Lawrence Berkeley National Laboratory

Recent Work

Title

THE SURFACE COMPOSITION OF THE SILVER-GOLD SYSTEM BY AUGER ELECTRON SPECTROSCOPY

Permalink

<https://escholarship.org/uc/item/24z4f7m2>

Author

Overbury, S.H.

Publication Date

1975-05-01

Submitted to Surface Science

LBL-3925
Preprint c. /

THE SURFACE COMPOSITION OF THE SILVER-GOLD SYSTEM
BY AUGER ELECTRON SPECTROSCOPY

S. H. Overbury and G. A. Somorjai

RECEIVED
LAWRENCE

BERKELEY LABORATORY

AUG 20 1975

May 1975

LIBRARY AND
DOCUMENTS SECTION

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-3925
c. /

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE SURFACE COMPOSITION OF THE SILVER-GOLD SYSTEM
BY AUGER ELECTRON SPECTROSCOPY

S. H. Overbury and G. A. Somorjai

Inorganic Materials Research Division, Lawrence Berkeley Laboratory
and Department of Chemistry; University of California
Berkeley, California 94720

Abstract

The surface composition of polycrystalline Ag-Au alloy foils is studied by Auger electron spectroscopy. The intensities of principal Auger peaks over a wide range of electron energies are obtained as a function of alloy bulk composition for the clean equilibrated surfaces. Their ratios are compared with ratios expected for a surface showing no surface segregation, and for a surface obeying the regular solution monolayer model that predicts silver surface segregation. The experimental results give evidence for enrichment of the surface with silver, but to an extent less than predicted by the regular solution model.

Introduction

It has long been speculated that the existence of differences in surface energies of metals can lead to selective adsorption or segregation at the surface of an alloy. Theories have been developed to describe thermodynamically the nature of this segregation in mixtures, both liquid and solid.^{1,2,3,4} With the advent of techniques which allow the surface layers of a solid to be probed quantitatively, the nature of surface segregation in alloys has become a topic of increasing interest and controversy.⁵

One of the most popular fields of study has been binary homogeneous solutions. Typical of such a system is Ag-Au. Silver is completely soluble in gold and, thus, they can be melted together in any proportion without phase separation. This is due to their practically identical lattice spacing, and the fact that they have the same crystal structure, similar melting points and electronic structures. In addition, Au and Ag are relatively unreactive and the clean alloy surfaces can be prepared and maintained without great difficulty. The surface energies are also different as may be expected since the heat of sublimation of Ag is about 20% lower than that of Au.⁶ Thus, the binary alloys of Au and Ag are good choices for studying equilibrium surface segregation in single phase disordered alloys.

Auger Electron Spectroscopy (AES) is a useful technique for elucidating the details of the depth distribution of composition in alloys. Many recent studies have revealed details of the attenuation of low-energy electrons in solids and have shown that the escape depths depend on energy in a manner that is nearly independent of the particular solid.^{7,8} This

fact suggests a method of analyzing the depth distribution of composition of an alloy from the surface inward. A relatively low-energy Auger electron (~ 100 eV) may be expected to yield information about the top one or two atomic layers whereas an electron of energy around 2000 eV may be expected to give information about the top 10-20 layers. Therefore, the relative intensities of Auger peaks at several different energies should contain the depth distribution information. In the work reported here, measurements have been made of relative intensities from Auger peaks of a wide energy range, for a series of equilibrated and clean Au-Ag alloys. The results are compared with the results expected from theory.

Experimental

Weighted quantities of 5 N Ag and 6 N Au were melted together on a water cooled copper hearth of an arc furnace. The resulting buttons were sealed into quartz tubes under an Ar atmosphere and were homogenized in a furnace. The samples were all annealed at about 1000°C for at least 100 hours. The samples were then cold rolled into foils of thicknesses between .010 and .015 cm, which was then cut into pieces of the desired size. No further etching or polishing was done.

The bulk composition of the samples was known from the amount of Au and Ag weighted out in preparing the samples. As a check, pieces cut from the foils were analyzed in solid form by X-ray fluorescence. This analysis suffered however from lack of a solid Au-Ag alloy standard. To correct this, the density of the sample with composition $x_b^{\text{Au}} = 0.65$ was determined using a pycnometer and a balance and the density was used to obtain the composition. This sample was used as a standard in the X-ray fluorescence. The results of the X-ray fluorescence and of the density determination agreed well with the compositions expected from the original preparation.

The six samples and foils of pure Ag and Au (which were rolled in the same manner as the alloys), were mounted together on a tantalum block. The block was designed in such a way that the surfaces of the samples would be normal to the axis of the Auger analyzer. In fact, the samples were slightly (less than 10°) off normal. The samples were connected to Cu braid heating leads using stainless steel screws and Ta pieces and were insulated with mica in such a way that the samples could be heated resistively to around 400°C. An IR pyrometer was used to estimate the

temperatures of the samples. The pyrometer was calibrated with a chromel-alumel thermocouple attached to the edge of one of the samples.

The samples were not polished, but since they were all prepared in the same manner, their surface "finish" may be expected to be comparable. In some cases heating and handling caused some buckling of the foils. The effect of this is to change the angles of portions of a sample relative to the analyzer. This introduces some uncertainty, but since the intensity ratios could be quite well-reproduced at various areas on the samples, this effect is believed to be unimportant.

The Auger measurements were performed on a Physical Electronics double pass type cylindrical mirror analyzer (CMA) using a co-axial 5 keV electron gun. A primary electron beam of 4000 eV was used with a beam current of 50 to 60 μ a. The electron gun was always warmed up for times sufficient to stabilize the output before measurements were made. Whenever measurements were made to compare absolute intensities from different samples the measurements were made in close succession to eliminate uncertainties due to drift in multiplier gain or in the electron gun output. A modulation potential of 2V p-p with a frequency of 4500 Hz was used.

Changing samples was effected by rotation about the manipulator axis and translation along this same axis. Fine adjustment could be made using two micrometer screws on the manipulator which gave linear translation perpendicular and collinear to the CMA axis. The spectrometer was found to be extremely sensitive to sample positioning. However, a method was developed for reproducibly positioning the sample. This involved setting the analyzer voltage to the voltage expected for the high-energy minimum

of the elastic peak and maximizing the negative deflection by moving the sample only along the axis with the micrometer screw. The reproducibility came from adjusting the analyzer voltage to the same value. Using this procedure the absolute intensities could be reproduced to within about 4% following any repositioning of the sample.

The polycrystalline foils were cleaned by argon bombardment using a 1.5 keV Ar^+ beam. This sputtering was found to always result in an enrichment in Au due to the higher sputtering coefficient of Ag. In separate experiments it was determined that this sputtering effect could be reproducibly annealed out. Heating to 400°C would anneal out the effects of sputtering in less than about 10 minutes whereas heating at 300°C would require closer to an hour to remove the effects. This information was obtained by monitoring the Au/Ag Auger intensity ratios as a function of heating times. Initially, the samples were contaminated with S, O, Cl, N, and C, which were removed by Ar bombardment. Typically, S, N, and Cl were reduced to below the detection limit while for some samples, especially the sample with $x_b^{\text{Au}} = 0.65$, very small amounts of O and C, believed to be less than 10% of a monolayer in all cases, were present. In some cases a trace of included Ar could also be seen. The Au, Ag and alloys were found to remain quite clean inside the UHV system (base pressure 1×10^{-9} Torr), with some very slow adsorption of nitrogen, especially on the Au-rich samples. The nitrogen could always be flashed off. The bulk, however, was a source of impurities, especially sulfur, and several cycles of sputtering and annealing were required to remove enough sulfur from the surface regions of the Ag-rich samples in order that they could be annealed without sulfur segregation.

It was found that the presence of the heating current in the sample affected the Auger spectrum obtained. This effect was caused by the heating current and was not due to variation of sample temperature. Therefore, all of the spectra were run with the heater current off. Upon turning off the heating current the temperature typically dropped from 400 to 200°C, within about a minute. The sample run may then be regarded as having been quenched from 400°C and to have surface compositions obtained by equilibration at that temperature.

After annealing the samples, a full scan of the Auger spectrum up to about 530 eV was taken to check for impurities, and at times the scans were extended to about 800 eV to check for Fe impurities from the stainless steel screws used in the heating connections. No Fe contamination was ever observed. Following a full scan the peak intensities were obtained by sweeping across the desired peaks several times to obtain an average value. In cases where peak intensities from an alloy were to be compared with those of a reference, the peak intensities of the reference were run immediately after the alloy. This was then followed by a full scan of the reference to determine that it too was clean.

Results

Spectra which are typical of the annealed samples and demonstrating the level of cleanliness obtained are shown in Fig. 1. The peak intensities were taken as the peak-to-peak values of the $dN(E)/dE$ curves. The peaks used in the analysis are all previously reported⁹ and were measured at 68 eV, 238 eV, and 2017 eV for Au and 348 eV for Ag. These energies will be used to label the peaks throughout the paper.

The measured intensities are given in Table I. All intensities are given as ratios of two peak intensities. Ratios of peaks of different energies are labelled R and are subscripted with the peak energies. For example, $R_{68;348}$ is the ratio of the intensity of the Au (68eV) peak to the Ag (348eV) peak from a particular alloy. In some cases "°" will be included as a superscript, (for example, $R^{\circ}_{68;348}$), to indicate that this ratio compares peak intensities from the pure silver and gold reference samples. The label ξ is used when comparing the intensities of a peak of one particular energy to that same peak in the pure Au or Ag references. For example, ξ_{68} is the ratio of the intensity of the Au (68eV) peak in an alloy divided by the intensity of the Au (68eV) from pure Au. At first glance ξ_{68} would appear to represent the atom fraction of Au in the region sampled by a 68 eV electron.

A correction which proved to be significant in some cases was applied to the data. In the spectrum of pure Ag a small peak was observed with a minimum at 237 eV, which thus overlapped the Au (238eV) peak. The peak was measured to be 0.003 times as intense as the Ag (348eV) peak. The Au (238eV) peak intensity from an alloy was thus corrected by subtracting

0.003 times the Ag (348eV) peak intensity (also from the alloy), from it. The actual (corrected) peak intensity was then lower than the measured intensity as much as 35% for the alloy sample richest in silver ($x_b^{\text{Au}} = 0.15$). The corrected values are given in Table I along with the uncorrected values.

A slight change was observed in the Au (58eV) peak which varied with alloy composition. A high-energy shoulder appeared in the peak, the intensity of which increased with Ag concentration. This peak was observed at 71 eV. Figure 2 illustrates the trend. The origin of the peak was not studied, but would appear to be due to alloy matrix effects. Its existence could affect a quantitative analysis in at least two ways. A growing shoulder could alter the shape of a peak, invalidating the assumption that peak-to-peak height is proportional to the Auger intensity. Secondly, the growth of this shoulder may represent a change in some Auger transition or ionization probability which would invalidate the assumption that the Auger intensity is proportional to the number of emitting atoms within the detected volume. Regarding the first of these possibilities, the peak at 71 eV appeared to be high enough in energy that it may well have not affected the peak shape of the peak at 68 eV. The second fact that this peak appeared to be enhanced by Ag concentration does not imply that the peak at 68 eV was altered. No trend was observed in the data which indicated that the behavior of the Au (68eV) was affected by this development. As such, the intensity values for this useful low-energy peak are used.

All the values presented in Table I are from clean samples believed to be fully equilibrated. For two samples upon which several measurements were made, standard deviations are given to demonstrate the amount of scatter in the data. This scatter is indicative of the error introduced

TABLE I

Auger Peak Intensity Ratios Obtained from Au, Ag and Au-Ag Alloys

$\frac{R_{Au}}{R_{Ag}}$	.15±.02	.33±.03	.41±.04	.51±.04	.65	.97±.02	pure Au and Ag
$R_{68;348}$	.112	.37±.03	.566	.725	1.36	16.6±1.	1.12±.01
$R_{238;348}$	.0085	.0184±.0005	.0265	.0362	.0674	.69±.01	.0521±.0006
$R_{238;348}^{corr.}$	.0055	.0153	.0236	.0333	.0647	.69±.01	.0521±.0006
$R_{2017;348}$	.0039	.009±.001	.013	.017	.035	.32±.01	.0236±.001
$R_{68;238}$	13.2	20.3±1.4	21.4	20.0	20.2	23.9±.9	21.5±.4
$R_{68;238}^{corr.}$	20.3	24.4	24.0	21.7	21.1	23.9	21.5
$R_{68;2017}$	29.0	42.6	44.	42.3	39.6	52.2	48.1
ξ_{68}	.10	.27±.020	.35	.41	.52	1.02±.02	---
ξ_{238}	.16	.28±.012	.35	.44	.55	.936±.003	---
$\xi_{238}^{corr.}$	.10	.24	.32	.41	.53	.936±.003	---
ξ_{2017}	.17	.32±.05	.36	.44	.59	1.00±.007	---
ξ_{348}	1.0	.79±.016	.69	.64	.43	.068±.001	---

-11-

in repositioning a sample after moving the manipulator to study another sample or reference. The cause of this scatter is the extreme sensitivity of the analyzer to sample position and also, possibly, the sample buckling mentioned earlier since, in general, different parts of the sample were examined after repositioning. To check for effects due to possible insufficient annealing or to changes in impurity levels, two sets of data are shown in Fig. 3. These data sets represent two independent trials in which all the samples and references were sputtered and annealed and all ratios remeasured. There is good agreement between these two independent trials. The data shown in Fig. 3 are also in good agreement with data collected in earlier experiments using different pieces cut from the same samples and in which the measurements were made using a LEED 4-grid optics type of Auger analyzer. Sputtering causes the surface composition to be removed from equilibrium and annealing re-equilibrates the surfaces. The good agreement between these two sets of data thus demonstrates that the samples were fully equilibrated.

The data given in Table I is plotted in Figs. 3a, 4, 5a, and 6. In Figs. 3 and 5 the ratios of the intensities of the various Au peaks divided by the intensities of the Ag peak are plotted vs. bulk composition of the various alloys. The ratios are normalized by dividing them by the appropriate ratio measured from the pure Au and Ag (denoted by R°). The bulk composition is plotted as a ratio also. In this manner, if the Auger peaks reflected directly the bulk atom fraction of the alloy, then the data points should fall on the dashed line given in Fig. 3 by

$$R = \frac{x_b^{\text{Au}}}{x_b^{\text{Ag}}} R^\circ.$$

This would be true regardless of the inherent absolute Auger intensities involved. This allows data from all Auger peaks to be compared directly.

In Fig. 5 the values of ξ_{68} , ξ_{238} , and ξ_{2017} for the Au peaks are plotted. In addition, ξ_{348} which is the value for the Ag peak is also plotted. The dashed lines in Fig. 4 correspond to $\xi = x_b$. The curves given in Figs. 3, 4, 5, and 6 are explained below.

Discussion

It is our aim to discuss the trends demonstrated in Figs. 3, 4, 5, and 6 by comparing these results with the results expected for a surface exhibiting no surface segregation and with a surface which obeys the regular solution model for monolayer surface segregation. The effects of backscattering and of attenuation in AES are the subjects of much current interest and the data here will be interpreted including these effects.

(a) The Regular Solution Monolayer Model

As mentioned earlier, if one component of a binary alloy has a lower surface free energy, then simple energy considerations predict a surface enrichment of that component at the surface. The theory of this effect has been described.¹ In most theories the monolayer approximation has been invoked which states that the effect of surface segregation is felt only in the top monolayer. In alloys, this approximation is rationalized by the short range interactions typically observed in metals. Other work has extended the theory by removing the monolayer approximation.² For a system obeying regular solution theory it has been shown that the composition of the surface monolayer is given by Eq.(1),¹

$$\frac{x_1^{\text{Au}}}{x_1^{\text{Ag}}} = \frac{x_b^{\text{Au}}}{x_b^{\text{Ag}}} \exp\left(\frac{(\sigma_{\text{Ag}} - \sigma_{\text{Au}})a}{RT}\right) \exp\left[\frac{\Omega(\ell+m)}{RT} \left(\left(x_b^{\text{Ag}}\right)^2 - \left(x_b^{\text{Au}}\right)^2\right) + \frac{\Omega\ell}{RT} \left(\left(x_1^{\text{Au}}\right)^2 - \left(x_1^{\text{Ag}}\right)^2\right)\right] \quad (1)$$

where x_1 and x_b are atom fractions in the surface monolayer and bulk, respectively. In this expression σ is the surface energy, a is the molar surface area, T is the absolute temperature, R the ideal gas constant, Ω is the regular solution parameter which is given from the alloy heat of mixing, ΔH_m , by¹⁰

$$\Omega = \Delta H_m / (x_b^{\text{Ag}} x_b^{\text{Au}}) \quad (2)$$

The packing parameter ℓ gives the fraction of an atom's nearest neighbors which are in the same plane parallel to the surface as the atom. Similarly, m is the fraction of nearest neighbors which are in an adjacent parallel plane. For instance, in an fcc lattice, an atom has twelve nearest neighbors, so a (111) plane has six nearest neighbors in the plane of an atom, and three nearest neighbors in the plane below the atom. Thus, in this case $\ell = 6/12$ and $m = 3/12$.

The lower surface energy of Ag leads through Eq.(1) to the prediction that there is an enrichment in Ag in the surface of a Au-Ag alloy. This can be tested by an intensity analysis of the Auger spectra obtained from Au-Ag alloys.

(b) The Attenuation of Auger Electrons

The attenuation depths of 348 eV electron in Ag have been measured and are found to be about 7.2 Å.¹¹ In addition, a 60 eV electron has been found to have an attenuation depth of less than or about equal to one monolayer in Ni,¹¹ while a 71 eV electron was found to have an attenuation depth of about 3.1 Å in Pb.¹² The value of 3.1 Å will thus be taken as the attenuation depth of a 68 eV electron in Au-Ag alloys. A 2017 eV electron may be expected to have an attenuation depth of around 30 Å,⁷ and thus, electrons of this energy sample the bulk more. Thus, if there is surface segregation in the surface monolayer, this should show up as a difference between the normalized intensity of the Au (2017eV) peak and the Au (68eV) peak. This information is hidden in the intensity ratios given in Table I.

It is useful to attempt to predict the values of these intensity ratios. To predict this type of information a simple model for Auger

excitation and emission from a solid can be proposed by making the following assumptions:

- (1) The ionization and Auger transition probabilities are independent of alloy composition; that is, there are no matrix effects.
- (2) Escape depths for the alloy system depend only on energy and not upon the composition of the alloy.
- (3) Escaping Auger electrons are attenuated exponentially. (Beer's Law).
- (4) Auger transitions are excited uniformly with depth throughout the region examined by Auger analysis. The excitation flux across any layer is proportional to rI_0 , where $r = 1 + n$ and n is the backscattering factor, and I_0 is the incident primary electron beam current. It will be assumed that backscattering factors for Ag-Au alloys vary linearly with alloy composition.
- (5) The number of Auger electrons generated in each layer is proportional to the number of the emitting type of atoms in that layer.

The first assumption is the most difficult to verify and has not been tested. The second assumption has been observed to be qualitatively correct with the development of a "universal" transmission curve.⁸ Assumption (3) has been reasonably demonstrated for Ag and Au.¹³ Regarding assumption (4), recent work has shown that Auger transitions are excited uniformly with depth by normally incident primary electrons of energy greater than 2000 eV.¹⁴ The statement that the backscattered portion of the excitation beam is uniform with depth is an approximation, but should be fairly good for observed low-energy Auger peaks from an unsegregated or monolayer segregated type of alloy. The fifth assumption is a priori assumed to be true.

Using the first, third, and fifth assumptions, an expression for the intensity of an Auger peak can be written as follows:

$$I(E) = \sum_{n=1}^{\infty} k(E, \dots) r N(x_n) \exp\left(-\frac{nd}{\lambda_E \cos \theta_0}\right) \quad (3)$$

which states that the intensity of an Auger peak at an energy E can be written as a sum of intensities from all layers within the solid. In this expression, $k(E, \dots)$ is a complicated function of the instrumental parameters and of properties of the solid. λ_E is the escape depth of an electron of energy E , and d is the interplanar spacing. The angle θ_0 is the acceptance angle of the Auger analyzer. For a CMA this is about 42° . This factor accounts for the fact that electrons detected by the analyzer from a depth nd have actually travelled a distance of $nd/\cos \theta_0$. (for the sample geometry used in this experiment). r is the backscattering coefficient defined above. $N(x_n)$ is the number of emitting type atoms at a particular depth nd . For the Au-Ag system, where the lattice parameter is independent of alloy concentration (within 0.3%)¹⁵ N is directly proportional to the atom fraction of the component, x_n , which will vary with depth if there is surface segregation. In the following the constant of proportionality will be included in $k(E, \dots)$. The second and fourth assumptions given above serve to state that $k(E, \dots)$, r and λ_E are independent of depth. Thus,

$$I(E) = k(E, \dots) r \sum_{n=1}^{\infty} x_n \exp\left(-\frac{nd}{\lambda_E \cos \theta_0}\right) \quad (4)$$

The values of the intensity ratios to be expected can be calculated from Eq.(4). For a surface with no segregation $x_n = x_b$, where x_b is the bulk atom fraction of the component of interest.

Then, for example, from Eq.(4) one can obtain the following:

$$\frac{R_{68;348}}{R^{\circ}_{68;348}} = \frac{I(68\text{eV, alloy})/I(348\text{eV, alloy})}{I(68\text{eV, Au ref.})/I(348\text{eV, Ag ref.})} = \frac{r_{\text{Ag}}}{r_{\text{Au}}} \cdot \frac{x_b^{\text{Au}}}{x_b^{\text{Ag}}} \quad (5)$$

Similarly, if there is a monolayer model type of surface segregation, and the top monolayer has composition x_1^{Au} and $x_1^{\text{Ag}} = 1 - x_1^{\text{Au}}$, while all deeper layers have composition x_b^{Au} and $x_b^{\text{Ag}} = 1 - x_b^{\text{Au}}$, then from Eq.(4) the following expression is obtained,

$$\frac{R_{68;348}}{R^{\circ}_{68;348}} = \frac{r_{\text{Ag}}}{r_{\text{Au}}} \left\{ \frac{x_1^{\text{Au}} \left(1 - \exp \left(-\frac{d}{\lambda_{68} \cdot \cos \theta_0} \right) \right) + x_b^{\text{Au}} \exp \left(-\frac{d}{\lambda_{68} \cdot \cos \theta_0} \right)}{x_1^{\text{Ag}} \left(1 - \exp \left(-\frac{d}{\lambda_{348} \cdot \cos \theta_0} \right) \right) + x_b^{\text{Ag}} \exp \left(-\frac{d}{\lambda_{348} \cdot \cos \theta_0} \right)} \right\} \quad (6)$$

These equations are used to obtain the theoretical curves in Fig. 3 and in Fig. 5. The case in which backscattering $\frac{r_{\text{Au}}}{r_{\text{Ag}}} = 1$ is neglected is the subject of Fig. 3. If there is no segregation, Eq.(5) gives the dashed "bulk ratio line" in Fig. 3 which applies to all ratios

($R_{68;348}/R^{\circ}_{68;348}$, $R_{238;348}/R^{\circ}_{238;348}$, and $R_{2017;348}/R^{\circ}_{2017;348}$). If there were segregation of the type given by (1), then (6) gives the curve for $R_{68;348}/R^{\circ}_{68;348}$ and an analogous equation gives the curve for $R_{2017;348}/R^{\circ}_{2017;348}$, both of which are shown in Fig. 3. In these calculations the following parameters were used in Eq.(1)^{16,17,6}

$$\sigma^{\text{Ag}} = 1728 - .48 T \text{ ergs/cm}^2$$

$$\sigma^{\text{Au}} = 2000. - .46 T \text{ ergs/cm}^2$$

$$\Omega = -1.75 \times 10^{11} \text{ ergs/mole}$$

$$l = \frac{1}{2}, \quad m = \frac{1}{4} \quad \text{fcc (111)}$$

$$T = 700 \text{ K}$$

The calculated surface composition for the parameters is shown in Table II.

TABLE II

Alloy Bulk Atom Fractions, x_b^{Ag} ,
and the Calculated Corresponding Surface Atom Fraction, x_1^{Ag}

x_b^{Ag}	x_1^{Ag}
.10	.251
.20	.418
.30	.558
.40	.681
.50	.786
.60	.870
.70	.932
.80	.970
.90	.991

In Eq.(6), the following values were used¹⁷

$$d = 2.31 \text{ \AA}$$

$$\lambda_{68} = 3.1 \text{ \AA}, \quad \lambda_{348} = 7.2 \text{ \AA}, \quad \lambda_{2017} = 30 \text{ \AA}$$

To include backscattering effects, the values for $r^{\text{Au}}, r^{\text{Ag}}$ are put into the calculation. These results are shown in Fig. 5 and will be discussed below.

Neglecting backscattering effects for the present time, the fact that all the points in Fig. 3 fall below the dashed bulk ratio line appears to be evidence for surface segregation of Ag. The curve for $R_{2017;348}/R^{\circ}_{2017;348}$ involves a high-energy Au peak which samples essentially the bulk Au composition, but also involves an Ag signal which samples the top 2-3 layers. Thus, this curve is slightly below the bulk ratio line, but not as far below as the curve for the more surface sensitive ratio, $R_{68;348}/R^{\circ}_{68;348}$. The experimental values for $R_{2017;348}/R^{\circ}_{2017;348}$ (the open circles in Fig. 3), are found to fit reasonably well to the curve predicted. However, the experimental values for the ratios $R_{68;348}/R^{\circ}_{68;348}$, (the triangles), do not fall upon their predicted curve. The triangles, however, are, in general, lower than the circles. This would seem to suggest surface enrichment of smaller magnitude than predicted by the regular solution model. For this explanation to be consistent, the values of $R_{238;348}/R^{\circ}_{238;348}$, (the squares), should be between the circles and the triangles because of the fact that a 238 eV electron may be expected to travel from depths greater than for a 68 eV electron, but not as great as for a 2017 eV electron. The squares should be quite close, however, to the triangles since λ_{238} should be quite close to λ_{68} . In fact, in about

half the instances the squares are below the triangles. This spread is probably attributable to experimental error. The samples with $x_b^{Au} = .97$ ($x_b^{Au}/x_b^{Ag} = 33$) is the only case where the circle is below the square or the triangle. The ordering of these points is different for the two sets of data indicated in Fig. 3. This fact and the suggested errors in Table I indicate that for this case the reversed ordering may not be significant. The closeness of these points is expected from the theoretical curves. The fact that the points as a group seem to be too low may be due to uncertainty in the bulk alloy composition. A bulk composition $x_b^{Au} = .96$ would put the points onto the predicted curves.

Confirmation of these trends can be obtained by looking at the values of ξ given in Table I and shown in Figs. 4 and 6. To predict the values of ξ expected from a surface exhibiting no segregation, it follows from Eq.(4) that,

$$\xi_E \equiv \frac{I(E, \text{alloy})}{I(E, \text{ref})} = \frac{r_{\text{alloy}}}{r_{\text{ref}}} x_t. \quad (7)$$

For a surface exhibiting monolayer model type segregation Eq.(4) gives the following:

$$\xi_E = \frac{r_{\text{alloy}}}{r_{\text{ref}}} \left[x_1 \left(1 - \exp \left(- \frac{d}{\lambda_E \cos \theta_0} \right) \right) + x_b \exp \left(- \frac{d}{\lambda_E \cos \theta_0} \right) \right]. \quad (8)$$

Neglecting, at present, the backscattering factors ($r_{\text{alloy}}/r_{\text{ref}} = 1$), the values of ξ_{68} and ξ_{2017} for Au and of ξ_{348} for Ag are calculated using (8) and the regular solution model as before, and are shown in Fig. 4. The surface with no segregation is given by (7) and is given by the dashed lines in Fig. 4. Again, the triangles (ξ_{68}) are, in general, below the circles (ξ_{2017}) as are the squares (ξ_{238}), but not so much as might be expected if segregation were as severe as predicted by the regular solution

model. The data for Ag does appear to follow regular solution model curve rather well, except the sample with $x_b^{\text{Au}} = .15$, which has an anomalously large value for ξ .

(c) The Backscattering Correction

In the above discussion, the effects of backscattering are neglected. In fact, there is a difference between the backscattering factors of pure Ag and Au. A study of these factors has been made by Smith and Gallon¹⁸ who measured the effects of backscattering on the Au (68eV) and the Ag (348eV) Auger signals. They found that for primary beam energies of 1000 eV and 2000 eV that $r^{\text{Au}}/r^{\text{Ag}} = 1.2$ and 1.3, respectively. For the present experiment, a rather bold extrapolation to 4000 eV may be made giving 1.5 for this ratio. This ratio may be expected to be dependent upon the energy of the Auger transitions, or more specifically, upon the ionization threshold of the Auger transition of interest. Simple considerations lead to the conclusion that for a given primary beam energy the backscattering factor of the higher energy Au (2017eV) peak might be smaller than that for the Au (68eV) peak.

It can be seen that introducing this factor into Eqs (5) and (6) serves to lower the predicted values for the curves given in Fig. 3. The backscattering also serves to enhance the values of ξ_{348} and weaken the values of ξ_{68} for an alloy. Physically, this can be seen as follows. The Au is a better backscatterer, and so it provides the surface region with a greater flux of exciting electrons. When Au is in an Ag matrix, the backscattered current to the Au atoms will be reduced. Thus, Au intensities from an alloy will be relatively weaker than from pure Au. This makes the observed Au/Ag ratios for an alloy smaller than expected from their bulk composition.

The backscattering factors for the Au (68eV) and the Ag (348eV) peaks given above have been applied and the results calculated for $R_{68;348}/R^{\circ}_{68;348}$ are shown in Fig. 5 for both a surface with no segregation and the regular solution model type of segregation. In addition, the values of ξ_{68} and ξ_{348} are calculated including backscattering and are shown in Fig. 6. Here the backscattering factor of the alloy was assumed to vary linearly with composition. The data in these figures is the same as given in Figs. 3 and 4.

In Fig. 5 it is seen that backscattering can account for the lowering of the triangles below the line $R_{68;348}/R^{\circ}_{68;348} = x_b^{\text{Au}}/x_b^{\text{Ag}}$. With this correction, the triangles are even farther from the regular solution model curve. The fact that the circles and the squares are above this line may then be attributed to one of two possibilities: (1) the backscattering factor is overestimated and there is actually some surface segregation and (2) the backscattering factor for the higher energy Au peaks are lower than for the Au (68eV) peak, as expected. This second possibility itself may be the cause of the observed trend in which the circles are generally above the triangles. Thus, effects due to backscattering may be difficult to distinguish from effects due to the segregation in this case.

Referring to Fig. 6 it can be seen that applying the backscattering factors again alters the interpretation. The triangles do not follow the curve predicted by the regular solution model, but in fact are close to the curve expected for the surface exhibiting no segregation. The same is true for the values of ξ_{348} . The spread in the values of ξ for Au might be explained by either of the two possibilities described above.

Our results do not rule out the possibility of surface segregation of Ag, but they do show that the extent of the segregation is smaller than predicted by the regular solution model with the parameters listed earlier. An actual upper limit to the extent to which surface segregation might be occurring is difficult to make because of the magnitude of experimental scatter. The task of assigning such an upper limit is further complicated by uncertainties regarding the effects of backscattering. Correcting the results for backscattering tends to lower the estimated Ag surface concentration.

An Auger study of the Au-Ag alloy oriented films has been completed in another laboratory.¹⁹ The results of that study indicated that there was no surface segregation of Ag, but the bulk and the surface compositions were the same. Thus, there seems to be a discrepancy between those results and the present results which indicate a slight enrichment of the surface layer with Ag. The origins of this discrepancy are not clear, although it may arise from the two different methods of sample preparation, (vaporized thin film vs. bulk alloy sample). Similar disagreement for other alloy systems underscores the difficulty of obtaining and interpreting Auger information and of obtaining clean and equilibrated surfaces.

Although the results presented here indicate that there is small surface segregation of Ag, the Ag-Au system does not follow closely the regular solution monolayer model. A possible cause for this is the large negative value of the regular solution parameter Ω . The primary assumption of regular solution theory is that the constituents are randomly distributed (Bragg-Williams approximation). This can be physically realistic only if Ω is small. A large negative Ω tends to result in ordering of the

system and short range ordering has been observed in Ag-Au alloys.^{20,21} This entropy effect contradicts the assumption utilized in the regular solution theory. In exploratory studies performed in this laboratory no evidence was found for temperature dependence of the Auger intensity ratios over the range 300-600°C, a fact which could be indicative of the presence of an important entropy effect. Theories have been developed to treat ordered alloy surfaces,³ but more experimental and theoretical work is necessary to elucidate their surface phase diagram.

Acknowledgment:

This work was supported by the U. S. Energy Research and Development Administration, and the National Science Foundation (Grant #MPS 74-13536).

We are indebted to Professor A. Hubbard and Dr. W. Siekhaus for assistance and for many enlightening discussions.

References

1. R. Defay, I. Prigogine, A. Bellemans, and D. H. Everett, "Surface Tension and Adsorption," John Wiley & Sons, Inc., New York, N.Y., 1966.
2. F. L. Williams and D. Nason, Surf. Sci., 45, (1974), 377.
3. R. A. Van Santen and W. M. H. Sachtler, J. Catal., 33, (1974), 202.
4. J. J. Burton, E. Hyman, and D. G. Fedak, J. Catal., to be published.
5. S. H. Overbury, P. A. Bertrand, and G. A. Somorjai, Chem. Revs., to be published.
6. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelly, "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley & Sons, Inc., New York, N.Y., 1963.
7. C. J. Powell, Surf. Sci., 44, (1974), 29.
8. I. Lindau and W. E. Spicer, J. Elect. Spect., 3, (1974), 409.
9. P. W. Palmberg et al., Handbook of Auger Electron Spectroscopy, (Physical Electronics Industries, Edina, Minnesota, 1972).
10. R. A. Swalin, "Thermodynamics of Solids," 2nd ed., John Wiley & Sons, Inc., New York, N.Y., 1972.
11. D. C. Jackson, T. E. Gallon, and A. Chambers, Surf. Sci., 36, (1973), 381.
12. J. P. Biberian and G. E. Rhead, J. Phys. F, 3, (1973), 675.
13. P. W. Palmberg and T. N. Rhodin, J. Appl. Phys., 39, (1968), 2425.
14. F. Meyer and J. J. Vrakking, Surf. Sci., 45, (1974), 409.
15. W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, Los Angeles, 1958.
16. H. J. Wasserman, J. S. Vermaak, Surf. Sci., 22, (1970), 164.
17. J. S. Vermaak and D. K. Wildsford, J. Phys. Chem., 72, (1968), 4150.
18. D. M. Smith and T. E. Gallon, J. Phys. D, 7, (1974) 151.

Ref., contd.

19. S. C. Fain, Jr. and J. M. McDavid, Phys. Rev. B, 9, (1974) 5099.
20. A. Van Den Beukel et al., Phys. Stat. Sol., 19, 177 (1967).
21. S. Radelaar, Phys. Stat. Sol., 27, K63 (1968).

Figure Captions

- Fig. 1. Derivative Auger spectra of Au-Ag alloys and of pure Au and Ag.
- Fig. 2. Peak shape of the Au (68eV) peak cluster as a function of bulk composition.
- Fig. 3. The experimental values for $R_{68;348}/R_{68;348}^{\circ}$ (Δ), for $R_{238;348}/R_{238;348}^{\circ}$ ($\square$) and for $R_{2017;348}/R_{2017;348}^{\circ}$ ($\circ$) are plotted vs. the ratio of the bulk atom fractions. The values predicted for no segregation (---) and the values predicted for surface segregation according to the monolayer regular solution model (—) are shown, assuming no backscattering effects. The curves are the same in (a) and (b), but the data are from independent trials. In each case the lower solid curve is predicted for $R_{68;348}/R_{68;348}^{\circ}$ and the upper solid curve is for $R_{2017;348}/R_{2017;348}^{\circ}$.
- Fig. 4. The experimental values for $\xi_{68}(\Delta)$ ($\equiv \frac{I(68\text{eV, alloy})}{I(68\text{eV, pure Au})}$), $\xi_{348}(\square)$, and $\xi_{2017}(\circ)$ for Au and $\xi_{348}(x)$ for Ag are plotted vs. the bulk atom fraction. The values predicted for no segregation (---) and the values predicted for the monolayer regular solution model (—) are shown, where backscattering factors are neglected. For Au, the lower solid curve is predicted for ξ_{68} and the upper is ξ_{238} . For Ag the solid curve is obviously predicted for ξ_{348} .
- Fig. 5. Data points are the same as in Fig. 3. The predicted curves are drawn to take into account backscattering effects. Values predicted for no surface segregation (---) and the predicted values for $R_{68;348}/R_{68;348}^{\circ}$ for the monolayer regular solution model (—) are shown.

Fig. Cap., contd.

Fig. 6. Data points are the same as in Fig. 4. The values predicted for $\xi_{68} \left(\equiv \frac{I(68\text{eV, alloy})}{I(68\text{eV, pure Au})} \right)$ and ξ_{348} for Ag for no segregation (---) and for the monolayer regular solution model (-) are shown. In this calculation, backscattering effects are included.

XBL 755-3000

Figure 1

XBL 755-2997

Figure 2

XBL 755-2999

Figure 3

XBL 755-2996

Figure 4

XBL 755-2998

Figure 5

XBL 755-2995

Figure 6

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720