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Autoionization and Auger features of clean and oxygen-exposed surfaces of Fe, Co and Ni

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The $M_{2,3}VV$ Auger and $3p$ core loss spectra for clean and oxygen-exposed surfaces of the transition metals Fe, Co, and Ni have been studied. All the peaks observed in the Auger spectra are accounted for in terms of both atomic and bandlike $M_{2,3}M_{4,5}M_{4,5}$ transitions and an autoionization emission involving the decay of a localized excited state. For the clean surfaces the localized excitation and subsequent deexcitation by autoionization emission is considered, within a quasiatomic model, to be $3p^63d^n \rightarrow 3p^53d^nd^* \rightarrow 3p^63d^{n-1}+ef$. However, upon oxidation of these surfaces, the splitting observed in the $3p$ core loss spectra and the energy of the observed autoionization peaks indicate changes in the nature of the excitation due to the chemical environment. This is contrary to the accepted notion for such quasiatomic processes, which are considered essentially unaffected by the chemical environment. Further, for these oxidized surfaces, the observed autoionization features are shown to be associated with the excitation of $3p$ electrons to a localized state at the bottom of the conduction band as opposed to the empty d states at the top of the valence band.

INTRODUCTION

The electronic structure of the transition metals has been of continuing interest to both experimentalists and theorists, not only because of their usefulness as catalysts, but also because their d bands defy easy categorization. The elements Fe, Co, and Ni are particularly interesting as their d bands bridge the gap, within the Hubbard model, between the change from bandlike to atomiclike behavior. In this paper we present results of a study of the $M_{2,3}VV$ Auger and the $3p$ core loss spectra for clean and oxygen-saturated (110) surfaces of these elements. Although numerous Auger studies have been performed on these surfaces, on the whole little useful electronic information has been extracted from the spectra. One of the problems associated with energy calculations for the $M_{2,3}VV$ spectra of these elements has been the anomalous features near, but above, the energy threshold which have, until recently, been assumed to be part of the $M_{2,3}VV$ Auger transition. Autoionization emission provides an explanation for these features.

Autoionization is the deexcitation of an excited atom by the emission of an Auger-like electron and is therefore generally associated with atomic spectra studies. It was first invoked to explain features in the electron spectra of solids in 1974 by Dufour and Bonnelle[1] in their work on Gd. Since then numerous studies of these features in other rare earths have been reported. Felton *et al.*[2] showed that for EuO the initial excitation can be observed in the electron loss spectra and the energy of the autoionization feature can thus be calculated. For the rare earths such quasiatomic behavior has been justified by the intrinsically localized nature of the f states involved in such processes. For the first transition-metal series Dietz *et al.*,[3] studying Ni, and later Davis and Feldkamp,[4] in their study of Cr, Mn, Fe, Co, and Ni, interpreted the line shape of the $3p$ core losses, of the clean surfaces, in terms of an atomic model involving $3p^63d^n \rightarrow 3p^53d^{n+1}$ excitation and its subsequent deexcitation $3p^53d^{n+1} \rightarrow 3p^63d^{n-1}+ef$. The peaks associated with the ef electrons emitted in such an autoionization process have only been recently identified with the features above the $M_{2,3}VV$ energy threshold for elements of the first transition-metal series.[5–8]

In our earlier paper on Fe,[8] we confirmed the presence of autoionization features for both the clean and oxidized surfaces. The behavior observed on oxidation was interpreted as being due to a change in the excitation from $3p \rightarrow 3d^*$ for the clean surface to $3p \rightarrow 4s^*$ in the oxidized surface. This is in marked contrast to the case of the rare earths on gas adsorption, where it has been argued that the quasiatomic nature of the autoionization process causes them to be effectively immune to changes in chemical enviornment. In this paper we extend our Fe study to that of Co and Ni and verify that the core excitation and autoionization energies do change on oxygen adsorption, and propose that the localized $3p$ excitations involved, for the oxidized surfaces, are not quasiatomic.

The identification of the autoionization peaks has enabled us to interpret and calculate, in a simple way, the energy position for every peak observed in the region of the $M_{2,3}VV$ Auger feature for both the clean and oxidized surfaces.

EXPERIMENTAL

Single-crystal samples of Fe, Co, and Ni were oriented by Laue back-reflection and polished to within $\frac{1}{4}$ degree of the [110] orientation. Experiments were performed in an ultrahigh vacuum system with a base pressure in the 10^{-10}-Torr range. Spectra were recorded using a Varian single-pass cylindrical mirror analyzer with a coaxial electron gun. Resolution of 1% was obtained using a 1.0-V peak-to-peak modulation on the external cylinder.

In vacuo cleaning of the samples was performed using

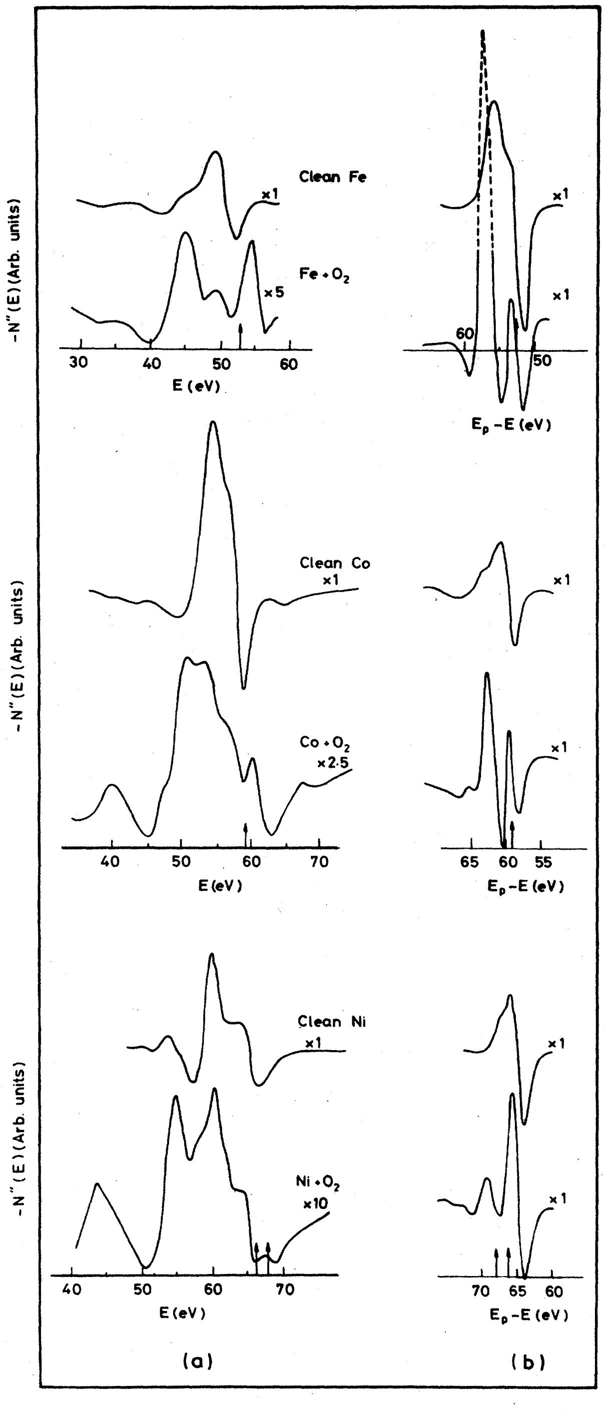

FIG. 1. (a) The $M_{2,3}VV$ Auger spectra. [$-N''(E)$ mode] of the clean and room temperature oxygen-saturated (110) surfaces of Fe, Co, and Ni. Note: the energy scale is referenced to the sample's Fermi level. (b) The clean and oxygen-saturated $3p$ core loss spectra of Fe, Co, and Ni obtained in $-N''(E)$ mode using 150 eV incident electrons. The energy scale is the loss energy measured from the peak of the elastically reflected primary beam. Arrows on the energy axes indicate the clean XPS binding energies of the $3p$ levels.

repeated cycles of argon-ion bombardment and resistive heating. Care was taken so that the crystals were not heated above their phase-transition temperatures. The Ni sample was cleaned such that no contaminant Auger peaks could be observed before or after experimental runs, while for Fe a small but detectable trace of carbon was always present. In the case of Co the major contaminants (C, S, O, Cl, and N) were removed below the level of detection; however, argon from the ion bombardment could only be partially removed as heating resulted in heavy Cl contamination and consequently the Co surface must be considered to be damaged.

Oxygen adsorption was performed at room temperature using high-purity (99.998%) oxygen introduced via a high-precision variable leak valve. During oxygen exposure the electron gun was switched off; however, the nude ionization gauge, located in a short-side tube near the sample surfaces, was on throughout the adsorption process.

Calibration of the energy axis, with respect to the sample Fermi level, was achieved by the use of an elastically reflected primary electron in a manner similar to that described by Powell *et al.*,[9] with their value of 59.4 eV for the clean Ni $M_{2,3}VV$ Auger peak used as the energy reference.

RESULTS

Figure 1 shows the features in the electron-excited electron spectrum associated with the creation of $3p$ core holes (the $3p$ core loss) and their annihilation by the $M_{2,3}VV$ Auger transitions for both the clean and oxygen-saturated (110) surfaces of Fe, Co, and Ni. Arrows on the energy axis mark Fuggle's[10] x-ray photoelectron spectroscopy (XPS) binding energies for the $3p$ levels which indicate the expected energy thresholds for the $M_{2,3}VV$ transitions and $3p$ core loss spectra.

The analysis of the peaks shown in Fig. 1 is based principally on energetic grounds. Peaks below the $M_{2,3}VV$ threshold are interpreted in terms of both atomic and bandlike $M_{2,3}M_{4,5}M_{4,5}$ transitions while those above the threshold are discussed in terms of autoionization processes. The $3p$ core loss features are identified with the excitation of $3p$ electrons to localized and nonlocalized states and the measured excitation and binding energies are used to calculate the autoionization and Auger energies.

CLEAN SURFACES

Table I shows, for the clean surfaces, a comparison of experimental and calculated peak energies with respect to the Fermi level of the sample. The atomiclike Auger energies were calculated using the expression

$$E(M_{2,3}M_{4,5}M_{4,5})=E_{3p}-2E_{3d}-U_{\text{eff}}\ .$$

Here E_{3p} is the $3p$ binding energy obtained from the threshold energy of our core loss spectra. We have chosen not to use published XPS binding energies for a number of reasons, foremost being the need for a consistent set of values, taken under the same experimental conditions, for both the clean and oxidized surfaces. As can be seen in

TABLE I: Experimental and calculated $M_{2,3}M_{4,5}M_{4,5}$ Auger and autoionization peaks for clean Fe, Co, and Ni. The $3d$ binding energies (E_{3d}) are derived from the peak positions in published photoemission results. E_{3p} is the $3p$ binding energy from the $3p$-core-loss threshold results (see Table II). U_{eff} is calculated from the energy of the principal Auger peak. $E_{(\mathrm{exc})3p}$ is the $3p$ excitation energy taken from the peak positions in the $3p$ core loss spectra. All values are in eV with kinetic energies referenced to the Fermi level.

			Fe		
$[E(M_{2,3}VV)]_{\mathrm{expt}}$	44.7	48.9		54.7	
$[E(M_{2,3}M_{4,5}M_{4,5})]_{\mathrm{calc}}$					
Atomiclike[a]	44.7	48.9			
E(Autoionization)[b]			52.6	54.6	
	$E_{3p}=52.9$; $E_{3d}=0.6,2.7$[c]; $E_{(\mathrm{exc})3p}=55.2,53.2$; $U_{\mathrm{eff}}=2.8$				
			Co		
$[E(M_{2,3}VV)]_{\mathrm{expt}}$	54.4	57.2		62.7	
$[E(M_{2,3}M_{4,5}M_{4,5})]_{\mathrm{calc}}$					
Atomiclike[a]	54.4				
Bandlike		57.8			
E(Autoionization)[b]			59.3	62.3	
	$E_{3p}=59.2$; $E_{3d}=0.7$;[d] $E_{(\mathrm{exc})3p}=63.0,60.0$; $U_{\mathrm{eff}}=3.4$				
			Ni		
$[E(M_{2,3}VV)]_{\mathrm{expt}}$	53.4	59.4	63.7		
$[E(M_3M_{4,5}M_{4,5})]_{\mathrm{calc}}$					
Atomiclike[a]		59.4			
Bandlike			63.7		
E(Autoionization)[b]				65.3	67.5
	$E_{3p}=65.3$; $E_{3d}=0.8$;[e] $E_{(\mathrm{exc})3p}=68.3,66.1$; $U_{\mathrm{eff}}=4.3$				

[a] $E(M_{2,3}M_{4,5}M_{4,5})=E_{3p}-2E_{3d}-U_{\mathrm{eff}}$.
[b] $E(\text{Autoionization})=E_{(\mathrm{exc})3p}-E_{3d}$.
[c] Reference 11.
[d] Reference 12.
[e] Reference 13.

Table II our values for the $3p$ binding energies are consistent with the two recently published XPS results for clean Fe, Co, and Ni surfaces. E_{3d} is the binding energies of the $M_{4,5}$ electrons taken as the peak positions from valence-band photoemission data (see Table I and references therein). U_{eff} is an empirical estimate of the energy associated with two holes localized in the d band, the hole-hole Coulomb interaction energy and the relaxation energy of the second hole. As Weightman points out,[15] U_{eff} can be misleading if its use is not justified. At approximately U_{eff} above the main peak, in the Ni and Co spectra there is a steplike shoulder which is associated with bandlike processes where U_{eff} approaches zero. In Fe, there is only a slight broadening to higher energy of the main peak; however, our value of U_{eff} is borne out by the good agreement between the experimental and calculated energy of the minor peak at 44.7 eV. Even when the use of U_{eff} is justified, care must be taken so that it does not mask inaccuracies in the energy scales of the Auger and photoelectron spectra. As the $M_{2,3}VV$ and L_3VV transitions result in the same final state, the U_{eff} values determined from the two transitions should be the same and a comparison of empirically determined values provides a useful check. The U_{eff} values determined from the $M_{2,3}M_{4,5}M_{4,5}$ transitions of 2.6, 3.4, and 4.3 eV (± 0.8 eV) agree, within experimental errors, with the values of 2.6, 3.7, and 5.3 eV (± 0.8 eV) determined by Yin *et al.*[16] from the L_3VV spectra of Fe, Co, and Ni, respectively. The apparent disagreement in the U_{eff} values for Ni is likely to be due to the L_3 binding energy value used by Yin *et al.* as a recent result from the $L_3M_{4,5}M_{4,5}$ transition by Martensson *et al.*[17] indicates a U_{eff} value of 4.6 eV.

TABLE II: Recent XPS $3p$ binding energies for clean Fe, Co, and Ni compared to our $3p$ binding energies which are derived from the $3p$-core-loss threshold for the clean and oxygen-saturated surfaces.

	Fe	Co	Ni	
	$M_{2,3}$	$M_{2,3}$	M_3	M_2
Clean XPS[a]	52.7	58.9	66.2	68.0
Clean XPS[b]	53.0	59.4	65.7	67.0
Clean CLS	52.9	59.2	65.3	
Oxidized CLS	52.9	58.9	65.0	

[a] Reference 10.
[b] Reference 14.

The only peak below the Auger threshold which cannot easily be accounted for in terms of either band or atomic-like $M_{2,3}M_{4,5}M_{4,5}$ transitions is the 53.4-eV peak in Ni. This peak has previously been assigned to a plasmon loss of the Auger electrons, which we feel, as did Baro *et al.*[18] is unlikely as its energy position relative to the Auger feature is too low. Also, similar peaks are not observed below other peaks in the electron spectrum of Ni or below the Auger features of Co and Fe as would be expected. $L_3M_{4,5}M_{4,5}$ Auger spectra of Ni shows three distinct features that have the same energies relative to the initial core-level binding energy as the three features observed in the $M_{2,3}M_{4,5}M_{4,5}$ spectrum. Martensson *et al.*[17] have analyzed the $L_3M_{4,5}M_{4,5}$ spectrum and assigned two of the features, the main peak and high-energy satellite, to atomic and bandlike Auger emissions. From their comparison of relative energy positions of the satellites observed in resonant photoemission with their calculations for two-, three-, and four-hole satellites they concluded that the third feature, the low-energy satellite, is a multiple-hole final-state satellite which arises from a localized cascade of Coster-Kronig transitions; for example, the L_3 hole produced by the $L_2L_3M_{4,5}$ Coster-Kronig transition decays, in the presence of the $M_{4,5}$ hole, via an $L_3M_{4,5}M_{4,5}$ transition leaving a final state with three $3d$ holes. A similar cascade process is also available to produce a multiple-hole satellite in the $M_{2,3}M_{4,5}M_{4,5}$ spectrum ($M_2M_3M_{4,5}$ followed by the $M_3M_{4,5}M_{4,5}$ transition) and we therefore interpret the feature at 53.4 eV in Ni as a multiple-hole Auger satellite.[19]

Anomalous features above the threshold energy for the $M_{2,3}VV$ transitions are clearly observed in the $N'(E)$ spectra from clean Fe (Ref. 7 and 8) and Co (Ref. 7) surfaces. These features are centered at 54.5 and 60.3 eV, respectively. For the $-N''(E)$ spectra shown in Fig. 1 this feature is only resolved for Co. In the case of Ni a similar feature cannot be observed in either the $N'(E)$ or $N''(E)$ mode; however, it should be noted that the half width of the negative excursion at 67.5 eV is nearly twice that of Fe and Co.

Recently, it has been proposed that these anomalous features for the first transition-metal series arise from autoionization emission[7,8] which results from the excitation of the $3p$ electron to a localized empty d state followed by a direct recombination emission of an electron from the d band ($3p^63d^n \rightarrow 3p^53d^nd^* \rightarrow 3p^63d^{n-1}+e$).

The energy of the autoionization emission can be calculated using the expression

$$E(3p \rightarrow 3d,3d) = E_{(\mathrm{exc})3p} - E_{3d}$$

in analogy with rare-earth calculations.[2] $E_{(\mathrm{exc})3p}$ is the excitation energy of the $3p$ electrons obtained from core loss spectra and E_{3d} is the $3d$ binding energy obtained from photoemission spectra. In principle the uncertainty in this calculation should be less than for the Auger peaks since it does not involve U_{eff}. The only difficulty arises in identifying the peak in the core loss spectra, which is associated with raising the $3p$ electrons to a localized state, as opposed to a nonlocalized state (in Gerlach's terminology,[20] an ionization loss).

The $3p$ core loss features for all three clean metal surfaces are asymmetric and are interpreted as double peaks in marked contrast to the symmetric single-peaked $3s$ and $2p$ core losses that we have observed. This double-peak structure is consistent with an ionization loss which produces a peak at a loss energy equivalent to the XPS binding energy, similar to the deeper core losses, and a resonance loss ($3p \rightarrow 3d^*$) which results in a peak at a loss energy equal to the excitation energy of the "atom." In the published $3p$ loss spectra[7] the trend is for the resonance loss energy to approach the ionization loss energy across the transition-metal series. Within a quasiatomic model this can be seen to be due to the empty d states approaching the Fermi level as the d band fills. In Fe and Co the lower loss energy peaks at 53.2 and 60.0 eV correspond to the XPS binding energy and consequently we have assigned the higher loss peaks at 55.2 and 63.0 eV to the $3p \rightarrow 3d^*$ resonance excitation. This assignment is borne out by the good agreement between the calculated autoionization energies and experimental energies of the anomalous peaks. For completeness, we have included in Table I the energies of the autoionization peaks which would arise if the lower-energy loss peaks were also associated with a localized $3p$ excitation. These calculated energies do not correspond to any observable features in the experimental spectrum.

In the case of Ni the assignment for the two core loss peaks is complicated by the possibility of spin-orbit splitting of up to 1.8 eV for the $M_{2,3}$ level. As can be seen in Table I the two CLS peaks have energies which correspond to Fuggle's XPS binding energies for the M_2 and M_3 levels. There is no evidence for splitting in our clean Auger results but this may be due to our inability to resolve the $M_2M_{4,5}M_{4,5}$ atomic Auger feature which should appear between the main $M_3M_{4,5}M_{4,5}$ atomic peak and the broad $M_{2,3}VV$ bandlike feature. We note that the bandlike feature of Ni has been assigned incorrectly to spin-orbit splitting in a number of recent studies.[7,21] If there is $M_{2,3}$ splitting in Ni, as seems likely, then the $3p$ core loss data cannot be interpreted by assigning the 66.1-eV peak to the ionization loss and the 68.3-eV peak to the $3p \rightarrow 3d^*$ excitation loss. It is more likely that the M_2 and M_3 ionization losses coincide with their respective excitation energies, which within the quasiatomic model, essentially means that the empty d states are at the Fermi level as expected for Ni. This in turn explains the inability to observe the expected dominant autoionization feature which is calculated to occur at the Auger threshold energy of 65.3 eV.

SURFACES AFTER OXYGEN ADSORPTION

It is not within the scope of this paper to discuss in detail all the changes that occur during oxygen adsorption on the three clean surfaces. For Co and Ni the changes are similar to those reported previously for Fe.[8] For oxygen exposures greater than 10 langmuirs (L) the Auger features undergo a general decrease in intensity, with line-shape changes below the energy threshold and growth in features above the energy threshold. The $3p$ core loss spectra also change for exposures greater than 10 L; features grow in intensity and two distinct peaks occur.

This result must be compared with the observed M_1, L_3, and L_2 core loss spectra which do not show a significant change in peak height or energy position on exposure to oxygen. As there is no decrease in the size of the core-loss features the decrease in the Auger feature cannot be attributed to "shadowing" of the substrate. This decrease is probably due to the electrons that take part in the bonding with oxygen being unavailable for the Auger process. Further, valence-band photoemission studies of the adsorption of oxygen on these transition-metal surfaces show that the growth in the oxygen $2p$ feature at approximately 6-eV binding energy occurs for oxygen exposures less than 10 L. Therefore, in the following analysis we feel justified in assuming that electrons of $2p$ character have no significant effect on the $M_{2,3}VV$ Auger features for the oxygen-exposed surfaces.

Listed in Table III are the experimental and calculated peak-energy positions for the surfaces exposed to saturation doses of oxygen. The referenced data used for these calculations are also shown. In the absence of valence-band difference spectra for Co and Ni on adsorption of oxygen, we have used, as the values of the $3d$ binding energies, the energy values of the peak positions obtained from the d-band photoemission results for the full oxides. In the case of the $3p$ binding energies for the oxidized surfaces there is no reliable photoemission data available for comparison with the core-loss threshold results which we have used in the Auger energy calculations. Table II shows that, on oxidation, the $3p$ threshold energy remains unaltered for Fe and decreases by 0.3 eV for Co and Ni. This is in marked contrast to the XPS chemical shifts reported for the deeper core levels which show large increases in binding energy on oxidation, for example, 3.8 eV and 1.6 eV for the $2p$ levels of Fe (Ref. 23) and (Ref. 24), respectively. This discrepancy may be due to the differences in the shielding of the $3p$ level in comparison to the deeper levels, as suggested by Carlson,[25] however, our core-loss threshold value for the $3s$ and $2p$ levels also show no significant increases in energy on oxidation suggesting that the discrepancy may be due to the differences in the shielding involved in the various techniques used for binding-energy determinations.

For the calculations shown in Table III, it has been assumed that U_{eff} is unaffected by oxidation. This assumption is justified by the excellent agreement between the experimental and calculated energy positions for peaks in

TABLE III: Experimental and calculated $M_{2,3}M_{4,5}M_{4,5}$ Auger and autoionization peaks for the oxygen-saturated Fe, Co, and Ni surfaces. For Ni and Co there are no reliable UPS data for comparable experimental conditions, therefore calculations are made with E_{3d} values of the probable full oxides. U_{eff} is assumed to be the same as for the clean surfaces.

Fe + O_2

$[E(M_{2,3}VV)]_{\text{expt}}$	44.7	49.1		54.5
$[E(M_{2,3}M_{4,5}M_{4,5})]_{\text{calc}}$[a]	44.7	49.1		
E(Autoionization)[b]			50.3	54.0

$E_{3p}=52.9$; $E_{3d}=0.5,2.7$;[c] $E_{(\text{exc})3p}=56.7,53.0$; $U_{\text{eff}}=2.8$

Co + O_2

$[E(M_{2,3}VV)]_{\text{expt}}$	47.7	51.0	53.3	54.4	57.2	60.3
$[E(M_{2,3}M_{4,5}M_{4,5})]_{\text{calc}}$[a]						
Clean remnant				54.5	57.2	
CoO	47.7	51.7				
Co_3O_4		50.3	53.5			
E(Autoionization)[b]					57.6	60.7

$E_{3p}=58.9$; $E_{3d}(CoO)=1.9,4.0$;[d] $E_{3d}(Co_3O_4)=1.0,2.5$;[d] $E_{(\text{exc})3p}=62.6,59.5$; $U_{\text{eff}}=3.4$

Ni + O_2

$[E(M_{2,3}VV)]_{\text{expt}}$	54.2	57.7	60.0	64.2	67.7
$[E(M_{2,3}M_{4,5}M_{4,5})]_{\text{calc}}$[a]					
Clean remnant			59.4	63.7	
NiO	54.0	57.9			
E(Autoionization)[b]				64.5	68.0

$E_{3p}=65.0$; $E_{3d}(NiO)=1.4,3.0$;[e] $E_{(\text{exc})3p}=69.4,65.9$; $U_{\text{eff}}=4.3$

[a] $E(M_{2,3}M_{4,5}M_{4,5})=E_{3p}-2E_{3d}-U_{\text{eff}}$.

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

[c] Reference 11.

[d] Reference 12.

[e] Reference 22.

the Auger spectra. In the past U_{eff} has either been considered to go to zero[21] or increase[22] on oxidation and, to our knowledge, our result of U_{eff} being essentially unaltered has not been addressed. When it is considered that U_{eff} arises from the d band being localized within a centrifugal barrier, which is principally dependent on the angular momentum quantum number, this result is not entirely surprising.

The $\text{Ni} + \text{O}_2$ results confirm that NiO is formed at the surface. The result for cobalt on the other hand appears to be different. Photoemission studies of oxygen adsorption suggest that CoO alone is formed.[12] The multipeaked Auger result suggests that both CoO and Co_3O_4 are present in significant amounts for the simple adsorption studies undertaken here (see Fig. 1 and Table III). This illustrates the usefulness of Auger spectra for both chemical and electronic information without the need for complex, and sometimes dubious, deconvolution. This advantage is derived in core-valence-valence spectra from the doubling of the energy separation for peaks observed in valence-band photoemission data. Apart from the oxide $M_{2,3}M_{4,5}M_{4,5}$ peaks there are also the remnants of both the atomic and bandlike clean Auger features in the oxygen-exposed $M_{2,3}VV$ spectra for each of the elements studied here. The sharp remnants of clean atomic features in Fe and Ni shift slightly to higher kinetic energies, by 0.2 and 0.6 eV, respectively. The UPS difference spectra for Fe (Ref. 11) show a 0.1-eV decrease in the binding energy in the clean d-band feature on oxygen adsorption, which accounts for the 0.2-eV Auger shift. We thus argue that a similar 0.3-eV shift to lower binding energy should be observed for the remnant of the clean Ni valence-band peak in photoemission spectra on oxygen adsorption.

Over the last decade there have been numerous interpretations proposed to explain the $M_{2,3}VV$ features for these transition metals on oxygen adsorption; for examples, in the case of Fe, see Ramsey and Russell[8] and references therein. In summary, these previous interpretations differ from those proposed by us due to one or a number of the following reasons: (1) attempting to introduce the oxygen $2p$ level into the $M_{2,3}VV$ feature, (2) assuming the anomalous features above the Auger threshold arise from the normal Auger transition, (3) inadequate data regarding core level binding energies and their shifts, and (4) treating elements individually.

As can be seen in Table III, our interpretation leads to the energy positions of all the observed peaks in the $M_{2,3}VV$ Auger features being accounted for within experimental error.

The $M_{2,3}$ loss spectra change dramatically on oxygen adsorption with both splitting and enhancement of the features. In all three transition metals the threshold peaks decrease slightly (by approximately 0.2 eV) in loss energy. In the case of Fe the higher loss energy peak is the dominant one whereas for Ni the lower loss energy peak is dominant. We have interpreted the two major loss peaks found for each oxidized surface as being due to exciting $3p$ electrons to the top of the valence band, and to the bottom of the conduction band, as the energy separation values for the core loss peaks are in agreement with the measured band gaps for these oxides.[26]

For each of the oxidized surfaces, peaks are observed above the $M_{2,3}VV$ threshold at energies which agree well with the autoionization energies calculated using the $3p$ loss energies associated with exciting the $3p$ electrons to the bottom of the conduction band. The size of these excitation losses qualitatively reflects the size of the resulting autoionization peaks. In Fe there is no significant change in the observed energy of the autoionization peak while for Co there is a 2.4-eV decrease in the energy of the peak on oxidation. In the rare earths there has been no reported changes in excitation or autoionization energies on gas adsorption. This has been attributed to the quasiatomic character of the autoionization process in solids. Zajac *et al.*[7] observed that the autoionization peak in Mn did not alter in energy on oxidation and suggested that the autoionization peaks in the transition metals remain pinned above the $3p$ binding energy while the $M_{2,3}VV$ Auger peaks decrease in energy. Our results show that the autoionization features, in the transition metals, are not inherently immune to changes in chemical environment as both the $3d$ binding energy and the $3p$ excitation energy do change markedly on oxidation. In the case of Fe, and probably Mn, the changes in $3d$ binding energy and $3p$ excitation energy effectively cancel out, resulting in the autoionization features remaining at constant energy. In Co this cancellation does not occur with the observed shift in the autoionization peak of 2.4 eV resulting.

The lower energy peak in the $3p$ loss spectra of the oxidized surfaces corresponds to exciting the $3p$ electrons to empty states at the top of the valence band. This is likely to be a $3p \rightarrow 3d^*$ transition which would be expected to be localized and hence deexcite with the emission of an autoionization electron also. As can be seen in Table III this would lead to peaks below the Auger threshold energy at 50.3, 57.6, and 64.5 eV for the oxides of Fe, Co, and Ni, respectively. If one considers that the relative sizes of the two peaks in the core loss spectrum reflect the relative sizes of the resulting autoionization peaks, then close inspection of the Auger features at these energies, while not proving their existence, certainly suggests that further experiments are in order.

The autoionization process in solids has up until now been considered quasiatomic and thus in essence due to the deexcitation of a localized Frenkel exciton. This is not only because of the analogy to similar features common in atomic spectra, but also because they have been associated with localized f states in the rare earths where excitation and emission spectra are apparently immune to changes in chemical environment. In the clean transition metals it has been shown that similar features occur. While the d states in the first transition-metal series are not as localized as the f states of the rare earths they are similarly bound within a centrifugal barrier and the analogy with the quasiatomic arguments of the rare earths is not unreasonable. For the insulating oxide surfaces of these transition metals we have shown that the observable autoionization peaks are associated with excitations to the bottom of the conduction band. If one pursues the analogy, as we have done in earlier papers,[8,27] then the excited $4sp^*$ state would necessarily be considered localized. We now feel that such a localized conduction-band electron is unlikely even in the presence of the $3p$ core hole. Therefore, we propose that, for the insulating transition-metal oxides, a "weakly bound" exciton exists (not a Frenkel exciton), where the $3p$ electron is raised to an excited state and remains bound in a hydrogenlike orbital around the core hole with the energy level of the excited electron being at the bottom of the conduction band but within the band gap. This type of exciton is unlikely in metals but, according to Peierls,[28] becomes increasingly probable as the material approaches that of an insulator.

CONCLUDING REMARKS

For the clean surfaces of Fe, Co, and Ni the energetic positions of the peaks associated with each of the $M_{2,3}VV$ Auger features have been calculated and found to be in excellent agreement with the experimental results. In Fe and Co the anomalous features above the Auger threshold have been identified as autoionization peaks associated with the decay of the localized $3p \rightarrow 3d^*$ excitation which is observed in the $3p$ core loss spectra. In Ni, the $3p \rightarrow 3d^*$ excitation cannot be unambiguously assigned due to the inability to resolve it from the ionization losses. This in turn explains the inability to observe the autoionization peaks in Ni as they would be expected to occur within the Auger feature.

The $M_{2,3}VV$ features for the oxidized surface have been interpreted in terms of $M_{2,3}M_{4,5}M_{4,5}$ transitions and autoionization peaks involving electrons which have been excited from the $3p$ level to a localized state at the bottom of the conduction band. The identification of the autoionization peaks has clarified the analysis of the oxidized Auger features enabling the energy of every peak observed in all three oxidized surfaces to be calculated. The agreement between experimental and calculated energies on oxidation is achieved by considering the $3d$ binding-energy changes observed in UPS spectra and U_{eff} values unchanged from the clean surface results.

In going from the clean metal surface to the insulating oxide surface we have shown that the excitation and the autoionization energies are affected by chemical environment. This result implies that the quasiatomic interpretation of autoionization in solids is not appropriate for our oxidized surfaces. Further, we have proposed that the $3p$ excitation and autoionization peaks observed involve $3p$ electrons raised to an excited state but remaining bound in a hydrogenlike orbital around the core hold. Autoionization involving quasiatomic excitation of the $3p$ electrons to localized $3d^*$ states at the top of the valence band should also be possible for these transition-metal oxides; however, since the energy of the features has been calculated to be below the $M_{2,3}VV$ energy threshold a comparison of electron- and photon-excited Auger spectra would be required to confirm their presence.

The results presented also have particular relevance to the resonant photoemission studies of the first transition-metal series as the creation of localized excited states, their subsequent decay by autoionization emission and the normal Auger emission all play a significant role in the photoelectron spectra at phonon energies in the region of the $3p$ binding energy. To our knowledge NiO is the only one of these three transition-metal oxides for which resonant photoemission experiments have been performed.[22] Thuler *et al.*[22] attributed the change in the energy of the resonant satellite, in going from Ni to NiO, to an increase in U_{eff} of $+3$ eV. This is not supported by our Auger results which suggest no appreciable change in U_{eff} occurs on oxidation. Hufner *et al.*[29] consider that the resonant satellite in NiO is due to an autoionization emission where, although the process leaves the same single-hole final state as direct d band photoemission, its energy is different from the direct photoemitted electron due to differences in screening. This is not supported by the good agreement between the autoionization energies we have obtained experimentally and those calculated using $3d$ binding energies obtained from direct photoemission results.

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