the resonant photoemission results of Chandesris *et al.*,[15] which show the photon energy at resonance to be 1.5 to 2.4 eV higher than the 3*p* binding energy. On formation of the oxide the two 3*p*-core loss peaks split. The loss energy of the first peak decreases by 0.2 to 53.0 eV, while the major peak shifts to higher loss energy. These peaks are assigned to 3*p* electrons being raised to the top of the valence band ($3p \rightarrow 3d$) and the bottom of the conduction band ($3p \rightarrow 4s$), respectively. This suggests a band gap of 3.7 eV, identical to the band gap reported for FeO.[22,23] Thus the changes of the resonant core excitations are seen to be due to changes in the final state. For the clean surface, 3*p* electrons are raised to localized *d* states while for the oxide the excited state is a 4*s* state which is sufficiently localized, by the presence of the incompletely screened 3*p* hole in the insulating oxide, to take part in a direct recombination process and emit band electrons which are manifested in the peak above the $M_{2,3}VV$ Auger feature.

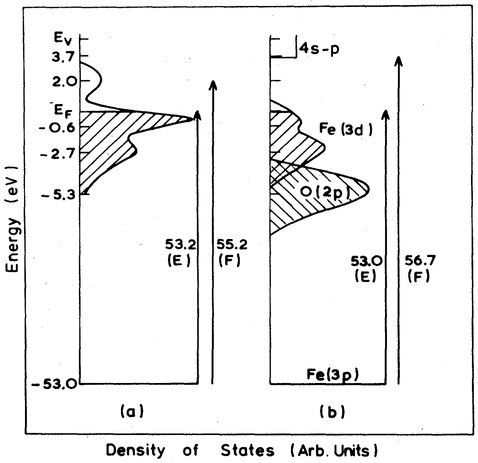

FIG. 5. An energy-level schematic of 3*p*-core loss processes for the Fe surface. The occupied density of states are a representation of the UPS electron distribution curves and the binding energies indicated are those used for the calculations shown in Table I. (a) Clean Fe(110) surface; (b) Fe(110) surface exposed to oxygen.

The core loss results for clean Fe (Fig. 4) show the excitation energy of 3*p* electrons to be 55.2 eV. In a direct recombination process this energy will be given to a 3*d* electron which will be emitted with an energy of 49.8 eV (see Table I). This result confirms the assignment of an autoionization peak made recently by Bader *et al.*[7] from literature comparisons, to the peak observed in a spin-polarized Auger study of clean iron at 50 eV.[24] The correlation of the 3*p* excitation peak, seen in the core loss result, with the peak above the $M_{2,3}VV$ Auger peak becomes clearer on addition of oxygen to the Fe surface as both features grow larger with increasing oxygen exposure and also undergo energy shifts which are seen to be consistent. The autoionization peak becomes prominent at 10-L exposure concomitant with the first changes in the 3*p*-core loss. At higher oxygen exposures it grows to rival the normal Auger features in size while the high 3*p*-loss feature also grows remarkably and undergoes a shift to higher loss energy. At saturation coverage of oxygen the 3*p* excitation energy is 56.7 eV; consequently, a direct recombination will emit *d*-band electrons resulting in a feature at 49.2 eV in agreement with the energy position of the anomalous peak above the threshold of the $M_{2,3}VV$ Auger transition.

Our results for both the clean and oxidized Fe surfaces clearly indicate an excitation of the 3*p* level to a localized quasiatomic state followed by direct recombination which emits a 3*d* electron with an energy higher than the normal Auger energy. Such processes have been invoked to explain similar features in the lanthanides, actinides, and recently in the first transition-metal series.[2,6,7,25,26] Very few of these studies show either growth or shift in these features (either core-loss, electron-excited autoionization, resonant photoabsorption, or resonant photoemission) on oxidation and it has been argued, for the rare earths,[25] that this is because of the highly localized nature of the final state which causes the autoionization channel to be virtually independent of environment.

Growth in core-loss resonances on absorption, such as the $3p$ loss, can be observed in the figures of a number of papers but little attention has been afforded them; for example, Er/O_2 $5p \rightarrow 5d$ (Fig. 3 in Ref. 27), Sc/N_2 $3p \rightarrow 3d$ (Fig. 2 in Ref. 28), and we have observed it in our core loss studies of Co/O_2 and Ni/O_2. In the resonant photoemission experiments on Ni/O_2 (Ref. 29) and Zn/Zn-Pc (Ref. 30) the resonant satellites are considerably stronger in the compounds than in the clean metals, and it is argued that this reflects an increase in the number of empty states available for excitation after bonding. We have observed L_2, L_3, M_1, and $M_{2,3}$ core losses in Fe, Co, and Ni for both clean and oxygen-saturated surfaces. While all $M_{2,3}$ ($3p$) losses show dramatic changes both in loss energy and size with oxygen absorption, the deeper M_1, L_3, and L_2 levels show no appreciable changes (Fig. 3). Such results make it clear that resonant excitations are not entirely dependent on the intrinsic nature of the excited state but are also dependent on the amount of overlap between the ground and excited states. Consequently, although an increase in the number of states available for excitation can be used as an explanation for the enhancement of the $3p$ resonance on oxidation, we point out that it could be due, in part, to weaker screening of the $3p$ hole on formation of the insulating oxide.

As in the case with growth there are few references to any significant energy shifts associated with oxidation in resonant core-excitation experiments. The notable exception to this is Ni, which has a resonant photoemission peak undergoing enhancement and a 3-eV shift on oxide formation along with a 2.9-eV shift in the $3p$-core loss.[31] Bertel *et al.*[6] show a shift in the autoionization feature of TiO_2; however, this is explained in terms of a change in the valence band as the $3p \rightarrow 3d$ excitation energy, observed in the electron loss spectra, is not affected. In uranium, where the autoionization peak is at an energy lower than calculated (but still well above the Auger threshold) and shifts on oxidation, Matthew[32] argues that this reflects the less localized nature of the actinides' $5f$ electrons compared to the lanthanides' $4f$ electrons. Such an argument for the first transition-metal series cannot be used, since greater changes would be expected at the low-Z end of the series (such as Ti,Sc) where the $3d$ states are less localized than at the higher Z end of the series.

The results presented here clearly demonstrate the presence of localized excited states associated with the excitation of the $3p$-core level. The changes observed in the $3p$-core loss and $M_{2,3}VV$ Auger feature indicate a change in the excited state from $3d$ to $4s$ in character on oxide formation: For the clean surface $3p^6 3d^n \rightarrow 3p^5 3d^n 3d^* \rightarrow 3p^6 3d^{n-1} + \epsilon f$ and for the oxide surface $3p^6 3d^n \rightarrow 3p^5 3d^n 4s^* \rightarrow 3p^6 3d^{n-1} + \epsilon f$. The resonant photoemission studies of Iwan *et al.*[30,33] and Thuler *et al.*[27] in Zn and Cu, with full d bands, are the only ones to suggest that an autoionization process can occur involving final states which are not intrinsically localized. We suggest that it is occurring in oxidized Fe and may well be an explanation for the 3-eV shift in the controversial resonant photoemission peak of Ni on oxidation.

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