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$N_{6,7}O_{4,5}O_{4,5}$ Auger spectrum of metallic Au

C. Verdozzi
Istituto Metodologie Avanzate Inorganiche, Consiglio Nazionale delle Richerche, I-00016 Monterotondo Scalo, Roma, Italy

M. Cini
Dipartimento di Fisica, Universita'di Roma II, via O. Raimondo, I-00173 Roma, Italy

J. F. McGilp
Department of Pure and Applied Physics, Trinity College, Dublin, Ireland

G. Mondio
Istituto di Struttura della Materia della Facolta' di Scienza, Università di Messina, Casella Postale 56, I-98166, Villa S. Agata (Messina), Italy

D. Norman
Science and Engineering Research Council, Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD, United Kingdom

J. A. Evans, A. D. Laine, P. S. Fowles, L. Duò, and P. Weightman
Department of Physics and Surface Science Research Centre, University of Liverpool, Liverpool L69 3BX, United Kingdom

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The spectral profiles of the $N_{6,7}O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ Auger transitions of metallic Au are calculated using a theory that gives a treatment of the influence of the $5d$ spin-orbit splitting on both the multiplet structure of localized $[5d^2]$ double-hole states and the $[5d]$ single-hole states in the d band. It has not been possible to obtain simultaneous agreement in the kinetic energies and spectral profiles of the Auger spectra. The theoretical profile is in good agreement with the experimental $N_{6,7}O_{4,5}O_{4,5}$ profile when the $U(^1G_4)$ correlation energy is taken to be 3.4 eV, though this predicts the spectrum to be 1.2 eV higher in kinetic energy than observed. Possible reasons for this discrepancy are discussed.

I. INTRODUCTION

The analysis of the core-valence-valence (CVV) Auger spectra of d-band metals can yield information on electron correlation energies and their dependence on the LSJ multiplet splitting $U(d^2;LSJ)$, the degree of localization of the $[d^2]$ double-hole states, and the local density of states of d character.[1-6] Considerable progress has been made in extracting this information from the CVV Auger spectra of the $3d$ and $4d$ elements Ni, Cu, Zn, Pd, Ag, and Cd and their alloys.[4-22] The Auger spectra of several systems involving these elements have now been analyzed within the context of the Cini-Sawatzky theory[1-3] in which the shape of a final-state component of the Auger multiplet structure is determined by the ratio $U(d^2;LSJ)/W$, where W is the single-electron d-band width. This ratio also determines the mixture of correlated $[5d^2]$ and uncorrelated $[5d],[5d]$ character in the two-hole final state.

Unfortunately a number of factors make it more difficult to extract similar information from the CVV Auger spectra of the $5d$ series Pt, Au, and Hg. To begin with, the optimum transitions[8,23,24] for obtaining this information for the $5d$ elements, the $N_6O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ groups, overlap due to the small $N_{6,7}$ spin-orbit splitting in the initial state [3.7 eV for Au (Refs. 8 and 25)] and the large $[5d^2]$ multiplet structure splitting[26,27] and $[5d]$ bandwidth.[28-30] In addition, unlike the situation for the $3d$ and $4d$ elements, the $5d$ spin-orbit coupling constant is large [$\xi_{5d}\sim 0.6$ eV for Au (Ref. 26) and, besides making significant contributions to both the $[5d]$ multiplet-structure splitting and $[5d]$ bandwidth, this gives rise to a theoretical difficulty in the analysis of the $N_{6,7}O_{4,5}O_{4,5}$ Auger profile. For the $3d$ and $4d$ elements the spin-orbit splitting has a small effect on the d-band density of states (DOS) and for the purposes of the Cini-Sawatzky analysis the $d_{3/2}$ and $d_{5/2}$ DOS's can be assumed to be identical. This simplification is not appropriate for the $5d$ elements and it is necessary to consider the relationship between the $[5d^2;LSJ]$ components and the $[5d_{3/2}]$ and $[5d_{5/2}]$ DOS's.

In this work we present an analysis of the $N_{6,7}O_{4,5}O_{4,5}$ Auger profile of metallic Au and of the profile of the $N_7O_{4,5}O_{4,5}$ group which has recently been determined separately using synchrotron radiation.[23] Our analysis includes a consistent treatment of the effects of the $5d$ spin-orbit splitting on both the $[5d^2;LSJ]$ multiplet structure and the $[5d_{3/2}]$ and $[5d_{5/2}]$ DOS's. In applying the

Cini-Sawatzky theory to the $N_{6,7}O_{4,5}O_{4,5}$ Auger profile of metallic Au we are unable to obtain simultaneous agreement between theory and experiment for both the shape and kinetic energy of the spectrum. We find that theory gives excellent agreement with the shape of the spectrum but at a predicted kinetic energy 1.2 eV higher than experiment. We discuss possible reasons for this shift.

II. EXPERIMENT

The experimental spectra to be analyzed in this work are taken from studies using synchrotron radiation by

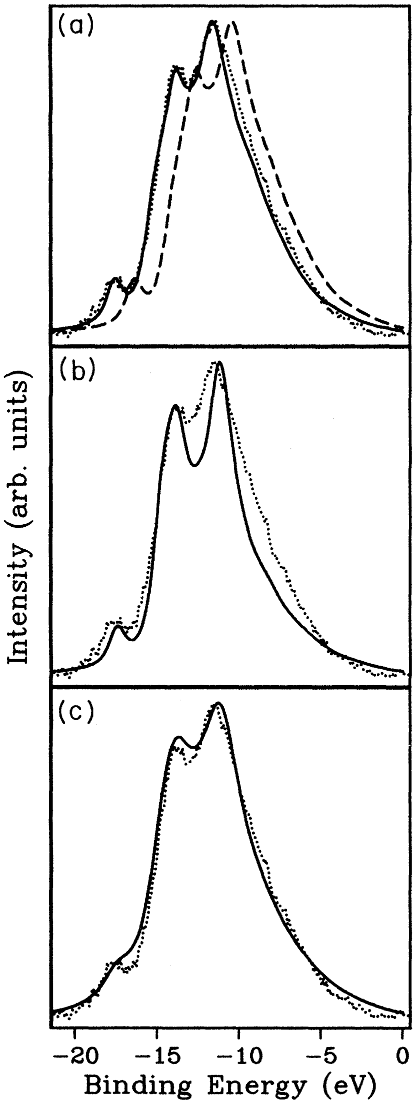

FIG. 1. The experimental profile of the $N_{6,7}O_{4,5}O_{4,5}$ Auger transitions of Au (Ref. 23) is shown by the dots. The energy scale is the binding energy of two-hole final states created by $N_7O_{4,5}O_{4,5}$ Auger transitions. The zero of this scale corresponds to the Fermi energy. The theoretical profile calculated with a value of $U(^1G_4)=3.4$ eV is shown by the dashed line in (a). The solid line in (a) is obtained by shifting the dashed line to higher binding energy by 1.2 eV. The profile calculated with a value of $U(^1G_4)=4.6$ eV is shown by the solid line in (b). The profile obtained from the theoretical profile shown in (b) by arbitrarily increasing the width of the Lorentzian lifetime broadening contribution to FWHM of 2.0 eV is shown by the solid line in (c).

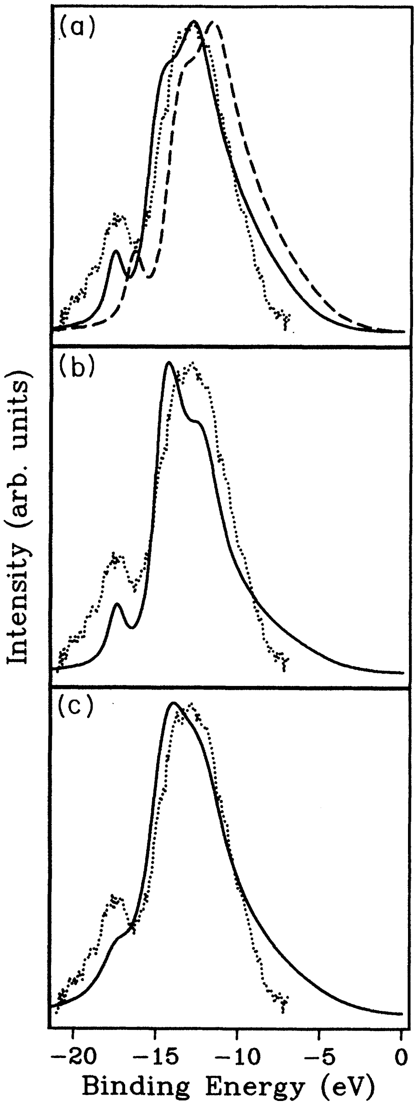

FIG. 2. The experimental profile of the $N_7O_{4,5}O_{4,5}$ Auger transitions of Au (Ref. 23) is shown by the dots. The energy scale is the binding energy of two-hole final states created by $N_7O_{4,5}O_{4,5}$ Auger transitions. The zero of this scale corresponds to the Fermi energy. The theoretical profile calculated with a value of $U(^1G_4)=3.4$ eV is shown by the dashed line in (a). The solid line in (a) is obtained by shifting the dashed line to higher binding energy by 1.2 eV. The profile calculated with a value of $U(^1G_4)=4.6$ eV is shown by the solid line in (b). The profile obtained from the theoretical profile shown in (b) by arbitrarily increasing the width of the Lorentzian lifetime broadening contribution to FWHM of 2.0 eV is shown by the solid line in (c).

Evans, Laine, Fowles, Duò, McGilp, Mondio, Norman, and Weightman.[23] These authors measured the $N_{6,7}O_{4,5}O_{4,5}$ Auger profile of metallic Au excited by photons of energy 115 eV. They obtained results in good agreement with the work of Nyholm, Helenelund, Johansson, and Hörnström,[24] who used 110-eV photon excitation. Evans *et al.*[23] also measured the $N_7O_{4,5}O_{4,5}$ Auger profile excited by photons of 86 eV which have insufficient energy to excite the Au N_6 core level. The $N_{6,7}O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ spectra lie on a smooth background of scattered electrons which rises rapidly to lower kinetic energy and which can be subtracted from the spectra using interpolation procedures. The $N_{6,7}O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ Auger profiles obtained after background subtraction[23] and with energy scales referenced to the binding energy of the two-hole final states are shown by the dots in Figs. 1 and 2 respectively. The experimental spectra of Evans *et al.*[23] were measured with an experimental resolution which can be represented by a Gaussian with a full width at half maximum (FWHM) of 0.5 eV.

III. THEORY

A theoretical analysis of the profile of the $N_{6,7}O_{4,5}O_{4,5}$ Auger transitions of metallic Au must consider the influence of a number of factors. We begin with the usual simplifying assumption that the transitions can be considered as a two-step process and that the influence of the initial state is restricted to a Lorentzian broadening arising from the lifetime of the initial core-hole states. The initial states for these transitions, the Au $[4f]$ states, are very narrow; McGuire's[31] calculations indicate a FWHM of 0.23 eV while Citrin, Wertheim, and Baer[32] find an experimental FWHM of 0.32 eV, a value which is near the limit of their experimental resolution. The conditions under which the assumption of a two-step process is valid have been investigated by Gunnarsson and Schönhammer[33] and would seem to be well justified in this case. This allows us to concentrate on the final-state contributions to the Auger profiles with a view to extracting useful information about the electronic structure of metallic Au.

The $N_6O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ groups are each an envelope of overlapping contributions from the *LSJ* multiplet structure of the final states and the kinetic energy of each component is given by

$$E^F_{\text{kin}}(N_{6,7}O_{4,5}O_{4,5})=E^F(N_{6,7})-E^F(O_{4,5}O_{4,5};LSJ) \tag{1}$$

where the binding energies of the initial and final states on the right-hand side are referenced, like the kinetic energy, to the Fermi level. For transitions in which the final states are in core levels it is usual[5] to express the binding energy of the two-hole final state in terms of the binding energies of the one-hole states. In this case this would be

$$E^F(5d^2;LSJ)=2E^F(5d)+F(5d^2;LSJ)-R \tag{2}$$

where $F(5d^2;LSJ)$ is equal to the sum of the atomic Coulomb integral between the two final-state holes, $F^0(5d5d)$, and combinations of $F^2(5d5d)$ and $F^4(5d5d)$ Slater integrals and the spin-orbit coupling constant ζ_{5d}, which depend on the particular *LSJ* quantum numbers of each component of the multiplet structure. The relaxation term R includes atomic and solid-state contributions to the Auger energy which arise from the failure of the independent particle description of atomic structure and the polarization of the solid-state environment of the emitting atom. In cases like the $N_{6,7}O_{4,5}O_{4,5}$ transitions of Au metal in which the final states are in a d band the $2E^F(5d)$ term in (2) becomes a self-convolution of the d-band single-electron density of states and the second two terms are combined into the on-site correlation energy $U(LSJ)$ which distorts the line shape of each multiplet structure component by an amount that depends on $U(LSJ)/W$.[1-3]

In order to calculate the Auger profile of the $N_{6,7}O_{4,5}O_{4,5}$ transitions of Au it is necessary to determine the energy $U(LSJ)$ and intensity $I(LSJ)$ of each component of the correlated final states, $[5d^2;LSJ]$. One can obtain a good idea of this structure from atomic-structure calculations[34] and from Aksela, Harkoma, Pohjola, and Aksela's measurement[27] of the Auger spectra of atomic Au. It is also necessary to determine the line shape of each component of the final state which, according to the Cini-Sawatzky theory, is determined by the ratio $U(LSJ)/W$. An important issue is the relative strengths of the atomic and crystal-field potentials in the final state. In this work we assume that, as for the $3d$ and $4d$ elements, we can neglect the influence of the crystal field of Au. This assumption allows us to describe the correlated final states in terms of the LSJ irreducible representations of the point group of spherical symmetry. It also means that in considering the influence of the large final-state spin-orbit splitting in Au we can work with the eigenvectors $[iJ\rangle$ obtained by diagonalizing the matrix of electrostatic and spin-orbit interactions between the *LSJ* terms of common J.

The Auger Hamiltonian can be written as

$$H=H_0+\sum_J\sum_{LS}U(LS)[LSJ\rangle\langle LSJ] \tag{3}$$

with $H_0=H_1+H_{\text{s.o.}}$ where $H_{\text{s.o.}}$ is the spin-orbit interaction and H_1 represents all other one-electron contributions. The second term in (3) is the on-site Coulomb repulsion. Following Refs. 35 and 36 the noninteracting two-hole Green's function is first computed in the *jj* picture and then cast into the *LSJ* picture by evaluating the matrix of electrostatic and Coulomb interactions between the two-hole states. In the absence of crystal-field effects the Auger spectrum is given by

$$A(E)=\pi^{-1}\sum_J\sum_{\lambda_J}I(\lambda_J)\text{Re}\Phi^J_{\lambda_J\lambda_J}(E)\ . \tag{4}$$

The Green's-function matrix $\Phi^J_{\lambda_J\lambda_J}(E)$ is given by

$$\Phi^J_{\lambda_J\lambda_J}(E)=-\langle\lambda_J](z+H)^{-1}[\lambda_J\rangle \tag{5}$$

where $z=E+i0^+$.

By a unitary transformation to the *LS* picture, the equation for the Green-function matrix becomes

$$\begin{aligned}&(1-\Phi_0^J U_J)\Phi^J=\Phi_0^J ,\\&(U_J)_{LS,L'S'}=-iU(LS)\delta_{LS,L'S'} .\end{aligned} \tag{6}$$

In Eqs. (6) the noninteracting Green's-function matrix Φ_0^J is related to the self- and cross-convolutions of S_0^J, the spin-orbit-projected bare propagator.[35]

We are now in a position to calculate the $N_6O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ Auger profiles, provided that we can determine the multiplet splittings $U(LSJ)$ and intensities $I(LSJ)$ and the spin-orbit-projected $[5d_{3/2}]$ and $[5d_{5/2}]$ densities of states, the latter entering the calculation by the S_0^J.

A. Multiplet splitting

It is now necessary to determine the multiplet splittings of the correlated $[5d^2]$ final states and the eigenvectors describing the various multiplet components in the intermediate-coupling (IC) scheme in terms of an $|LS\rangle$ basis set. It has been established (Ref. 21 and references therein) that for systems with filled d bands the final-state $[d^2]$ multiplet splittings are not observably different in the metallic and free-atom states for $3d$ and $4d$ elements. Experience in analyzing the spectra of $3d$ and $4d$ elements also indicates that the valence electrons of s and p character do not introduce any additional structure into the $[d^2]$ multiplet.[37] In order to determine the eigenvectors for our analysis we need the values of the $F^2(5d5d)$ and $F^4(5d5d)$ Coulomb integrals and the ζ_{5d} spin-orbit coupling constant. For $4d$ elements it was possible to determine the values of the equivalent parameters from an analysis of the observed atomic multiplet splittings.[9,10] However, this technique did not produce a consistent set of parameters when applied to the optical data on the multiplet splitting of the Au $5d^86s^2$ configuration (Ref. 26 and shown in brackets in Table I) probably because of configuration-interaction effects. The Auger spectra of free-atom Au has been measured by Aksela *et al.*[27] though in this case the final state is $5d^86s^1$ and the $6s$ electron introduces additional splittings into the multiplet structure. In order to determine the Au $5d^8$ splittings from the results of Aksela *et al.*[27] we expressed the experimental splittings in terms of the $F^2(5d5d)$, $F^4(5d5d)$, and $G^1(5d6s)$ Coulomb and exchange integrals and the ζ_{5d} spin-orbit coupling parameter in an IC description of the $5d^86s^1$ configuration. Solving these expressions gave the values of those parameters shown in Table I. The main part of Table I shows the splittings of the terms of the $5d^8$ configuration obtained using those parameters which we assume are relevant to the screened $[5d^2]$ configuration in Au metal.

B. Multiplet intensities

The work of McGilp, Weightman, and McGuire[38] on the $N_{6,7}O_{4,5}O_{4,5}$ Auger transitions of Tl, Pb, and Bi established that the $5d$ spin-orbit coupling has a strong influence on the intensity distribution among the components of the multiplet structure. Accordingly the intensities of the final-state components were calculated in IC (Ref. 34) using the formalism of McGilp *et al.*[38] with eigenvectors determined from the diagonalization of the matrices of the electrostatic and spin-orbit interactions between terms of common J and making use of McGuire's results[39] for the Auger matrix elements. These relative intensities are also shown in Table I. They may be compared with the experimental intensities of the corresponding components of the Auger spectrum of atomic Hg (Ref. 40) which are shown in brackets in the table.

In calculating the overall $N_{6,7}O_{4,5}O_{4,5}$ Auger profile it is necessary to take account of the different total intensities of the two Auger groups. We weighted the intensity of the $N_7O_{4,5}O_{4,5}$ and $N_6O_{4,5}O_{4,5}$ groups in the ratio 1.0:0.699, a result found from the study of the spectrum of Hg.[40]

C. Lifetime effects

The Auger profile given by Eq. (3) does not include contributions from the lifetime broadening in the initial

TABLE I. Multiplet structure of Au $[5d^2]$. (1) The $|LS\rangle$ terms are mixed by spin-orbit coupling. The components are identified by the $|LS\rangle$ term that makes the largest contribution to the mixed state. (2) Calculated in intermediate coupling using $F^2(5d,5d)=6.65$ eV, $F^4(5d,5d)=5.74$ eV, and $\zeta_{5d}=0.64$ eV. (3) Optical splittings (Ref. 26). (4), (6) Calculated in intermediate coupling by Wright (Ref. 34) using the formalism of Ref. 38. (5), (7) Experimental results for Hg (Ref. 40).

Component	Splittings (eV)		Relative intensities			
			N_6 group		N_7 group	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
$^1S_0$	-3.51	(3.69)	1.06	(1.02)	0.48	(0.38)
$^1D_2$	-0.63	(0.84)	1.46	(1.64)	0.19	(0.19)
$^1G_4$	0.0	(0.00)	1.28	(1.23)	1.00	(1.00)
$^3P_1$	0.52	(0.28)	0.01	(0.63)	0.49	(0.36)
$^3F_2$	0.90	(0.39)	0.64	(0.79)	0.61	(1.15)
$^3P_0$	0.87	(0.74)	0.64	(0.07)	0.48	(0.23)
$^3F_3$	1.58	(1.14)	0.47	(0.54)	0.35	(0.51)
$^3P_2$	2.16	(1.59)	0.04	(0.05)	1.20	(1.30)
$^3F_4$	3.01	(2.59)	0.11	(0.15)	0.87	(0.97)

and final states. As discussed previously the initial-state contribution is expected to be small, ~0.3 eV. The contribution from the lifetime broadening of the two-hole final states is harder to determine. In free-atom Au spectra the component width found experimentally by Aksela *et al.*[27] is ~0.35 eV, a figure which includes instrumental contributions. This value is probably derived almost entirely from the initial-state contribution since in the free atom the two-hole final states $5d^8 6s^1$ can only decay by collisions with other Au atoms or with the walls of the container. However, it is clear from studies of a wide range of elements (see the discussion in Ref. 21) that correlated $[d^2]$ hole states in metals experience an additional lifetime broadening of ~1 eV. This probably arises from the decay of the final states by Auger and other processes involving electrons in the *d* and *sp* bands. A similar lifetime broadening seems to affect the noncorrelated final states produced by Auger processes in wide band materials[41] and calculations of the lifetime broadening of simple metal *sp* bands by Landsberg[42] also indicate a lifetime contribution of this order. In view of these considerations we convolute the calculated Auger profile obtained by evaluating Eq. (3) with a Lorentzian of FWHM 1 eV to represent these lifetime contributions. In order to facilitate the comparison with experiment the theoretical profiles were also convoluted with a Gaussian of FWHM 0.5 eV representing the instrumental resolution.

IV. RESULTS AND DISCUSSION

In calculating the profile of the $N_{6,7}O_{4,5}O_{4,5}$ Auger spectrum of Au using the theory described previously we have only two free parameters, the total intensity of the whole spectrum and $U(^1G_4)$ the on-site correlation energy for two 5*d* holes localized in a $^1G_4$ state on one Au atom. The values of $U(LSJ)$ for the other components of the multiplet structure are determined from $U(^1G_4)$ using the splittings shown in Table I. The value of $U(^1G_4)$ determines both the shape of the Auger spectrum and its overall kinetic energy. We find we are unable to get simultaneous agreement between theory and experiment for both the spectral shape and position of the spectrum. By varying $U(^1G_4)$ we can get agreement with either the shape or the position of the spectrum. This is demonstrated in Fig. 1. Figure 1(a) shows the excellent agreement in spectral shape obtained with a value of 3.4 eV for $U(^1G_4)$. In this figure the calculated profile, shown by the solid line, has been arbitrarily shifted 1.2 eV to lower kinetic energy from its true position shown by the dashed line. In Fig. 1(b) we obtain good agreement in the kinetic energy of the spectrum, but a poor agreement in spectral profile, with a value of 4.6 eV for $U(^1G_4)$.

In seeking an explanation for the discrepancy noted above we first observe that our experimental results for the position of the three discernible peaks in the spectrum agree to within experimental error with those of Powell[8] and Nyholm *et al.*[24] We also note that it is extremely unlikely that the uncertainty in the background subtraction could account for the difference between the theoretical and experimental profiles shown in Fig. 1(a). We can eliminate the possibility that the discrepancy arises from small errors in the multiplet structure since the only discernible difference between calculations employing the results of splittings and intensities determined by different procedures (Table I) is a slight overestimate of the intensity of the weak isolated peak on the high-binding-energy side of the spectrum, which is known to be associated with the $^1S_0$ component of the $N_7O_{4,5}O_{4,5}$ group, when the component intensities are taken from our calculations. For this reason the calculated profiles shown in Fig. 1 use the relative intensities derived from Hg, but the difference between the two calculations is small and the experimental result for the intensity of this feature is sensitive to the details of the background subtraction procedure. An important point to note is that apart from the small uncertainty in the intensity of the $^1S_0$ component of the $N_7O_{4,5}O_{4,5}$ group its width is reproduced by the calculation, indicating that our representation of the experimental and lifetime broadening contributions is essentially correct.

In an earlier study Nyholm *et al.*[24] calculated the profile of these transitions within the Cini-Sawatzky formalism using a $[5d]$ band DOS obtained from x-ray photoelectron spectroscopy, final-state multiplet splittings obtained from optical data,[26] and multiplet intensities measured for the corresponding transitions in free-atom Hg.[40] These authors were able to reproduce the position of the Auger spectrum but only by treating the FWHM of the Lorentzian and Gaussian broadening contributions as adjustable parameters. Their theoretical profile reproduced the slope of the low-binding-energy region of the spectrum quite successfully but disagreed in the region between the two main peaks and to high binding energy. Nyholm *et al.*[24] speculated that the disagreement they obtained between theory and experiment might arise from contributions from shake up processes in the experimental spectrum or from approximations in their theoretical procedure. In this latter category they identified possible errors arising from their assumptions about the multiplet structure but placed most emphasis on the effects of neglecting the spin-orbit splitting in the $[5d]$ band DOS. Our work shows that calculating the multiplet splittings and intensities in a more sophisticated way does not give results (Table I) which are very different from those used by Nyholm *et al.*[24] and cannot be the source of the disagreement they obtained between the theoretical and experimental profiles or of the shift which we observe. Our analysis treats the contributions from the $[5d_{3/2}]$ and $[5d_{5/2}]$ DOS's separately, giving a better representation of the physical situation and this coupled with our estimate of the broadening contributions has shown up the discrepancies shown in Fig. 1. We can obtain a similar degree of agreement between theory and experiment to that obtained by Nyholm *et al.*[24] by adopting their procedure of arbitrarily increasing the lifetime broadening in the final state. This is shown in Fig. 1(c) where the spectrum has been broadened with a Lorentzian of FWHM 2.0 eV. However, although the use of the lifetime broadening as a free parameter improves the agreement between theory and experiment, the final result is not in as good agreement with the experimental profile as that shown in Fig. 1(a) which corresponds to a lifetime broadening contribution consistent with the value found from the analysis of a large number of $3d$ and $4d$ systems.

In Figs. 2(a) and 2(b) we show comparisons between theory and experiment for the $N_7O_{4,5}O_{4,5}$ profile. The theoretical profiles are calculated assuming values of $U(^1G_4)$ of 3.4 and 4.6 eV and correspond to the theoretical profiles for the $N_{6,7}O_{4,5}O_{4,5}$ Auger group shown in Figs. 1(a) and 1(b), respectively. As in Fig. 1(a) the dashed profile in Fig. 2(a) corresponds to the calculated position of the spectrum, the solid line is the result of a shift by 1.2 eV to lower energy. The theoretical results for the $N_7O_{4,5}O_{4,5}$ profile are not as good as those obtained for the $N_{6,7}O_{4,5}O_{4,5}$ group possibly due to the presence in the experimental spectrum of contributions from energy loss processes accompanying the photoelectron spectrum of the Au $5d$ band which occurs to high kinetic energy of these transitions when they are excited by photons of 86 eV.[23] It is also possible that photon excitation so close to threshold will lead to the Auger spectrum being influenced by postcollisional-interaction effects. The background subtraction process applied to the experimental results for the $N_7O_{4,5}O_{4,5}$ profile (Fig. 2) results in a higher predicted intensity for the low-energy $^1S_0$ component than obtained from the background-subtracted spectrum of the $N_{6,7}O_{4,5}O_{4,5}$ profile (Fig. 1). This difference is a measure of the uncertainty in the background-subtraction procedure which is severe in this low-energy region. The theoretical profiles shown in Fig. 2 correspond to the results obtained for the whole group shown in Fig. 1 and have been evaluated using the relative intensities of multiplet components obtained from the Hg spectrum (Ref. 40 and Table I). In the $N_7O_{4,5}O_{4,5}$ case slightly better results are obtained using multiplet intensities obtained from the IC calculations (Ref. 34 and Table I) since these predict a higher intensity for the $^1S_0$ component. As in Fig. 1 the best agreement with experiment is obtained by shifting the profile calculated with a value of 3.4 eV for $U(^1G_4)$ to lower kinetic energy. The theoretical profiles in Figs. 2(a) and 2(b) both disagree with the experimental slope of the spectrum to higher kinetic energy, which may be a result of errors in the background subtraction or energy loss accompanying the valence-band photoelectron spectrum, but the shifted profile shown in Fig. 2(a) is in better agreement with the general distribution of intensity in the spectrum.

We have now established that our calculation of the Auger line shape is unable to account simultaneously for the position and shape of either the $N_{6,7}O_{4,5}O_{4,5}$ or the $N_7O_{4,5}O_{4,5}$ spectrum of metallic Au. The new feature incorporated into our use of the standard Cini-Sawatzky theory is the separate treatment of the $[5d_{3/2}]$ and $[5d_{5/2}]$ spin-orbit-split DOS's. We now show that this extension of the theory is not the source of the observed shift. We note that the center of gravity of the Auger profile depends on the binding energy of the local $5d$ hole, E_{5d}, on spin-orbit and Coulomb interaction parameters but is independent of hopping terms. The binding energies of the first moments of Christensen's[29] subbands are $E_{5/2}=3.8$ eV and $E_{3/2}=5.245$ eV. They correspond to a local level $E_{5d}=4.379$ eV with spin-orbit parameter $\zeta_{5d}=0.572$ eV. Using the values of the Slater integrals and the characteristics of the multiplet structure shown in Table I we calculate the center of gravity of the $N_7O_{4,5}O_{4,5}$ group from $2E_{5d}+S_iI_iE_i$ as 11.09 eV, compared with a value for the first moment of the calculated, unbroadened, spectrum as 11.35 eV. The difference between these two figures, which is attributable to rounding errors and numerical imprecision in the treatment of singularities in components of the multiplet structure, is small compared with their difference from the experimental value of ~13.5 eV. Since the broadening contributions should not shift the calculated position of the spectrum at all we can conclude that neither the introduction of a spin-orbit-split DOS nor the possibility of numerical errors in the computer code can explain the 1.2-eV discrepancy with experiment. Our calculation does depend on the accuracy of Christensen's results for the single-electron DOS in Au. However, the center of gravity of the Au d band given by Christensen's results, 4.44 eV, is in good agreement with experiment (we obtain ~4.54 eV from an analysis of the experimental data of Ref. 43 and Citrin *et al.*[32] obtain ~4.8 eV for the bulk DOS of Au) and although there could be a contribution to the observed shift from this source it could not account for the whole of the 1.2-eV discrepancy.

In seeking an explanation for the observed shift we first consider the possibility that the experimental results are dominated by surface effects. This is quite possible since the spectrum occurs at low kinetic energy in the region of the broad minimum in electron escape depths. Fortunately the changes in the surface electronic structure of Au have been investigated using high-resolution x-ray photoelectron spectroscopy (XPS) by Citrin *et al.*[32] They find that the surface component of the initial $[4f]$ states is less bound by 0.40 ± 0.02 eV compared with the bulk and that the center of gravity of the Au d band at the surface is less bound by 0.5 eV. It is not possible to repeat our analysis using the surface electronic structure since we need the spin-orbit-split DOS's of the d band and these have not been determined experimentally. However, it is easy to see that surface effects, if present, will increase the discrepancy between theory and experiment. This is because the d-band DOS enters into the calculation as a self-convolution of the single-electron DOS. This will result in a shift of ~1.0 eV to lower binding energy compared to the bulk. The resulting increase in the predicted kinetic energy of the Auger profile due to this shift is only partially compensated by the reduced binding energy of the surface-shifted initial state, and so to a first approximation surface effects are expected to shift the calculated Auger profile a further 0.6 eV higher in kinetic energy.

Given the agreement in spectral profile shown by the shifted spectrum in Fig. 1(a) it is reasonable to assume that there is some additional interaction not included in the Cini-Sawatzky treatment which is responsible for this shift. One possibility is that dynamic screening influences the position of the spectrum. However, a study of dynamic effects[44] indicates that the additional channels introduced into the decay usually result only in a change in shape of the spectrum and if anything in a shift to higher kinetic energy, the opposite direction to that which is required.

A more likely possibility is that the merging of the two-hole interaction terms and the screening terms of Eq. (3) into a single on-site correlation term $U(LSJ)$ in the Hamiltonian of Eq. (3) oversimplifies the description of the Auger process in condensed matter. Since the on-site term $U(LSJ)$ is used as a free parameter in calculating the Auger profile any true on-site contributions from atomic interactions or screening by the environment are automatically included in the analysis and cannot be the origin of the observed discrepancy. However, if there were more distant screening contributions they could account for the observed shift. We briefly describe this possibility in two different though not necessarily distinct ways. To begin with we can adopt the traditional separation of the hole-hole interaction and relaxation contributions to the last two terms on the right-hand side of Eq. (2) described in Ref. 5. If we group the hole-hole interaction and atomic relaxation contributions into $U(LSJ)$ we are left with an extra-atomic relaxation termed R_S^{ea}, the S denoting[5,45,46] that this term is a static screening term which represents the difference between the screening of a double-hole state $R^{ea}(d^2)$ and twice the screening of a single-hole state, $2R^{ea}(d^1)$. If the screening is linear $R_S^{ea}=2R^{ea}(d^1)$ and it should be accurate to include these terms into $U(LSJ)$ and expect the standard form of the Cini-Sawatzky theory, treating $U(LSJ)$ as a free parameter, to predict both the position and the shape of the Auger profile. However, if the screening is less than linear we should write the last two terms on the right-hand side of Eq. (2) as $U(LSJ)+R_S^{ea}$ and with R_S^{ea} reduced in value and then we would obtain a shift in the theoretical spectrum to lower kinetic energy as required. If we adopt a local atomic description of the likely screening configurations then we expect the local configuration to become $5d^{10}6s^2$ in the presence of the core-hole and something like $5d^8 6s^2 6p^1$ in the final state. It is quite possible that the $6p$-like screening orbital will be more extended and provide less efficient on-site screening than the $6s$-like orbital with a consequent shift of the whole spectrum to lower kinetic energy as required. This would be a similar effect to the well-known reduction in the value of the relaxation contribution to the binding energy of core-hole states that accompanies the change in the character of the screening orbital at the end of the $3d$ series.[5,47–50]

In terms of the Cini-Sawatzky theory, what is required is an extension of the theory to include the radial dependence of the $U(LSJ)$ term. As presently constructed the Hamiltonian assumes that the two holes are screened on site in the sense that they do not interact at all when they are some distance apart. Since the Auger matrix element includes the wave function of the on-site core hole in the initial state we expect that the effects of any radial dependence of $U(LSJ)$ would be restricted to nearest neighbors and this is confirmed by theoretical studies on clusters in which it is found that a cluster consisting of at most the next-nearest neighbors gives identical results to those found for an extended solid.[51] A $U(r,LSJ)$ interaction sensitive to nearest-neighbor distances could explain the observed shift; if in the limits of this interaction $U(r,LSJ)$ had an on-site value U_0 and a value U_n for holes on adjacent sites then we would expect to observe a profile described by the standard Cini-Sawatzky theory but with an effective U, $U_{\rm eff}=U_0-U_n$ and the whole spectrum shifted to lower kinetic by U_n. Of course, assuming that the adjacent hole configurations can be represented by a constant shift U_n is a simplification and one would expect that the inclusion of a distance dependence of the interaction would also result in some inhomogeneous broadening.

V. CONCLUSIONS

We have shown that the standard form of the Cini-Sawatzky theory is unable to account simultaneously for both the kinetic energy and the spectral profile of the $N_{6,7}O_{4,5}O_{4,5}$ and $N_7O_{4,5}O_{4,5}$ Auger transitions of metallic Au. The theory gives excellent agreement with the spectral profile of the $N_{6,7}O_{4,5}O_{4,5}$ transitions though these are predicted to occur 1.2 eV higher in kinetic energy than observed experimentally. This shift may be loosely attributed to relaxation contributions arising from nonlinear screening. It is possible that an extension of Cini-Sawatzky theory to include the distance dependence of the screening and electron correlation interactions will be able to account for both the kinetic energy and the spectral profile of the Au $N_{6,7}O_{4,5}O_{4,5}$ transitions.

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