Sublifetime-resolution Ag L_3 -edge XANES studies of Ag-Au alloys

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High-resolution Ag L_3 -edge XANES for a series of Au-Ag alloys, AuAg₃, AuAg, and Au₃Ag, have been obtained by monitoring the intensity of the highly energy-resolved Ag $L_3M_{4,5}M_{4,5}(^1G_4)$ Auger line. The experimental results reveal features that were previously unresolved with total electron yield techniques and confirm previous observations that Ag gains d charge and Au loses d in Au-Ag alloys. Full-scale multiple scattering calculations for the Ag L_3 -edge XANES of Ag and AuAg yield semiquantitative agreement with the experiment. The results show that in the case of wide band metals, the Auger yield of a well-separated narrow final state can indeed be used to improve the resolution of XANES near the threshold. The implication of the results to electron charge redistribution upon alloying is discussed. [S0163-1829(98)02235-8]

I. INTRODUCTION

The characteristic emissions, i.e., fluorescence photons and electrons associated with the creation and deexcitation of an atomic inner-shell vacancy, are modified markedly if the energy of the exciting photon is varied in the threshold region. Recent experimental and theoretical progress in the study of resonant inelastic x-ray scattering has led to a better understanding of these phenomena.¹⁻⁴ The resonant scattering is treated as a single second-order process embedding the one-electron excited state as a virtual intermediate step with essentially no relaxation if the intermediate-state lifetime Γ_i is short. This implies energy conservation in the excitation from the initial ground state to the final scattering state. Consequently, the available excess energy is shared by the two emitted particles, the “primary” photoelectron and the “secondary” fluorescence photon or Auger electron. If the final-state lifetime is relatively long, i.e., $\Gamma_f < \Gamma_i$, it is possible to reduce the effect of the intermediate-state lifetime broadening. This becomes apparent for intermediate excitation into discrete localized states or bandlike states near the Fermi level (in metals) where a characteristic sublifetime line narrowing is observed in high-resolution fluorescence and Auger spectra.²⁻⁶

In transmission or total yield experiments, there is no final-state selection and all spectral features are broadened due to the core-hole lifetime Γ_i . This is particularly undesirable for XANES studies where the information-rich, inherently narrow near-edge structure is smeared out. It is thus natural to consider utilizing the final state induced narrowing for XANES experiments in order to reduce the intrinsic lifetime broadening. Experimentally, this is accomplished by monitoring the yield corresponding to a narrow final state, e.g., a particular fluorescence or Auger line when the photon energy is tuned across the absorption edge. For the experiment to be successful, it is required that the combined photon

and analyzer energy resolution is smaller than the core-hole lifetime broadening. Thus the measurement demands a very bright photon source and an efficient detection scheme. The first study of this kind was reported by Hämäläinen *et al.*⁵ who used the Dy L_α fluorescence to measure the L_3 edge of Dy compounds. Additional fine structure in the spectra was indeed observed, which is unresolved in the corresponding transmission data. However, while this experiment is conceptually simple and straightforward, the interpretation of the data generally is not.³ For narrow-band solids, such as the rare-earth metals and compounds, the coupling of the core hole to the valence shell in the intermediate excited state results in a complex final-state structure. The measured yield modulation for a constant final state (fluorescence) energy as a function of excitation photon energy in this case is not directly related to a one-electron density of states.

The situation is much more manageable for wide-band materials.^{2,3,6} This is evident from a detailed study of the resonant Auger electron emission from Ag by Drube *et al.*² where a single-particle band structure picture can explain the line-shape modulations in the resonance regime. It has been further recognized that the x-ray absorption spectra for most 3d and 4d metals can well be described using a one-electron band structure approach.⁷ Reduced lifetime constant final-state XANES spectra from these materials can therefore be expected to provide direct information on the partial unoccupied densities of states.⁶ It should be noted that the above-stated argument also applies to conventional XANES.

For the Ag-Au alloy system discussed here, it is well known that the single-particle approximation is valid in x-ray-induced excitation processes so that many-body effects are relatively unimportant; in addition, we are interested in changes in a series of closely related metallic alloys, so that any effect of the corehole would be further minimized.

The AuAg alloy system has been traditionally a prototype for the study of Friedel charge screening and the interaction

of noble metal d bands.^{8–13} This system continues to be of great interest to experimentalists and theorists alike as instrumentation techniques and computational tools, respectively, advance. Of particular interest is the nature of charge redistribution at the atomic site when alloys are formed. Photoemission and Au¹⁹⁷ Mössbauer techniques have been used extensively in the studies of the occupied electronic states of this system, especially at the Au site. It has been shown that significant charge redistribution occurs upon alloying and it can be understood in terms of a compensation mechanism (rehybridization) in which Au loses d charge and gains s charge while Ag loses s charge and gains d charge¹¹ so that there is only a small net charge flow onto the Au site in accord with electroneutrality (atoms tend to be neutral locally in metallic systems) and electronegativity (Au is the most electronegative element) considerations. The notion of d -charge depletion at the Au site and d -charge gain at the Ag site in these alloys has been recently confirmed with total electron yield (TEY) XANES measurements at both the Au $L_{3,2}$ (Ref. 12) and the Ag $L_{3,2}$ edges.¹³ Despite the usefulness of these TEY measurements in affirming the direction of the charge transfer, the XANES features are hampered by core-hole lifetime broadening.

Here we report a partial Auger electron yield measurement of the Ag L_3 -edge XANES for a series of AuAg alloys: Au_{0.25}Ag_{0.75}, Au_{0.5}Ag_{0.5} and Au_{0.75}Ag_{0.25} (henceforth denoted AuAg₃, AuAg, and Au₃Ag, respectively) and show that this technique can indeed be used to obtain meaningful Ag XANES with better resolution within a few eV of the threshold. Charge redistribution upon alloy formation from the Ag perspective has been studied by examining the systematic change in the Auger yield just above the threshold. A multiple scattering (MS) technique has been used to calculate the Ag L_3 -edge XANES for the Ag metal and the AuAg alloy. Excellent agreement between experiment and theory is obtained within the first 15 eV of the threshold.

II. EXPERIMENTS AND CALCULATION

The experiments were performed at the x-ray wiggler beamline, BW 2 (Ref. 14) at HASYLAB. The photon flux at the focal spot ($\sim 1 \times 1 \text{ mm}^2$) was $1 \times 10^{12} \text{ s}^{-1}$ within a bandwidth of $\Delta E = 0.7 \text{ eV}$ at 3350 eV. The alloys were prepared with a stoichiometric amount of ultrapure metals as described elsewhere.^{12,13} The alloy samples were rolled followed by annealing and were mounted in a UHV chamber. Clean surfaces were obtained by Ar sputtering and moderate heating cycles prior to the measurement. Electrons were collected with a hemispherical electron energy analyzer ($\Delta E = 0.5 \text{ eV}$). The Si(111) double crystal monochromator was calibrated at the L_3 edge of pure Ag at the documented value of 3351.0 eV. The accuracy in the calibrated energy is within 0.1 eV.

Partial Auger yield XANES measurements were made by monitoring the intensity of the main 1G_4 line ($\Gamma_f = 0.58 \text{ eV}$) of the L_3 - $M_{4,5}M_{4,5}$ Auger transition.² A typical set of Auger spectra excited on and above resonance is shown in Fig. 1. In the threshold-excited spectrum ($\Delta h\nu = 0 \text{ eV}$) several distinct lines are resolved. They can be assigned to $3d^8$ final-state components when compared to calculated values as indicated.¹⁵ The highest transition rate is

FIG. 1. High-resolution Ag $L_3M_{4,5}M_{4,5}$ Auger spectra excited with photon energy at and above the L_3 edge. Note the pronounced line narrowing for the threshold excited spectrum. The relative final-state energies and transition rates are reproduced from Ref. 15.

obtained for the 1G_4 line, which is also well separated from other stronger components. Therefore it is chosen for the experiment. The resonant line narrowing is clearly evident by comparing the above-threshold-excited spectrum. Also notice the pronounced asymmetry in the resonance spectrum, which is caused by the Fermi energy cutoff in the intermediate state. In fact, the high-energy flank of the line corresponds to the Fermi edge broadened by the final-state lifetime and the experimental width. Likewise, the small bump on the low-energy side can be related to structure in the one-electron density of states.² The additional broad peak appearing in the off-resonance case is a satellite emission likely due to shakeup in the final state. This emission does not significantly affect the 1G_4 intensity.

The 1G_4 line final-state energy was accurately determined from the measured Auger electron energy distribution with excitation energy far above the threshold. It should be noted that postcollision interaction-induced energy shifts of the Auger lines were not observed in these materials within the experimental accuracy.

The Ag L_3 -edge XANES for a fcc Ag metal and a fcc AuAg alloy have also been calculated using a full-scale multiple scattering scheme. The detailed description of the computational scheme is published elsewhere.¹⁶ The full multiple-scattering algorithm we used has been discussed previously.¹⁷ For phase shift calculation, we obtained a crystal muffin-tin (MT) potential with touching MT spheres. We used the muffin-tin approximation according to a Mattheiss prescription with Slater exchange parameters. Atomic charge densities were obtained with the help of the self-consistent Dirac-Slater method. The procedure for the MT potential construction and MT radii selection was described in detail previously.¹⁶ Ag metal has fcc structure with a lattice parameter equal to 4.0862 Å.¹⁸ In the first approximation we treated the AgAu alloy as having the same lattice but with Au atoms substituting for half of the Ag atoms. In the calculation clusters with up to 6 shells were used. The structures of the clusters are summarized in Table I. The values of MT spheres radii are 1.445 Å (Ag) and 1.441 Å (Au). The MT constants (part of the averaged crystal potential if the

TABLE I. Structure parameters of the clusters around the Ag site employed in the calculation for Ag metal and AgAu alloy in a fcc lattice.

Shell number	Sphere radii (Å)	AuAg alloy		
		Ag metal No. of atoms	No. of Ag atoms	No. of Au atoms
1	2.8894	12	8	4
2	4.0862	6	2	4
3	5.0046	24	8	16
4	5.7788	12	8	4
5	6.4608	24	16	8
6	7.0775	8	0	8

vacuum level energy is zero) were found to be -13.35 eV for the Ag site and -14.04 eV for the Au site.

In the calculation we included phase shifts with orbital momentum up to 4, but even with $l=3$ there is almost no change in the calculated spectra. In order to compare theoretical spectra with the experimental data, one needs to take into account the contributions that cause the broadening of the spectra. These are the energy-dependent mean free path of the photoelectron⁷ and the experimental resolution (the effective resolution is ~ 1.1 eV). We included all of these factors in the imaginary part of the complex potential used in the calculation. The results indicate that there was little difference going from 5 to 6 shells. The calculation presented here are based on 6 shells (87 atoms in a fcc lattice).

Both $p \rightarrow d$ and $p \rightarrow s$ dipole channels were evaluated. The calculation shows that the Ag L_3 -edge XANES was dominated by the $p \rightarrow d$ channel, primarily due to matrix element effects; that is that the transition matrix element corresponding to the $p \rightarrow d$ transition is much larger than that for the $p \rightarrow s$ transition. This is illustrated in Fig. 2 where both channels together with the overall spectrum are displayed.

III. RESULTS AND DISCUSSION

A. General considerations

Figure 3 shows the Ag L_3 -edge XANES for a series of AuAg alloys together with that of Ag metal. The spectra have been normalized to unity edge jump¹⁹ and are aligned at the point of inflection, E_0 , so that the Fermi levels for the alloys are at the same energy position as that of the metal. It should be noted that E_0 (before alignment) exhibits a linear chemical shift to lower photon energy as Ag becomes more diluted in Au. This indicates that the Ag site is better screened in the alloy. These shifts show the same trend as the chemical shifts of the Ag $3d$ level for the same series of alloys.^{12,13} These parameters, together with those reported previously for the Au site are given in Table II. It is interesting to note that all spectra show a distinct three-peak pattern within the first 10 eV (inset) above the threshold. The intensity of the first peak increases slightly in the alloys while the intensities in the region of the second and the third peaks decrease markedly as Ag becomes more dilute in Ag; this is accompanied by a dispersion of the second and the third peaks to lower and higher photon energy, respectively. At higher photon energies (>20 eV about the threshold),

FIG. 2. Ag L_3 -edge XANES for fcc Ag metal obtained with the multiple scattering calculation. The $p \rightarrow d$ and $p \rightarrow s$ channels are also shown separately.

however, no dispersion is noticeable. It should also be noted that although both Auger yield and TEY show the same trend, the small difference in the intensity of the first peak was not detectable in TEY XANES,¹³ where the difference in intensity was dominated by the second and the third peak.

Figure 4 compares the experimental Ag L_3 -edge XANES of Ag metal, recorded with both partial Auger yield (1G_4 line) and total electron yield, together with the theoretical spectra based on MS and band calculation.⁷ In the MS calculation the spectrum is broadened with the effective resolution of the Auger yield while the band calculation was con-

FIG. 3. Ag L_3 -edge XANES for Ag, AuAg₃, AuAg, and Au₃Ag recorded with the partial Auger yield.

TABLE II. Relevant parameters for the AuAg alloys relative to the metal.

Alloy	White line area (10^4 eV cm $^{-1}$) ^a				Ag ^b		Au ^c	
	ΔA_1	ΔA_2	ΔA	ΔE_0	$\Delta BE(3d)$	Δh_t	$\Delta BE(4f)$	Δh_t
AuAg ₃	0.13	-0.328	-0.198	-0.15	-0.11	-0.04 ₁	0.13	0.089
AuAg	0.16	-0.705	-0.544	-0.25	-0.18	-0.09 ₆	0.07	0.073
Au ₃ Ag	0.095	-1.26	-1.163	-0.46	-0.25	-0.17 ₈	0.034	0.034

^aUncertainty $\approx 5\%$.^bFrom Ref. 13, Δh_t was obtained by scaling the TEY results: $\Delta h_t(\text{Auger})/\Delta h_t(\text{TEY}) = \Delta A(\text{Auger})/\Delta A(\text{TEY})$.^cFrom Ref. 13.

voluted with a resolution typical of the TEY measurement. Two features are apparent. First, the improvement in resolution in the Auger yield data is significant as can be seen in the much steeper rise of the threshold and the narrower width of the resonances. Second, the MS calculation not only reproduces the first three resonances very accurately but also predicts all the structures derived from the band calculation of Müller⁷ albeit the discrepancy in positions compared to the experiment increases progressively beyond the threshold region. Such a discrepancy for the Slater type exchange potential for pure Ag densities of states has also been found previously.¹⁷ For better agreement, one needs to use a more sophisticated energy-dependent exchange potential like the Dirac-Hara potential.²⁰ In the following, we will compare the results for the alloy AuAg with that of Ag metal.

B. Ag L_3 -edge XANES and charge redistribution

Figure 5 shows the XANES region just above the threshold for AuAg and Ag as obtained from both experiment and

FIG. 4. Comparison of Ag L_3 -edge XANES obtained with the partial Auger yield (1G_4), total electron yield, multiple scattering calculation, MS (this work), and band calculation (Ref. 7). The MS spectrum was convoluted with the effective resolution of the Auger yield experiment while the band calculation is convoluted with the resolution corresponding to the TEY experiment.

MS calculation and the difference curves (alloy metal). It has been shown that this region is of particular importance to charge redistribution considerations.¹³ The question as to how wide a region above the threshold should be used in charge transfer considerations has been discussed previously.¹³ The spread is due largely to core-hole lifetime contributions convoluted into the unoccupied densities of states and instrument resolution. Our experience with TEY measurements indicates that the region of interest is typically 10–15 eV for $3d$ - $5d$ transition metal $L_{3,2}$ edges, respectively, and in the case of Ag, is ~ 12 eV.^{13,2}

What is clearly noticeable from Fig. 5 is that the MS calculation predicts semiquantitatively the difference curve between the alloy and the metal; that is, that the integrated

FIG. 5. Comparison of Ag L_3 -edge XANES between AuAg and Ag: upper panel, experiment; lower panel, multiple scattering calculations. All spectra are normalized to the edge jump. The difference curves are also shown.

area under the difference curve exhibits the same pattern as observed and decreases upon alloying (the negative area is considerably larger than the positive area). Our calculations show that the transition matrix element in the energy interval of the Ag L_3 edge is a slowly changing, monotonic function of energy. In the dipole approximation the x-ray-absorption coefficient is proportional to the projected density of states times the square of the transition matrix element; in the present case, we can use the shape of the Ag L_3 edge and the area under the difference curve to infer the change in the distribution of the unoccupied densities of states in the conduction band of the alloys at the Ag site. In addition, the transition is dominated by the $p \rightarrow d$ channel (Fig. 2), therefore the difference curve reflects primarily changes in the distribution and the average count of the d holes at the Ag site in the alloys, hence the direction of d -charge redistribution.

A reduction in area under the curve (Fig. 5, ΔA) indicates that Ag gains d charge upon alloying (the smaller the resonance intensity, the smaller the d hole count, the larger a gain in d charge). This observation is in agreement with the E_0 and Ag 3d binding energy shift as well as previous measurements.^{10–13} It is also in good accord with the calculation of Lu *et al.*²¹ who show that within the muffin-tin sphere Ag gains d and loses s charge while Au loses d and gains s charge. The small positive area change is observed experimentally for the first time for Ag as the result of high resolution and is attributed to the redistribution of the unoccupied d states above the Fermi energy. It is interesting to note that this behavior is entirely reproduced by the MS calculation. Similar patterns have recently been observed at the Cu L_3 edge for a series of Cu-Au alloys.²²

The above analysis confirms the validity of the procedures and arguments used in the discussion the $L_{3,2}$ edge of noble metals that do not normally exhibit intense white lines.^{12,13} The analysis of the other Ag-Au alloy spectra confirms the previously observed trend that Ag gains d charge when diluted in Au.¹² Results relevant to the Ag site are summarized in Table II and shown in Fig. 6 where the chemical shifts and area under the curve ΔA (ΔA_1 and ΔA_2 are the positive and the negative areas and $\Delta A = \Delta A_1 + \Delta A_2$) are plotted as a function of alloy composition (Au atomic fraction).

It can be seen that the area under the difference curve becomes more negative upon dilution, and this is accompanied by a decrease in the Ag 3d binding energy and the threshold energy E_0 . This result indicates d charge gain at the Ag site upon alloying. Thus Ag must lose sp -type conduction charge to satisfy electroneutrality and electronegativity considerations since Ag is less electronegative than Au and a small net charge flow from Ag to Au is expected.

Figure 7 plots the change of d hole count Δh_t between the alloy and the pure element and their corresponding core-level shifts at both the Ag and the Au site. The difference in d hole count for Ag was estimated from the area under the difference curve, ΔA , within the first 12 eV above the threshold. One can write the following expressions:^{23,24}

$$\Delta A_2 = CE_2(\Delta h_{3/2}/3), \quad (1)$$

$$\Delta A_3 = CE_3(\Delta h_{5/2} + \Delta h_{3/2})/15, \quad (2)$$

FIG. 6. Correlation of chemical shifts and area under the curve, $\Delta A = (\Delta A_1 + \Delta A_2)$ with alloy composition; subscripts 1 and 2 denote the positive and negative area, respectively, of the difference curve.

where C includes the fine-structure constant, the number density, and the square of the matrix element and is to a good approximation a constant. E_2 and E_3 denote the threshold energy of the edges and $\Delta h_{5/2}$ and $\Delta h_{3/2}$ the difference in $d_{5/2}$ and $d_{3/2}$ hole counts (total d hole count difference, Δh_t , is the sum of the two). For most transition metals the ratio of $d_{5/2}$ and $d_{3/2}$ hole counts is close to 1.5, a statistical value but for the noble metals there may be significant deviations and the ratio sometimes varies from compound to compound. Although we have only measured the L_3 edge in the high-resolution experiment, we can scale it to the TEY measurements¹³ where both L_3 and L_2 data were available, so that $\Delta A/\Delta h_t$ is a constant in both measurements. This procedure yields the total d hole count at the Ag site from the

FIG. 7. Correlation of XPS binding energy shifts and d hole count difference at the site vs composition of Au in Au-Ag alloys. The dotted line represents the correlation previously obtained for these alloys using TEY (Ref. 13).

Auger yield measurement (Fig. 7). The Au results are from a previous study.¹² One can easily see from Fig. 7 that Ag gains and Au loses d charge when diluted into each other and that the core-level binding energy shifts in the same direction as the d hole count (a negative value means gaining d charge and decreasing binding energy). This is because the binding energy is largely determined by the significant difference in the Coulomb integrals, $F(\text{core}, d) - F(\text{core}, \text{non-}d)$ where core is $4f$ and $3d$, and $5d$, $6s$ and $4d$, $5s$ are the d and non- d charges, respectively, for Au and Ag. Extrapolations of the d hole count difference correlations yield a d hole count difference of 0.13 (a loss of d charge relative to pure Au) and -0.24 (a gain of d charge relative to pure Ag) respectively for Au and Ag in infinite dilution.

It is interesting to compare the infinite dilution result for Ag (gains 0.24 d charge) with the calculated maximum d hole count available in pure Ag that can be filled. Theory²¹ shows that the d hole count in pure fcc Ag is 0.349, the maximum d vacancy possible that can be filled. The alloying trend indicates that although the Ag d band gets increasingly filled upon dilution, the Ag d band can never be totally filled even in infinite dilution. This result is in line with results reported for the Pd-Ag system.²⁵ It is also interesting to compare the infinite dilution results with Fermi surface measurement in dilute alloys. Templeton and Coleridge⁹ reported Friedel phase shifts for these alloys and found that d charge flows from Au onto Ag and s charge flows from Ag to Au. Our results are in good agreement with their observation.

IV. CONCLUSION

Selecting the narrow Ag $1G_4$ final state of the Ag $L_3M_{4,5}M_{4,5}$ Auger transition as a monitor, we have carried out a sublifetime resolution constant-final-state measurement of the Ag L_3 -edge XANES for a series of Ag-Au alloys. We have also performed a multiple scattering calculation of the Ag L_3 -edge XANES for fcc Ag metal and a AuAg alloy. The calculation is in excellent agreement with the experiment and the results not only confirm earlier total electron yield observations that Au loses d charge and Ag gains d charge upon alloying but also reveals features at the Ag L_3 edge previously unresolved in TEY. Thus we have shown that this kind of constant final-state measurement is indeed a viable tool to advance the understanding of XANES features in situations where the intermediate excitation can be described within the one-electron approximation. Experimentally, this technique should be applicable to a large number of systems containing $4d$ metals such as bimetallic, magnetic, and catalysts materials, and metal silicides.

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