DETERMINATION OF THE SURFACE COMPOSITION OF
BINARY ALLOYS BY AUGER ELECTRON SPECTROSCOPY:
THE GOLD-SILVER AND GOLD-TIN SYSTEMS

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DETERMINATION OF THE SURFACE COMPOSITION
OF BINARY ALLOYS BY AUGER ELECTRON SPECTROSCOPY:
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ABSTRACT

Auger electron spectroscopy was exploited as a means of determining the surface phase diagram of Au-Ag and Au-Sn alloys. Polycrystalline Au-Ag alloy foils of a wide range of composition (atom fractions of .15 to .97) were cleaned and equilibrated in ultra high vacuum. Using two different types of energy analyzers for comparison, the intensities of the Auger emission from transitions at several energies were measured and normalized to those of pure Au and Ag. A model developed to describe the intensity of Auger emission was applied to the intensities and the surface monolayer compositions of the alloys were thus determined. The Auger data was consistent with enrichment of Ag in the surface monolayer, but to an extent which is less than predicted by the regular solution model. The results were discussed in terms of other theories which were reviewed in the text. The effects of uncertainties in electron attenuation and backscattering were considered. Ingots of Au-Sn with bulk composition between 50 and 99 at % Au were prepared by solidification from the melt, cut and polished for Auger analysis. The bulk structure and composition of these complex alloys were characterized by electron microprobe, x-ray

diffraction, x-ray fluorescence and optical microscopy. The samples were cleaned and equilibrated in ultra high vacuum and the intensities of the Auger emission from transitions at several energies were measured and normalized to those of pure Au and pure Sn. Using the intensity model, the normalized Auger intensity ratios were used to determine the surface monolayer composition. Enrichment of Sn was found in the surface monolayer for disordered ζ (86.7 at % Au) and α (99.0 at % Au) phase alloys. The highly ordered δ (50.0 at % Au) phase alloy was found to exhibit no surface segregation. The surfaces of two phase alloys (δ and ζ) were found to be describable by the lever rule. The results were interpreted in terms of the bulk structures, ordering properties, and driving force for segregation of the alloys. In addition to the surface composition of the clean and equilibrated alloys, the effects of ion sputtering upon the surfaces of Au-Ag and Au-Sn alloys were also investigated and selective sputtering of Ag and Sn respectively was found.

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1. INTRODUCTION

In the past ten years there has been increasing interest in studying the surface properties of alloys. Interest in this problem has typically arisen among two separate disciplines working with slightly different points of view. One of the disciplines consists of chemists who are interested in studying catalysis on alloy surfaces, and the other consists of metallurgists who are interested in understanding the properties of alloy materials.

Since heterogeneous alloy catalysis occurs at the free surface, a fundamental understanding of the mechanism of alloy catalysis requires characterization of the alloy surface. Certainly a fundamental step in characterizing an alloy surface is to specify its composition. Usually alloys are described by their bulk compositions, but it is in fact the surface composition that is important in determining the activity and selectivity of alloy catalysts. It has long been realized that there are thermodynamic reasons why one component in an alloy may segregate to the surface yielding a surface composition which is not the same as the bulk composition. It is therefore of interest to determine the surface composition of alloys and to try to understand how this varies with the more commonly known bulk composition.

The metallurgists are also interested in the surface compositions of alloys but for different reasons. The macroscopic properties of alloy materials are greatly affected by the properties of grain boundaries, which are internal surfaces. The segregation of impurities, or of one

alloy component to the grain boundary leads to dramatic and usually undesirable changes in the strength of alloys. The nature of segregation to grain boundaries and to free surfaces are expected to be similar, so it is of interest for metallurgists to understand the fundamentals of segregation to a free surface.

With the development of Auger electron spectroscopy and related techniques it has, in principle, become possible to directly determine the composition of a free surface. As such these techniques have been applied with increasing frequency to problems of immediate industrial interest. But it is of greater interest to use these techniques as an experimental monitor in developing theories to explain the energetics of surface segregation. The ultimate goal of such studies is to be able to predict the surface composition of an alloy from the well known bulk thermodynamics and properties of the alloy and the component metals.

The experiments described in this thesis represent an initial step in achieving this goal. The purpose here is to test some of the simpler theoretical models and to look for effects which may be of importance in determining the nature of surface segregation. The first part of this thesis reviews the theory which has been proposed to describe surface enrichment. This is followed by a review of the experiments which have been done to test these theories. The third chapter provides a description of Auger electron spectroscopy including both experimental aspects and the development of the model which describes the intensity of Auger emission. In the fourth and fifth chapters, the experiments done to determine the surface phase diagram of the Au-Ag and the Au-Sn systems

are described. In each chapter the intensity model is applied to the measured intensities to determine the surface composition of the alloys. The surface compositions are then discussed with regard to theoretical predictions. The sixth chapter describes the effects of sputtering upon alloy surfaces; results which were obtained incidentally as the experiments were done. The last chapter summarizes the information obtained from these experiments and suggestions are made for possible future work.

2. LITERATURE REVIEW

The concept that the formation of a surface requires energy is not at all new. Water droplets take a spherical shape in order that their surface area to volume ratio will be minimized, thereby lowering the surface energy to the least possible value. The tendency to reduce surface area leads to a concept of surface tension, since to reduce its area a liquid exerts a pull in the direction tangential to its surface. Through study of this phenomena it was realized that in a liquid mixture, if the component with the lowest surface tension were to migrate preferentially to the surface, the surface energy, which is the product of the surface tension and the area of the surface, would be lowered. It was further realized that in solids also it requires extra energy to create a surface, and therefore in solid solutions there might be a migration to the surface of whichever component would lower the surface energy. Such a migration would obviously result in a surface with its own composition, distinct from that of the bulk.

Theories have been developed to describe this behavior. All theories (except one) attempt to calculate the surface composition that will produce the lowest surface free energy of the alloy. They differ only in the way in which they describe the alloy and the way in which they calculate the surface free energy. Section 2.1 gives a review of the theories that have been developed. With the theories as a guide it is of interest to compare their predictions with experiment.

Section 2.2 briefly describes the various methods by which surface compositions can be measured and section 2.3 reviews the results of most of the published work undertaken to determine the surface composition of alloys.

2.1 Theory of Surface Segregation

One of the simplest ways of describing the surface is the monolayer model in which the surface is defined to consist of a single monolayer one atom thick.¹ To predict the composition of the surface of a liquid mixture, some solution model must be applied to it. Certainly one of the simplest models is that of the ideal solution. For an ideal solution, it can be shown¹ that if two liquids with surface tensions σ^A and σ^B are mixed together, and form a surface with area a , then the atom fractions x_1^A and $x_1^B = 1 - x_1^A$ of components A and B in the first (surface) monolayer, will be given by Eq. 2.1:

$$RT \ln \left(\frac{\frac{x_1^A}{x_1^B}}{\frac{x_b^A}{x_b^B}} \right) = -(\sigma^A - \sigma^B)a \quad . \quad 2.1$$

In addition to the surface tension difference, the surface composition depends upon the bulk compositions x_b^A and x_b^B and upon the temperature T .

The left side of Eq. 2.1 derives from the configurational entropy of mixing of an ideal solution at the surface, and the right side derives from the remainder of the free energy required to form the surface. It is most convenient to rewrite Eq. 2.1 in the following form:

$$\frac{x_1^A}{x_1^B} = \frac{x_b^A}{x_b^B} \exp \left(-\frac{(\sigma^A - \sigma^B)a}{RT} \right) \quad . \quad 2.2$$

It is readily seen that if the surface tensions of A and B are the same, then the surface composition will be identical to the bulk, while if they are different, the component with the lower surface tension will be enriched at the surface. The surface tension here is treated as an empirical property of the liquid surface which can be measured straight forwardly. In a solid, it is also possible to measure a surface free energy, analogous to σ_a , and this quantity can be inserted straight into Eq. 2.2 to obtain a theoretical estimate of the surface composition of an alloy.

An alternative approach, described by Williams,^{2,3} and by Van Santen and Boersma,⁴ which is physically more elucidating is to treat the solid as a sum of the pairwise bond enthalpies, H_{AA} , H_{BB} and H_{AB} , between nearest neighbor atoms. The solid is treated as a semi-infinite block, and the atoms at the surface have an incomplete coordination sphere. Since bonding results in a lowering of the energy of the system, the minimum energy situation can be achieved by placing the weaker bonding component in those positions where the coordination is the lowest, i.e., at the surface. Summing all the bonding energies and including the configurational entropy (still assumed to be ideal), an expression for the free energy of the system is obtained. This free energy is minimized with respect to the surface composition and provides the following result:

$$\frac{x_1^A}{x_1^B} = \frac{x_b^A}{x_b^B} \exp\left(-\frac{(H_{\text{sub}}^A - H_{\text{sub}}^B)(Z_v/Z)}{RT}\right). \quad 2.3$$

H_{sub}^B and H_{sub}^A are the heats of sublimation of the solid and arise from approximating the bond energies H_{AA} and H_{BB} by the molar heats of sublimation of the pure solids A and B divided by the number of pairwise bonds broken in sublimating the solid. Z_v is the number of would be nearest neighbors in the missing atomic plane above a surface atom (vertically bonded) while Z is the number of nearest neighbors that an atom in the bulk of the solid has. For example, in an fcc solid each atom has 12 nearest neighbors so $Z = 12$, while at a (111) surface, three of these are missing so $Z_v = 3$. Eq. 2.3 states that the component with the lowest heat of sublimation will be present in excess at the surface. Eqs. 2.2 and 2.3 are identical if the following correlation is made:

$$(\sigma^A - \sigma^B)_a = (H_{\text{sub}}^A - H_{\text{sub}}^B)(Z_v/Z) \quad 2.4$$

Arguments of this type have lead to attempts to correlate experimental surface energies with measured heats of sublimation.^{5,6}

In Fig. 2.1 is shown such a correlation. Again for an fcc(111) face, one would expect that $\sigma_a \equiv \sigma_{\text{sm}} \approx H_{\text{sub}} \cdot (3/12) = .25 H_{\text{sub}}$. The data actually lead to the result $\sigma_{\text{sm}} \approx .16 H_{\text{sub}}$. The agreement is fairly good considering the simplicity of this approach to a surface where the actual nature of the electron structure and bonding are much more complicated. Nevertheless, this correlation is used frequently to quickly predict which component will segregate to the surface, since heat of sublimation data are more readily available and more accurate than surface free energy data. However, this can lead to confusion and inaccuracies, as in the case of Cu and Au where the heat of sublimation of Au is larger, yet Au appears to have the lower surface energy.⁷

Fig. 2.1 Correlation between molar surface free energy and heat of sublimation. (Reference 5)

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Metallic alloys are not ideal solutions, since they generally have some finite heat of mixing.⁸ In the derivation of Eq. 2.3, this heat of mixing was ignored by assuming that the bond energy between unlike atoms, H_{AB} is equal to the average of the bond enthalpies between like atoms, i.e., by assuming that

$$H_{AB} - \frac{H_{AA} + H_{BB}}{2} = 0 \quad . \quad 2.5$$

If we assume that this is not true, but that instead

$$H_{AB} - \frac{H_{AA} + H_{BB}}{2} = \frac{\Omega}{N_0 Z} \quad 2.6$$

where N_0 is Avogadro's number, then if $\Omega/N_0 Z$ is a constant, we have the next simplest approximation of a solution. This is the regular solution model⁶ and Ω , the regular solution parameter, is directly related to the heat of mixing, ΔH_m , of a regular solution by the relation

$$\Omega = \Delta H_m / x_b^A x_b^B \quad . \quad 2.7$$

Therefore, from heat of mixing data, which is in many cases readily available, the parameter Ω and the bond energy H_{AB} can be estimated. The derivation leading to Eq. 2.3 can be redone, but this time making use of the assumption in Eq. 2.6. Again the surface is treated as being one layer thick, and a well defined surface structure must be assumed. The result is given in Eq. 2.8.

$$\frac{x_1^A}{x_1^B} = \frac{x_b^A}{x_b^B} \exp \left\{ - \frac{(H_{sub}^A - H_{sub}^B)(Z_v/Z)}{RT} + \frac{\Omega}{RT} \left[\frac{Z_v + Z_\ell}{Z} \left[(x_b^B)^2 - (x_b^A)^2 \right] + \frac{Z_\ell}{Z} \left[(x_1^A)^2 - (x_1^B)^2 \right] \right] \right\} \quad 2.8$$

In this implicit equation, Z_ℓ is the number of nearest neighbor atoms which are in the plane of the atom (laterally bonded). For example, for an fcc (111) face, $Z_\ell = 6$.

For Au-Ag alloys, the quantity $\Omega = \Delta H_m / (x_b^{Au} x_b^{Ag})$ is constant to within 17% throughout the entire composition range,⁸ which is about as close to regular behavior as found in any metallic alloys. Eq. 2.8 was applied to the Au-Ag system and the results are shown in Fig. 2.2. The calculation was done for an fcc (111) face, and surface energy data was used instead of the heats of sublimation (so that Eq. 2.4 is inserted into 2.8).

The most artificial aspect of this model is the monolayer approximation, and in fact it is unnecessary to restrict all layers deeper than the top monolayer to have the bulk composition. Williams presented a four-layer model in which the top four layers are allowed to have a composition different than the bulk, while the fifth and deeper have the bulk composition.^{2,3} The results of the derivation are four coupled implicit equations relating the surface compositions of the four layers to T , Ω , H_{sub} , x_b and the crystal structure parameters. To demonstrate, the results of calculations which were made for the Au-Ag system and the liquid Pb-In system⁹ are shown in Figs. 2.2 and 2.3 respectively. The surface enrichment in each of the top four layers is plotted as a function of x_b . The surface enrichment fades away quite rapidly with depth into the surface as might be expected for this model which considers only nearest neighbor bonding. Further, if as in Ag-Au $\Omega < 0$ (which by Eq. 2.6 implies attractive interactions between unlike atoms) then there is a reversal

Au-Ag
T = 300 °K

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Fig. 2.2 Surface enrichment for a (111) face of Au-Ag at 300°K as predicted by the monolayer regular and the four-layer regular solution models. (Reference 9)

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Fig. 2.3 Surface enrichment for Pb-In at 600°K as predicted by the monolayer regular and the four-layer regular solution models. The surface is assumed to have an fcc(111) orientation whether liquid or solid. (Reference 9)

in enrichment in adjacent layers. That is, Ag enrichment occurs in the first layer, but Ag depletion takes place in the second layer. This represents a tendency towards ordering of the alloy. For Pb-In where $\Omega > 0$, the attraction between like atoms is on the average greater than between unlike atoms, so that Pb, the component with the lower surface energy, clusters at the surface. If $\Omega = 0$, the depth distribution collapses to only a single monolayer type of segregation.

Although Williams only considered four layers at a vacuum-solid interface, there has been a variety of other theoretical work dealing with up to infinitely many layers.¹⁰⁻¹³ The work has usually been applied to regular liquid solutions at a solid-liquid or a liquid vapor interface, although in defining the liquid phase, the liquid takes on a quasi-crystalline aspect in that it is partitioned into layers. In these cases the liquid is usually taken to be of semi-infinite extent.

In solids there arise phenomena due to small particle effects and due to kinks, edges and other surface defects, which have no analogy in liquids. Furthermore, it appears that these surface defects may be of great importance, especially in catalysis.¹⁴ Burton, Fedak and Hyman approached this problem,¹⁵ again within the regular solution approximation. For a microcluster in which $\Omega = 0$ (ideal solution) they arrived at an equation more general than Eq. 2.3, in which the term (Z_v/Z) in Eq. 2.3 is replaced by $(Z - Z_i)/Z$. This simply takes into account that the surface site may have any number of nearest neighbors, Z_i . The lower the coordination of a particular site, the

greater is the tendency for segregation. Thus in alloy microclusters, sites at edges and corners are more enriched in the segregating species than are the sites on flat terraces.

Burton, Hyman and Fedak¹⁵ also studied thin films of various thicknesses for alloys in which there is a miscibility gap ($\Omega > 0$). In this case the films were thin enough that segregation to the surface leads to a non-negligible depletion of the bulk. These are the first calculations mentioned here to take this mass balance into account, since others theories have assumed an infinite bulk. The results are shown in Fig. 2.4 for parameters modeled after a 50 at % Au-Ni alloy. The results indicate enrichment of Au at both surfaces of the film in all cases except the trivial two layer film. The Au-Ni bulk phase diagram has a miscibility gap below $T_c = 1100^\circ\text{K}$. For $T > T_c$ the segregation of Au takes place only in the surface region, with a core that approaches the bulk composition as the film thickness increases. For $T < T_c$ the films exhibit phase separation with the Au rich phase accumulating at the surface and the Ni rich phase accumulating at the center.

This structure, consisting of a film with an outer shell of one phase and an inner shell of another was suggested by Sachtler and Jongpier¹⁶ in their explanation of experimental findings in Cu-Ni alloys. Their "cherry" model suggests that during simultaneous deposition of thin films at temperatures $T < T_c$, the two phases will nucleate and grow separately. As the film equilibrates, the more easily diffusing species will diffuse to coat the crystallites of the other phase.

Fig. 2.4 Calculated compositions, x_i^{Au} , of each layer of thin films of infinite extent and thicknesses of 2,4,10 or 18 layers. The calculation was done for fcc(111) films with bulk composition of 50 at% Au-Ni using the regular solution model at various temperatures: a) 500°K, b) 900°K, c) 1100°K, d) 1300°K, and e) 1700°K. The temperature of the miscibility gap is 1100°K. (Reference 15)

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The resulting "cherry" has a shell enriched in the more easily diffusing species which is also usually the most surface active species since rates of diffusion usually increase with a decrease in bonding strength. This effect is illustrated in Fig. 2.5.

In the theories presented up to now, the driving force for segregation has been the fact that the surface is a site of reduced coordination. In solids there is another driving force for segregation and that is the reduction of strain. McLean¹⁷ has pointed out that a solute which is of a different size than the solvent lattice creates a strain in the lattice. At a grain boundary there are open sites where more space is available to the atoms. By migrating to these sites a solute can reduce the strain energy. McLean used the ideal solution model and arrived at an expression identical to Eqs. 2.2 or 2.3 except that the argument of the exponential involves a difference between the strain energy caused by a solute atom located at the grain boundary and one located within the bulk. To estimate this energy, McLean pointed to a treatment by Pines¹⁸ who used elastic theory to calculate the elastic distortion energy caused by a solute in a lattice.

Two difficulties arise from McLean's treatment. This theory applies to a dilute solute only, since the strain energy term may be expected to depend upon the composition in the bulk. The second is that the treatment was developed for a grain boundary, and unless there is some sort of surface reconstruction it is not clear that the sites at a free surface are actually much roomier than the sites within the lattice.

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Fig. 2.5 The cherry model of alloy film formation. (Reference 16)

The form of all of the equations given so far have been

$$\frac{x_1^A}{x_1^B} = \frac{x_b^A}{x_b^B} \exp\left(-\frac{Q}{RT}\right) \quad 2.9$$

where Q resembles an activation energy and has been referred to as a heat of segregation or a retrieval energy.¹⁷ Q in the ideal solution model is a constant enthalpy due to the reduced coordination at the surface, while in the strain theory of McLean, Q is a constant strain energy term. In the regular solution model Q is an enthalpy which takes account of the pairwise bonding in the solid and because of this Q takes on a composition dependence in this model.

In fact, Q corresponds to a free energy of segregation¹⁹ and in an exact treatment would contain all enthalpy and entropy changes associated with segregation, except of course the ideal configurational entropy term which is already included in the expression.

Seah and Lea¹⁹ have extended these models by adding terms due to vibrational entropy, ΔS_{vib} and an anharmonic vibrational entropy term ΔS_{anh} to Q . They show that $-T\Delta S_{\text{vib}}$ varies linearly with T and $-T\Delta S_{\text{anh}}$ varies as T^2 , so that Q in Eq. 2.9 can have a temperature dependence. Their values for the free energy of segregation $Q \equiv \Delta G$ for the first layer of dilute Sn in Fe is given in Fig. 2.6. This value for ΔG is different for grain boundary segregation than for free surface segregation.²⁰ At 550°C this free energy leads to segregation of up to two full monolayers of Sn for bulk compositions of Sn less than the solubility limit as shown in Fig. 2.6. Seah used a solid state analog of a two layer BET adsorption isotherm to relate the surface composition

Fig. 2.6 Upper: Calculated and experimental temperature dependence of the free energy of segregation of Sn to free surfaces and grain boundaries of Fe-Sn alloys. Lower: The Sn surface composition x_B versus the Sn bulk composition x_C for equilibrium free surface and grain boundary segregation in Fe-Sn. (Reference 19)

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Fig. 2.6

to the bulk composition and ΔG . The segregation level x_B shown in Fig. 2.6 is the total surface adsorption level and is plotted versus the bulk solute composition x_C .

In another approach,²¹ Sundarem and Wynblatt avoided making any assumption about the configurational entropy of an alloy by using Monte Carlo techniques. Their model involves assigning an initial compositional configuration to an alloy. The energy of the configuration can then be calculated by using the standard pairwise bonding approximation. Then atom pairs are chosen at random, and the atoms switched according to the Boltzmann probability $\exp(-(E_2 - E_1)/kT)$ where E_1 and E_2 are the configurational energies before and after the exchange. This process is repeated in some appropriate manner until convergence to the equilibrium properties is obtained. Some results calculated are shown in Fig. 2.7 for films ten layers thick. With this model it is quite easy to consider any structural configuration (i.e., thin films, semi-infinite slabs, cubo-octahedron, etc.), and the mass conservation requirement is trivially satisfied. For an infinite slab of Au-Ni, their method gives results virtually identical to those obtained by Williams³ using his model described above.

Starting with a rather different point of view,²² Burton and Machlin have pointed to similarities between solid-liquid solution equilibrium and solid-solid surface solution equilibrium. In a dilute alloy, the liquid formed at the melting point may have a higher or lower concentration of solute as determined by the phase diagram. Burton and Machlin have proposed that if it is the case that this liquid is enriched in the solute, then it might also be true that this

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Fig. 2.7 Layer compositions, C_A , for 10 layer thin films of (100) surface orientation for $V_1 = \Omega/NZ < 0$ (left) and for $V_1 > 0$ (center). A comparison of two different faces for $V_1 = -kT/5$ (ordering alloy) and for $V_1 = +kT/5$ (clustering alloy) is given on the right. (Reference 21)

solute will enrich the liquid-like free surface of the solid alloy. If the melt has a lower concentration of solute than the solid, then segregation of the solute to the surface is not expected. These predictions are illustrated in Fig. 2.8. This theory is qualitative only and was applied quite successfully to predict only whether or not segregation would occur in a number of dilute alloys which have been studied experimentally.

Van Santen and Sachtler⁷ have done theoretical work on strongly ordered alloys, that is, in cases where $-2\Omega/Z \gg RT$. They used the pairwise bonding scheme to obtain the energy of a particular configuration, but derived a special entropy of mixing term which was a function of the long range ordering parameter S . They applied their model to Pt_3Sn , Au_3Cu and Cu_3Au which are structurally isotypic. They calculated the surface energy for low index planes and derived expressions for the energy required to swap a surface atom with an unlike atom from the second layer. These energies depended upon S , Ω , H_{AA} , H_{BB} , H_{AB} and the crystal orientation. Their values for the solid surface energies, σ , showed the expected dependence upon the crystal orientation, i.e., $\sigma(111) < \sigma(100) < \sigma(110)$. Using a statistical thermodynamic approach they obtained an expression for the change of the entropy of mixing associated with surface enrichment. Combining this entropy and the energy term and minimizing this free energy with respect to the surface composition they obtained the probable enrichment in the first layer. On the basis of these calculations they predict strong enrichment of Sn at the surface of Pt_3Sn and of Cu at the surface of Au_3Cu and Cu_3Au .

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Fig. 2.8 Predictions of which alloys will segregate based upon the alloy bulk phase diagram. (Reference 21)

The theories given above refer to clean binary alloys. All real metals and alloys contain impurities and it is commonly observed that impurities segregate to the surface in prodigious quantities. Segregation of S, P, Ca, C and other impurities to the surfaces of "pure" metals appears in virtually every surface study and many studies have been devoted solely to this phenomena.²³⁻²⁶ As trace impurities in a metal can be regarded as a very dilute alloy system, this behavior should be interpretable within the framework given above.

The case of impurities at the surface of binary alloys is then really that of a ternary alloy. Very little theoretical effort has been put into this subject. Qualitatively it is possible that the absorbed impurity may bond more strongly with one component of the alloy than the other. This could result in the less strongly bonding component being replaced at the surface by the bound species. Williams^{2,3} has considered this possibility by adding an additional term to the surface enthalpy. This impurity-induced segregation is expected to occur only at high enough temperatures that diffusion in the bulk can occur, as with all segregation. Another effect of impurity segregation is the site competition which Seah and co-workers have discussed.^{19,20} In their studies of Fe-Sn-S, they found that at grain boundaries there was no competition between Sn and S for sites, while at a free surface there was competition with S displacing Sn at the surface. These possible effects of impurities must be considered before a complete understanding of alloy surface phenomena will be achieved.

2.2 Methods for Determining Surface Composition

Before the fairly recent (since 1968) development of electron and ion spectroscopy, the composition of an alloy in the extreme surface regions could be determined only indirectly. Three of the more common ways are mentioned here. The first means commonly used was that of surface titration.²⁷ If one component of the alloy will strongly chemisorb a particular species but the other component will not, then a measurement of the uptake of the gaseous species by an alloy determines the surface composition of the active component. A second method is to measure the work function of the alloy.²⁸ The work function of the alloy is strongly dependent upon surface composition, but the drawback to this method is that nobody fully understands the relation between work function and composition, which causes a calibration problem. Another method²⁹ has been to measure the surface energy of a solid alloy and relate this by means of some fundamental equation, such as the dilute approximation of the Gibbs adsorption isotherm, to the surface composition. This is essentially the inverse of the entire problem discussed in Section 2.1 and so is certainly not satisfactory.

With the development of Auger electron spectroscopy (AES) ion scattering spectroscopy (ISS),³⁰ x-ray photoelectron spectroscopy (XPS),³¹ soft x-ray appearance potential spectroscopy (APS),³² Rutherford scattering,³³ and other related techniques, it has become possible to not only verify the cleanliness of an alloy but to also measure directly the surface composition. These methods (with the exception of Rutherford scattering) rely upon the strong interactions

of low energy (< 1 keV) electrons or ions with solids to give them their extreme surface sensitivity (1-100 Å). AES is the most popular technique at present due to the ability to use the common low energy electron diffraction (LEED) analyzer to perform AES. ISS is the most surface sensitive technique and may yet become a very popular method for performing alloy surface composition measurements if quantitative and reliable methods of sputter profiling and a more quantitative understanding of charge neutralization can be developed. XPS is not as surface sensitive as AES and it is usually applied more to problems of electronic structure which cannot be studied as readily with AES. APS gives virtually the same information as AES but it is not now in common use. The equipment needed to do Rutherford scattering experiments is only available to a few groups.

The alloys studied in completion of this thesis, and indeed most of the alloy systems studied to date have been examined by AES. Chapter 3 is devoted to experimental details and methods of using AES as a means of determining surface composition.

2.3 Survey of Experimental Results

The development of techniques of electron and ion spectroscopy has sparked an interest in studying the surface composition of alloys. When Auger electron spectroscopy (AES) started to come into common use, many workers started to apply it to problems in catalysis, grain boundary segregation, semiconductor and metal contacts and numerous other fields. As a large number of very applied problems were attacked with AES, a broad base of information began to accumulate

and greater sophistication in the use of AES as a quantitative tool developed. As applied problems were solved a further interest developed in the fundamental problem of the energetics of surface segregation, the prediction of the surface phase diagram, and in developing and testing theories such as those given in the first part of this chapter.

It is therefore of interest to review the information which is known about alloys, keeping in mind that it is a fundamental understanding that is of interest. In the remainder of this chapter, a survey of work pertaining to the alloy surface composition problem is presented. The summary is divided up by binary alloy systems, and will be approached in order of increasing complexity of the alloy bulk phase diagram. The alloy systems with the simplest bulk thermodynamics, to which the ideal or regular solution theories might apply will be considered first. Systems which have been studied include Ag-Pd, Ag-Au, Au-Pd, Ni-Pd and Fe-Cr. Next alloys with ordered phases or low temperature miscibility gaps such as Au-Cu, Cu-Ni, Au-Ni, and Au-Pt will be considered. More complicated alloys in which there is complete phase separation or intermetallic compounds formed such as Pb-In, Au-In, Cu-Al, Pt-Sn, Fe-Sn and Au-Sn will then be reviewed. In many of the studies of the complex alloys, only a specific phase, such as dilute In in Au were studied. In such an alloy the problem is reduced to that of a fairly simple solution. In this summary, the information that will be highlighted will be whether the alloys studied were cleaned and fully equilibrated and an evaluation of the

analysis techniques used, their virtues and difficulties will be given. The surface composition of each clean and equilibrated alloy and the effect of sputtering and reactions with adsorbed impurities are the answers of ultimate interest.

Before beginning this summary, some of the physical properties of these alloy systems are given in Table 2.1. In the theories given in Section 2.1, some important parameters are the difference in the heats of sublimation³⁴ and the relative size difference of the pure components,³⁵ and the heat of mixing of the alloys.⁸ These are given along with some phase diagram information⁸ in Table 2.1. For these alloys the value of the heat of mixing is a function of composition, and Ω as defined by Eq. 2.7 is usually not very constant (non-regular behavior). As such only the largest absolute value of Ω throughout the composition range is reported. Whether segregation of one of the components will take place is qualitatively predicted by three theories in Table 2.1. The strain theory of McLean¹⁷ and the "phase diagram" theory of Burton and Machlin²² apply to dilute solutes and their predictions are given for the two possible dilute cases in each alloy. The regular solution theory prediction applies to the entire composition range. In cases where the strain and the regular solution theories disagree, the expected result is that of a compromise between the two opposing tendencies. It is hoped that the Table may be a helpful reference in reviewing the results of the studies described below.

Table 2.1. Summary of alloy data and predicted segregation.

Alloy A/B	Phase diagram	$H_{\text{sub}}^A - H_{\text{sub}}^B$ (kcal/g.at)	$\frac{r^A - r^B}{\langle r \rangle} \times 100$	$(\Delta H_m / x_b^A x_b^B)_{\text{max}}$ cal/g.at	predicted segregation			
					solute	strain	phase diagram	regular solution
Ag/Pd	Simple	-22.6	+ 4.9	$-7600 (\pm 200)$ $x^{\text{Pd}} \rightarrow 0, 1200^\circ\text{K}$	Ag	Ag	Ag	Ag
					Pd	Pd	None	
Ag/Au	Simple	-23.9	+ .2	-4850 $x^{\text{Au}} \rightarrow 0, 800^\circ\text{K}$	Ag	None	Ag	Ag
					Au	None	None	
Au/Pd	Simple	- 3.7	+ 4.7	-9500 $x^{\text{Au}} = .8, 298^\circ\text{K}$	Au	Au	Au	small
					Pd	Pd	None	
Ni/Pd	Simple	+11.8	- 9.9	+1460 to -2240, 1273°K	Ni	Ni	Ni	Pd
					Pd	Pd	Pd	
Fe/Cr	low T phase	+4.5	+ 1.6	+5600 $.1 < x^{\text{Fe}} < .9, 1600^\circ\text{K}$	Fe	small	Fe	small
	Y-loop				Cr	small	Cr	
Au/Cu	low T ordered phases	+6.2	+12.1	-5650 $x^{\text{Au}} = .3, 800^\circ\text{K}$	Au	Au	Au	Cu
					Cu	Cu	Cu	
Cu/Ni	low T miscibility gap	-21.7	+ 2.5	+2800 $x^{\text{Cu}} \rightarrow 0, 973^\circ\text{K}$	Cu	Cu	Cu	Cu
					Ni	Ni	None	
Au/Ni	Miscibility gap	-15.5	+14.6	+7650 $x^{\text{Au}} = .3, 1150^\circ\text{K}$	Au	Au	Au	Au
					Ni	Ni	Ni	
Au/Pt	Miscibility gap	-47.9	+ 3.8	—	Au	Au	Au	Au
					Pt	Pt	None	
Pb/In	Intermediate phase	-11.2	+ 7.7	+1240 $x^{\text{Pd}} = .5, 315^\circ\text{K}$	Pb	Pb	Pb	Pb
					In	In	In	
Au/In	Complex	+29.3	-11.9	Complex	Au	Au	—	In
					In	In	In	
Al/Cu	Complex	- 3.6	+11.3	Complex	Al	Al	Al	small
					Cu	Cu	—	
Pt/Sn	Complex	+63.2	- 8.7	Complex	Pt	Pt	—	Sn
					Sn	Sn	Sn	
Fe/Sn	Complex	+27.5	-17.5	Complex	Fe	Fe	—	Sn
					Sn	Sn	Sn	
Au/Sn	Complex	+15.3	- 4.8	Complex	Au	Au	Au	Sn
					Sn	Sn	Sn	

Ag-Pd

In studies by Bouwman, Lippits and Sachtler,³⁶ work function measurements indicated that Ag segregates to the surface of equilibrated thin films (x_b^{Ag} from .14 to .90). This was deduced not so much by the dependence of the values of the work function upon composition, but by the initial work function change upon adsorption of CO, which increases non-linearly with bulk Pd composition. It was also found that prolonged exposure to CO led to chemisorptive induced segregation of Pd to the surface.

A later study by Christman and Ertl³⁷ of the dependence of the Auger intensities on the angle between the surface and the primary beam showed no evidence for surface segregation in equilibrated thin films throughout the full range of compositions. That this method could detect a composition gradient was shown for a sample said only to be insufficiently annealed. One might not expect this method to be very sensitive to a monolayer type of segregation, so that a knowledge of the depth to which this inhomogeneous sample enriched in Ag would be helpful. They also found a linear relationship between Auger intensity and lattice parameter (proportional to the bulk composition).

Wood and Wise³⁸ studied supported Ag-Pd catalysts and found Ag enrichment at the surface. No efforts to clean the samples in the vacuum system were made and no Auger spectra were provided. The oxygen signal present was assumed to be from the alumina substrate only,

and the Handbook of Auger Electron Spectroscopy was used as reference to normalize the Auger intensities. Use of this handbook is of dubious value, since the intensity ratios may be expected to be a function of the experimental conditions used and may vary from analyzer to analyzer. Their results agreed with the regular solution model, and they explained the disagreement between their results and those of Christman and Ertl as due to crystallite size effects.

Another study³⁹ determined that sputtering Ag-Pd alloys resulted in an enrichment of Pd on the surface, due to the sputter rate of Ag being 1.89 times larger than that of Pd. Fractured surfaces of Ag-Pd rods, broken in vacuum had surface compositions equal to the bulk, as determined by comparison of the Auger intensities with those of pure Ag and pure Pd.

Ag-Au

Because of its very regular properties, this system is one that was chosen for study by the author,⁴⁰ and the results of that study were that for clean and equilibrated alloys, there seems to be some segregation of Ag, but less than is predicted by the regular solution theory. Part of the evidence for surface segregation was that the normalized Auger intensities depended upon the Auger electron energy, and hence the sample depth. This behavior is indicative of surface segregation (Chapter 3). It was also found that sputtering caused an enrichment in Au in the surface region, due to preferential sputtering of Ag. Details of this study are the subject of Chapter 4.

Fain and McDavid⁴¹ made work function measurements of vapor deposited Au-Ag films throughout the entire composition range and found that the work function varied non-linearly with composition in a manner suggestive of Ag enrichment at the surface. To check this possibility they measured intensities from different energy Auger peaks, but did not find the energy dependence indicative of a surface composition gradient. They did, however, observe this sort of dependence for an unequilibrated thin (two monolayers film of Ag evaporated onto an alloy). They therefore concluded that there was no segregation of Ag to the surface of their equilibrated films.

Using ion scattering spectrometry (ISS), Nelson⁴² found that there was surface segregation of Ag to the surface of alloy foils, and he claimed good agreement with the regular solution model. The cleanliness of the samples after annealing does not seem to have been carefully confirmed, and long annealing can cause sulphur segregation and a resultant enrichment of Ag at the surface.

Färber and Braun^{43,44} studied the surfaces of scribed, broken and sputtered alloys, and confirmed that sputtering enriches the surface in Au compared to the other treatments. No surfaces shown to be fully cleaned and equilibrated were studied.

Au-Pd

This system was investigated by Wood and Wise³⁸ who studied microspheres with compositions of 40, 60 and 80 at % Pd and alloy catalysts supported upon alumina with bulk compositions of about 22, 35, 55 and 75 at % Pd. They found considerable scatter in the Auger intensities

due to the roughness and heterogeneity of the samples. Nevertheless, the average values of the Auger intensities of the Pd(331 eV) and the Au(71 eV) (for the microspheres only) Auger transitions were obtained and compared with similarly prepared samples of pure Au and Pd. They found no evidence for segregation of either component to the surface, although prolonged heating in oxygen did have the effect of altering the surface composition.

Alloy foils of Au-Pd were studied with AES by Jablonski et al. All foils were polished in the same manner, cleaned in UHV by sputtering, equilibrated by heating, and the Auger intensities from both low and high energy Auger peaks were obtained and compared with intensities from pure Au and Pd. The surface monolayer compositions were calculated from the normalized Auger intensity ratios by taking full account of attenuation of the Auger electrons. A marked surface enrichment in Au was found throughout the entire composition range. Sputtering was found to enrich the surface in Pd.

Ni-Pd

Stoddart and Moss⁴⁶ studied Ni-Pd films of a wide bulk composition range vapor deposited onto substrates which were initially at room temperature and were not further heated (except by the deposition process). These films showed segregation of Pd to the surface, although there were some S and Cl impurities present. The principle evidence for segregation was the variation of the intensity ratio of a low energy to a high energy Ni peak. Taking attenuation into account, they analyzed this variation and obtained a surface monolayer

composition. They found that it was necessary to use low energy Auger peaks when comparing alloy Auger intensities to those of pure Ni and Pd, or the surface enrichment would not be clearly observed. This is evidence that the enrichment takes place only in the extreme surface region. The surface enrichment in Pd that they found was smaller than expected from the ideal solution model and the heats of sublimation. The question of whether the films were fully annealed was not directly discussed in the paper. Two of the films mentioned in this study were sintered at 400°C for one hour, but the results on these films seemed to be absent from most of the figures, and were not otherwise discussed.

In other work,³⁹ it was found that due to the fact that Ni sputters .63 times slower than Pd, sputtering Ni-Pd alloys results in a surface enrichment of Ni. Use of the high energy Ni Auger peak indicated that fractured surfaces have a surface composition equal to the bulk.

Fe-Cr

Leygraf et al.⁴⁷ studied single crystals of Fe, Cr and $\text{Fe}_{.84}\text{Cr}_{.16}$ with (110) and (100) orientation. When the sputtered (100) alloy was annealed for 15 minutes at temperatures between 675 and 1175°K, a constant Cr composition of about 31 ± 4 at % Cr and about 69 ± 5 at % Fe in the region sampled by 500 and 700 eV electrons (top 9-10 Å) was found. This enrichment in Cr was accompanied by the presence of S and is somewhat larger than expected from the ideal solution model and the differences in the heats of sublimation. In other experiments

related in the paper, it is not proven or likely that the surface was in equilibrium with the bulk. Heating the alloy in low pressure O_2 seemed to cause an increase in Cr in the surface region as was explained from the greater stability of Cr_2O_3 over $\alpha-Fe_2O_3$. Samples which were annealed for too short a time or at low temperatures after sputtering seemed to give very high Cr compositions which may indicate that there is selective sputtering of Fe in this alloy.

Au-Cu

This system has been studied by several workers and is interesting because at temperatures well below the melting point it forms ordered phases in the regions of 25, 50 and 75 at % Au, while maintaining miscibility in all proportions.

The earliest Auger studies of Au-Cu by Palmberg and Rhodin⁴⁸ showed that a thin Au film could be diffused into Cu at 300°C but they did not look at bulk alloys as such. The work of Potter and Blakely⁴⁹ indicated that there might be a surface enrichment of Au in Au_3Cu and possibly in AuCu also, for clean samples annealed at 500°C. The evidence was the dependence of the Cu(730 eV)/Cu(60 eV) intensity ratio upon bulk composition. For Cu_3Au there seemed to be no surface segregation. Their work also indicated that there is no dependence of the Auger intensity upon crystal orientation.

The work of Sundarem et al.⁵⁰ and of Braun and Färber⁵¹ could not provide very definite information regarding the surface composition but reached conflicting conclusions regarding the effects of sputtering. Sundarem's paper did indicate that the presence of S impurity tends to increase the Cu/Au Auger intensity ratio.

Van Santen et al.⁵² found that heating Au_3Cu which had been fractured in situ did not affect the Cu/Au intensity ratios, but that heating fractured AuCu_3 led to an increase in the Cu/Au ratio between 350 and 500°C, followed by a decrease at temperatures above 500°C. The changes in the ratios correlated with buildup of S followed by its disappearance above 500°C. This is in agreement with Sundarem's results. Van Santen believed that the fractured state corresponded to a surface composition equal to the bulk. This would indicate that no segregation is observed for Au_3Cu , while for AuCu_3 segregation of Cu is observed when S is present.

Fain and McDavid⁵³ used an intensity model essentially identical to that presented in Chapter 3 below to determine that, for clean and equilibrated alloy films with bulk compositions between $x_b^{\text{Au}} = .15$ and $.71$, there is strong segregation of Au to the top monolayer. Their data for Au Auger peaks from three different energies were internally consistent and proved that the second layer had essentially the same composition as the bulk. To the author's knowledge this is the only quantitative Auger analysis in the literature to take full account of attenuation and determine a two layer surface composition profile. The results are noteworthy and are shown in Fig. 2.9.

Cu-Ni

This system is the most widely studied of all alloys for reasons of its catalytic importance, and has been a source of confusion, most of which seems finally to be sorted out. The components are miscible in all proportions at higher temperatures but it is now believed

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Fig. 2.9 The experimentally determined first (●) and second (○) layer Au atom fractions of Au-Cu alloy films. (Reference 53)

that there is a miscibility gap below about 322°C ^{54,55} brought about by the positive heat of mixing.

The controversy started with work function measurements of Sachtler and Dorgelo⁵⁴ which indicated that a Cu rich phase was coating a Ni rich phase in their evaporated films. This configuration, described as the cherry model, was brought about by the fact that the films were equilibrated at low temperature, and resulted in a work function which was invariant throughout a wide range of composition lying within the proposed miscibility gap.

Later Auger studies⁵⁶ were made on Cu-Ni alloys which were prepared at high temperature and resulted in surface compositions which varied continuously between pure Cu and pure Ni. The problem was further confused by the fact that the most surface sensitive low energy Auger peaks in Cu-Ni are too close to be resolved easily, so that studies were made using the higher energy Auger peaks. This led experimenters to believe that the surface composition was identical to the bulk.^{56,57,58} Other workers^{59,60} assumed that uncleaned surfaces had surface compositions equal to the bulk and found that the normalized Auger intensities varied non-linearly with surface composition. It was found that heat treatments and sputtering of the alloys altered the surface composition with sputtering generally tending to increase Ni at the surface, but heating of the sputtered surfaces resulted in an increase in Cu.⁶⁰⁻⁶³ Using sputtered surfaces and compositions obtained from Auger, it was found that the work function

of Cu-Ni alloys varied linearly with composition,⁶⁴ seemingly in conflict with Sachtler's results. Due to impurities which most certainly were present in calibrating the Auger measurements, these results are probably not fully accurate.

As studies on Cu-Ni and other alloys progressed, there developed a greater understanding of the effects of sputtering and of impurities upon the surface composition, and an appreciation of how using high energy Auger peaks can be misleading. Finally, using the low energy Auger peaks, Helms^{65,66} determined that indeed clean and annealed alloys of 50 and 90 at % Ni do show segregation of Cu to the surface as expected and that sputter cleaning and the presence of oxygen does affect the surface composition. Using ion scattering spectroscopy, a technique which may be expected to be even more surface sensitive than AES, Brongersma and Buck⁶⁷ found segregation of Cu to the surface of an alloy of 50 at % Cu held at 730°C. A surface composition of about 85 at % Cu was found for this alloy, somewhat lower than that found by Helms at 650°C. It has been shown that segregation of Cu could explain CO flash desorption experiments⁶⁸ and that segregation according to the ideal solution model could explain ethylene hydrogenolysis results.⁶⁹ The conflicting results of Sachtler's work function studies seem to be due purely to the bulk sample preparation.

Au-Ni

The expected surface segregation of Au was found in two separate Auger studies. Williams⁷⁰ found that for alloys of three different bulk compositions ($x_b^{\text{Au}} = .005, .035 \text{ and } .23$) he got good agreement with predictions of the regular solution, taking the heats of sublimation as a driving force. The samples were prepared by electrodeposition of Au onto Ni foils, presumably at room temperature. It is interesting to notice that at least one of the samples was within the miscibility gap. No attenuation effects were taken into account in using the Auger data to obtain surface compositions.

Burton^{71,72} measured the temperature dependence of the Au(69 eV)/Cu(61 eV) Auger intensity ratio in a sample with nominally 1 at % Au in the bulk and obtained a heat of segregation of 12 ± 2 kcal/g·at. He found that the surface monolayer could vary from 1 to 100% Au as a function of temperature, but evidence from comparing low and high energy Auger peaks indicated that the segregation was localized to only the top monolayer. Together, both Williams and Burton found that the presence of S, H and O impurities resulted in an enrichment of Ni at the surface, as is expected from a chemisorption type of segregation.

Au-Pt

To the author's knowledge, no Auger or other modern techniques have been applied to this alloy system. However, the work function measurements made by Bouwman and Sachtler⁷³ are interesting because they reenforce the results found by Sachtler and Dorgelo⁵⁴ in their

Cu-Ni studies. Bouwman and Sachtler found that films of a wide bulk composition range prepared by simultaneous evaporation of Pt and Au had work functions which varied smoothly between the values for pure and pure Au. Upon sintering the films at 300°C, the work function was found to be nearly constant between 15 and 88 at % Pt. These results were attributed to the Kirkendall effect¹⁶ in which the Au diffuses faster than Pt and coats the Pt crystallites resulting in a skin of the Au rich phase engulfing a core of Pt rich phase. This behavior is exactly analagous to that found on Cu-Ni films annealed at low temperatures. They also found that prolonged exposure to CO caused a gradual increase in the work function which is attributed to chemisorption induced segregation of Pt to the surface.

Using a technique of chemisorptive titration, Kuijers et al.⁷⁴ confirmed the results of Bouwman and Sachtler.

Pb-In

The surface of Pb-In alloys were studied by Berglund and Somorjai,⁷⁵ and this work is unique among these considered in this review in that they studied liquid alloys. As such there could be no strain effects contributing to segregation. Measuring the Pb(92 eV)/In(403 eV) Auger intensity ratio indicated that there was the expected enrichment of Pb to the surface for alloys of 28.6, 44.5 and 60.5 at % Pb, although the extent of the segregation was not estimated and attenuation effects were not included. Further confirmation of enrichment was given by the temperature dependence of the Pb/In Auger intensity ratio, which increased with decreasing temperature as expected from

the ideal solution model. For the 44.6 at % Pb sample it was found that the presence of CO did not affect the intensity ratio, but exposure to O₂ resulted in a decrease of the ratio. This was attributed to the volatility of PbO at the temperatures studied (260-500°C).

In an Auger study of Pb-In oxide films, Chou et al.⁷⁶ found that In is preferentially oxidized, resulting in an oxide film enriched in In, in good qualitative agreement with the results of Berglund and Somorjai. For alloys with > 30 at % In, the surface contained only In₂O₃ in agreement with their thermodynamic predictions of the stability of In₂O₃ in contact with a Pb-In film.

Au-In

Only one brief paper is published on this alloy system, and deals with a film of nominally 2 at % In in Au. Thomas⁷⁷ found a strong segregation of In in this film. Sputtering the film resulted in a decrease of the In Auger peak to a value corresponding to approximately the bulk composition. Upon discontinuing the sputtering, the In signal increased and the Au Auger signal decreased to a value corresponding to about 15 at % in the region scanned by the Au(71 eV) peak. This diffusion takes place at room temperature and with a time constant of about two minutes!

Cu-Al

One phase alloys of 1, 5 and 10 at % Al dissolved in the Cu lattice were studied by Ferrante.⁷⁸ He cleaned his single crystal samples by cycles of sputtering and annealing. Following sputtering he annealed the samples for 30 minutes at various temperatures between

room temperature and 700°C. Comparing the resulting Auger intensities ratios with those of a sputtered sample, he concluded that there was segregation of Al to the surface in accordance with expectations, since Al strains the Cu lattice, and since Al has the lower heat of sublimation. The analysis is clouded by the use of a sputtered surface for a reference intensity ratio when roughness and selective sputtering effects may be present. As such no trustworthy surface compositions could be obtained. In a later paper,⁷⁹ Ferrante studied the temperature dependence of the low energy Al/Cu Auger intensity ratio and obtained a heat of segregation of 1380 cal/g•at for Al segregation in a sample with bulk composition of 10 at % Al.

Pt-Sn

This system has a complicated phase diagram with intermetallic compounds forming at PtSn, Pt₃Sn and at other bulk compositions. Both PtSn and Pt₃Sn are strongly ordered and have rather large negative heats of formation (-14. kcal/g•at and -12. kcal/g•at respectively).

Alloys of PtSn and Pt₃Sn were studied with Auger by Bouwman et al.⁸⁰ The intensity ratio Sn(428 eV)/Pt(236 eV) from the alloy was used as a monitor. Calibration was performed by comparing with the intensity ratios of alloy rods of PtSn and Pt₃Sn which were fractured in vacuum. The fractured surface was found to be clean and the resulting intensity ratios were consistent between PtSn and Pt₃Sn. Using these reference intensity ratios but without taking attenuation into account, overall surface compositions of 68 ± 5 and

equilibrated at various temperatures. The Auger intensities were calibrated carefully by three independent means,⁸² taking full account of electron attenuation. They found up to two full monolayers of Sn adsorbed at the surface for both the grain boundaries and the free surface, though the free surface showed greater segregation of Sn as shown earlier in Fig. 2.6. The temperature dependence of the measured compositions indicated that the free energy of segregation varied as a function of temperature (Fig. 2.6). They also found that S decreases the amount of Sn at the free surface due to site competition.

Au-Sn

This complex system was one chosen by the author for study⁸³ and is the subject of Chapter 5. Briefly previewing the results, it was found that strong segregation of Sn occurs when Sn is the solute in the Au lattice and in the hcp ζ phase which forms at about 86 at % Au. The strongly ordered δ (50 at % Au) phase shows no evidence for Sn segregation which is interpreted as being due to the strong ordering in that compound. No evidence is found for phase redistribution (such as in the "cherry model") for two phase alloys with composition between the δ and the ζ phase alloys.

41 $\pm$ 5 at % Sn were found for equilibrated surfaces of PtSn and Pt₃Sn respectively. Equilibration was performed at 500°C and led to the appearance of some C. They also found that sputtering causes enrichment of the surface in Pt. Oxidation at 200 and 500°C gave further enrichment in Sn. Reduction at 500°C resulted in a surface composition of 64 and 35 at % Sn for PtSn and Pt₃Sn respectively.

Later, using x-ray photoelectron spectroscopy, Bouwman and Biloen⁸¹ again determined the surface composition of reduced PtSn and Pt₃Sn. The higher energy photoelectrons gave a deeper sampling depth than the Auger electrons, so comparison of these two experiments allowed them to obtain a crude surface composition profile. Their data for PtSn was found to be consistent with a hypothetical surface configuration which had a top layer enriched in Sn sitting above a layer depleted in Sn. However, the fit to the data was very coarse and the layer thickness' (6-11 Å for PtSn and 11-20 Å for Pt₃Sn) do not seem physically probable.

Fe-Sn

Very dilute alloys of Sn (< 1 at % Sn) were studied with Auger by Seah et al.^{19,20,82} Fe-Sn has a very complex phase diagram, but in these studies only the single phase primary Fe solution was studied. Sn is expected to segregate to the surface. Seah and Hondros²⁰ looked at the grain boundary composition by cleaving a well annealed sample (which fractured in vacuum along grain boundaries) and examining the cleaved surfaces. Seah and Lea¹⁹ studied the segregation of Sn to the free surface cleaned by sputtering and

3. AUGER ELECTRON SPECTROSCOPY

The technique of Auger electron spectroscopy was used as a means of determining the surface composition of the alloys discussed in this thesis. The following chapter is devoted to describing this technique in detail. In section 3.1 some selected basic facts about AES are provided. In section 3.2 a description of the Auger spectrometers and vacuum systems used for these studies is given and experimental details relating to the experiments described in later chapters are provided. Finally in section 3.3 is given a detailed description of how to use the information obtainable from AES quantitatively to obtain the surface composition or depth profile of an alloy.

3.1 Some Fundamentals of Auger Emission

When a solid is bombarded with a primary beam of energetic electrons (1-5 keV) a large number of the atoms in the near surface region (top 100-200 Å) are ionized. These ionized atoms relax rapidly by a process in which another electron "falls" into the vacancy in the ionized atom. The energy which results from the process is either emitted as a photon or transferred to another electron as kinetic energy. The energetic electron produced by the latter process is called an Auger electron and if it escapes from the solid without energy loss it can be detected electrostatically. The energy of this electron is characteristic of the type of atom and so can be used to identify the types of atoms present. The creation, detection and interpretation of this emission process is Auger electron spectroscopy.⁸⁴

A study of the distribution of emitted electrons, $N(E)$, can yield a tremendous amount of physical information about the type and quantity of atoms present, the electronic structure of the solid, the processes of transport and relaxation of energetic electrons in a solid and many other phenomena. In addition to the Auger electrons however, a solid bombarded by an energetic primary beam will emit a broad background of electrons which have energies ranging between almost zero and the primary energy. This broad background consists of elastically and inelastically scattered primary electrons, Auger electrons and secondary electron emission.^{84,85} The number of Auger electrons which leave a solid without energy loss is very small compared to the immense background. To enhance this signal the distribution of scattered electrons is usually differentiated electronically,⁸⁶ using the modulation techniques described in the next section.

The physical aspect of AES which has caused so much interest in this technique is entirely the fact that it is surface sensitive. Electrons of energies from 50-2000eV interact strongly with solids. The inelastic mean free paths or escape lengths of low energy electrons in various solids are shown in Fig. 3.1.^{87,88,89} The values given in the Figure are tabulated from many experimental measurements, and due to the difficulty in measuring them the values have fairly large uncertainties. Nevertheless, when plotted on a log-log plot the mean free paths in metals seem to be nearly independent of the type of metal, and depend only upon the energy. The low energy electrons around 50 eV have the minimum escape depth of only about 4 Å, while the escape depths increase gradually with energy above 50 eV to about 30 Å for a 2000 eV electron.

These facts have been exploited fully in these studies.

3.2 The Auger Electron Spectrometer

Since AES is a surface technique, and since the surfaces of clean solids are very reactive it is necessary to perform the measurements in an ultra-high vacuum (UHV) system. In the course of the studies described in this thesis, three separate UHV systems were used. Chronologically, the first system was equipped with a retarding field analyzer (RFA) which was used for making the initial measurements on Au-Ag alloys. A system with a double pass cylindrical mirror analyzer (CMA) was used for making the confirming measurements upon Au-Ag alloys. Both sets of measurements are reported in Chapter 4. The third system contained a single pass CMA and was used to make all measurements on the Au-Sn alloys reported in Chapter 5. These analyzers were all mounted upon distinct UHV systems. As an example, the design and geometry of the third system will now be described in some detail.

The basic system was designed by the author and was purchased and/or built and assembled during the summer of 1975 by Weylon Wong, Emery Kozak and the author. The design of the system is standard. The vacuum was obtained by means of three pumps. The system was rough pumped by two sorption bottles (Varian/Vacuum Division, Palo Alto, Ca.) which are capable of pumping the system to about 10^{-2} to 10^{-3} torr. At this pressure it is possible to start an ion pump which was used for most of the pumping. This ion pump as a Varian 400 l/sec triode pump and was separated from the main chamber by a 6" gate valve. Inside the main

chamber was a water cooled titanium sublimation pump used at very low pressures as a getter. The pressure in the chamber was measured by a Varian nude filament ionization gauge bolted into the sample chamber. The system was capable of achieving a base pressure of 5×10^{-10} torr and routinely maintained a vacuum of 1×10^{-9} torr with all filaments on. A photo and schematic of the system are shown in Figs. 3.2 and 3.3.

The main chamber (Physical Electronics Industries, Edina Minnesota; Chamber Model 44) contained the samples mounted on the sample supports shown in Fig. 3.4. The supports were designed so that up to six samples could be mounted in the UHV at one time. A precision manipulator (Huntington Mechanical Laboratories, Inc., Mountain View, Ca.; manipulator model PM-602) was used to correctly position the samples in front of the CMA. This manipulator has three orthogonal translational degrees of motion in addition to rotation (about the axis of the manipulator shaft) and tilt motions. A stainless steel plate was bolted onto a rod using alumina insulators in such a way that the plate was electrically isolated from the rod, and this rod was attached to the central shaft of the manipulator. The actual sample holders were made of tantalum and were bolted to the stainless steel plate. With supports of this type the samples could be placed in front of the CMA in such a way that the plane of the sample surface was perpendicular to the axis of the CMA. Each sample holder could hold up to three samples. One side of each sample was electrically isolated from the Ta block holders and was connected to a Cu braid as shown in Fig. 3.4. To heat the samples, current was passed through the braid, across the sample and into the

Fig. 3.2 Photograph of the Auger electron spectrometer used to make the Au-Sn measurements. (Top) A- Ion pump B- Swing gate valve (Bottom) C- Cylindrical mirror energy analyzer D- Precision sample manipulator E- Sputter ion gun F- Sapphire leak valve G- Titanium sublimation pump

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Fig. 3.2

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Fig. 3.3 Schematic of the Auger electron spectrometer used to make the Au-Sn measurements.

Fig. 3.4 Photograph and schematic of the sample holder used for the Au-Sn measurements. A- Copper common heating lead B- Insulating four hole washer (Al_2O_3) C- Stainless steel manipulator shaft extension D- Tantalum sample support frames E- Copper heating lead F- Samples (only two shown) G- Stainless steel screw and nut H- Copper lug I- Mica washer J- Al_2O_3 sleeving.

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Fig. 3.4

Ta holder and the stainless steel plate. This plate was common to all samples and a Cu braid was attached to the plate as a current return. In addition, thermocouples were frequently used by spot welding the junction to the back of a sample. The thermocouple and the heating leads were attached to electrical feedthroughs mounted on mini-conflat flanges (Varian) and bolted on the manipulator. The temperatures of the samples with thermocouples could be used to calibrate an Infrascopes (Huggins Inc. Model #31C00-04) which was then used to estimate the temperatures of the remaining samples.

The single pass CMA (Physical Electronics, Model #10-150) contained a 0-5000 eV electron gun which was co-axial with the analyzer and was used as an excitation source. This geometry simplifies the intensity analysis as will be described in section 3.3. The samples could be sputter cleaned with energetic ions by using a commercially available sputter ion gun (Physical Electronics, Model #04-161). The ion beam was incident at a grazing angle of about 70° from the surface normal. An ion energy of 1.5 keV was used and the gun produced a total beam current of about $20\mu\text{A}$ collected at the sample but the flux density and distribution was unknown. Prep grade Argon (Matheson Gas Products) was used for sputtering and was introduced to the chamber through a sapphire leak valve (Varian) from a gas manifold. The manifold was pumped by a mechanical forepump. A liquid nitrogen cold trap and a molecular sieve trap were included in the line between the forepump and the gas manifold.

The electronics for controlling the CMA and the integral gun were

purchased in a package along with the analyzer (Physical Electronics; Auger System Controller 11-500A and Auger Gun Control 11-010). Other electronics included a high voltage power supply for biasing the electron multiplier and a lock-in amplifier (Princeton Applied Research; Model #JB-5) for phase sensitive detection of the output of the CMA electron multiplier. The output of the lock-in was monitored with an x-y recorder or infrequently an oscilloscope. A D.C. variable current power supply was used for resistively heating the samples.

The other two systems mentioned earlier which were used for making the measurements on the Au-Ag alloys were quite similar to the above system with the principle differences being the types of analyzers used. A comparison of the different analyzers will now be made.

A retarding field analyzer has four concentric hemispherical wire mesh grids and a hemispherical collector plate concentric with the grids.⁹⁰ These elements are biased as shown in Fig. 3.5. The sample is positioned at the center of the five hemispheres. The electron beam is either directed through a drift tube which extends through the grids and collector plate or is incident at a grazing angle from outside the analyzer. The former geometry was used here. The single pass CMA consists of two co-axial cylinders which are biased as shown in Fig. 3.5.^{91,92} The electron beam is either directed along the axis of the cylinders, or it may be incident at a grazing angle.

The electron beam excites the sample and a spectrum of electrons, $N(E)$, are emitted. Auger measurements are made by placing a negative D.C. potential V and a small A.C. modulation, $k\sin(\omega t)$, onto the second and third grids of the RFA or onto the outer cylinder (mirror) of the

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Fig. 3.5 Comparison of the retarding field and the cylindrical mirror types of Auger analyzers.

CMA.

For the RFA only electrons with energy greater than $V(\pm k)$ will pass through the grids and strike the collection plate. The analyzer then acts as a high pass cutoff filter. The CMA on the other hand is a differential detector. Of the electrons passing into the entrance slit of the analyzer only those with a particular small energy range, $E \pm \Delta E$, determined by V and the characteristics of the analyzer will pass through the exit slits. For the CMA, this relationship is approximately $E \pm \Delta E \approx 1.76e(V \pm k)$. This difference in the range of collected energies leads to important differences between the two analyzers.

The purpose of the modulation is to obtain a derivative of the $N(E)$ spectrum. Chang⁸⁴ has shown that the collected current, I , can be written as follows:

$$I = I_0 + \left[I'k + \frac{I'''k^3}{8} + \dots \right] \sin(\omega t) - \left[\frac{I''k^2}{4} + \frac{I''''k^4}{48} + \dots \right] \cos(2\omega t) + \dots \quad 3.1a$$

$$\approx I_0 + I'k \sin(\omega t) - \frac{I''k^2}{4} \cos(2\omega t) + \dots \quad 3.1b$$

Here the primes refer to differentiation with respect to the D.C. potential V . The second equation approximates the first if the modulation amplitude k is sufficiently small. The value of the frequency of ω to be used is largely unimportant. For the RFA a frequency of around 1000 Hz was used while for the single pass CMA $\omega \approx 6000$ Hz was chosen. Since the CMA is a differential detector it is clear that the collected current is proportional to $N(E)$ so that $I' \approx N'(E)$. With a lock-in amplifier it is possible to phase sensitively detect the component, A_1 , of the collected current which has frequency ω . For a CMA it follows

from Eq. 3.1b that $A_1 \approx kI' \approx kN'(E)$ so it is seen that the derivative of the electron distribution curve can be obtained by detecting the first harmonic of the collected current. Since the RFA is a cut off filter, $I' N(E)$ so it is necessary to detect the component A_2 of frequency 2ω to obtain the $N'(E)$ curve, since $A_2 \approx I''k^2/4 \approx N'(E)k^2/4$. This is the first difference between the two types of analyzers. Note that in both cases the signal depends upon the amplitude of the modulation voltage, k , but for the RFA the signal depends upon k^2 while for the CMA the signal varies linearly with k . The signal can be increased by increasing k , within the limit that k is small enough (compared to the peak width) that higher order terms in Eq. 3.1a are negligible.

A second and most important difference between the analyzers is that the CMA is much more sensitive than the RFA. This arises from the fact that shot noise is the greatest contributor to the electronic noise, and the shot noise current is proportional to the square root of the collected current. In an RFA a greater current is collected so more noise is obtained for the same amount of signal than for the CMA. This results in the CMA having a signal to noise ratio which is about 100 times larger than that of the RFA.⁸⁴ This allows less intense Auger peaks (such as the 2024 eV Au peak) to be more quantitatively studies. This also allows the use of higher scanning speeds and/or lower electron beam currents, and the use of smaller modulation amplitudes. The resolution of the analyzer can be no better than the modulation amplitude so resolution may be limited by the need to use a higher modulation amplitude to see a weak signal. For the RFA used in the Au-Ag system the sensitivity needed required the use of 10 V

p-p modulation, while the measurements made with the CMA were done with a modulation of 2 V p-p. There are many other factors involved in the resolution of the two types of analyzers which will not be discussed here.

Another important difference is the angle of collection. A CMA collects a cone of electrons at an angle $\theta_o = 42.3^\circ$ plus or minus some angle (probably about 6°)⁹² which depends upon the geometry of the exit slits. The RFA collects all electrons between the smallest angle which misses the drift tube of the normal electron gun and the outside edge of the analyzer (about 60° for the 4-grid RFA used here). If there is angular anisotropy in the Auger emission which varies with alloy composition, crystallite orientation, roughness, heat treatment, etc., the RFA will be insensitive to the effect, but the CMA will be affected. This is a disadvantage of the CMA for quantitative purposes. The RFA has the distinct advantage in this regard in that it can be used for doing low energy electron diffraction (LEED) experiments thereby allowing the simultaneous use of two techniques. This fact is the principle reason that the RFA is in more common use than the CMA. LEED can be done with a CMA but the technique seems somewhat inconvenient.⁹³

The CMA is critically sensitive to the placement of the sample.⁹⁴ Small movement of the sample away from the focal point along the line defined by the axis of the analyzer results not only in a shift of the peak position and in peak distortion, but also causes a decrease in the signal intensity to an extent which depends upon the energy. The

effect is demonstrated in Fig. 3.6. The RFA is not nearly as sensitive to this placement and the sample may be moved several millimeters without noticeable effect. This is no real disadvantage of the CMA since it is possible to place the sample in the correct analysis position by maximizing the measured intensity of the elastic peak with respect to sample placement. Problems can arise due to uncontrolled sample movement such as buckling due to expansion during heating. This necessitates occasional checks of the sample position.

The shape of the Auger spectra obtained from a CMA and RFA are also different. At low energies the RFA accurately shows the large background due to secondary emission. Use of the peak to peak height in the derivative spectra as a measure of intensity at low energies is affected by the sloping background. The CMA does not show this sloping background due to the fact that it distorts the spectra at low energies. This distortion is due to the energy dependent transfer function of the analyzer and the energy dependence of the electron multiplier gain.⁸⁴ This distortion is also expected to affect the relation between peak to peak height and Auger intensity. The assumption will be made that the distortion is similar for all alloys. Spectra recorded with a CMA and an RFA are given in Fig. 3.7 for comparison.

The double pass CMA which was used for re-measuring the Au-Ag intensity ratios consists essentially of two mirror analyzers put back to back with the electron multiplier behind the exit slits of the second analyzer. Such an analyzer is sold by Physical Electronics and most of what has been said about the single pass CMA applies to the double

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Fig. 3.6 Effect upon shape, position and relative intensity of the elastic peak due to sample displacement, d , along the axis of the cylindrical mirror analyzer.

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Fig. 3.7 Comparison of Auger spectra of an Au-Ag alloy ($x_b^{\text{Au}} = .65$) obtained with retarding field and cylindrical mirror types of energy analyzers.

pass. The only real operational difference is that the double pass CMA is even more sensitive to sample position making it frustrating to do experiments with any but a very precisely repositionable manipulator.

3.3 Analysis of Auger Intensities

Auger has principally been used as a means of performing qualitative analysis of surfaces; i.e. to identify or verify the presence of various atomic species. For this purpose AES is quite certainly the best of all available techniques. Also of interest is the use of AES as a means of quantitatively analyzing a surface to determine how much of an impurity or alloying component is present. This endeavor has occupied the time and efforts of a growing number of workers in the last eight years and in many cases has obtained some measure of success although the methods currently used still have shortcomings and difficulties.

An understanding of quantitative AES begins with an expression describing the intensity of Auger emission.⁹⁵ The current, I_E , of Auger electrons arising from a transition observed at energy E , may be phenomenologically divided up into intensities from each atomic layer in the solid. This description arises naturally from considering flat perfect surfaces of infinite extent as in some of the models described in Chapter 2. This concept is not as well defined for rough surfaces or small clusters, but in spite of this the results will be applied to the rough polycrystalline samples used in this study. The intensity from each layer may then be described by breaking the Auger process into the following three steps; 1) excitation, 2) emission and 3) collection. Each step will now be considered.

The standard means of excitation is by bombardment with electrons of energy E_p and current I_p . For the studies in this thesis E_p was 2 or 4 keV and I_p was usually 15-50 μ A spread over an area of about 1 mm². The number of atoms ionized in the i^{th} layer near the surface may be expected to be proportional to the expression given in Eq. 3.2 below.

$$\text{ionization events} \sim I_p g_p(\theta_p, \phi_p) \rho_i \sigma_i(E_p) p_i(E_p) r_i(E, E_p) \quad 3.2$$

Here ρ_i is the number of atoms per unit area in the i^{th} layer and the function $g_p(\theta_p, \phi_p)$ takes the geometric and anisotropic factors in the excitation into account and depends upon the angles of incidence θ_p and ϕ_p of the primary beam. σ_i is the cross section for ionization of an atom by electrons of energy E_p . p_i is an energy dependent factor which accounts for the attenuation of the primary beam and r_i is a backscattering factor which takes into account that electrons which have been elastically and inelastically scattered may contribute to the ionization.

The excited region of the solid is penetrated by a beam of electrons incident at fixed angles θ_p and ϕ_p whose intensity decreases with depth due to inelastic and elastic scattering of the primary beams. This region also consists of a plasma of electrons of nearly continuous energies and momentums. The terms $\sigma_p(E_p) p_i(E_p)$ in Eq. 3.2 takes account of the ionization by the column of primaries while the general term $r_i(E, E_p)$ takes account of the excitation by the plasma. This backscattering term is very complicated and contains the energy dependence of the ionization cross section of the solid and may be expected to vary with depth.^{96,97}

To use Eq. 3.2 approximations must be used. Typically it is

assumed that there is no anisotropy in the excitation process. Because of attenuation, the more grazing the incident angle θ_p the more energy will be deposited in the surface region from which Auger electrons can be collected. This suggests the form $g(\theta_p, \phi_p) \sim 1/\cos \theta_p$.⁹⁵ In fact experiments have shown that this model is only partly correct.^{98,99} In the experiments done in this thesis the primary beam was normal to the sample ($\cos \theta_p = 1$) so $g(\theta_p, \phi_p)$ will be taken as unity. Eq. 3.2 may be further simplified by assuming that the primary beam intensity or its ionization capability is independent of depth within the region detected by collecting the Auger electrons. The basis for this assumption is the fact that the escape length of an electron with energy $E_p = 4$ keV is large and the average inelastic collision results in only a small energy loss, leaving the primary electron still energetic enough to efficiently ionize. More importantly, this assumption has been experimentally justified.¹⁰⁰ With these assumptions, Eq. 3.2 simplifies to the following form:

$$\text{ionization events} \sim I_p \sigma_I(E_p) \rho_i r_i(E, E_p) \quad 3.3$$

The emission process, the second step in this scheme, is much simpler, and is given in Eq. 3.4.

$$\text{probability of emission} \sim P_A q_i(E, \theta) \quad 3.4$$

The probability of emission is the product of the probability, P_A , that an ionized atom undergoes an Auger process and emits an electron, and the likelihood $q_i(E, \theta)$ that the Auger electron emitted at an angle θ from layer i will escape to the surface without an inelastic collision. P_A is characteristic of the type of atom involved and the energy E of the

Auger transition¹⁰¹ and is assumed to be independent of angle. The attenuation of the electron is usually assumed to be exponential with a characteristic attenuation depth λ_E which depends upon the energy, so Eq. 3.4 becomes the following.

$$\text{probability of emission} \sim P_A \exp(-(i-1)d/\lambda_E \cos\theta) \quad 3.5$$

Here d is the interlayer spacing of the solid, so an atom in the i^{th} layer is at a depth of $(i-1)d$. If the Auger electron is emitted at an angle θ measured from the surface normal, it must travel through the solid a distance $(i-1)d/\cos\theta$ to escape from the solid.

It is important to note that this form holds only if each layer fully covers the layer below it. This is true in a close packed plane such as in the (111) face of an fcc solid. For the (110) face, the surface consists of ridges and troughs so that the atoms at the bottom of the troughs while in the second layer are not attenuated fully by the first layer. This fact leads to the necessity of applying this model only to close packed planes. This causes difficulties in the Au-Sn studies as will be seen in Chapter 5. It is also important to note that the model assumes that the surface is atomically flat and smooth. If there is roughness, the emission will be affected.

Holloway¹⁰² has studied the effects of roughness on Auger emission and has found that even very slight roughness (root mean square displacement of $.28\mu\text{m}$) could reduce the Auger intensity by up to 40% depending upon the angle of incidence of the primary beam and the collection angle. He found that the effects of roughness were least when a normally incident primary beam was used. This is the configuration used in these

experiments.

To get the total emission Eq. 3.5 should be integrated over all angles collected. Eq. 3.4 assumes that the emission is isotropic and that the emitted electrons are not diffracted or otherwise attenuated anisotropically. Experiments show that this may not be true for single crystals.^{98,99} For the polycrystalline samples used in these studies the presence of crystals of many orientations should eliminate anisotropies.

Finally the collection process, which is the third step of the emission process adds terms which take into account that the detector intercepts a solid angle Ω and so only collects $\Omega/4\pi$ of the emitted Auger electrons. This fraction is further attenuated by the transmission, T , of the detector. For a CMA such as used in these experiments, only electrons emitted at an angle near $\theta_0 \approx 42.3^\circ$ are collected where θ_0 is measured from the axis of the analyzer. If the sample is mounted so that the sample surface is perpendicular to the axis of the analyzer, then θ in Eq. 3.5 becomes θ_0 . For the calculations below, an average value of $\theta_0 = 42.3$ is assumed. For this narrow angle detector the factor $\Omega/4\pi$ effectively derives from integrating Eq. 3.5 over the angle θ .

Combining the number of ionization events times the probability of emission and collection and summing over all the layers of the pure solid gives Eq. 3.6 for the intensity I_E^O of an Auger peak at energy E .

$$I_E^O = \sum_{i=1}^{\text{layers}} I_p g_p(\theta_p, \phi_p) \rho_i^O \sigma_i^O(E_p) p_i^O(E_p) r_i^O(E, E_p) P_{Aq_i}^O(E, \theta) (\Omega/4\pi) T \quad 3.6$$

Here the superscript "o" denotes values characteristic of a pure solid. Making the assumptions suggested above the expression simplifies to the following expression for the absolute Auger intensity from the pure solids.

$$I_E^o = I_p \sigma_I^o(E_p) P_A^o(\Omega/4\pi) T \sum_{i=1}^{\text{layers}} \rho_i^o r_i^o(E, E_p) \exp \left(- \frac{(i-1)d^o}{\lambda_E \cos \theta_o} \right) \quad 3.7a$$

$$\equiv k^o(E, \dots) (a_1^o + a_2^o + a_3^o + \dots) \quad 3.7b$$

where, for convenience, $I_p \sigma_I^o(E_p) P_A^o(\Omega/4\pi)$ is written as $k^o(E, \dots)$ and $\rho_i^o r_i^o(E, E_p) \exp \left(- \frac{(i-1)d^o}{\lambda_E \cos \theta_o} \right)$ is written as a_i^o . This formula can be applied

to alloys if ρ_i^o is replaced by $\rho_i x_i$ where x_i is the atom fraction of the emitting species in the i^{th} layer and ρ_i is now the total number of both types of atoms per unit area. This yields for an alloy the following:

$$I_E = I_p \sigma_I(E_p) P_A(\Omega/4\pi) T \sum_{i=1}^{\text{layers}} \rho_i r_i(E, E_p) \exp \left(- \frac{(i-1)d}{\lambda_E \cos \theta_o} \right) x_i \quad 3.8a$$

$$\equiv k(E, \dots) (a_1 x_1 + a_2 x_2 + a_3 x_3 + \dots) \quad 3.8b$$

In this equation ρ_i and d may be expected to vary with composition of the alloy. Difficulties arise from the fact that $\sigma_I(E_p)$, P_A , $r_i(E, E_p)$ and λ_E might also depend upon alloy composition. The dependences of these four quantities upon composition will be referred to as matrix effects, and very little is known about them.

Progress has been made in calculating or measuring ionization cross sections,¹⁰³ backscattering factors,^{96,97} Auger transition probabilities,¹⁰¹ and attenuation lengths⁸⁷ in pure solids, but in

general it is still not possible to calculate the absolute Auger current. In fact it is not even easy to measure the Auger current! The reason is that the Auger current is superimposed upon a much larger background so that modulation techniques and a rather sophisticated analyzer must be used. Typically the peak to peak height in the derivative spectra or some appropriately integrated Auger feature is used as a measure which is taken to be proportional to the Auger intensity. The former measure is used in these studies. Theoretical work has shown under what conditions the proportionality holds for both CMA and RFA types of Auger analyzers.^{90,84} In fact, if the Auger peak shape changes (as it might with alloying or change in oxidation state) or if too large a modulation voltage is used the proportionality may break down. Small modulation voltages were used in this work and the peak shapes were checked as a function of alloy composition.

To avoid many of the problems of absolute intensity measurement, it is common to use standards which provide reference intensities for calibration. For the alloys studied below, the references used were the intensities, I_E^0 , from samples of the pure components prepared in similar manner to the alloys. The drawbacks to this method is that it requires that there be no matrix effects. The factors $\sigma_I(E_p)$ and P_A might be expected to be independent of matrix but no data exists to confirm this. The escape depth λ_E is taken as independent of composition, an approximation which is suggested by the "universal" nature of the curve shown in Fig. 3.1.

Other workers have attempted to use other means of calibration.⁸²

Typical methods include sputtering, scribing, or cleaving of alloys in an attempt to obtain a surface which has the same composition as the bulk. Each of these methods has difficulties, for instance sputtering may lead to preferential removal of one of the components as will be discussed in Chapter 6. Other techniques involve depositing some species onto a substrate and comparing the Auger intensity with the amount deposited as measured by some other means such as with a quartz crystal oscillator¹⁰⁴ or by ellipsometry,⁹⁵ or by radiometric techniques. These techniques also are uncertain due to matrix effects.

With the various pitfalls and approximations labeled above, the means by which surface information was obtained in this thesis will be described. The information that is available from the experiments are the intensities of each of the Auger peaks in the spectrum of an alloy and the corresponding intensities in the reference samples. To cancel the effects of instrumental drift and for purposes of normalization, these are always measured as ratios.

Two types of ratios are of use. The ratio of the intensity of a peak at an energy E in the alloy divided by the intensity of the same peak in the pure reference will be denoted as ξ_E . The ratio of the intensity of a peak at an energy E to another peak at energy E' will be referred to as $R_{E/E'}$. This ratio may be measured from one alloy sample or from one or both pure references in which case the superscript ^o in $R_{E/E'}^o$ will denote that the ratio is for the pure reference. Summarizing, the following definitions are given:

$$R_{E/E'} = I_E/I_{E'} \quad 3.9a$$

$$R_{E/E'}^O = I_E^O/I_{E'}^O \quad 3.9b$$

$$\xi_E = I_E/I_E^O \quad 3.9c$$

These ratios are all measured experimentally. The $R_{E/E'}$ types of ratios are the easiest to measure since only one sample is involved. If E and E' refer to Auger transitions from the same component, then $R_{E/E'}^O$ is also easy to measure. The ratios ξ_E and $R_{E/E'}^O$ (when E and E' derive from different components) are harder to measure since two samples (the alloy and the reference or both references) must be prepared and positioned in turn in front of the analyzer.

It is possible to calculate ξ_E . Using Eqs. 3.7, 3.8 and 3.9 it follows that:

$$\xi_E = \frac{k(E, \dots)(a_1 x_1 + a_2 x_2 + \dots)}{k^O(E, \dots)(a_1^O + a_2^O + a_3^O + \dots)} \quad 3.10$$

To calculate ξ_E it is merely a matter of putting in the proper values for k, k^O , a_i , a_i^O and the depth distribution, i.e. the compositions in each layer, x_i . The depth distribution is the information of interest here and we want to extract it from the experimental values of $R_{E/E'}$, $R_{E/E'}^O$ and ξ_E .

Two methods are exploited. One may suggest hypothetical depth distributions which are then used to calculate the intensity ratios. These ratios are then compared with the experimental results and the depth distribution varied to give the best fit. An alternate method is to use the experimental data to directly calculate the depth distribution.

In Chapters 4 and 5 both methods are used to obtain the composition profile and estimate the uncertainty of the results.

To use Eq. 3.10 some assumptions are made. The first assumption is that ionization cross sections, Auger transition probabilities and the instrumental factors remain constant and are independent of composition. This assumption implies that:

$$I_p \sigma_I^0(E_p) P_A^0(\Omega/4\pi) T = k^0(E, \dots) = k(E, \dots) = I_p \sigma_I(E_p) P_A(\Omega/4\pi) T \quad 3.11$$

The second assumption is that below some depth the composition of each layer of the alloy becomes equal to the bulk composition x_b . The Auger intensity obtained from below that depth can be summed to give an expression of the following form:

$$\xi_E = \frac{(a_1 x_1 + a_2 x_2 + \dots + a_{k-1} x_{k-1} + a_b x_b)}{(a_1^0 + a_2^0 + a_3^0 + \dots)} \quad 3.12$$

From Eq. 3.8 and using the properties of a geometric series it can be seen that:

$$a_i = \rho_i r_i \exp\left(-\frac{(i-1)d}{\lambda_E \cos \theta_o}\right) \quad (\text{for } i < k) \quad 3.13a$$

$$a_b = \rho_b r_b \sum_{i=k}^{\text{layers}} \exp\left(-\frac{(i-1)d}{\lambda_E \cos \theta_o}\right) = \rho_b r_b \frac{\exp(-(k-1)d/\lambda_E \cos \theta_o)}{1 - \exp(-d/\lambda_E \cos \theta_o)} \quad 3.13b$$

From Eq. 3.7 it is seen that if the pure solid has the same value of ρ^0 , r^0 and d^0 in each layer then

$$\sum_{i=1}^{\text{layers}} a_i^0 = \sum_{i=1}^{\text{layers}} \rho_i^0 r_i^0 \exp\left(-\frac{(i-1)d^0}{\lambda_E \cos \theta_o}\right) = \rho^0 r^0 \left(1 - \exp\left(-\frac{d^0}{\lambda_E \cos \theta_o}\right)\right) \quad 3.14$$

It is now possible to write out an expression for the Auger intensity ratio ξ_E , in terms of contributions from each layer. This is done by substituting Eqs. 3.14 and 3.13 into 3.12. For example, Au, Ag and Au-Ag alloys have nearly identical lattice parameters (within .25%) and have the same crystal structures. Therefore, $\rho_i = \rho_{Au}^0 = \rho_{Ag}^0 = \rho_{alloy}$. For the (111) crystal face, each plane is separated by 2.35 Å, and the values of the escape depths λ_E for various energies can be obtained from Fig. 3.1. The intensity values ξ_E for a hypothetical composition profile can be obtained from the equations shown in Table 3.1. It is assumed arbitrarily that the fourth and all deeper layers have the bulk composition. The energies $E = 71, 241, 2024$ and 356 eV correspond to transitions in the Auger spectrum of Au-Ag alloys as will be discussed in Chapter 4.

It is seen from Table 3.1 that for a low energy Auger transition at 71 eV, about 55% of the signal comes from the top monolayer, while for a higher energy Auger peak at 2024 eV only about 10% of the signal comes from the top layer. For this high energy transition, as much as 73% of the signal comes from deeper than the third layer. The principle uncertainty in these equations, within the framework of the model, are the values for the escape lengths λ_E , and a lack of knowledge of the form or magnitude of r and r^0 .

Now that the values of ξ_E can be calculated, it is easy to calculate values for the normalized intensity ratios $R_{E/E'} / R_{E/E'}^0$, by using Eq. 3.15 given below.

Table 3.1. Auger intensities for Au-Ag alloys.

$\rho_i = .139 \text{ atoms/\AA}^2$	$\lambda_{71} = 4 \text{ \AA}$
$d = 2.35 \text{ \AA}$	$\lambda_{241} = 6 \text{ \AA}$
$\cos\theta_0 = .740$	$\lambda_{356} = 8 \text{ \AA}$
	$\lambda_{2024} = 30 \text{ \AA}$
$\xi_{71} = [.548 X_1 + .248 X_2 + .112 X_3 + .092 X_b][r(71\text{eV}, E_p)/r^0(71\text{eV}, E_p)]$	
$\xi_{241} = [.471 X_1 + .249 X_2 + .132 X_3 + .148 X_b][r(241\text{eV}, E_p)/r^0(241\text{eV}, E_p)]$	
$\xi_{356} = [.328 X_1 + .220 X_2 + .148 X_3 + .304 X_b][r(356\text{eV}, E_p)/r^0(356\text{eV}, E_p)]$	
$\xi_{2024} = [.101 X_1 + .090 X_2 + .081 X_3 + .728 X_b][r(2024\text{eV}, E_p)/r^0(2024\text{eV}, E_p)]$	

$$R_{E/E'} / R_{E/E'}^O \equiv R/R_{E/E'}^O = \xi_E/\xi_{E'}, \quad 3.15$$

which follows directly from Eq. 3.9. The ratios $R_{E/E'}$ and $R_{E/E'}^O$ (like the values I_E and I_E^O) can not be calculated without knowledge of all the factors in Eq. 3.7 and 3.8.

It should be noted that in Eq. 3.12 if $x_1 = x_2 = x_3 = \dots = x_b$ and if $a_i = a_i^O$, then $\xi_E = x_b$ and similarly $R/R_{E/E'}^O$ is equal to the ratio of the bulk atom fractions of the components associated with the Auger peaks at E and E'. In Au-Sn, it will be shown that in general $a_i \neq a_i^O$, so that even if there is no segregation it is not necessarily true that $\xi_E = x_b$.

The model provided above takes into full account attenuation of Auger electrons and it has capability of including backscattering effects as well. In section 2.3 above, it was frequently pointed out which workers did take full account of attenuation by using a model similar to the above. In the cases where attenuation was not considered, the standard practice was to measure some intensity ratio ξ_E and assume that $\xi_E = x_s$ where x_s is the "surface composition". As just shown ξ_E is weighted over a sizable depth. Here can be seen the source of considerable confusion as in the Cu-Ni case discussed above. In interpreting the results of studies made of Au-Ag and Au-Sn given below, peaks of several energies are used, and consideration is taken of attenuation and the possible effects of backscattering. The difficulties encountered point the way towards future work.

4. THE AU-AG SYSTEM

As mentioned in Chapter 2, the Au-Ag system is quite a simple one. Silver is completely soluble in gold so they can be melted together in any proportion without phase separation. This is in part due to their practically identical lattice spacing, and the fact that they have the same crystal structure, similar melting points and electronic structures. The heat of mixing is within 17% of being parabolic with composition $[\Delta H_m = -(4850 - 800 x_{Au})x_{Au}(1-x_{Au}) \text{ at } 800^\circ\text{K}]^8$ which is the form for a regular solution. 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.³⁴ For these reasons the binary alloys of Au and Ag were chosen to test the theories given in Chapter 2.

This chapter provides details of the experiments done to determine the surface composition of clean equilibrated Au-Ag alloys. Section 4.1 provides experimental details which were not given in Chapter 3 that are specific to the Au-Ag studies. Section 4.2 provides the results of experiments performed using a system which contained a retarding field analyzer (RFA) for doing AES. Section 4.3 provides the results of confirming experiments done with the system containing the double pass cylindrical mirror analyzer (CMA). Section 4.4 compares the results and analyzes them to obtain the desired information about the surface composition.

4.1 Sample Preparation and Experimental Details

Weighed quantities of 5 N Ag and 6 N Au were melted together on a water cooled 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 were then cut into pieces of the desired size. Pieces of pure Au and Ag were rolled and cut in the same manner for use as references.

The samples were not polished or etched further, but since they were all rolled in the same manner, their surface finish may be expected to be comparable. In some cases heating in the UHV 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 bulk composition of the samples was known from the amount of Au and Ag weighed out in preparing the samples. As a check, pieces cut from the foils were analyzed in solid form by x-ray fluorescence by Bob Giaque of Lawrence Berkeley Laboratories. This analysis suffered however from lack of a solid Au-Ag alloy standard. To correct this, the density of the sample with composition $x_b^{\text{Au}} = .65$ was determined using a pycnometer with water as the displacement liquid and the density was used to obtain the composition. This

sample was used as a standard in the x-ray fluorescence. The results of these determinations are summarized in Table 4.1. The prepared compositions will be assumed to be correct.

Initially the samples were contaminated with S, O, Cl, N and C which were removed by Ar^+ ion bombardment. After initial ion bombardment, impurities (especially S) readily diffused into the sample's detected volume upon heating the sample to above 200°C . Several cycles of bombardment followed by heating served to sufficiently rid the samples of impurities such that heating to 600°C could be accomplished without immediate detectable impurity segregation. Even so, the possible presence of impurities (S, C, Cl and O) was monitored by AES in all experiments. At the low pressures obtained, essentially no adsorption of ambient gas was observed on Ag, Au or their alloys. Impurities on the surface seemed to be due to segregation from the bulk or surface diffusion from dirtier regions.

In the RFA system the first samples tried were fixed on an alumina block. This support caused charging problems, which were only partly corrected when a film of Cu was evaporated onto it. One sample ($x_b^{\text{Au}} = .40$) was completed on this sample mount. A more satisfactory sample support was made from tantalum and was used for all other samples. Up to three samples could be mounted on the block sample support at one time. The samples were insulated in such a way that they could be heated independently by passing a direct current through them. Thermocouple leads of Pt and Pt-10% Rh were spot welded together and onto the backs of some of the sample foils.

Table 4.1. Bulk analysis of Au-Ag alloys.

Sample #	at % Au		
	Prep comp.	X-ray fluor.	pycnometer
1	30.3	33 ± 3	65.2 ± .9
2	45.5	51 ± 4	
3	65.0	65	
4	14.9	15 ± 2	
5	39.5	41 ± 4	
6	96.9	97 ± 2	

The temperatures of the remaining samples were crudely estimated from the heating current. Details of the AES measurements are given in Table 4.2.

In the CMA system the six samples and foils of pure Ag and Au were mounted together on a tantalum support as shown in Fig. 4.1. The support was designed with the intention that the sample surfaces would be normal to the axis of the Auger analyzer, but in fact the samples were slightly (less than 10°) off normal. The samples could be heated resistively to around 400°C . An infrared pyrometer was used to estimate the temperatures of the samples.

4.2 Auger Intensity Measurements: RFA

The samples which were mounted in the RFA spectrometer were of use for determining important properties of the Au-Ag system. The techniques for cleaning and equilibrating the samples and measuring the intensity were developed and a set of normalized Auger intensity ratios were ultimately obtained. Exemplary spectra are shown in Fig. 4.2 which indicate the degree of cleanliness that could be obtained from the originally quite dirty surfaces. The Auger peaks used in this analysis were the Au peaks found at about 71 and 241 eV and an Ag peak at about 356 eV. The Ag(356 eV) and the Au(71 eV) peaks are both actually unresolved doublets and the total peak to peak heights were used as a measure of the intensity. The Au peak known to be at about 2024 eV^{105} was too weak to be detected with this system when the excitation energy was set to 3000 eV.

Table 4.2. Typical operating conditions, Au - Ag measurements.

Analyzer	RFA - 4 - grid	Double pass CMA
Base pressure	$2-3 \times 10^{-9}$ torr	1×10^{-9} torr
Gun angle	Normal	Normal (axial)
Primary energy	2030 eV	4000 eV
Beam current	40 μ a	50 μ a
Sample angle	Normal	Normal ($\pm 10^\circ$)
Mod. voltage	10 V p-p	2 V p-p
Mod. frequency	1000 Hz	4500 Hz
Scan rate	40 eV/min	.5 eV/sec
Time constant	1 sec	100 msec
Lock-in Amp.	P.A.R. JB-5	P.A.R. HR-8

Fig. 4.1 Sample holder used to support Au-Ag alloys for measurements made in the spectrometer containing the double pass cylindrical mirror analyzer.

Fig. 4.1

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Fig. 4.2 Exemplary spectra of an Au-Ag alloy foil showing impurity levels before (bottom) and after (top) cleaning.

While cleaning the samples it was discovered that ion bombardment of a room temperature alloy always resulted in an increase in the Au/Ag Auger intensity ratios over the equilibrated values. This could be due to sputter damage, removal of an altered (segregated) surface layer or selective sputtering of one of the components. These possibilities will be assessed in Chapter 6. The effect of sputtering could be reproducibly annealed out at temperatures as low as 300°C. This effect was observed for all samples, and is demonstrated in Fig. 4.3. For all samples it was found that at 400°C the Au/Ag intensity ratios dropped very rapidly (within a few minutes) from the sputtered value and then reached a value which remained constant within experimental error for long (> 30 minutes) periods of further heating. This behavior was interpreted as the attainment of equilibrium between the surface and the bulk, and the final values for the intensity ratios are taken as the equilibrium values.

The process of sputtering and annealing was repeated many times until the sample could be fully equilibrated without the appearance of impurities. The equilibrium intensity ratios thus obtained are given in Table 4.3a. These ratios are each averaged from several measurements in which the sample was sputtered, heated long enough to assure that it had reached equilibrium and was then determined by Auger to be sufficiently clean. The reported uncertainties are the standard deviations of the averaged measurements. Some samples could not be cleaned as completely as some others in which impurities were undetectable by AES, but in all cases the impurity Auger peak intensities

Fig. 4.3 The change in an Au/Ag Auger intensity ratio when a freshly sputtered alloy is annealed at various temperatures.

Table 4.3. RFA - Annealed values

a) Experimental ratios

x_b^{Au}	$R_{71/356}$	$R_{241/356}^{\text{unc}}$	$R_{71/241}^{\text{unc}}$	$R_{241/356}$	$R_{71/241}$
.15	.105 $\pm$.017	.018 $\pm$.003	6.1 $\pm$ 1.7	.011 $\pm$.002	10.2 $\pm$ 2.8
.30	.757 $\pm$.029	.037 $\pm$.003	20.6 $\pm$ 1.8	.031 $\pm$.002	24.2 $\pm$ 2.1
.40	1.41 $\pm$.03	.061 $\pm$.006	23.2 $\pm$ 2.5	.055 $\pm$.005	25.8 $\pm$ 2.8
.46	2.38 $\pm$.08	.074 $\pm$.005	32.5 $\pm$ 3.4	.068 $\pm$.005	35.3 $\pm$ 3.7
.65	5.06 $\pm$.42	.127 $\pm$.012	39.8 $\pm$ 1.3	.121 $\pm$.011	41.9 $\pm$ 1.4
.97	55.3 $\pm$ 2.4	1.21 $\pm$.07	45.6 $\pm$ 5.7	1.21 $\pm$.07	45.6 $\pm$ 5.7
Au & Ag	4.30 $\pm$.16	.088 $\pm$.005	48.6 $\pm$ 1.5	.088 $\pm$.005	48.6 $\pm$ 1.5

b) Normalized ratios

$x_b^{\text{Au}} / x_b^{\text{Ag}}$	$R/R^{\circ}_{71/356}$	$R/R^{\circ}_{241/356}$	$R/R^{\circ}_{71/241}$
.176	.024 $\pm$.004	.12 $\pm$.02	.21 $\pm$.06
.429	.176 $\pm$.009	.35 $\pm$.03	.50 $\pm$.05
.667	.328 $\pm$.014	.61 $\pm$.06	.53 $\pm$.06
.852	.55 $\pm$.03	.77 $\pm$.06	.73 $\pm$.08
1.86	1.18 $\pm$.11	1.4 $\pm$.1	.86 $\pm$.04
32.3	12.9 $\pm$.7	13.7 $\pm$.9	.94 $\pm$.12

were greatly reduced over those obtained before cleaning the samples as demonstrated in Fig. 4.2. In addition there was no noticeable difference observed in the intensity ratios between samples of the acceptable cleanliness and those somewhat dirtier, indicating that the effect of any of these residual impurities was small.

A correction was necessary for the Au(241 eV) peak which was found to overlap a very small peak in the Ag spectra. The intensity of the Au peak was corrected by subtracting an amount proportional to the intensity of the Ag(356 eV) peak. The intensity ratios corrected for this peak overlap are also given in Table 4.3a.

The annealed intensity ratios (corrected for peak overlap) were normalized and are given in Table 4.3b and plotted in Fig. 4.4. The dashed lines in this figure indicate the values that would be expected if the surface composition were identical to the bulk.

It was deemed necessary to make yet another correction to the data. Because of the low resolution in these spectra and the fact that the Au(71 eV) peak lies on a very steep background it was believed possible that this peak's intensity is affected by the sloping background in a way which varies from sample to sample. To correct this, suitable spectra of each alloy and of pure Au were chosen and approximate backgrounds were drawn in using the shape of the background above and below the Au(71 eV) peak. The difference between the actual feature and the estimated background was manually replotted and a new intensity was measured from the (larger) redrawn Auger peak. The ratio of this new intensity divided by the old intensity was used

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Fig. 4.4 The normalized Auger intensity ratios obtained from clean and equilibrated Au-Ag alloys using the RFA but uncorrected for background. Both Au/Ag (left) and Au/Au (right) ratios are shown. If there were no surface segregation the data would be expected to fall upon the dashed line.

as a multiplicative factor to correct the values in Table 4.3 for the corresponding sample. The corrected values are given in Table 4.4 and are plotted in Fig. 4.5. This correction has the largest effect on the samples with the least amount of Au.

Attempts were made to look for a temperature dependence of the Auger intensity ratios. These efforts were complicated by the fact that the D.C. heating caused fields which affected the Auger intensities in a manner which depended upon the Auger energy, requiring that the heater be turned off to record Auger intensities. This helped restrict the temperature range of the study to about 300 to 600°C. The lower limit is imposed by the necessity to equilibrate the alloy in a reasonable time. The upper limit is imposed by the following factors. First, the vapor pressure of Ag reaches about 10^{-7} torr at 600°C¹⁰⁶ so the surface composition is expected to be altered by rapid evaporation at higher temperatures. Second, segregation of impurities to the surface becomes a problem at higher temperatures. Finally, the surface equilibration takes place so rapidly at 600°C that the sample can re-equilibrate as the temperature falls after the heater is turned off to make the measurements. The highest temperature measurements are really averages over a temperature range. These problems are discussed in greater detail in temperature dependence studies of the Au-Sn alloys.

Table 4.4. RFA Background Correction.

x_b^{Au}	.15	.30	.40	.46	.65	.97	
$R_{71/356}$	$.105 \pm .017$	$.757 \pm .029$	$1.41 \pm .03$	$2.38 \pm .08$	$5.06 \pm .42$	55.3 ± 2.4	$4.30 \pm .16$
$R_{71/356}^{\text{cor}}$	$.46 \pm .07$	$1.59 \pm .06$	$2.38 \pm .05$	$3.90 \pm .13$	$6.88 \pm .57$	70.2 ± 3.0	$4.94 \pm .18$
$R/R_{71/356}^{\text{cor}}$	$.093 \pm .016$	$.322 \pm .021$	$.482 \pm .020$	$.789 \pm .039$	$1.39 \pm .14$	$14.2 \pm .8$	- -
$R_{71/241}$	10.2 ± 2.8	24.2 ± 2.1	25.8 ± 2.8	35.3 ± 3.7	41.9 ± 1.4	45.6 ± 5.7	48.6 ± 1.5
$R_{71/241}^{\text{cor}}$	$45. \pm 12.$	50.8 ± 4.4	43.6 ± 4.7	57.9 ± 6.1	57.0 ± 1.9	57.9 ± 7.5	55.9 ± 1.7
$R/R_{71/241}^{\text{cor}}$	$.80 \pm .22$	$.909 \pm .083$	$.780 \pm .087$	$1.04 \pm .11$	$1.02 \pm .05$	$1.04 \pm .14$	- -

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Fig. 4.5 The normalized Auger intensity ratios obtained from clean and equilibrated Au-Ag alloys using the RFA data corrected for background. Both Au/Ag (left) and Au/Au (right) ratios are shown. If there were no surface segregation the data would be expected to fall upon the dashed line.

Within this temperature range, the results of attempts to find a temperature dependence in three different alloys were largely negative. Within the errors of the experiment, no temperature dependence could be found for the samples with $x_b^{\text{Au}} = .15$ and $.65$. In some cases a slight drifting of the intensity ratios was observed upon changing temperature, but this was neither reversible nor reproducible and could in some cases be attributed to impurity segregation. For the sample with $x_b^{\text{Au}} = .97$, there was evidence for a reversible 8% increase in the value of $R_{71/356}$ as the temperature was increased through a range estimated from the heating current to be from about 400°C to about 600°C. Since some fast re-equilibration may have taken place as the sample cooled from 600°C, the effect of turning the heater off to perform the Auger measurement is to freeze in the composition of a temperature somewhat lower than 600°C, thus effectively reducing the actual temperature range of the measurements. This 8% increase in $R_{71/356}$ is just larger than the experimental uncertainty in the value reported in Table 4.4.

4.3 Auger Intensity Measurements: CMA

Because of the large background present in the RFA spectra and because the Au(2024 eV) peak could not be seen, it was determined to check these results by comparison with results obtained from another type of analyzer. The CMA is sensitive enough to observe the high energy Au peak. Although it merely replaces the steep low energy background of an RFA with a distorted background, the sensitivity of the analyzer allows for the use of low modulating voltages and

corresponding higher resolution can be achieved. With the increased resolution the Au(71 eV) peak becomes narrower, so the effect of the background and distortion is reduced. An independent verification of the RFA results would also reduce the possibility of unknown determinant errors.

In view of this, more samples cut from the same rolled foils as before were mounted in the spectrometer containing the double pass CMA. The samples were cleaned and equilibrated as before by heating to 400°C for up to an hour. Sample spectra are given in Fig. 4.6. These again show the level of cleanliness that could be achieved. The increased resolution is apparent also since now the doublet structure of the Au(71 eV) and the Ag(356 eV) peaks can be seen. The peak to peak intensity of only the first peak in the Ag doublet was used here as the measure of the Auger intensity, and the position of this first minimum was measured at 348 eV. The high energy Au peak (not shown in Fig. 4.6) was found at 2017 eV which is somewhat lower than reported by Palmberg.¹⁰⁵ The two low energy Au peaks were measured at 68 eV and 238 eV. These energies are a bit lower than before which is possibly due to a calibration error in one of the spectrometers. This discrepancy is probably not due to an error in sample positioning since great care was taken to position the samples correctly. It is unlikely that the discrepancies are due to a source which could seriously affect the Auger intensities, which are the quantities of interest here. Having noted the measured energies, for convenience the peaks will be henceforth labeled with the energies 71, 241, 356 and 2024 eV.

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Fig. 4.6 Exemplary spectra of clean Au-Ag alloys and the Au and Ag references as collected by the double pass CMA. (Reference 40)

With the increase in resolution, a high energy shoulder was observed on the Au(71 eV) peak. This structure was present in the alloys but appeared to be absent from pure Au and Ag as shown in Fig. 4.7. The nature of this peak was not studied and the effect on the Au(71 eV) intensity is not known, but is likely to be quite small.

The intensity ratios obtained using this apparatus are given in Table 4.5a. The measured intensity ratios are averages over a few trials, between some of which the sample was sputtered and re-equilibrated. The Au(241 eV) peak was corrected for the overlap with a small Ag peak as with the RFA data, and both the corrected and the uncorrected values are given in the table. The extra effort was taken in these measurements to obtain values for the ratios ξ_E (Section 3.3) which are also given in Table 4.5a.

It can be seen that the values for the non-normalized R ratios are quite different than those measured by the RFA (Table 4.3a). This is because these ratios are dependent upon the resolution and the characteristics of the analyzer used. The normalization procedure should of course completely cancel these differences, so that the normalized ratios R/R^0 which are given in Table 4.5b should be comparable with the values in Table 4.3b or the normalized ratios in Table 4.4. The normalized ratios are plotted in Fig. 4.8 and 4.9.

XBL 755-2997

Fig. 4.7 Variation of the low energy Auger spectrum as a function of bulk composition of Au-Ag alloys. (Reference 40)

Table 4.5. CMA annealed values.

(a) Experimental ratios							
$\frac{Au}{x_b}$	.15	.30	.40	.46	.65	.97	Pure Au and Ag
$R_{71/356}$	.112	.37 $\pm$.03	.566	.725	1.36	16.6 $\pm$ 1.	1.12 $\pm$.01
$R_{241/356}^{unc}$	.0085	.0184 $\pm$.0005	.0265	.0362	.0674	.69 $\pm$.01	.0521 $\pm$.0006
$R_{241/356}$	.0055	.0153	.0236	.0333	.0647	.69 $\pm$.01	.0521 $\pm$.0006
$R_{2024/356}$	.0039	.009 $\pm$.001	.013	.017	.035	.32 $\pm$.01	.0236 $\pm$.001
$R_{71/241}^{unc}$	13.2	20.3 $\pm$ 1.4	21.4	20.0	20.2	23.9 $\pm$.9	21.5 $\pm$.4
$R_{71/241}$	20.3	24.4	24.0	21.7	21.1	23.9	21.5
$R_{71/2024}$	29.0	42.6	44.	42.3	39.6	52.2	48.1
ϵ_{71}	.10	.27 $\pm$.020	.35	.41	.52	1.02 $\pm$.02	- -
ϵ_{241}	.16	.28 $\pm$.012	.35	.44	.55	.936 $\pm$.003	- -
ϵ_{241}	.10	.24	.32	.41	.53	.936 $\pm$.003	- -
ϵ_{2024}	.17	.32 $\pm$.05	.36	.44	.59	1.00 $\pm$.007	- -
ϵ_{356}	1.0	.79 $\pm$.016	.69	.64	.43	.068 $\pm$.001	- -

(b) Normalized ratios						
	.176	.429	.667	.852	1.86	32.3
$R/R_{71/356}^c$	.100	.330	.505	.647	1.21	14.8
$R/R_{241/356}^c$	.105	.294	.453	.639	1.24	13.2
$R/R_{2024/356}^c$	.165	.381	.551	.720	1.48	13.5
$R/R_{71/241}^c$	.944	1.13	1.116	1.000	.981	1.112
$R/R_{71/2024}^c$	.603	.886	.915	.879	.823	1.085

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Fig. 4.8 The normalized Auger intensity ratios obtained from clean and equilibrated Au-Ag alloys using the double pass CMA. Both Au/Ag (left) and Au/Au (right) ratios are shown. If there were no surface segregation the data would be expected to fall upon the dashed line.

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Fig. 4.9 The Auger intensity ratios ξ_E obtained from clean and equilibrated Au-Ag alloys using the double pass CMA. If there were no segregation the data would be expected to fall upon the dashed lines.

4.4 Intensity Analysis and Discussion of the Surface Composition

In analyzing these results, the following four questions will be discussed: 1) how do the results from the CMA compare to those from the RFA, 2) what surface composition do they imply, 3) how does this surface composition compare with the theoretical surface composition, and 4) how could the uncertainties in the escape depths and the backscattering coefficients affect the results.

In principle the CMA and the RFA should certainly give the same results. The only three normalized ratios which can be compared are those involving the two low energy Au peaks and the Ag peak. A visual comparison between Figs. 4.4 and 4.8 indicate that there is good agreement only for the ratio $R/R_{241/356}^0$. The two ratios involving the Au(71 eV) peak do not agree well. But when the CMA data is compared with the RFA data in which the background correction was applied to the low energy Au peak, a very good qualitative agreement is found with all three ratios (compare Fig. 4.5 with Fig. 4.8). This demonstrates that the background correction was indeed necessary for the RFA data.

A more qualitative comparison was made by numerically comparing the relative differences in each of the eighteen ratios (three ratios for each of six samples) with the expected combined errors in the measurements. This was done by assuming that the CMA data had the same relative errors as given for the RFA data. It was found that 12 of the 18 ratios are equal for both sets of data within the experimental uncertainty. This is expected since the uncertainties used are standard deviations which approximate about a 65%

confidence level. In about half the cases (10 out of 18) the CMA ratio is lower than the RFA ratio. It is therefore concluded that the CMA and RFA data sets are in agreement.

It is now of interest to try to extract the surface composition from this data. With the CMA data, if the ξ_E values are used, it is possible in principle to obtain a four layer depth composition profile. This is because each of the ratios for the four different energies provides an independent equation (as in Table 3.1) which is set equal to the experimental ratio. (The ratios R/R^0 are just ratios of these equations, according to Eq. 3.15.) The four equations for ξ_E can be solved simultaneously for the unknown composition of the top four layers. In practice, this does not work well, since small inaccuracies in the data inevitably lead to atom fractions which are outside the range from 0 to 1.

Some numerical procedure must be found for varying the layer compositions to give the best fit between the calculated intensity ratios and those measured experimentally. A four dimensional minimization of this nature is quite an unwieldy problem, so the monolayer approximation was evoked by setting $x_2 = x_3 = x_b$ and thus truncating the equations in Table 3.1 so that x_1 is the only variable. The surface monolayer composition is now overdetermined so it must be varied to give the best fit to all ratios. This was done by setting the monolayer expressions for a particular intensity ratio (obtained from Eq. 3.15 and the truncated equations obtained from Table 3.1) equal to the measured value and solving for the surface

monolayer composition. This was done for both the CMA data and the RFA data modified by the background correction. The calculated surface Au atom fractions for each ratio are given in Table 4.6 along with the parameters used in the calculations.

It can be seen that some ratios consistently give fairly reasonable values, while other ratios do not. The ratio ξ_{2024} gives poor results. This is expected because large variations in the monolayer composition have only a small effect on this deeply probing peak. That is, small errors in the measured intensity ratio result in large variations in the calculated surface composition. The difficulty is enhanced by the fact that the Au(2024 eV) peak is of low intensity and so has a fairly sizeable uncertainty. ξ_{356} also gives fairly poor results which may be due to the fact that 356 eV is the next most deeply probing energy. The two ratios $R/R^{\circ}_{71/241}$ and $R/R^{\circ}_{71/2024}$ are both ratios of Au peaks only and give poor results for reasons which are not entirely clear. The remaining ratios give surface monolayer compositions which are in fairly good agreement and these were averaged to give for each alloy the "best value" given in Table 4.6. It can be seen that both data sets yield surface monolayers which are enriched in Ag relative to the bulk compositions. There is also generally fair agreement between the "best values" obtained from the two data sets. These are plotted in Fig. 4.10 as a function of bulk composition. This is the experimentally determined surface phase diagram of Au-Ag.

Table 4.6. Calculated surface monolayer composition - x_1^{Au}

CMA Data						
x_b^{Au}	.15	.30	.41	.46	.65	.97
71/356	.04	.20	.26	.32	.41	.87
241/356	.02	.11	.17	.28	.39	.85
2024/356	.08	.15	.16	.25	.42	.85
71/241	.10	>1.0	>1.0	>1.0	.56	>1.0
71/2024	.03	.22	.32	.34	.40	>1.0
ξ_{71}	.06	.25	.31	.37	.41	>1.0
ξ_{241}	.06	.16	.20	.34	.36	.89
ξ_{2024}	.36	.52	.02	.26	.06	>1.0
ξ_{356}	<0.0	0.0	.13	.16	.40	.86
Best value	.05 $\pm$.02	.17 $\pm$.06	.22 $\pm$.06	.31 $\pm$.06	.40 $\pm$.05	.87 $\pm$.02

RFA Data						
x_b^{Au}	.15	.30	.41	.46	.65	.97
71/356	.03	.18	.24	.42	.49	.86
241/356	.04	.20	.34	.40	.47	.86
71/241	.01	.14	.01	>1.0	>1.0	>1.0
Best value	.04	.19	.29	.41	.48	.86

Fig. 4.10 The surface monolayer Au atom fraction as determined from the RFA and the CMA Auger intensity ratios are shown. The data obtained by Nelson using ISS (Reference 42) is also shown. The surface compositions predicted by the regular solution model using $(\sigma^{Au}-\sigma^{Ag})_a = 1.26 \times 10^{11}$ ergs/g.at and $\Omega = -1.75 \times 10^{11}$ ergs/g.at (—) and using $(\sigma^{Au}-\sigma^{Ag})_a = .405 \times 10^{11}$ ergs/g.at and $\Omega = +.293 \times 10^{11}$ ergs/g.at (---) are given.

These results may now be compared with other experimental results reported for the Au-Ag system. Following the Auger measurements, pieces of two of the alloy foils were sent to G.C. Nelson of Sandia Laboratories who analyzed them using low energy ion scattering spectroscopy (ISS).⁴² The surface monolayer compositions which he obtained are also shown in Fig. 4.10 and can be seen to agree well with the results calculated from the CMA Auger intensities by neglecting backscattering effects. Using AES, Fain and McDavid⁴¹ found no evidence for Ag segregation on Au-Ag films. This discrepancy may be due to differences between epitaxially grown thin films and bulk polycrystalline film foils used here. A similar situation is found for Au-Cu when results from single crystals are compared with the results from thin films.

The solid line in Fig. 4.10 gives the surface composition predicted by the regular solution monolayer model given by Eq. 2.8 and using the substitution in Eq. 2.4. The values for the parameters used in this calculation are as follows:^{107,108,8}

$$\begin{aligned}
 \sigma^{\text{Ag}} &= 1728 - .48 T \text{ ergs/cm}^2 \\
 \sigma^{\text{Au}} &= 2000 - .46 T \text{ ergs/cm}^2 \\
 \Omega &= -1.75 \times 10^{11} \text{ ergs/g at} \\
 a &= 4.4 \times 10^8 \text{ cm}^2/\text{g at} \\
 T &= 700^\circ\text{K} \\
 Z_v &= 3, Z_1 = 6, Z = 12 \text{ -- fcc(111)}
 \end{aligned}
 \tag{4.1}$$

It can be seen that this model overestimates the extent of the Ag segregation for all but the sample with $x_b^{Au} = .97$. At 700°K, about the temperature at which the samples were equilibrated, these values for the surface energy give

$$(\sigma^{Au} - \sigma^{Ag}) a = 1.26 \times 10^{11} \text{ ergs/g}\cdot\text{at} \quad .$$

From heats of sublimation data³⁴ it is found that

$$(H_{sub}^{Au} - H_{sub}^{Ag}) Z_v/Z = 2.49 \times 10^{11} \text{ ergs/g}\cdot\text{at} \quad .$$

Using this last quantity as the driving force for segregation, as suggested by Williams, would overestimate the actual segregation even more than the surface tension data. Thus, according to both models, the segregation observed is less than predicted by the monolayer regular solution model.

The value $(\sigma^{Au} - \sigma^{Ag})$ was varied in Eq. 2.8 to give the best possible fit to the data in Fig. 4.10. The best fit was found to be with

$$(\sigma^{Au} - \sigma^{Ag}) a = .73 \times 10^{11} \text{ ergs/g}\cdot\text{at} \quad .$$

This indicates that the driving force for the segregation is a little more than half of what is expected from the surface energy data.

Changing the value of the parameter Ω has the effect of changing the shape of the surface composition curve. As Ω varies, the segregation (according to the regular solution model) is enhanced in one composition range. Varying both Ω and $(\sigma^{Au} - \sigma^{Ag}) a$ in the regular solution model equation gave the following best least squares values:

$$(o^{\text{Au}} - o^{\text{Ag}}) a = .405 \times 10^{11} \text{ ergs/g}\cdot\text{at}$$

$$\Omega = + .293 \times 10^{11} \text{ ergs/g}\cdot\text{at}$$

The surface compositions predicted for these parameters are given in Fig. 4.10 by the dashed-dotted curve. The fact that the best fit value for Ω is positive, which is physically unrealistic, indicates that the regular solution model does not fit the shape of the data. This may be partly due to the fact that in Au-Ag, Ω as calculated from Eq. 2.7 depends upon composition. This variation was not considered in these calculations since it represents non-regular behavior. The reason that the data cannot be fit better with the regular solution model is apparent from Fig. 4.10. The two samples with a dilute solute ($x_b^{\text{Au}} = .15$ and $x_b^{\text{Au}} = .97$) show relatively more Ag segregation than the samples of intermediate composition. The regular solution model cannot fit all three regions at once. This hints at a solute effect such as suggested by the strain theory¹⁷ (which should not apply to the particular case of Au-Ag) or the "phase boundary" theory suggested by Burton.²² The latter theory predicts segregation of Ag only at the Au rich ends which does not agree with these results. So it therefore appears that none of the simpler theories give a detailed fit of the Au-Ag results.

It is now of interest to discuss the results of the temperature dependence studies. Using the regular solution monolayer model and the parameters given in Eq. 4.1, it is possible to calculate the temperature dependence of the surface monolayer compositions predicted by that model. Using the equations in Table 3.1 and Eq. 3.15 as

before, it is possible to calculate the predicted change in $R/R^\circ_{71/356}$ brought about by altering the temperature. In changing the temperature from 700 to 900°K which matches the range used in the experiments (400-600°C) it is calculated that the values of $R/R^\circ_{71/356}$ may be expected to change by only about 7% for a sample with $x_b^{Au} = .15$ and about 6% for a sample with $x_b^{Au} = .65$. These variations are less than the uncertainties given for the experimental intensity ratios. Thus the reason no temperature dependence could be seen for these samples is likely due to the fact that the temperature dependence is a small effect compared to the errors present in the experiments. This is especially true since the Ag enrichment and therefore also the temperature dependence are actually overestimated by the regular solution model. For a sample with $x_b^{Au} = .97$, the regular solution model predicts about a 14% increase in $R/R^\circ_{71/356}$ in going from 700 to 900°K. For this sample the increase is large enough that it might be observable in these experiments. The 8% increase observed in going from 400°C to a composition characteristic of something less than 600°C may be real and in fact qualitatively agrees with that expected for the Ag enrichment observed.

Finally it is necessary to point out two potential difficulties in this analysis. The first is created by the lack of accurate electron escape depths. For instance the escape depths of a 356 eV electron has been reported as 5.4 Å in Ag,¹⁰⁹ 8 Å in Au,⁴⁸ 7.2 Å in Ag,⁸⁷ 8.2 Å in Ag,¹¹⁰ and 10 Å in Ag.¹¹¹ Even if the assumption that the escape depth is independent of bulk composition is correct, the proper value is seldom known to better than about $\pm 30\%$.

In computing the values for x_1^{Au} given in Table 4.6 the values of 4, 6, 8 and 30 Å were assumed for the energies 71, 241, 356 and 2024 eV respectively. To show the effect of uncertainty in these escape depths, the calculation of the surface monolayer atom fractions were repeated with various selected values for the escape depths. It was found that increasing λ_{71} from 3 Å to 5 Å resulted in an average decrease of about 16% in the calculated Au monolayer surface compositions. Increasing λ_{356} through the range from 7 to 10 Å resulted in an average decrease of about 7-8% in the calculated monolayer Au atom fractions. Qualitatively, then, the expected uncertainties in the escape lengths leads to an uncertainty on the order of 10 to 20% in the calculated surface composition. The extent to which the results from each ratio is affected depends upon the particular ratio involved. For example, the surface monolayer composition obtained from $R/R_{71/356}^{\circ}$ is less sensitive to changes in λ_{356} than is that obtained from $R/R_{2024/356}^{\circ}$. This point will be discussed in greater detail in Chapter 5.

The possible effects of backscattering have been neglected up to this point. The backscattering coefficient, $r^{\circ}(E, E_p)$ for 356 eV electrons in Ag and 71 eV electrons in Au have been measured.⁹⁷ It was found that for a primary beam energy $E_p = 1000$ eV that $r_{\text{Au}}^{\circ}(71 \text{ eV})/r_{\text{Ag}}^{\circ}(356 \text{ eV}) = 1.1$, while at $E_p = 2000$ eV (the energy used in the RFA studies) $r_{\text{Au}}^{\circ}(71 \text{ eV})/r_{\text{Ag}}^{\circ}(356 \text{ eV}) = 1.2$. No data was given for a primary energy of 4000 eV (the energy used in the CMA experiments) but extrapolation from the lower energies yields $r_{\text{Au}}^{\circ}(71 \text{ eV})/r_{\text{Ag}}^{\circ}(356 \text{ eV}) = 1.4$. The validity of this extrapolation is of course questionable,

but it is instructive to see the effects of assuming this value. The backscattering coefficients for Au-Ag alloys are also unknown, so it will be assumed to vary linearly with composition between the values for pure Au and Ag. Further, backscattering will be assumed to be constant in all layers, and due to lack of information it will be assumed that

$$r_{Au}^{\circ} \equiv r_{Au}^{\circ}(71\text{eV}, E_p) \cong r_{Au}^{\circ}(356\text{eV}, E_p)$$

$$r_{Ag}^{\circ} \equiv r_{Ag}^{\circ}(356\text{eV}, E_p) \cong r_{Ag}^{\circ}(71\text{eV}, E_p) .$$

Making these assumptions, it is found that

$$\frac{r(71\text{eV}, E_p)}{r^{\circ}(71\text{eV}, E_p)} \equiv \frac{r_{\text{alloy}}}{r_{Au}^{\circ}} = \frac{r_{Au}^{\circ} x_b^{\text{Au}} + r_{Ag}^{\circ} x_b^{\text{Ag}}}{r_{Au}^{\circ}} = x_b^{\text{Au}} + (1. - x_b^{\text{Au}}) \frac{r_{Ag}^{\circ}}{r_{Au}^{\circ}}$$

and similarly that

$$\frac{r(356\text{eV}, E_p)}{r^{\circ}(356\text{eV}, E_p)} \equiv \frac{r_{\text{alloy}}}{r_{Ag}^{\circ}} = x_b^{\text{Ag}} + (1. - x_b^{\text{Ag}}) \frac{r_{Au}^{\circ}}{r_{Ag}^{\circ}}$$

These factors are then used in the monolayer equations obtained from Table 3.1 and using these the monolayer composition is found as before (i.e., as in Table 4.6). This time, however, the only ratios which should be used are ξ_{71} and ξ_{356} (when available) and $R/R_{71/356}^{\circ}$ since the backscattering factors apply to these energy peaks. This was done for the CMA data using $r_{Au}^{\circ}/r_{Ag}^{\circ} = 1.4$ and for the RFA data using $r_{Au}^{\circ}/r_{Ag}^{\circ} = 1.2$ and the calculated surface monolayer compositions are shown in Fig. 4.11. The error bars on the CMA data indicate only the agreement between the compositions obtained from each of the three different ratios.

XBL769-9310

Fig. 4.11 The surface monolayer Au atom fraction as determined from the RFA and the CMA Auger intensity ratios by making a correction for the possible effects of backscattering. The dashed line denotes where the surface and the bulk compositions are equal.

If these corrections are valid, it can be seen that the effects of backscattering are quite serious. The backscattering may be responsible for effects attributed to surface segregation in Fig. 4.10. This disturbing possibility is based upon insufficient measurements of the magnitude of backscattering coefficients and upon an oversimplified model for backscattering and seems unlikely in view of the confirming ISS results. A great deal more work must be done before corrections of this nature can be made with confidence.

5. THE AU-SN SYSTEM

Most of the alloy systems discussed in Chapter 2 and the Au-Ag system which was studied in Chapter 4 are alloy systems which have fairly simple bulk thermodynamics. The bulk properties of these alloys can be described fairly well by regular solution theory. Most alloy surface studies to date have been on such systems. Less work has been done to characterize the surface phase diagram of alloys that form strong compounds or have otherwise complex bulk phase diagrams.

The Au-Sn system was chosen as a suitable example of this type of alloy. Sn has a much smaller surface free energy than that of Au (685 ergs/cm² for Sn versus about 1400 ergs/cm² for Au near their melting points)^{112,108} and on this basis Sn may be expected to segregate to the surface. In addition there is a considerable atomic size difference between pure Au and pure Sn,³⁵ so that strain effects may be expected to lead to segregation in some instances. The bulk phase diagram given in Fig. 5.1 indicates also that there is complex bulk behavior for this system with at least three distinct phases forming between the composition of 50.0 at % Au and pure Au. The bulk structures of each of these phases have been well characterized.⁸ The δ phase is a very strongly ordered phase having a hexagonal type of structure (B8, isotypic with NiAs) which exists over a very narrow range of composition at 50.0 at % Au. The ζ phase is simply a hexagonally close packed lattice (A3, isotypic with Mg) with Au and Sn randomly distributed on the lattice. This phase forms at compositions between 83.5 at % Au and 89. at % Au.¹¹³ The

XBL 767-8584

Fig. 5.1 Bulk phase diagram of the Au-Sn system. (Reference 8)

primary α phase is simply the face centered cubic Au lattice with the Sn solute substitutionally mixed in. The maximum solubility of Sn in Au is 7. at % Sn.⁸

The following questions arise. Is there a segregation of one of the components to the surface of a one phase alloy such as the δ , the ξ , or the α phase alloys, and if there is, then why does the segregation occur and to what extent? If there are two phases present, are both phases present at the surface in amounts expected from the lever rule as shown at the top of Fig. 5.2 or is there some sort of phase redistribution at their surface which causes one phase to coat the surface as shown in the lower part of Fig. 5.2?

Alloys throughout the composition range from 50 to 99 at % Au were prepared and studied by Auger electron spectroscopy with the goal of answering these questions. The first section of this chapter deals with the preparation of the Au-Sn samples. The second section deals with experiments performed to characterize the bulk of the samples. Section 5.3 describes in detail the procedures and results of the Auger experiments performed to characterize the surfaces of the samples. The fourth section is devoted to an analysis of the Auger intensities with the goal of determining quantitatively the surface composition of the alloys. And finally, the last section presents a physical interpretation of the results.

5.1 Sample Preparation

Alloys of Au and Sn were prepared by melting together weighed amounts of high purity Au (6N) and Sn (4N), calculated to give the atom

LEVER RULE

PHASE REDISTRIBUTION

XBL7610-9404

Fig. 5.2 Two possible configurations of the surface of a two phase alloy.

percent compositions given below. The sample with 99 at % Au was melted down in an arc furnace and was homogenized by the stirring action of the arc and by flipping the ingot several times. The remaining samples were sealed under Ar or an Ar (98%)-H₂(2%) mixture in quartz tubes. The 50.0 at % Au and the 86.7 at % Au samples were melted at 480 and 800°C respectively, with vigorous shaking to insure thorough mixing and were then quenched in ice water. The two alloys were then homogenized at 260°C for over two weeks. The 65.0 at % Au and the 79.9 at % Au alloys were melted and remelted with vigorous shaking at 500° and 650°C respectively and then quenched in ice water. No further homogenization was done on these samples. The 61.0 at % Au and the 75.5 at % Au were melted down but were then removed from their tubes and crushed up. The resulting powder and chips were re-encapsulated and held at 650°C for several hours with occasional shaking, air quenched and then homogenized at 250-279°C for 7 days.

Following these treatments, the alloys were coarse ground and filed down to the desired shapes. The polycrystalline surfaces to be studied were polished with a series of emery papers of decreasing grit size, and then final polishing was done with 1 μ m diamond paste on a polishing wheel moistened with kerosene. Attempts to polish the samples with .03 μ m alumina on a Syntron failed due to the appearance of terraces and ridges on some samples due presumably to their brittleness. To obtain consistency therefore, all samples were polished to 1 μ m only.

Samples of pure Au and pure Sn were used to give reference intensities to obtain information about the surface composition of the bulk alloys. Chunks of 6N Au were melted into a button which was mashed flat,

cut to size and polished, ultimately with 1 μ m diamond paste. Sn samples were prepared by cutting a piece from a larger 4N Sn ingot, coarse grinding to size and polishing, ultimately with 1 μ m diamond paste.

5.2 Characterization of the Bulk

It seems certain that whatever the composition of a sample surface may be, it will certainly be dependent upon the structure and composition of the bulk. Thus it is important to determine this information for each sample. The problem is simplified by the fact that for the Au-Sn system the bulk phase diagram has been worked out. This allows one to predict the structure of the alloys upon preparation by the reasonably complicated process of solidification from the melt.

Three conditions were desired of the Au-Sn alloys: 1) the overall total composition be known, 2) the one phase alloys be homogeneous and 3) the two phase alloys have a uniform distribution of the two phases.

With regard to the first point, when solidifying an alloy from a melt it is often observed that solute rejection occurs along the advancing solid-liquid interface, due to a number of types of phenomena.¹¹⁴ In a rapidly quenched alloy ingot, this can lead to a core of a composition differing from the outer regions. Since the Au-Sn samples used in this study were prepared by rapid solidification and the outer portions of each was ground away to obtain a polished surface of the desired shape, it is possible that the final sample may not have the composition of the

original ingot. Thus it is important to check the final bulk composition of the sample to verify that the undesired bulk segregation is not occurring.

With regard to the second point, the information of interest is the surface composition of a fully equilibrated alloy, which for an alloy of overall composition within a one phase region, implies complete bulk homogeneity.

Finally, regarding point three, the desire to use AES to look at both phases in the two phase alloys simultaneously, requires that the individual crystallites of the two phases be small compared to the width of the primary electron beam, ($\sim 1\text{mm}$) so that a statistical amount of each phase at the surface can be obtained. From this, an average surface composition is obtained. It might also be desirable to determine the surface composition of the individual crystallites. This however, was impossible due to the low spatial resolution of the Auger apparatus used in these studies.

To these ends, the bulk techniques of electron microprobe, optical microscopy, x-ray diffraction and x-ray fluorescence were combined to characterize and confirm the bulk structure and composition as is now described.

Electron Microprobe and Optical Microscopy

Following the final polishing, some of the samples were put into an electron microprobe available at Lawrence Berkeley Laboratories and operated by Richard Lindberg. The microprobe has the capability of performing two useful tests in this case. It is excellent for scanning the surface and showing the phase structure of a two phase alloy. It also can be used along with now standard analysis procedures¹¹⁵ to obtain

an approximate alloy composition at any particular point along the sample. Electron microprobe data was obtained for the 61.0, 75.5, 50.0 and 86.7 at % Au samples. The electron microprobe data obtained for these samples was used to interpret the optical micrographs obtained for all samples.

For the 61.0 at % Au and the 75.5 at % Au samples, a scan of intensity of collected electrons as a function of position of the electron probe was obtained. Due to the higher back-scattering power of the Au rich phase, the two phases can be distinguished by the technique and a picture of the phase structure is obtained. An example of this is given in Fig. 5.3. By recording intensity of Sn or Au x-rays as a function of the position of the electron probe a similar type of map may be made of the surface. Both of these modes were applied to the two alloys and showed that the alloys consisted of intermeshed irregularly shaped crystallites of the order of 5-20 μ m in size. In addition it was possible to fix the 1 μ m diameter electron probe within a particular crystallite and obtain a chemical analysis.

The microprobe also had an optical microscope attachment with cross-hairs which pin-pointed the position of the electron beam. Patches of contrasting brightness could be observed whose shape correlated with those obtained in the scan of collected electron current or collected x-ray intensity as a function of position. These patches could thus be taken as the individual crystallites of the δ and ζ phases. Using the optical microscope, the electron probe could be placed in the center of a bright or dark patch and a quantitative analysis performed at that point. This

Fig. 5.3 The surface of a 61 at% Au-Sn sample as observed by backscattered electrons in an electron microprobe (top) and as viewed with an optical microscope (bottom).

-125-

20 μ

40 μ

XBB 765-4017

Fig. 5.3

was done for several randomly chosen patches. The results are shown in Table 5.1.

In interpreting these results it should be remembered that the spatial resolution of the electron microprobe when well focused is about $1\mu\text{m}$ both in width and in analysis depth. In addition the electron beam expands below the surface. Thus in measuring the composition of a small patch with a size of a few microns it is expected that the analysis will unavoidably also include portions of adjacent phases. Thus due to this error it is expected that the Au atom fractions obtained for the δ phase will be too high, and those of the ζ phase will be too low. Further the effect will be greatest for the smallest patches. Thus the Au at % obtained for the ζ phase should be lower for the 61.0 at % sample than for the 75.5 at % Au sample. The Au at % of the δ phase would be too high for the 75.5 at % Au sample, but better for the 61.0 at % sample. This is in excellent agreement with the results.

Following the Auger analysis of these samples (to be discussed later) photographs of them were taken through a metallographic microscope available at Lawrence Berkeley Laboratory. Polarizers were used to enhance the contrast. With this method, due to the different optical properties of the two phases a quick check of the phase structure could be obtained. A photograph obtained in this way is shown in Fig. 5.3 along with the data obtained from the electron microprobe.

These results for the 61.0 at % Au and the 75.5 at % Au samples indicate that the desired conditions stated above have been obtained. The samples are shown to be a mixture of the ζ and δ phase as expected

Table 5.1 Electron Microprobe Data

	wt. % Au	two phase alloys		at. % Au
		wt. % Sn	Σ wt. %	
61.0 at % Au				
optically light	64.5 $\pm$ 1.6	37.8 $\pm$.5	102.3	50.7 $\pm$.6
optically dark	89.3 $\pm$ 2.7	12.0 $\pm$.4	101.3	81.8 $\pm$.7
75.5 at % Au				
optically light	67.3 $\pm$ 2.2	35.5 $\pm$ 1.2	102.8	53.4 $\pm$ 1.6
optically dark	93.1 $\pm$ 1.2	10.9 $\pm$.09	104.0	83.7 $\pm$.2
	wt. % Au	one phase alloys		at. % Au
		wt. % Sn	Σ wt. %	
86.7 at % Au				
center	96.6 $\pm$ 1.1	5.5 $\pm$.2	102.1	91.3 $\pm$.3
1st corner	86.0 $\pm$.8	4.2 $\pm$.2	90.2	92.5 $\pm$.3
2nd corner	95.5 $\pm$ 2.0	7.2 $\pm$.2	102.7	88.9 $\pm$.3
3rd corner	94.1 $\pm$.8	5.3 $\pm$.2	99.4	91.5 $\pm$.2
4th corner	94.1 $\pm$ 1.2	6.1 $\pm$.1	100.2	90.3 $\pm$.2
50.0 at % Au				
center	68.4 $\pm$ 1.2	36.4 $\pm$.4	104.8	53.1 $\pm$.6
1st corner	61.6 $\pm$ 1.6	29.8 $\pm$.6	92.4	55.4 $\pm$.4
2nd corner	67.6 $\pm$ 1.3	36.1 $\pm$.6	103.7	53.0 $\pm$.5
3rd corner	66.2 $\pm$ 1.8	35.5 $\pm$.1	101.7	53.0 $\pm$.7
4th corner	61.8 $\pm$ 1.0	29.2 $\pm$.3	91.0	56.0 $\pm$.5

from the bulk phase diagram, and the combination of the two techniques verify that the phases are distributed uniformly as might be expected for quenched hyper and hypo eutectic mixtures. Further the size of the individual phase crystallites are shown to be small compared to the size of the Auger electron beam (about 1 mm).

Although no electron microprobe analysis was done on the 65.0 at % Au or the 79.9 at % Au sample, optical micrographs were recorded using polarized light and following the Auger measurements. By comparing these with the results of the 60.0 at % Au and the 75.5 at % Au results it was found again that the phase structure was small and the distribution approximately uniform. Optical micrographs of the 79.9 at % Au sample at two magnifications are shown in Fig. 5.4.

On a separate date, the one phase alloys, the 50.0 at % (δ phase) and the 86.7 at % Au (ζ phase) alloys were run on the microprobe. No sort of phase segregation could be seen optically or by monitoring the x-ray intensity as a function of position of the two samples. An analysis of the x-ray intensity at a few places on each sample gave the results shown in Table 5.1. For both of these samples the at % Au obtained were higher than expected and the values varied by 3-6% at various points on the sample. In addition the wt % of Au and Sn did not add up to 100% but this sum varied by up to 12%. This variation could be caused partly by sample roughness, since the samples were polished with 1 μ m diamond paste so the scratches may be comparable to the size of the electron beam. This discrepancy is probably not due to impurities since there was no evidence for persistent impurities in the Auger data

→ 50 μ ←

79.9 at. % Au-Sn

→ 50 μ ←

86.7 at.% Au-Sn

XBB 766-5127

Fig. 5.4 Optical micrographs of two Au-Sn alloys at two different magnifications.

X-ray Fluorescence

As a further check upon the bulk composition of the samples, they were all analyzed using x-ray fluorescence. Following all other measurements, the edge of each sample was sliced off with a diamond saw. These slices were dissolved in aqua regia and given to Bob Giaouque of Lawrence Berkeley Laboratories for analysis by a method developed in his lab.¹¹⁶ The results are shown in Table 5.2. Only the Sn content in each sample was analyzed, so no material balance was obtained. The errors given indicate deviations of two separate trials. The results confirm quite well that the samples are of the presumed composition.

X-ray Diffraction

Additional information was obtained by applying x-ray diffraction techniques to the samples. At LBL there was available an x-ray diffractometer which operated with Cu K_α radiation, and it was set up so that flat polished samples such as these could be run routinely. Two of the samples (99.0 at % Au and the 50.0 at % Au) were run before they were mounted in the UHV for Auger measurements, but the others were all run sometime after the Auger measurements. Pieces of pure Au and Sn were also x-rayed.

In Table 5.3 there is a listing of all the reflections expected from pure Au, pure Sn and for the δ and ζ phases of Au-Sn alloys. The positions of the lines (2 θ values) and the intensities of the lines, normalized to the most intense line, are shown. The data for the pure Au, pure Sn and the δ phase are taken from the Powder

Table 5.2 Results of X-Ray Fluorescence Measurements

Prep composition at % Au	x-ray fluorescence at % Au
50.0	48.9 $\pm$.10
61.0	60.7 $\pm$.16
65.0	64.7 $\pm$.03
75.5	75.3 $\pm$.02
79.9	79.8 $\pm$.02
86.7	86.8 $\pm$.05
99.0	99.1 $\pm$.02

Table 5.3 Powder Diffraction Data

Pure Au		Pure Sn		δ phase		ζ phase	
2 θ	I/I _{max}	2 θ	I/I _{max}	2 θ	I/I _{max}	2 θ	I/I _{max}
38.2	100	30.6	100	23.8	50	35.6	-
44.4	52	32.0	90	28.8	45	37.7	-
64.6	32	43.8	34	40.5	100	40.4	-
77.6	36	44.9	74	41.7	65	52.8	-
		55.3	17	48.6	8	63.9	-
		62.5	23	51.5	10	69.9	-
		63.8	13	53.8	4	75.3	-
		64.5	20	55.6	10	76.6	-
		72.4	15	59.6	25	78.4	-
		73.2	15	66.0	10		
		79.4	20	68.4	8		
				71.9	4		
				73.0	6		
				75.4	20		
				76.3	8

Fig. 5.5 X-ray diffraction spectra obtained from the Au-Sn alloys.

Diffraction file.¹¹⁷ The ζ phase was not listed in this file, but the structure is known to be hexagonally close packed, and the lattice parameters are known.¹¹³ With this knowledge, and using the structure factor for an hcp lattice (or simply looking up the allowed reflections for another hcp substance such as Mg) the positions of the allowed reflections for the ζ phase alloy can be calculated. These are also shown in the Table.

Typical diffractometer scans are given in Fig. 5.5. The 2θ values were taken directly from the chart recording and are the positions of the intensity maxima. The intensities are in arbitrary units and are normalized to be consistent between spectra, although since the measurements were made on various days, comparison of intensities between spectra is probably not completely trustworthy. The peaks may be assigned as being due to a particular phase by comparison of the 2θ values with the values given in Table 5.3.

It was discovered that the powder intensities could not be reproduced. This is undoubtedly due to the fact that in a fine powder a nearly continuous distribution of crystallite orientations is assumed and is actually achieved in practice. These samples were not powdered but were flat polished ingots with various thermal histories. The grain sizes have been shown to be of sizes ranging from 10 to 200 μm in diameter, which is somewhat larger than the size range necessary to achieve uniform powder rings.¹¹⁸ The intensity ratios between different reflections may therefore be different than obtained in a powder picture. A diffractometer scan of the pure Sn showed this effect.

There was a very high background and the peak intensity ratios were very different than that expected from a powder print. The strongest peak was at $2\theta = 32.1^\circ$ and the peaks were about $.1$ to $.2^\circ$ too high. The Au showed the expected intensity ratios in the region scanned but the peak positions were again all about $.2^\circ$ too high.

The one phase δ alloy showed almost nothing in the x-ray scan between $2\theta = 27$ and 50° except the background. (Fig. 5.5) A previous sample which had been prepared to be 50 at % Au was run and showed nearly the same behavior, but exhibited a small peak at $2\theta = 40.8^\circ$. The δ phase alloy was lump annealed for a long period of time which tends to lead to large grain growth which would interfere with the measurements. The ζ phase alloy had a low background and showed a large number of peaks which could be assigned to expected peak positions although in some cases the deviations were as great as $.5^\circ$ from the calculated values. The peaks at $2\theta = 40.5$ and 52.9° contain lower angle components (at 39.8° and 52.5° respectively) which are of greater intensity. The nature of these peaks is not clearly understood. The 99.0 at % Au sample showed only Au peaks present and of about the intensity expected.

The peak positions and intensities from the two phase alloys are shown in Fig. 5.6 along with the results from the 86.7 at % Au sample and the expected results for a powdered δ phase alloy (Table 5.3). Comparison with the expected peak positions verifies the presence of both δ and ζ phase reflections in the two phase alloys. All but possibly seven of the δ phase reflections were seen in the spectra

of the alloys for $2\theta < 120^\circ$. Virtually all of the ζ phase reflections were observed. The intensity of a particular line varies from one alloy to the next, but seldom is there a trend with composition.

There are, in some of the alloys, peaks which are not adequately described as δ or ζ phase reflections. There are peaks present at $2\theta = 25.2^\circ$ and 93.5° which could not be assigned. These peaks were quite weak, however, and were only observed in one alloy each. As such they were deemed unimportant.

For the 79.9 at % Au sample there were low intensity peaks at $2\theta = 44.4, 64.5$ and 77.5° which could be attributed to Au reflections. In addition there was a peak at $2\theta = 38.0^\circ$, the angle of another Au peak, but this could also be due to the ζ phase reflection expected at 37.7° . These peaks at $44.4, 64.5$ and 77.5° were not observed in the other two phase alloys (except a small peak at 77.6° in the 60.0 at % Au alloy). During solidification the 79.9 at % Au sample may pass through a peritectic halt, according to the phase diagram given in Fig. 5.1. In the preparation of this alloy, the primary α phase is the first to precipitate out. Rapid quenching of this sample, while resulting in small grain size, must also result in some amount of α phase left unequilibrated.¹¹⁹ These reflections were absent in the 86.7 at % Au sample, which also solidifies through the same peritectic halt. Therefore, the two week homogenization served to equilibrate this sample.

The most disturbing features which were observed were peaks at $2\theta = 32.6^\circ$ and at 31.4° . The peak at 32.6° was very strong in the

60.0 at % Au and less strong in the 65.0 at % Au sample. The only diffraction peak expected in that region is that of Sn which has peaks at $2\theta = 30.6$ and 32.0° . There were no other features due to Sn in the spectra, and these peaks were not quite in the right position ($.5^\circ$ too high). Further, it is difficult to explain how an inclusion of Sn could have survived the heat treatments given these alloys. If there is Sn, it is impossible to tell how much is present. There is the possibility that these reflections could be due to the low temperature γ phase, shown in the phase diagram in Fig. 5.1. However, very little is known about this phase, so it is difficult to verify this hypothesis.

5.3 Auger Intensity Measurements

For performing the Auger intensity measurements, the samples were mounted in the ultra-high vacuum system containing the single pass CMA. This system was described in detail in Chapter 3. Typical operating conditions for the Auger analysis are given in Table 5.4. The 61.0 at % Au, the 75.5 at % Au, the first pure Au and both pure Sn samples were mounted using Ta foils. However, for these samples there were occasional difficulties with Ta impurities sputtered on to the surfaces so the remaining samples were mounted with Au foil supports. Pt and Pt-10 % Rh thermocouple wires were mounted to the backs of the samples or onto their supporting foils.

5.3.1 Equilibrium Auger Intensity Ratios

Pure Au and Sn

The samples of Au and Sn were mounted simultaneously in the UHV system

Table 5.4 Typical Operating Conditions, Au-Sn Measurements

Analyzer	single pass CMA
Base pressure	1×10^{-9} torr
Gun angle	Normal
Primary energy	4000 eV
Beam current	15 μ a
Sample angle	Normal
Modulation voltage	2 V p-p
Modulation freq.	5600 Hz
Scan rate	1. V/sec
Time constant	.1 sec
Lock-in amp	P.A.R. JB-5

and both were sputtered and annealed until an acceptable degree of cleanliness was obtained. The troublesome impurities were carbon and oxygen on the Sn, and carbon and Sn on the Au. These impurities seemed to diffuse onto the surface from the bulk or from surrounding areas. Spectra of Au and Sn showing the maximum acceptable levels of impurities are shown in Fig. 5.7. All data considered were obtained from samples of this cleanliness or better.

The values desired were the intensity ratios of Au to Sn and Au to Au peaks. Upon cleaning and annealing, the intensities of three Au peaks observed at 71 eV, 241 eV and 2024 eV (not shown in Fig. 5.7) and one Sn peak observed at 431 eV were measured in rapid succession. From the intensity ratios and using the lock-in amplifier scaling factors, the intensity ratios, $R_{E/E'}^O$, were computed. ($R_{E/E'}^O$ = intensity of Auger peak at energy E, divided by the intensity of the Auger peak at energy E'. The superscript refers to ratios obtained from pure Au and pure Sn.)

There are several immediately apparent sources of error in these measurements. To avoid effects due to drift in instrumental factors such as beam current, multiplier gain and modulation amplitude, only intensity ratios were used and these ratios were measured by scanning the two peaks involved in quick succession. Pure Au and Sn (and the alloys) were all polished in the same manner to minimize effects due to surface roughness. Measurements were repeated and averaged for a few different places on the samples to further minimize effects due to roughness or any type of inhomogeneity. A source of error is introduced by the analyzers sensitivity upon the perpendicular distance from the sample. This distance was set by

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Fig. 5.7 Exemplary Auger spectra of the Au-Sn alloys and of pure Au and Sn. (Reference 83)

maximizing the intensity of a 2000 eV elastic peak, and was checked repeatedly. The samples were sputtered and annealed several times and the ratios remeasured again at a few different locations. After every measurement the cleanliness of the samples was re-checked. All of the values for these different measurements were tabulated and averaged to give the final values included in Table 5.5.

In addition to these precautions, actually two sets of pure Au and Sn were run, as at one point the Au sample was removed from the UHV and completely repolished, and an altogether new sample of Sn was cut and polished and used. The first Sn sample had a greater amount of O present which was never fully removed. The second set showed a slight decrease of 6-8% in the Au to Sn ratios, as is consistent with attenuation of the Sn Auger electrons by surface oxygen on the first Sn sample. The Au/Sn ratios from the first set were not used, but the Au/Au ratios were averaged from both samples. The average values included in Table 5.5 are the average of 12 values for the Au/Sn ratios and of 26 values for the Au/Au ratios. The errors are the standard deviation of the data set and are indicative of the uncertainty introduced by the factors listed above.

Cleaning and Equilibrating the Alloys

The alloy surfaces were cleaned by sputtering with 1.5 keV Ar ions. As with the pure Au and Sn the troublesome impurities were C and O, most of which seemed to come from the bulk or from diffusion from the surroundings. Spectra which show the maximum acceptable levels of impurities are given in Fig. 5.7. All data considered were obtained from samples of this

Table 5.5 Auger Intensity Ratios

a) Experimental ratios

at % Au	$R_{71/431}$	$R_{241/431}$	$R_{2024/431}$	$R_{71/241}$	$R_{71/2024}$
Pure Au&Sn	.558 $\pm$.016	.0568 $\pm$.0014	.0395 $\pm$.0016	9.73 $\pm$.18	13.97 $\pm$.62
50.0	.505 $\pm$.013	.0500 $\pm$.0010	.0316 $\pm$.0010	10.10 $\pm$.14	15.99 $\pm$.42
61.0	.667 $\pm$.016	.0683 $\pm$.0013	.0487 $\pm$.0008	9.71 $\pm$.11	13.6 $\pm$.50
65.0	.657 $\pm$.016	.0678 $\pm$.0025	.0490 $\pm$.0023	9.69 $\pm$.19	13.41 $\pm$.40
75.5	.782 $\pm$.033	.0835 $\pm$.0020	.0640 $\pm$.0020	9.35 $\pm$.20	12.20 $\pm$.30
79.9	.886 $\pm$.029	.0977 $\pm$.0034	.0780 $\pm$.0036	9.09 $\pm$.12	11.39 $\pm$.35
86.7	.931 $\pm$.084	.105 $\pm$.009	.0870 $\pm$.0084	8.83 $\pm$.19	10.69 $\pm$.36
99.0	1.64 $\pm$.03	.186 $\pm$.003	.154 $\pm$.002	8.79 $\pm$.09	10.62 $\pm$.27

b) Normalized ratios

x_b^{Au}/x_b^{Sn}	$R/R^O_{71/431}$	$R/R^O_{241/431}$	$R/R^O_{2024/431}$	$R/R^O_{71/241}$	$R/R^O_{71/2024}$
1.00	.905 $\pm$.035	.880 $\pm$.028	.800 $\pm$.041	1.04 $\pm$.024	1.14 $\pm$.06
1.56	1.19 $\pm$.04	1.20 $\pm$.04	1.23 $\pm$.05	.998 $\pm$.022	.973 $\pm$.056
1.86	1.18 $\pm$.04	1.19 $\pm$.05	1.24 $\pm$.08	.996 $\pm$.027	.960 $\pm$.051
3.08	1.40 $\pm$.07	1.47 $\pm$.05	1.62 $\pm$.08	.961 $\pm$.027	.873 $\pm$.044
3.97	1.59 $\pm$.07	1.72 $\pm$.07	1.97 $\pm$.12	.934 $\pm$.021	.815 $\pm$.044
6.52	1.67 $\pm$.16	1.85 $\pm$.17	2.20 $\pm$.23	.908 $\pm$.026	.765 $\pm$.043
99.0	2.94 $\pm$.10	3.27 $\pm$.10	3.90 $\pm$.16	.903 $\pm$.019	.760 $\pm$.039

cleanliness or better.

The sputtering of the samples was always found to remove the surface of the alloys from equilibrium, as in the case of Au-Ag alloys. Sputtering always results in an increase in the Au/Sn intensity ratios. This fact gives a means of determining temperatures at which the samples can be readily equilibrated. By annealing at a particular temperature and monitoring the Auger intensity ratios, the rate of return to equilibrium can be determined. This procedure was done for each sample. An exemplary result is given in Fig. 5.8. Generally the samples were sputtered at room temperature for 1500 to 2000 secs, resulting in an increase in the $R_{71/431}$. Following sputtering the Ar was removed from the chamber and the sample was heated as quickly as possible to the desired temperature. The value of $R_{71/431}$ was then recorded as a function of heating time after reaching temperature. As shown in Fig. 5.8, at 150°C there is an initial rapid decrease in the value of $R_{71/431}$ with time. The intensity ratio then remains constant, within experimental error, for times long compared to the time of the initial decrease. As before, this behavior is interpreted as the full equilibration of the surface with the bulk.

The Alloys

Having obtained the state attributed to equilibrium, the Auger intensities of the principle Au and Sn peaks were recorded. From these intensities, the intensity ratios given in Table 5.5 were obtained. To obtain these ratios, all the precautions regarding instrumental drift, sample positioning, surface roughness, etc. mentioned in considering the pure Au and Sn measurements, were taken. Each of the ratios given are

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Fig. 5.8 The changes of the Au/Sn intensity ratio $R_{71/431}$ observed when a freshly sputtered alloy is annealed at various temperatures. (Reference 83)

averages of many measurements made at various positions on the sample surfaces, and after various cycles of sputtering and annealing. The errors given are the standard deviations of the data sets. Values obtained for measurements for which the sample was not sufficiently clean or in which there was reason to suspect that the sample was not fully equilibrated were not included. These values were used to determine the effect of these factors on the measured values. All measurements refer to samples equilibrated at 150°C except the 99. at % Au sample which was equilibrated at 200°C.

It is important to clarify this last statement. The samples were annealed at 150°C (200°C) for times long enough to reach equilibrium, according to the above arguments. However, for every case averaged into Table 5.5, the samples were allowed to cool to temperatures as low as room temperature before the measurements were made. This point will be discussed below.

As was pointed out in Chapter 3, it is important to the analysis that the shapes of the Auger peaks do not change with alloy composition. To check this, the Auger peaks from some of the alloys were checked by scaling the peaks to equal intensities and recording them on an expanded energy scale. The Sn (431 eV) peak was found to have an identical shape for the 50.0, 65.0, 79.9, and 86.7 at % Au samples and this shape was identical to that of pure Sn. However, two loss peaks were observed at 416.5 and 402.5 eV in the pure Sn which correspond to losses of about 14.5 and 28.5 eV below the 431.0 eV Sn peak. The 14.5 eV loss has been reported by Seah¹²³ as a characteristic Sn plasmon loss and the loss at

28.5 eV probably corresponds to twice the plasmon frequency. As expected, these losses were not observed on any of the Au-Sn alloys. These changes, well below the Sn (431 eV) peak, should not interfere with the intensity analysis. The shape of the Au (71 eV) peak for the 50.0, 65.0, 75.5, 80, 79.7 and 86.7 at % Au alloys were compared with each other and with pure Au. Virtually no change in shape was observed except the peaks from the alloys seemed to be slightly narrower in the region above the high energy minimum (73 to 80 eV) with the δ phase (50.0 at % Au) seemingly narrower than the ζ phase (86.7 at % Au) alloy. The shape of the Au (241 eV) and the Au (2024 eV) peaks from the 75.5 at % Au sample were compared with those of pure Au and no change in shape was observed.

5.3.2 Temperature Dependence of the Intensity Ratios

The Two Phase Alloys

In view of the temperature dependent surface composition predicted by the regular solution model, temperature dependent behavior was searched for in some of these alloys. There was however, one important experimental difficulty. As found in the Au-Ag studies, resistance heating of the samples results in electromagnetic fields created by the heating current, which affects the observed Auger intensities in a manner that depends upon the energy of the Auger peak and the magnitude of the current. This effect was observed for AC and DC heating. The presence of the heating current therefore affects intensity ratios in a manner which is temperature (heating current) dependent. To circumvent this problem, the experiments were performed in the following manner.

The sample was heated at the desired temperature an arbitrary length of time. The heater was then turned off and the Auger intensity ratio quickly measured as the sample cooled. This could be repeated several times to assure that the sample was fully equilibrated or to improve the statistics, and then the temperature would be changed and the process continued. A diagram of some typical experiments is given in Fig. 5.9. The intensity ratio that was used as a probe in all these measurements was $R_{71/431}$ since it is the most sensitive to surface composition changes and involves the most intense peaks. To record this ratio required 25 seconds at the scan rates used in these experiments. The rate at which one of the samples cooled is shown in Fig. 5.10. These curves are fairly typical of each of the samples studied. In 25 seconds, a sample initially at 210°C will cool about 35°, whereas a sample initially at 90°C will cool about 12°. The intensity ratios are therefore characteristic of a temperature known only to be within a certain range. The temperatures given in Fig. 5.9 were measured before the heater was turned off. The temperature was recorded with a thermocouple in the case of the 79.9 at % Au sample, and with an Infra-red pyrometer for the others discussed below. The absolute temperatures are uncertain by probably ± 10 -15°, but the scaling between two temperatures is probably more accurate. The temperature range employed in these studies was limited from below by diffusion rates and from above by the eutectic temperatures of the samples (270°C). Because of possible temperature inhomogeneities in the sample and the uncertainty in the measured temperature, temperatures above about 220°C were avoided.

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Fig. 5.9 Values for the Au/Sn intensity ratio as monitored during a series of heat treatments.

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Fig. 5.10 The cooling rate of one of the Au-Sn samples following a sudden termination of the heating current. The minimum time required to measure the Auger intensity ratio $R_{71/431}$ is denoted by $t_{\min.}$

In making the measurements, the peak which is scanned first will be characteristic of a slightly higher temperature than that scanned second. This effect can be minimized by constantly reversing the order of measurements. This was done in the experiments shown in Fig. 5.9. This reversal resulted in a regular zig-zagging of the data points about the lines drawn at the average value for each temperature. It was found, almost without exception and on all samples, that if the Au (71 eV) peak was scanned first, $R_{71/431}$ was less than if the Sn (431 eV) peak was scanned first.

The results of experiments of this kind are given in Fig. 5.11 for three samples, including the experiments detailed in Fig. 5.9. The average value of $R_{71/431}$ at each temperature as defined above is given. The error bars characterize the spread resulting from reversing the order of measurements referred to above. The dashed lines and arrow serve to show the procedure by which the experiments were performed and demonstrate the reversibility and reproducibility of the observed trends. In each case trial 1 is distinct from trial 2, in that after trial 1 the sample was completely cooled and then resputtered before trial 2 was begun.

The experiments indicate that there is a temperature dependence of the Au/Sn ratio which correlates increasing Sn with increasing temperatures. The trend is observed for all three samples although the effect is least for the 65.0 at % Au sample. As discussed below, this sample has less Sn segregation than the other two and so may be expected to have the smallest temperature dependence. The other two samples have roughly the same temperature dependence. The fact that samples can be cycled

Fig. 5.11 The Auger intensity ratio, $R_{71/431}$ as a function of temperature for three Au-Sn alloys.

between the highest and lowest temperatures reinforces the conclusions obtained from the annealing curves given in Fig. 5.8, that the surface has obtained equilibrium with the bulk at these low temperatures. The measurements made at the highest temperatures, because of sample cooling, are actually indicative of slightly lower temperatures than are assigned them. At lower temperatures this is not as serious. This effect tends to hide the temperature dependence. Therefore, the actual temperature dependence may be expected to be somewhat greater than that experimentally determined.

The displacement observed between the results of trial 1 and trial 2 in each case, are fairly typical of the scatter observed whenever the samples were re-sputtered, or whenever a different portion of the sample was examined. This scatter is characterized by the errors given in Table 5.5, and is believed to be due to many combined factors including surface roughness, and the fact that the samples are two phased and are inhomogeneous on a micro-scale.

The intensity ratios recorded during these temperature dependence studies were lower than the values reported in Table 5.5. The values in the Table 5.5 were recorded by heating the samples to 150°C (200°C for the 99.0 at % Au) followed by a fairly long waiting period of from several minutes to perhaps hours, before the peaks were scanned. In making these measurements it was presumed that the surface was frozen to the configuration of the surface at or slightly below 150°C. These temperature dependence measurements indicate that the measurements in Table 5.5 may represent the surface composition at a lower temperature. The weakness

of this argument is that the values in Table 5.5 seem to be so much higher than those of Fig. 5.11 as to be unobtainable even at room temperature.

Beside this result, there are two things that are particularly puzzling about these data. The first is the fact that the values of $R_{71/431}$ depend so strongly upon the order in which the peaks are measured. This could be in part due to the fact that the sample is cooling as the measurements are being made, if it is assumed that the sample can equilibrate fast enough to follow the temperature decrease. But this explanation is not very likely since the same effect was observed at 70°C in the 79.9 at % Au with a deviation as large as at any other temperature. At 70°C it is not likely that the sample can equilibrate rapidly, as is affirmed qualitatively in Fig. 5.8 for other samples. In addition, at 70°C the sample temperature drops about 10° during the measurements. According to the rate of change of $R_{71/431}$ with T indicated in Fig. 5.11, a 10° variation would not result in a change in R which is as great as the spread in the data.

The second puzzling result is that the value of $R_{71/431}$ decreases with increasing T. The equilibrium measurements indicate there is segregation of Sn at the surface of the ζ phase as will be discussed below. If this segregation takes place according to any model similar to the regular solution model, it is expected that an increase in T would lessen the surface segregation and thus increase the value of $R_{71/431}$. This is opposite to what is observed.

Because of these results, it was conjectured that some experimental anomaly may be interfering. One possibility considered was that heating

caused the sample to buckle toward or away from the analyzer. By checking the sensitivity of the measured value of $R_{71/431}$ to reasonable sample movements, it was found that this could not account for these effects. The data seem to suggest that the effects of fields caused by the heating fall off slowly. This would account for the difference obtained between measuring the Au peak first versus measuring the Sn peak first, especially since the low energy Au peak is affected more by the current. This would also account for the lowering of these $R_{71/431}$ values below those reported in Table 5.5. It is extremely difficult, however, to imagine how the influence of the heating current could remain up to 30 seconds after the power supply has been switched off.

The ζ Phase Alloy

Temperature dependence experiments, performed in the same manner as described above, were undertaken for the 86.7 at % Au sample. For this one phase alloy, results were found which did not show the reproducible trends of the two phase alloys. Four separate trials, numbered chronologically in Fig. 5.12, were performed in a temperature range from about 120 to 260°C. Each trial is distinct in that the sample was sputtered at least once between trials. The results seem to indicate that the sample is undergoing some complicated equilibration process. A fairly detailed thermal history of the sample, after being mounted in the ultra-high vacuum system, is contained in Fig. 5.12.

Prior to trial 1, the sample was sputtered and annealed in cycles. The average value of $R_{71/431}$ (for samples annealed at 150°C and then allowed

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Fig. 5.12 The Auger intensity ratio $R_{71/431}$ as a function of the thermal history of the ζ phase alloy.

to cool) was 1.07 and is given in Fig. 5.11 along with the standard deviation of the distribution. Prior to trial 1 the sample had not been heated to above 170°C except during bulk preparation described in section 5.1. After heating to 210°C in trial 1, the average value of $R_{71/431}$ dropped about 12% to .935. Three other experiments were run to look for temperature dependence up to 260°C. After completion of these three, the value for $R_{71/431}$ made as before and based on 15 measurements was $.873 \pm .043$.

A variation in the $R_{71/431}$ values for the sputtered sample was also observed. For the sputtered surface, the measured values of $R_{71/431}$ were higher before trial 1 was completed than after (7.2 - 11.8 before versus 5.3 - 7.0 after) for roughly equivalent sputtering conditions.

The data might seem to indicate that for this sample, unlike the two phase alloys discussed above, there is some slow bulk equilibration process which is going on, in addition to the comparatively rapid equilibration of sputter damage that occurs at 150°C. But, the sample was homogenized at 260°C for over two weeks before it was mounted in the vacuum system. How could heating in ultra-high vacuum for relatively short times at 220°C further equilibrate the sample? The x-ray diffraction spectra recorded after the Auger measurements, indicate that none other than the ζ phase was present in the sample. The composition of the sample, confirmed by x-ray fluorescence, falls within a one phase region which has been studied very carefully. These facts tend to negate any argument that the surface behavior is due to bulk equilibration. Nevertheless, the values of $R_{71/431}$ did decrease as a result of trials 1 and 2, although

they seemed to have stabilized somewhat by the time trial 4 was completed. The values given in Table 5.5 for this alloy take into account all measurements made before and after trial 1, and the quoted uncertainties reflect the uncertainty described here.

5.4 Analysis of the Auger Intensities

5.4.1 Qualitative Study of the Intensity Ratios

The equilibrium Auger intensity ratios are plotted in Fig. 5.13 and Fig. 5.14. The ratios are normalized by dividing by the intensity ratios in pure Au and pure Sn. The normalized ratios in Fig. 5.13 are Au/Sn ratios and are plotted versus the ratio of the bulk atom fractions. If the surface composition were always equal to the bulk composition, one would expect (to a first approximation) that these normalized ratios would be equal to the ratio of the bulk atom fractions and the data points would fall upon the dashed line in Fig. 5.13. The data for the 50.0 at % Au sample falls near this dashed line but the deviation from the dashed line increases with increasing Au composition. Deviation below the dashed line indicates enrichment of Sn in the region sampled by the Auger electrons. For the 86.7 at % Au sample ($x_b^{\text{Au}}/x_b^{\text{Sn}} = 6.5$) the lowering of the $R/R_{71/431}^{\text{O}}$ below the values of $R/R_{2024/431}^{\text{O}}$ is indicative of greater Sn segregation to the region sampled by the 71 eV Auger electrons. Since a 71 eV electron is established to have a lower escape depth than the 2024 eV electron in metals, this indicates segregation of Sn to the surface. Therefore, both this dispersion and the overall low values of the Au/Sn ratios for the ζ phase alloy are strong evidence for segregation of Sn to the surface in

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Fig. 5.13 The Au/Sn intensity ratios are plotted versus the ratio of the bulk atom fractions. The dashed line is given by $R/R^0 = x_b^{Au}/x_b^{Sn}$. The dot-dashed curve gives the three intensity ratios calculated using the intensity model for the case in which the surface composition is equal to the bulk. The solid curves give the predicted intensity ratios if there is segregation in the ζ phase ($x_1^{Au} = .43$). The upper solid curve is for $R/R^0_{2024/431}$ and the lower solid curve is for $R/R^0_{71/431}$. (Reference 83)

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Fig. 5.14 The normalized Au/Au intensity ratios are plotted versus the bulk Au atom fraction. The dashed line is given by $R/R^\circ=1$. The dot-dashed curve gives the intensity ratio calculated using the intensity model for the situation in which the surface composition is equal to the bulk. Upper is for $R/R^\circ_{71/241}$ and the lower is for $R/R^\circ_{71/2024}$. The solid curves give the predicted intensity ratios if there is segregation in the ζ phase ($x_1^{Au}=.43$). Upper solid curve is for $R/R^\circ_{71/241}$ and the lower is for $R/R^\circ_{71/2024}$. (Reference 83)

this phase.

Attention should also be called to the data in Table 5.5 for the 99 at % Au sample which is not plotted in Fig. 5.13. Here also the normalized ratios $R/R_{71/431}^0 < R/R_{241/431}^0 < R/R_{2028/431}^0 < 99$. which is evidence for segregation of Sn in the α phase alloy.

For the δ phase by contrast, the different energy Au peaks give about the same information and the points lie close to the dashed line indicating that the surface composition is possibly identical to the bulk. The values for the two phase regions vary smoothly between these one phase values.

In Fig. 5.14 the normalized Au/Au ratios are plotted versus bulk composition. Again, because of the difference in escape depths λ_E (generally accepted as $\lambda_{71} < \lambda_{241} < \lambda_{2028}$) variation of the normalized ratios from the value 1.0 may be interpreted as surface segregation. For the ζ phase alloy, the lowering of both ratios $R/R_{71/241}^0$ and $R/R_{71/2024}^0$ below the dashed line, and the trend $R/R_{71/241}^0 < R/R_{71/2024}^0$ are evidence for segregation of Sn to the surface. The same is true for the α phase sample. For the δ phase alloy, the data would seem to indicate an enrichment of the surface in Au, but this is not consistent with the normalized ratios being less than 1.0 in Fig. 5.13. The two phase alloys have values varying quite smoothly between the δ and the ζ values.

5.4.2 Quantitative Analysis of the Intensity Ratios

Although a great deal of interesting qualitative information can be obtained by looking only at the trends in the data, the goal of present

day Auger electron spectroscopy is to try to quantify the results. The remainder of this section will be devoted to using the intensity ratios to obtain the surface composition of the alloys.

To attempt to estimate the extent to which the indicated segregation may be taking place, the model for the intensity of Auger emission which was developed and discussed in Chapter 3 will be used. Hypothetical surface compositions will be suggested and will be used along with reasonable values for the various parameters to calculate the Auger intensity ratios. The resulting ratios will be compared with the experimental ratios. The hypothetical surface composition which is found to give the best fit will be suggested as the true surface composition. The extent to which the results depend upon the parameters entering into the calculation will also be calculated.

The ζ Phase

As was pointed out in Chapter 3, Eqs. 3.7a and 3.8a can really only apply to close packed planes. In pure Sn (and in the δ phase) there are no close packed planes. Nevertheless, the expression was applied to the most densely packed planes in these solids, as derived from the crystal structure and lattice parameters of the crystals.³⁵ If we neglect matrix effects, then the normalization results in a cancellation of the term $I_0(\sigma_{I^P A} \frac{\Omega}{4\pi} - T)$ and the values of λ_E are constant for all bulk composition. The parameters to be used in these calculations are shown in Table 5.6.

The calculation was performed for the ζ phase alloy (86.7 at % Au) assuming that surface segregation takes place only on one surface monolayer

Table 5.6 Parameters Used to Calculate Auger Intensities

Sample	Crystal Face	Atom Density, $\rho_i^\dagger$ Atoms/ $\text{\AA}^2$	Interlayer Spacing, $d_i^\dagger$ $\text{\AA}$
Sn	(100)	.108	2.910
δ phase	(110)	.097	2.157
ξ phase	(001)	.135	2.38
α phase*	(111)	.139	2.354
Au	(111)	.139	2.354

$$\lambda_{71} = 4 \pm 1 \text{ \AA}$$

$$\lambda_{241} = 8 \pm 2 \text{ \AA}$$

$$\lambda_{431} = 12 \pm 2 \text{ \AA}$$

$$\lambda_{2024} = 30 \pm 5 \text{ \AA}$$

$$r_i = 1 \text{ (no backscattering effects)}$$

$$\theta_o = 42^\circ$$

*For these purposes the lattice parameters of the α phase may be assumed to be equal to those of the pure Au.

$\dagger$ The density and interlayer spacing were taken to be the same in every layer of an alloy, even if there was segregation.

(monolayer approximation). The calculated normalized Au/Sn intensity ratios are shown as a function of the first layer composition in Fig. 5.15. If the first layer composition is the same as the bulk ($x_1^{\text{Au}} = x_b^{\text{Au}} = .867$), then the three different ratios are equal, but if the first layer composition is different than the bulk, then the normalized ratios show the dispersion discussed above. Note however that at $x_1^{\text{Au}} = x_b^{\text{Au}}$, the normalized Au/Sn ratios are not equal to the ratio of the bulk atom fractions ($x_b^{\text{Au}}/x_b^{\text{Sn}} = 6.52$) but instead are equal to about 4.2. This is a result of the fact that the pure Au, pure Sn and the ζ phase alloys all have different crystal structures and interplanar spacings, which means that the coefficients $a_i \neq a_i^\circ$ in Eq. 3.12. Thus from this calculation it is seen that even if the surface composition were equal to the bulk, the normalized ratios would not fall upon the dashed line in Fig. 5.13 but would fall upon the dashed-dotted curve in that figure. Actually this same effect can lead to somewhat different values for the three different Au/Sn normalized ratios even when the surface is identical to the bulk. This effect was observed in the calculations but was too small to appear in Fig. 5.15.

The experimental values of the normalized ratios are taken from Table 5.5 and are denoted by arrows in Fig. 5.15. The point where a calculated curve crosses the experimental values determines the monolayer composition which fits that data point. The three Au/Sn ratios give three monolayer compositions, corresponding to 38, 40 and 41 at % Au indicating a large segregation of Sn to the surface of this alloy with bulk composition of 86.7 at % Au. The fact that the three data

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Fig. 5.15 The calculated values of R/R^0 as a function of the first monolayer composition for the ζ phase alloy. The arrows mark the experimentally observed intensity ratios taken from Table 5.5b.

points give such excellent agreement seems to indicate that the monolayer approximation is valid. The two Au/Au ratios also give first monolayer compositions which are in fair agreement (not shown in Fig. 5.15).

The same calculations can be performed for different values of the escape depth, and then this graphical method yields again the values for x_1^{Au} . This process provides an estimate of how an uncertainty in the escape length will affect the proposed surface composition. These calculations were performed and the results for the Au/Sn ratios are shown in Fig. 5.16. Here the value of the obtained x_1^{Au} as a function of the escape length used in the calculation is given for constant values of R/R° given by the experimental values. The slopes of these curves provide a figure of merit for the dependence of the calculated surface composition on escape length.

Similarly the slopes of the curves in Fig. 5.15 give a means of estimating the extent that the calculated surface composition depends upon the experimental uncertainty in the measured normalized intensity ratios. Using these values it is now possible to assign an uncertainty in the calculated surface monolayer composition by statistically adding the uncertainties from escape lengths and from the experimental data. This was done and the results are shown in Table 5.7. In this, the uncertainties in the escape lengths are taken from Table 5.6 and the uncertainties in the data are taken from Table 5.5. From Table 5.7 a surface monolayer composition of 43 ± 10 at % Au is proposed.

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Fig. 5.16 The effect of varying the escape lengths λ_E upon the calculated monolayer composition obtained from the three normalized Au/Sn intensity ratios.

Table 5.7 Surface Monolayer Compositions and Uncertainties

E/E'	$x_1^{\text{Au}} (\times 100)$	<u>ζ phase</u>			
		uncertainty due to: (at %)			
		λ_E	$\lambda_{E'}$	exp scatter	Σ unc.
71/431	41.0	± 3.6	± 3.2	± 5.1	± 7
241/431	38.0	± 3.2	± 4.2	± 6.6	± 8
2024/431	40.0	± 0.9	± 5.2	± 9.5	± 11
71/241	54.5	± 10.4	± 8.5	± 7.7	± 16
71/2024	43.5	± 11.1	± 1.5	± 7.3	± 13

E/E'	$x_1^{\text{Au}} (\times 100)$	<u>α phase</u>			
		uncertainty due to: (at %)			
		λ_E	$\lambda_{E'}$	exp scatter	Σ unc.
71/431	40.0	± 3.2	± 5.4	± 1.5	± 6
241/431	36.5	-----	± 7.0	± 2.0	$> \pm 7$
2024/431	36.5	± 0.5	± 8.1	± 2.8	$\pm 9.$
71/241	60.0	± 14.5	-----	± 6.2	$> \pm 16$
71/2024	48.5	± 9.5	± 1.5	± 7.5	± 12.2

This proposed surface composition is of course uncertain due to other factors, the effects of which are difficult to predict. In all of this discussion, the backscattering effects were completely neglected. Chapter 4 pointed out how this effect can lead to uncertainty in interpretation. Applying the principles of that discussion, it appears that neglecting backscattering corrections would lead to a Au surface composition which is too low. In addition, the calculations were not done for any but a monolayer type of segregation, and in fact a unique surface depth profile could not be determined from this limited data. The problems already mentioned of applying these equations to the non-closest packed Sn solid are difficult to test, and indeed performing this calculation for crystal parameters other than those listed in Table 5.6 does alter the results somewhat. Finally there are all of the initial assumptions inherent in the use of Eq. 3.8 which were discussed in Chapter 3.

The α phase

The data given in Table 5.5 for the α phase alloy (99.0 at % Au) shows all of the expected properties for a sample with Sn segregated to the surface. Specifically, the normalized Au/Sn ratios are much less than the ratio $x_b^{\text{Au}}/x_b^{\text{Sn}}$, and there is a difference between ratios of different energies. Thus, this sample can be analyzed in the same manner as the ζ phase alloy, but again the same uncertainties apply. Using the monolayer approximation, the same calculations were performed as before, and the results are shown in Table 5.7. For this alloy a monolayer surface composition of 46 ± 10 at % Au is proposed.

It may be seen that the data given in Table 5.7 for both the α phase and the ζ phase would be more self consistent if the value of λ_{241} was assumed to be about 6 Å (instead of 8 Å). For the ζ phase this would bring the value of x_1^{Au} obtained from $R/R^\circ_{71/241}$ down from 54.5 to 40.5 at % Au. In addition, it can be seen from Fig. 5.16 that the value of x_1^{Au} obtained from $R/R^\circ_{241/431}$ would increase to about 41.5 at % Au and all data would then be more consistent. Similarly for the α phase, using $\lambda_{241} = 6$ Å would bring the value of x_1^{Au} obtained from the values of $R/R^\circ_{241/431}$ and $R/R^\circ_{71/241}$ closer to 40 at % Au.

The δ phase alloy

Applying this sort of intensity analysis to the δ phase (50.0 at % Au) alloy is not as fruitful. The closeness of the intensity ratios to the dashed line in Fig. 5.13 indicates that the surface composition is close to the bulk, but the spreading in the intensity ratios given in Fig. 5.14 for the δ phase alloy is an indication that there may be some segregation of Au to the surface. As such, the normalized intensity ratios were calculated for this phase, again using the parameters in Table 5.6, but this time assuming a monolayer segregation of Au to the surface. The results are summarized in Fig. 5.17 where the calculated intensity ratios are plotted as a function of the surface monolayer composition. As before the data is given by the arrows.

The Au/Au ratios indicate that the composition of Au is about 65 to 70 at % in the first layer. However, the values calculated for the three Au/Sn ratios are so much lower than the experimental

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Fig. 5.17 The calculated values of R/R^0 as a function of the first monolayer composition for the δ phase alloy. The arrows mark the experimentally observed normalized intensity ratios taken from Table 5.5 (b).

intensities that they are inconsistent with only a monolayer segregation of Au in any amount. This inconsistency is likely due to some fault in the intensity model rather than inconsistency in the data. Using the parameters for a less closely packed crystal plane in the δ phase lowered the calculated Au/Sn intensity ratios still further. It therefore seems that if somehow a more closely packed plane than the (110) were used for the δ phase, then the Au/Sn ratios might become consistent with some monolayer composition. As discussed in Chapter 3, the intensity model assumes that emission from each layer is fully attenuated by the layers above it, so calculations should be done for the closely packed surfaces. The fact that there are no closest packed planes in the δ phase may be responsible for the fact that it is impossible to obtain a surface monolayer composition from the present intensity analysis.

In view of the problems, the original qualitative interpretation of the data is chosen. The surface has nearly the same composition as the bulk for the δ phase alloy, although there is some evidence for very slight enrichment of Au.

The two phase alloys

For the two phase alloys, the major question of interest is whether both phases are present at the surface in the amounts expected from their abundance in the bulk or whether there is phase redistribution. To check these possibilities a hypothetical surface composition was assumed in which both δ and ζ phases were present at the surface according to their stoichiometrical amounts in the bulk, i.e. according

to the lever rule. Each phase was assumed to be segregated as found above ($x_1^{\text{Au}} = x_b^{\text{Au}}$ for the δ phase and $x_1^{\text{Au}} = .43$ for the ζ phase). The intensity ratios expected for this surface composition were calculated and are shown in Figs. 5.13 and 5.14 as solid curves. For comparison the calculations were also made for a surface in which the lever rule was assumed but that $x_1^{\text{Au}} = x_b^{\text{Au}}$ in both phases. This bulk composition curve is shown in Fig. 5.13 and 5.14 as a dot-dashed curve. The solid curves fit the data very well at the ζ phase end, and poorly at the δ end as expected from the discussion above. Because of the poor fit at the δ end, it is difficult to tell whether the two phase alloys follow the trend expected if the lever rule were obeyed.

To correct this situation the lever rule was applied directly to the measured experimental intensity ratios of the δ and ζ phase alloys. So for a given bulk atom fraction x_b^{Au} , the expected intensity ratio R/R° (two phase) is given by the following:

$$R/R^\circ(\text{two phase}) = \left(\frac{.867 - x_b^{\text{Au}}}{.367} \right) R/R^\circ(\delta \text{ phase}) + \left(\frac{x_b^{\text{Au}} - .500}{.367} \right) R/R^\circ(\zeta \text{ phase})$$

This expression is actually not exactly correct since it is the phase boundary composition (83.5 at % Au) which should be used in the calculation. Nevertheless, the calculation was performed and the results are shown in Fig. 5.18 along with the experimental data. The curves must trivially pass through the one phase endpoints. The good agreement between the calculated curves and the two phase data quite convincingly demonstrate that there is little or no phase redistribution at the surface.

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Fig. 5.18 The solid and dashed curves show the result of applying the lever rule directly to the experimental intensity ratios obtained for the δ and the ζ phase alloys. (Reference 83)

5.5 The Surface Composition

The δ Phase (50 at % Au)

The Auger data seems to indicate that the surface composition is identical to that of the bulk for this alloy. This seems surprising at first since due to the lower surface energy of pure Sn, it is expected that Sn should segregate to the surface. This contradiction can be explained by consideration of the bulk structure of the δ phase alloy. This alloy is very strongly ordered and remains so up to the melting point.⁸ If the surface segregation is to take place, this order must be defeated by interchanging Au and Sn atoms. For this alloy then it appears that the ordered lattice is stable enough to be energetically favored over the disordered state brought about by surface segregation.

In work done by Bouwman et al^{80,81} the surface composition of a PtSn alloy which has the same structure as the δ phase AuSn alloy⁸ was studied and in that case they found that there was segregation of Sn to the surface. For this alloy apparently the tendency for Sn to segregate to the surface is strong enough to bring about the disordering. For the Au-Cu system, which forms ordered compounds at about 25, 50 and 75 at % Au, the long range ordering is weak enough that it breaks up before the melting point is reached.⁸ Fain and McDavid⁵³ found surface segregation of Au, the component believed to have the lower surface energy, for films of a wide bulk composition range.

It would be ideal to be able to predict these results by comparing quantitatively the tendency for the alloy to remain ordered and the tendency for segregation to occur. The driving force for segregation may be expected to be related to the difference between the surface energy

of the pure components, or to the difference in their heats of sublimation. The tendency of the alloy to order should be related to ΔH_m , the heat of mixing of the alloy, or better to $\Omega = \Delta H_m / x^A x^B$ where x^A and x^B are the atom fractions of the two components in the alloy. The ratio $|H_{\text{sub}}^A - H_{\text{sub}}^B| / |\Omega|$ may be of use in predicting whether segregation takes place in an alloy. This ratio is 1.05 for AuSn. For PtSn, the heat of mixing at 298°K is -58.6 kJ/g·at¹²⁰ which gives a value for this ratio of 1.13. This larger ratio indicates that for PtSn the tendency towards segregation is somewhat greater than for the AuSn alloy, in agreement with the experimental results.

The point of this discussion is to indicate that the strength of bonding between unlike atom pairs in the alloy is of importance in predicting the surface composition. Qualitative information about this effect can be obtained from the alloy heats of mixing, but much theoretical and experimental work is necessary before this effect will be fully understood.

The ζ Phase (86.7 at % Au)

For the ζ phase alloy, contrary to the δ phase alloy, there is no long range ordering in the bulk and all lattice points are equivalent whether occupied by Au or Sn.⁸ For this alloy the value of $|H_{\text{sub}}^A - H_{\text{sub}}^B| / |\Omega|$ ranges from 2.07 to 2.21 at 273°K, which is larger for the δ phase alloys of Au-Sn and Pt-Sn. Here then it is expected to be easier for the Sn to segregate to the surface of the alloy. The Auger intensity data for this sample is consistent with there being a monolayer of only about 43 at % Au sitting on top of the bulk. It should be

pointed out that this composition does not exist in the bulk phase diagram and as such the layer may be thought of as a distinct surface phase. It would be of interest to study the structure of this surface phase by a technique such as LEED.

There are possibly two driving forces causing this segregation. The first is the fact that pure Sn has a lower surface free energy than Au. Secondly, the effects of lattice strain might also enter, since the Sn is somewhat dilute in a lattice where the nearest neighbor distance (2.91 Å) is smaller than that in pure Sn (3.01 Å).³⁵ Segregation of Sn to the surface sites where there are fewer nearest neighbors can relieve this strain. This solid state effect which is often ignored in regular solution theories of surface segregation, has been cited as a driving force of segregation in other dilute alloys.⁷⁸ Any theory that predicts the surface composition of alloys must take both effects into account.

The Two Phase Alloys

The agreement between the experimental intensities and the intensities expected from the lever rule, demonstrated in Fig. 5.18, provides at least circumstantial evidence that no phase redistribution has taken place upon the surface. This is really not very surprising. In the cases in which such phase redistribution has been observed, such as the Cu-Ni⁵⁴ and Au-Pt⁷³ films described by Sachtler's cherry model, it is likely that the presence of only one phase on the surface was a result of diffusion and was not representative of equilibrium mixing as is the case here. It is hard to imagine a driving force that could impose phase redistribution since it is expected that the effects of the surface can in metals be

relieved within a few atomic layers.

The possibility that small crystallites of α phase might have been present in the 79.9 at % sample, and the possibility that the γ phase might have been present in all of the "two phase" alloys, have been ignored in this discussion. It is quite difficult to say how the existence of these phases could affect the results and these conclusions.

The α Phase

The Auger data for this alloy indicates strong segregation of Sn to the surface. Here again the driving force for segregation is likely due partly to the lower surface free energy of Sn, but in this case possibly the more important driving force is the relief of lattice strain caused by the large Sn atoms dissolved substitutionally in the Au lattice. Burton's phase diagram theory²² also would predict segregation of Sn in this sample.

The Surface Phase Diagram

It is of interest to use this data to construct a surface phase diagram. Surface phase diagrams of binary alloys can be quite complicated because there are so many variables. If more than the top monolayer has a composition different from the bulk, then one variable is required for each layer. In addition, these compositions may depend upon crystal face and will certainly depend upon temperature, at least over a wide temperature range. (Pressure as a variable is ignored.) As with the Au-Ag case, the monolayer approximation will be assumed and the surface monolayer composition will be that of the average over crystal faces since the experimental data is for polycrystalline samples. The surface phase

diagram then becomes a plot of $x_1^{\text{Au}} \equiv x_s^{\text{Au}} = x_s^{\text{Au}}(x_b^{\text{Au}}, T)$. In Fig. 5.19 is a portion of a constant temperature slice of such a phase diagram. The temperature would vary along the y-axis perpendicular to the plane of the figure. The bulk structure is given along the x-axis and is a single line cut from the bulk phase diagram shown in Fig. 5.1. The entire bulk phase diagram would be contained in the x-y plane. In Fig. 5.19 the surface monolayer composition is plotted along the z axis as a function of bulk composition at a temperature of 150°C.

In the surface monolayer, there are two surface phases present between bulk composition of $x_b^{\text{Au}} = .50$ and $x_b^{\text{Au}} = .835$. These are labeled δ_s and ζ_s since they derive from the bulk structures δ and ζ but have undetermined structures. The dashed-dotted lines indicate that both phases are present but each phase has its own surface composition which is invariant throughout the bulk composition range. The solid diagonal line between the two phase boundaries gives the average surface composition and indicates that the lever rule is obeyed at the surface in this two phase field. If the lever rule were not obeyed, then this line would become a curve which bowed closer to the surface composition of the more surface active phase. Through the narrow ζ phase region the surface composition is shown as constant at the value determined for the 86.7 at % Au alloy. In fact there is probably a variation in x_s^{Au} throughout this region but the data is not complete enough to determine this. Such a variation is shown for the α phase. A hypothetical curve is drawn through the surface composition determined for the 99 at % Au sample. (Liberty is taken with the fact that for this alloy the surface composition

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Fig. 5.19 A constant temperature slice of the Au-Sn surface phase diagram.

was actually determined at 200°C.) This curve demonstrates that the surface Au atom fraction must approach unity as $x_b^{\text{Au}} \rightarrow 1$. Surface structural changes are possible in this region. Speculative guesses are made as to the nature of the two phase $\zeta + \alpha$ field and of the two phase region for $x_b^{\text{Au}} < .5$. As with the Au-Ag bulk phase diagram (Fig. 4.10) a dashed line shows the hypothetical case in which $x_s^{\text{Au}} = x_b^{\text{Au}}$. This line is not part of the surface phase diagram but is put in to show off the enrichment of Sn in the surface monolayer.

This phase diagram summarizes the experimentally determined Au-Sn surface compositions in a compact way. Such surface phase diagrams have been constructed for simpler systems such as for the Au-Ag system (Fig. 4.10) and the Au-Cu system (Fig. 2.9). The diagram for Au-Sn is the first to be proposed for a complex alloy where several different phases are present both in the bulk and at the surface. In the future such phase diagrams will undoubtedly become more common and will improve as more information about the structure, composition and temperature dependence of various surface phases is obtained.

6. EFFECTS OF SPUTTERING

In both the Au-Ag and the Au-Sn alloys it was found that sputtering resulted in an increase in the Au composition at the surface compared to that in the equilibrated alloy. In the course of making the equilibrium measurements on the alloys, Auger intensity data was collected from sputtered samples. It is of interest to use this data to obtain information regarding the effects of sputtering an alloy surface.

6.1 The Au-Ag System

In Table 6.1 (a) are given the experimental intensity ratios obtained with the RFA from the alloy foils following sputtering at or near room temperature. In view of the discussion in Chapter 4, these ratios were corrected not only for the peak overlap at the Au(241eV) peak, but also for the background in the Au(71eV) peak and were then normalized to give the ratios in Table 6.1 (b). No sputter data was collected with the CMA.

The intensity ratios provided in Table 6.1 were unfortunately obtained under a variety of sputtering conditions. The sputter times ranged from about 10 minutes up to several hours depending upon the effectiveness of the sputtering as judged by the rate at which an impurity peak disappeared or the rate at which the Au/Ag intensity ratios increased. Originally a sputter ion gun (Varian) with a maximum energy of about 370 eV was used for some of the samples. The sputtering yields at this energy are low, so longer sputtering times (from one to several hours) were used. It was found that the efficiency

Table 6.1 Auger intensities from sputtered Au-Ag alloys

a) Uncorrected experimental ratios

x_b^{Au}	$R_{71/356}$	$R_{241/356}$	$R_{71/241}$	sputtering energy (eV)	sputtering time (min)
.15	.87 $\pm$.08	.031 $\pm$.002	28 $\pm$ 3	1500	10 - 20
.30	2.5 $\pm$.4	.074 $\pm$.008	33 $\pm$ 2	370	60 - 360
.40	3.6 $\pm$.9	.095 $\pm$.019	38 $\pm$ 3	370	60 - 1020
.46	5.9 $\pm$.7	.148 $\pm$.017	40 $\pm$ 1	370	60
.65	14. $\pm$ 2	.31 $\pm$.05	46 $\pm$ 2	1500	10 - 15
.65	13. $\pm$ 2	.27 $\pm$.03	48 $\pm$ 2	370	60 - 360
.97	157. $\pm$ 17	3.2 $\pm$.4	49 $\pm$ 2	1500	10 - 17

b) Normalized ratios*

$x_b^{\text{Au}}/x_b^{\text{Ag}}$	$R/R^\circ_{71/356}$	$R/R^\circ_{241/356}$	$R/R^\circ_{71/241}$
.176	.31 $\pm$.03	.28 $\pm$.02	1.08 $\pm$.12
.429	.76 $\pm$.13	.78 $\pm$.09	.97 $\pm$.07
.667	.99 $\pm$.24	1.0 $\pm$.2	.98 $\pm$.08
.852	1.5 $\pm$.2	1.6 $\pm$.2	.95 $\pm$.03
1.86	3.3 $\pm$.5	3.4 $\pm$.6	.99 $\pm$.05
1.86	3.1 $\pm$.4	3.0 $\pm$.4	1.03 $\pm$.05
32.	36. $\pm$ 4	36. $\pm$ 5	1.01 $\pm$.05

* corrected for peak overlap at 241 eV and background at 71 eV

of this gun could be improved by biasing the sample negatively, effectively increasing the ion energy. Later, another sputter ion gun (Physical Electronics) capable of generating Ar^+ ion energies of 1500 eV was used to obtain more efficient sputtering. Times on the order of 10 to 20 minutes were typically used for this source. In the RFA system the sample had to be rotated into the ion beam and various different angles of incidence were used. The sputtering efficiencies did seem to be better for grazing angles than for near normal angles of incidence. For neither gun was the ion flux, flux density or the point on the sample of highest flux density known. The data given in Table 6.1 are averages from several independent measurements and the uncertainties given are the standard deviations of the distributions. The magnitude of the uncertainties probably reflect mostly the variation in the sputtering times.

It is of interest to use this data to speculate as to the possible effects of sputtering. One possible result of sputtering is to remove the top layers at a constant rate and without regard for the composition, leaving the bulk alloy exposed. This is the simplest possibility and is the basis for some work in which the sputtered surface is used as a reference for calibrating the surface composition of an unsputtered alloy.

It has been shown experimentally that different solids have different sputter efficiencies. Wehner^{121,122} has made measurements for many solids including Au, Ag and Sn for Ar bombardment with ion energies from 50 - 600 eV, and indeed their sputter efficiencies are different.

As such, in binary alloys it may be expected that the species with the highest sputter yield may be removed preferentially, leaving a surface enriched in the other component. If the sputtering yield is denoted by y , then the surface composition, x_s , of a sputtered surface may be given by Eq. 6.1

$$\frac{x_s^{Au}}{x_s^{Ag}} = \frac{x_b^{Au}/y^{Au}}{x_b^{Ag}/y^{Ag}} \quad 6.1$$

which can be rewritten as the following:

$$x_s^{Au} = \frac{Y (x_b^{Au}/x_b^{Ag})}{1 + Y (x_b^{Au}/x_b^{Ag})} \quad 6.2$$

where $Y = y^{Ag} / y^{Au}$. This model makes the unlikely assumption that the sputter yield of a species is independent of the matrix it is in. It also provides no information about the depth profile of the enrichment.

Another possible effect of sputtering is that the surface might be altered by the formation of pits, towers, vacancies, dislocations and implanted Ar. It is very difficult to predict how the formation of such exotic topography will affect the Auger intensity ratios.

The data in Table 6.1 make it possible to assess these three possibilities. If the effect of sputtering were to strip away the Ag rich segregated surface leaving an exposed surface having the bulk composition, then it would be expected that the normalized Au/Ag ratios would be equal and they would equal the ratio of the bulk atom fraction, x_b^{Au}/x_b^{Ag} , while the Au/Au ratio, $R/R_{71/241}^0$, would be expected to be equal to unity. From Table 6.1 (b) it is easily seen that the

Au/Ag ratios are all significantly greater than the ratio of the bulk atom fractions. This fact indicates that there is an enrichment of Au in the surface region which implies that Ag is preferentially sputtered. As with the equilibrated alloys, to obtain information about the depth profile of the composition requires information from various different energies. Here there is no data from the Au(2024 eV) peak so only comparison of the 71 and the 241 eV peaks gives depth information. Due partly to the experimental scatter, it is difficult to see a trend in the data which might yield information about the composition profile brought about by the selective sputtering of Ag.

In view of this, for a first approximation it will be assumed that

$$R/R^{\circ}_{\text{Au/Ag}} = x^{\text{Au}}_s / x^{\text{Ag}}_s \quad 6.3$$

where x_s is the "surface composition." If there is a composition gradient, the x_s will be a weighted average of the composition in each of the layers sampled by the Auger electrons. The surface compositions obtained from the ratios $R/R^{\circ}_{71/356}$ and $R/R^{\circ}_{241/356}$ using Eq. 6.3 are shown in Fig. 6.1. The resulting surface compositions show the expected enrichment in Au.

Wehner's results indicate that for normally incident 400 eV Ar^+ ions, pure Ag sputters with an efficiency of about 1.3 times greater than pure Au. Using this ratio in Eq. 6.2 gives the expected surface enrichment shown by the solid curve in Fig. 6.1 labeled $Y=1.3$. It appears that the selective sputtering occurs to an extent even greater than predicted by the 400 eV sputter yields for pure Au and Ag. This may be due in part to the off-normal angles of incidence used in these

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Fig. 6.1 The surface enrichment in Au of sputtered Au-Ag alloys as determined from two normalized Auger intensity ratios. The solid curves give the predicted enrichment for the cases in which Ag sputters 1.3 and 1.7 times more efficiently than Au.

experiments. This may also mean either that the sputter yields depend upon the matrix in which the sputtered species is located, or that the model in Eq. 6.1 is a poor description of what is actually happening. The Au-Sn data given later indicates that for that system possibly the latter is true.

The effects of the supposed increase in surface roughness brought about by sputtering are hard to estimate. One might expect the lowest energy Auger peaks to be attenuated more strongly than the higher energy peaks. If this is true, then the increased roughness would cause a decrease in the ratios $R_{71/356}$ and $R_{241/356}$. Correcting for this factor would give surface compositions even more enriched in Au.

To check for roughness effects, the absolute intensity of the Au(71 eV) peak from a pure Au sputtered sample was compared to that obtained after annealing the sample for about 700 seconds near 400°C. There was a slight increase in the intensity after annealing but the increase was less than 6%, which was about the same size as the experimental error. Intensity changes of this magnitude could not be responsible for the large apparent Au enrichment, especially since only intensity ratios are used and it might be expected that ratios are less sensitive to roughness than absolute intensities. It should be pointed out that sputtered data was normalized using the reference ratios R° obtained from pure Au and Ag samples which had been annealed. The difference between using these ratios instead of those obtained from sputtered Au and Ag (which might be a more proper reference) is expected to be small for the reasons given above. The fact that the

normalized intensity ratios for the sample with $x_b^{\text{Au}} = .97$ indicates nearly no Au enrichment is very good evidence for the fact that the reference ratios R° are indeed correct. That is, for this sample sputtering can not yield a strong enrichment in Au; it must give something close to the bulk values which is what the normalized intensity ratios correctly show.

Finally it should be restated that these surface compositions, calculated from Eq. 6.3, are weighted averages of the compositions in all of the layers sampled by the Auger electrons. If the enrichment in Au actually occurs in only the top monolayer, then the enrichment of this monolayer would be even larger than indicated by the data points in Fig. 6.1. However, the ratio $R/R^\circ_{71/241}$ is close to or even possibly less than unity for all alloys, which is not consistent with a monolayer type of enrichment in Au. Also, as mentioned above, the two Au/Ag ratios do not show the proper difference to be consistent with only a monolayer type of enrichment.

6.2 The Au-Sn System

The experimental and normalized Auger intensity ratios obtained from sputtered Au-Sn alloys are given in Table 6.2. The sputtering was done with ion energies of 1500 eV at a grazing angle of incidence (about 70° off normal) which was constant for all alloys. Sputtering times ranged from 20 to 90 minutes. Upon one occasion, the ratio $R_{71/431}$ was monitored as a function of sputtering times and it was found that after an initial rapid increase, the ratio continued to increase although rather slowly. As such, the ratios in Table 6.2

Table 6.2 Auger intensities from sputtered Au-Sn alloys.

a) Experimental ratios

x_b^{Au}	$R_{71/431}$	$R_{241/431}$	$R_{2024/431}$	$R_{71/241}$	$R_{71/2024}$	Sputtering times (sec)
.500	.88 $\pm$.02	.097 $\pm$.002	.073 $\pm$.001	9.1 $\pm$.2	12.1 $\pm$.3	1500-1600
.610	1.25	.127	.090	9.8	13.8	1425
.650	1.03 $\pm$.07	.114 $\pm$.009	.083 $\pm$.007	9.0 $\pm$.1	12.5 $\pm$.5	1700-2100
.755	2.31 $\pm$.10	.241 $\pm$.011	.169 $\pm$.008	9.6 $\pm$.1	13.7 $\pm$.3	1900-2900
.799	6.1 $\pm$ 1.5	.62 $\pm$.14	.430 $\pm$.09	9.7 $\pm$.3	14.3 $\pm$.5	1500-2850
.867	8.1 $\pm$ 2.2	.84 $\pm$.22	.58 $\pm$.16	9.6 $\pm$.2	13.8 $\pm$.5	1600-5200
.990	37. $\pm$ 8.	4.1 $\pm$.9	2.9 $\pm$.6	9.4 $\pm$.1	13.3 $\pm$.3	1500-4700

b) Normalized ratios

$x_b^{\text{Au}}/x_b^{\text{Sn}}$	$R/R_{71/431}^{\circ}$	$R/R_{241/431}^{\circ}$	$R/R_{2024/431}^{\circ}$	$R/R_{71/241}^{\circ}$	$R/R_{71/2024}^{\circ}$
1.00	1.58 $\pm$.06	1.71 $\pm$.06	1.84 $\pm$.08	.94 $\pm$.02	.87 $\pm$.04
1.56	2.24	2.23	2.29	1.00	.99
1.86	1.85 $\pm$.14	2.01 $\pm$.2	2.09 $\pm$.19	.92 $\pm$.02	.89 $\pm$.05
3.08	4.14 $\pm$.2	4.24 $\pm$.2	4.28 $\pm$.27	.99 $\pm$.02	.98 $\pm$.05
3.97	10.8 $\pm$ 2.7	10.9 $\pm$ 2.5	10.9 $\pm$ 2.4	.99 $\pm$.04	1.02 $\pm$.06
6.52	14. $\pm$ 4.	14.9 $\pm$ 3.9	14.8 $\pm$ 4.	.99 $\pm$.03	.99 $\pm$.06
99.0	66. $\pm$ 14.	72. $\pm$ 19.	73. $\pm$ 15.	.97 $\pm$.02	.95 $\pm$.05

are probably not quite steady state values. The principle source of spread in the data seems to be due not so much to variation in the sputtering time as to the placement of the samples, since various positions were tried to achieve optimal sputtering. Because of the grazing angle of the sputtering, small movements of the sample along the axis of the CMA resulted in large displacements of the ion beam across the sample, so that the actual ion flux at the surface of the samples varied. The uncertainties given in Table 6.2 are standard deviations of the data from all occasions on which the samples were sputtered.

In spite of these difficulties, the qualitative information of interest can be obtained. The surface Au composition was obtained from the normalized Au/Sn intensity ratios using Eq. 6.3, and these are shown in Fig. 6.2. The data indicates that sputtering does enrich the surface in Au for most of the alloys. For the 99 at% Au sample, virtually no enrichment in Au is expected and the data indicates this. The data shows that for at least two of the samples the high energy Au peak indicates greater enrichment of Au than do the low energy Au peaks, i.e. there is a trend in which

$$R/R^{\circ}_{2024/431} > R/R^{\circ}_{241/431} > R/R^{\circ}_{71/431} > x_b^{\text{Au}}/x_b^{\text{Sn}} .$$

and

$$R/R^{\circ}_{71/2024} < R/R^{\circ}_{71/241} < 1 .$$

These sequences indicate that the composition of Au increases with depth, but that there is enrichment of Au (over the bulk value) even in the region sampled by the Au(71 eV) electrons. It therefore appears

XBL7610-7599

Fig. 6.2 The surface enrichment in Au of sputtered Au-Sn alloys as determined from three normalized Auger intensity ratios.

as if the Au enrichment caused by sputtering not only occurs in more than one layer, but it increases with depth for some distance before decreasing back to the bulk value. The data are not accurate enough to provide a composition profile, and in fact the apparent inverted composition gradient may actually be a result merely of a roughened surface combined with selective sputtering in only the top layer.

It should be pointed out that the decrease in the surface enrichment for the 65.0 at % Au sample seems to be real. This could suggest that matrix effects in the sputtering yields may be important for this sample. Wehner has reported that at normal incidence the sputter yield for Sn seems to be even lower than that for pure Au for energies from 50 to 600 eV which is interesting in view of these results which indicate that Sn is selectively sputtered from a Au-Sn matrix. These facts and the evidence for the effect of sputtering extending for deeper than one layer indicate that the simple model suggested by Eq. 6.3 is insufficient to explain these sputter results.

7. SUMMARY AND SUGGESTED FUTURE WORK

In concluding the results and discussions of these studies, two main subjects will be considered. The first topic will be a summary of the information that has been learned from these experiments, both from a general and a more specific point of view. This includes not only facts learned about alloys, but also about the techniques used in the study. The second topic will be a discussion of the questions which have arisen and the experiments which are suggested by the results of this work.

Most generally, the experiments have shown that surface segregation of the component with the lowest surface free energy does occur. When this work was begun, this concept was appreciated, but had not yet really been directly or conclusively proven. In addition, the experiments have shown that AES can be used (in favorable cases) to obtain at least semi-quantitative information about the extent of the surface segregation. The techniques of AES have improved in the last few years and will continue to improve as more is learned about attenuation, back-scattering and matrix effects. Here the effect of the attenuation of the Auger electrons, which was included in the intensity expression proposed by Meyer and Vrakking,⁹⁵ was applied to alloys and the necessity for the simultaneous collection of information from Auger peaks of as wide an energy range as possible was realized. To study the equilibrium segregation of binary alloys necessarily requires that the alloys be both binary (i.e. clean) and equilibrated. Much of the

confusion in the literature comes from experiments performed upon samples that do not satisfy these criteria.

More specifically, the following things have been learned.

Sputtering can be used as a means of cleaning alloy samples and its disruptive effect upon the surface can be exploited to determine the temperatures at which the surface can be equilibrated with the bulk (about 400°C for Au-Ag and about 150°C for Au-Sn). The sputtering does lead to preferential sputtering of one of the components in these binary system (Sn and Ag in Au-Sn and Au-Ag respectively) so sputtering can not be used as a reference state for normalized Auger intensity data. It was found that surface impurities can also affect the Auger intensities and thus must be removed.

From the Au-Ag studies it was found that the regular solution model does not accurately predict the surface composition of a very simple alloy. Segregation of Ag was found to be present, but the driving force is only about two thirds of that expected from the surface energies of pure Au and Ag. The discrepancy is attributed to solid state effects which may also be responsible for an apparently enhanced segregation near the limits of dilute solutes. These solid state effects which enter into the free energy of segregation may include some entropy effects such as due to the presence of short range ordering in the alloys or to the change in the vibrational entropy between atoms at the surface and in the bulk. There may also be strain effects due to different elastic properties of Au and Ag at the surface. A comparison of results measured with two types of Auger analyzers pointed to the

fact that instrumental effects (such as the perturbation of a high background) can lead to confusion. The consideration of possible backscattering corrections indicated the importance of further work to measure and understand backscattering factors.

From the studies of the Au-Sn system it was learned that surface segregation can be detected not just by the absolute values of Auger intensity ratios, but also by the dispersion between intensity ratios involving different Auger energies. This dispersion was also present in the Au-Ag system which showed less segregation, but was not as pronounced. It was found that using the intensity model, the data from different energies for the ζ and the α phase alloys could be fit very consistently to a monolayer segregation, giving evidence to the suspected property that the segregation takes place only in a narrow surface region. It was shown that the uncertainties in the analysis due to the imprecise knowledge of the electron escape depths could be estimated. It was found that systems involving changes in structure and density with bulk composition required careful analysis which takes account of the atomic densities. Effects of applying the intensity model to surfaces other than closest packed planes were also observed.

The most important physical fact obtained from the Au-Sn studies was the discovery that the presence of strong long range ordering can prevent segregation (as in the δ phase) whereas the segregation may occur for a disordered alloy (as in the ζ phase). The strong segregation found in the α and ζ phase is in agreement with that expected

from considering the surface energies of pure Au and Sn, and the relatively larger effect in the α phase attributes to the effect of strain in the segregation. The fact that the two phase ($\delta + \zeta$) alloys were found to obey the lever rule again provides evidence that the surface segregation is localized to only the surface or near surface atomic monolayers. Above all, the results of the Au-Sn studies show that consideration of the bulk phase diagram and bulk alloy properties is essential in predicting the surface phase diagram of an alloy.

Future studies of alloys might be expected to move in two possible directions. The first possibility is to study semi-quantitatively a wide variety of phenomena which occur at alloy surfaces. The second direction is to work hard on making AES more quantitative. Both of these possibilities will be discussed below.

Important information about alloys can be obtained without a full quantitative treatment by studying the temperature dependence of the alloy's surface composition. This dependence is expected to be described by Eq. 2.9. Burton⁷¹ has shown that for a very dilute alloy, this expression can be written as an Arrhenius type of equation. Measuring only the temperature dependence of an unnormalized Auger intensity ratio can give the heat of segregation Q . In this way, without knowing the actual surface composition, information about the driving force for segregation can be obtained and compared with theoretical estimates. Non-linearity in the Arrhenius plot might yield information about the temperature dependence of Q as expected from the entropy terms suggested by Seah.¹⁹ Experiments of this type

would require carefully designed sample holders which would allow the sample to be held at high temperature without introducing electromagnetic fields which would affect the Auger analysis. The difficulties with these experiments is first that for non-dilute alloys the value of Q is not easy to extract from the data, and second that the experimental errors are usually non-negligible compared to the extent of the measured effect.

Other studies might center upon studying liquid alloys. In the Au-Ag system studied above, it is believed that solid state effects enter into the segregation. In liquids, these effects and the effects of surface roughness are absent. Comparison between the surface composition of the solid and liquid phase of an alloy in addition to the temperature dependence of these compositions may provide interesting information on the energetics of segregation. Solid state effects might also be elucidated by studies of small alloy particles, but Auger data from such samples would be hard to interpret properly.

The effects of ordering might also be successfully studied. It may be useful to observe the Auger intensities at temperatures above and below the critical temperature of an alloy known to undergo a bulk order-disorder transition. This could be extended to order-order and even solid-liquid phase transitions. It might also be interesting to study a series of very similar ordered alloys which maintain long range order. For instance, the δ phase Au-Sn alloy discussed above could be compared with PtSn, NiAs and other structurally isotypic compounds to determine for which ones the ordering is dominant in

inhibiting surface segregation. The effect of ordering upon surface segregation is also generally lacking a good theoretical framework.

This points to another possible means of understanding alloys. If enough reliable data is accumulated it may be possible to separate out a series of alloys in which one particular property, such as the heat of sublimation, of one of the components varies widely while other important properties remain nearly constant. This would of course permit speculation about the significance of the particular property. Not only the type of components but also the concentration can be varied in a series. This sort of empiricism requires identification of all physical properties expected to be important in determining the nature of the surface segregation.

Still more experiments may be done to study how the presence of impurities on the alloy surface may alter the surface composition. This may yield information about the surface site competition and about chemisorptive induced segregation. This problem is complicated experimentally by the attenuation of Auger electrons caused by the impurity.

The other direction toward which future work may be expected to move is that of striving to make AES more quantitative. To improve the techniques of AES a number of suggestions can be made. Of first importance is to perform experiments to test and measure the effects of backscattering. Smith and Gallon⁹⁷ have shown how to measure backscattering coefficients from solids. It would be interesting to measure the backscattering coefficients, r , for the pure solids and

the alloys of binary systems for which the surface compositions have been determined by Auger. The conclusions of those studies could be judged in view of the new backscattering information. The value of r should be measured as a function of the energy of the primary beam and for Auger transitions of various energies. In addition, these measurements can be made for alloys of various compositions. The effects of backscattering can also be tested more simply by careful measurements of ξ_E as a function of the primary energy. Any change in ξ_E with E_p is indicative of either a change in (r/r^0) or of a matrix effect in which the energy dependence of the ionization cross section is different for an alloy than for a solid.

Other problems which complicate the use of Auger to determine the surface composition of alloys is that of possible matrix effects. In the analysis here, these effects have been assumed to be absent, but in fact this assumption should be checked. The effect of alloying upon the ionization cross sections, Auger probability and escape depths should somehow be measured. The problem is that making such measurements will undoubtedly be very difficult, especially that of measuring any composition dependence of the escape depth. This is due basically to the fact that the Auger intensities carry too much information and it is practically impossible to uncouple it all.

One of the principle difficulties of doing quantitative AES is that there are no good standards. In view of this, one approach to improving the technique is to continually search for specimens which may serve as standards. For example, if it is possible to grow a very

thin film known to be continuous and of uniform thickness, then it is possible to measure escape depths of Auger electrons emitted from the substrate and the film. This method has in fact been exploited.⁴⁸ Such films may also be used to study the effects of backscattering and possibly other important parameters entering into the Auger intensity expression. Other surface morphologies such as vaporized grids, uniform sandwiches, controlled roughness, cleaved single crystals exhibiting layers of alternating composition such as GaAs(111), etc. may possibly be used as standards to study the various factors involved in the Auger intensities.

Another approach that may be useful in elucidating the alloy problem is to use complementary information from a second technique such as ion scattering spectroscopy (ISS). These two techniques (ISS and AES) have a different set of difficulties, so the use of both techniques simultaneously may yield information by supplementing weaknesses of one technique with the capabilities of the other.

APPENDIX

The computer was used frequently as an aid in interpreting the Auger data. Variations on two basic programs were used in these studies. The first program, REGSOL, was used to calculate theoretical surface compositions for alloys which obey the regular solution model. The second program, AUGINT, was used to calculate the expected Auger intensities from a hypothetical surface configuration.

The program REGSOL is shown below for the case of Au-Ag alloys. The surface monolayer compositions predicted by the ideal solution monolayer model (XIM) and the regular solution monolayer model (XRM) are calculated as a function of bulk composition (XBULK). The compositions in each of the top four layer (XW1, XW2, XW3 and XW4) as predicted by William's³ four-layer regular solution model are also given. The program uses a form of Newton's method to find the roots. The output for a particular temperature (700°K) is provided along with the program.

The program AUGINT as applied to Au-Sn alloys is shown below along with some of the output. The program is shown for the calculation of nine possible normalized Auger intensity ratios, ξ_E and $R/R^\circ_{E/E'}$ (denoted by XC(E) and E/E' respectively in the output) for the energies $E = 71, 241, 2024$ and 431 eV. The intensities are calculated assuming that the first layer compositions X1 are the same as the bulk composition. The crystal parameters which include the atomic density, RHO, and the interlayer spacing, D, are specified

for each of the δ , ζ , pure Au and pure Sn phases. The program repeats the calculation for various values of the escape lengths, LAMBDA.

Many forms of AUGINT were used depending upon the particular calculations desired. By altering the input format or various lines in the program, surface monolayer compositions, escape lengths, crystal parameters or bulk compositions could be altered so that the calculated intensity ratios could be visually compared with the experimental data. Backscattering or multilayer effects could also be included by altering the second line of the program.

REGSOL

```

      PROGRAM REGSOL(INPUT,OUTPUT,TAPE6=OUTPUT)
      REAL XI(100),XR(100), XDB(100),XW(4,100)
      SUR(AA)=F+ALOG(G*AA/(1.-AA))
      DIF1(A1,A2)= E+SUR(A1)-CD*A1-CC*A2
      DIF2(A1,A2,A3)=SUR(A2)-CC*A1-CD*A2-CC*A3
      DIF3(A2,A3,A4)= SUR(A3)-CC*A2-CD*A3-CC*A4
      DIF4(A3,A4)= SUR(A4)+FE-CC*A3-CD*A4
      DIFP(AAA)=1./AAA+1./(1.-AAA)-CD
      READ 300,WORD1,WORD2,AREA
120    READ 301,OMEGA
126    READ 202,ZL,ZV,Z,EL,EV
      300  FORMAT(A5,2X,A3,2X,E11.3)
      301  FORMAT(F5.0)
      202  FORMAT(2X,F2.0,2X,F2.0,2X,F3.0,2X,F2.1,2X,F3.2)
144    R=1.9872
145    T=300
147    303  SIG1=2000.-.46*T
152    SIG2=1720.-.48*T
154    DELSIG=(SIG1-SIG2)*AREA*(1./4.18*10.**(-7))
164    WRITE(6,111) WORD1,WORD2
      111  FORMAT(//////,14HFOR THE SYSTEM,A3,1H-,A3)
173    WRITE(6,110) WORD1,SIG1
203    WRITE(6,110) WORD2,SIG2
      110  FORMAT(16HSURFACE TENSION OF,2X,A3,1H=,F5.0,2X,8HJOYNES/CM)
213    WRITE(6,116) AREA
      116  FORMAT(13HSURFACE AREA=,E11.3,1X,10HCM*CM/MOLE)
221    WRITE(6,112) OMEGA,T
      112  FORMAT(34HREGULAR SOLUTION PARAMETER, OMEGA=,F6.0,
11X,8HCAL/MOLE,/,12HTEMPERATURE=,F5.0)
231    WRITE(6,117) Z,ZV,ZL
      117  FORMAT(25HSTRUCTURAL PARAMETERS ARE,/,10X,2HZ=,2X,F2.0,/,
110X,12HZ VERTICLE =,2X,F2.0,/,10X,9HZ LAYER =,2X,F2.0,/)
243    WRITE(6,113) WORD2
      113  FORMAT(2HX=,A3,/)
251    WRITE(6,114)
      114  FORMAT(8HXBULK=,7X,4HXIM=,6X,4HXRM=,6X,4HXX1=,6X,4HXX2=,6X,
14HXX3=,6X,4HXX4=,6X,2HN=)
      C  THIS PART CALCULATES THE IDEAL FIRST LAYER CONCENTRATION
255    DO 10 K=1,49
260    XB=.02*K
261    XDB(K)=XB
263    EI=(XB/(1.-XB))*EXP(DELSIG/(R*T))
274    XI(K)= EI/(1.+EI)
      C  THIS PART CALCULATES THE MONOLAYER REGULAR SOLUTION SURFACE CONCEN.
276    XR(K)= XI(K)
277    6  X1=XR(K)
301    ER1= EXP(OMEGA*(EV+EL)*((1.-XB)**2-XB**2)/(R*T))*EXP(OMEGA*EL*(
1X1**2-(1.-X1)**2)/(R*T))
327    FXR=X1/(1.-X1)-CR1*EI
331    DFXR=1./((1.-X1)**2)-(2.*OMEGA*EL/(R*T))*EI*ER1
341    XR(K)=X1-FXR/DFXR
345    IF(ABS(XR(K)-X1).GT..001) GO TO 6
      C  THIS PART COMPUTES THE WILLIAMS DEPTH DISTRIBUTION
355    CC=2.*OMEGA*EV/(R*T)
357    CD=2.*OMEGA*EL/(R*T)
361    E=-DELSIG/(R*T)-.5*CC

```

REGSCL

```

364      EE=-CC*XB
366      F=XB*(CD+2.*CC)
370      G=(1.-XB)/XB
372      X1=XB
373      X2=XB
374      X3=XB
374      X4=XB
375      N=0
377      30  N=N+1
401      XW(1,K)= X1-DIF1(X1,X2)/DIFP(X1)
413      XW(2,K)= X2-DIF2(XW(1,K),X2,X3)/DIFP(X2)
430      XW(3,K)= X3-DIF3(XW(2,K),X3,X4)/DIFP(X3)
445      XW(4,K)= X4-DIF4(XW(3,K),X4)/DIFP(X4)
460      DO 34 J=1,4
462      IF(XW(J,K)-1) 32,31,31
467      31  XW(J,K)=.9999
473      32  IF(XW(J,K)) 33,33,34
477      33  XW(J,K)=.0001
503      34  CONTINUE
505      ER1=DIF1(XW(1,K),XW(2,K))
513      ER2=DIF2(XW(1,K),XW(2,K),XW(3,K))
523      ER3=DIF3(XW(2,K),XW(3,K),XW(4,K))
533      ER4=DIF4(XW(3,K),XW(4,K))
542      ERRT=ABS(ER1)+ABS(ER2)+ABS(ER3)+ABS(ER4)
551      IF(ERRT.LT..01) GO TO 35
554      IF(N.GT.20) GO TO 35
565      X1=XW(1,K)
565      X2=XW(2,K)
566      X3=XW(3,K)
567      X4=XW(4,K)
571      GO TO 30
571      35  WRITE(6,115) XDB(K),X1(K),XR(K),XW(1,K),XW(2,K),XW(3,K),XW(4,K),N
115      FORMAT(F5.3,7X,F5.3,5X,F5.3,5X,F5.3,5X,F5.3,5X,F5.3,5X,F5.3,5X,13)
626      10  CONTINUE
630      T=T+100
632      IF(T.LT.1100) GO TO 303
635      END

```


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FOR THE SYSTEM AU- AG

SURFACE TENSION OF AU= 1678 DYNES/CM

SURFACE TENSION OF AG= 1392 DYNES/CM

SURFACE AREA= 4.400E+08 CM*CM/MOLE

EQUILAR SOLUTION PARAMETER, OMEGA= -4200 CAL/MOLE

TEMPERATURE= 700

STRUCTURAL PARAMETERS ARE

Z= 12

Z VERTICLE = 3

Z LAYER = 6

X= AG

XBULK=	XIM=	XPM=	XW1=	XW2=	XW3=	XW4=	N=
.020	.151	.069	.069	.019	.020	.020	3
.040	.256	.123	.124	.036	.040	.040	3
.060	.357	.170	.171	.052	.061	.060	3
.080	.451	.212	.214	.068	.081	.080	3
.100	.492	.251	.254	.084	.102	.100	3
.120	.543	.287	.291	.100	.122	.120	3
.140	.585	.322	.327	.116	.143	.140	3
.160	.624	.355	.361	.132	.164	.160	3
.180	.657	.387	.394	.148	.185	.179	3
.200	.685	.418	.425	.164	.206	.199	3
.220	.711	.447	.455	.181	.227	.219	3
.240	.733	.475	.485	.197	.248	.239	3
.260	.754	.504	.514	.214	.269	.258	3
.280	.772	.532	.542	.230	.290	.278	3
.300	.789	.556	.569	.248	.311	.298	3
.320	.804	.584	.595	.265	.331	.318	2
.340	.818	.610	.621	.283	.352	.338	2
.360	.830	.634	.645	.301	.373	.357	2
.380	.842	.656	.670	.319	.395	.377	2
.400	.853	.681	.693	.337	.417	.397	2
.420	.863	.704	.715	.355	.439	.417	2
.440	.872	.725	.737	.375	.455	.437	2
.460	.881	.745	.758	.394	.475	.457	2
.480	.889	.767	.778	.413	.495	.477	2
.500	.897	.786	.797	.433	.515	.497	2
.520	.904	.805	.815	.453	.535	.517	2
.540	.911	.822	.832	.474	.555	.537	3
.560	.917	.839	.849	.495	.575	.557	3
.580	.925	.855	.865	.516	.594	.577	3
.600	.929	.875	.876	.538	.614	.597	3
.620	.934	.885	.892	.560	.633	.617	4
.640	.939	.898	.904	.582	.652	.637	4
.660	.944	.910	.916	.605	.672	.658	4
.680	.949	.921	.925	.628	.691	.676	7
.700	.953	.932	.936	.651	.710	.696	7
.720	.957	.941	.945	.675	.729	.718	7
.740	.961	.950	.952	.698	.748	.739	7
.760	.965	.957	.960	.722	.767	.759	7
.780	.969	.964	.966	.746	.786	.779	7
.800	.972	.970	.972	.771	.805	.799	7
.820	.975	.976	.977	.794	.824	.819	7
.840	.979	.980	.981	.818	.843	.840	7
.860	.982	.984	.985	.842	.862	.860	7
.880	.985	.985	.988	.866	.882	.880	6
.900	.987	.991	.991	.890	.901	.900	6
.920	.990	.993	.994	.913	.921	.920	6
.940	.993	.996	.996	.936	.940	.940	6
.960	.995	.998	.997	.958	.960	.960	6
.980	.998	1.000	.999	.979	.980	.980	6

AUGINT

```

PROGRAM AUGINT(INPUT,OUTPUT)
REAL FLAM(4),RHO(4),XCD(4),XCZ(4),R(4,4),XCI(4)
F1(D1,D2,E)=RH*(1.-EXP(-D1/(E*.743)))*(X1+X2*EXP(-DZ/(E*.743)))/
1 (1.-EXP(-DZ/(E*.743)))
READ 101,(RHO(I),I=1,4)
37 READ 101,DAU,DSN,DD,DZ
53 9 READ 103,(ELAM(I),I=1,4)
61 IF(FLAM(1).EQ.0) GO TO 8
100 FORMAT(F6.3,2X,F6.3,2X,F6.3,2X,F6.3)
101 FORMAT(F8.4,2X,F8.4,2X,F8.4,2X,F8.4)
62 PRINT 201,RHO(1),DAU,RHO(2),DSN,RHO(3),DD,RHO(4),DZ
201 FORMAT(////,7HR4D AU=,F6.5,10X,5HDAU =,F6.4,/,7HR4D SN=,
1 F6.5,10X,5HDSN =,F5.4,/,10HR4D DELTA=,F6.5,7X,7HDELTA=,
2 F6.4,/,9HR4D ZETA=,F6.5,9X,6HZETA=,F6.4)
112 PRINT 203,(ELAM(I),I=1,4)
203 FORMAT(11HLAMBDA 71=,F6.1,/,11HLAMBDA 241=,F5.1,/,
112HLAMBDA 2024=,F4.1,/,11HLAMBDA 431=,F6.1)
120 PRINT 202
202 FORMAT(///,2X,2HXB,9X,5HXC(71),5X,7HXC(241),4X,8HXC(2024),
15X,7HXC(431),6X,6H71/431,5X,7H241/431,4X,8H2024/431,6X,6H71/241,
25X,7H71/2024)
124 X1=.5
125 X2=.5
126 RH=RHO(3)/RHO(1)
131 DO 1 I=1,3
132 1 XCD(I)=F1(DAU,DD,ELAM(I))
143 RH=RHO(3)/RHO(2)
145 XCD(4)=F1(DSN,DD,ELAM(4))
153 X1=.837
154 X2=.837
154 RH=RHO(4)/RHO(1)
157 DO 2 I=1,3
160 2 XCZ(I)=F1(DAU,DZ,ELAM(I))
171 X1=.163
172 X2=.163
173 RH=RHO(4)/RHO(2)
176 XCZ(4)=F1(DSN,DZ,ELAM(4))
204 DO 3 K=1,7
205 XA=.5+.05*(K-1)
211 DO 4 I=1,4
224 4 XCI(I)=(.837-XB)/.337*XCD(I)+(XB-.5)/.337*XCZ(I)
231 DO 5 I=1,3
236 5 R(I,4)=XCI(I)/XCI(4)
241 R(1,2)=XCI(1)/XCI(2)
242 R(1,3)=XCI(1)/XCI(3)
245 PRINT 200,XB,(XCI(I),I=1,4),(R(I,4),I=1,3),R(1,2),R(1,3)
200 FORMAT(F6.3,9F12.3)
264 3 CONTINUE
266 XB=.867
267 X1=.867
270 X2=.867
271 RH=RHO(4)/RHO(1)
274 DO 5 I=1,3
275 6 XCI(I)=F1(DAU,DZ,ELAM(I))
306 X1=.133
307 X2=.133
AUGINT
310 RH=RHO(4)/RHO(2)
313 XCI(4)=F1(DSN,DZ,ELAM(4))
321 DO 7 I=1,3
326 7 R(I,4)=XCI(I)/XCI(4)
331 R(1,2)=XCI(1)/XCI(2)
332 R(1,3)=XCI(1)/XCI(3)
335 PRINT 200,XB,(XCI(I),I=1,4),(R(I,4),I=1,3),R(1,2),R(1,3)
354 GO TO 9
355 8 STOP
357 END

```

HO AU=.13930
 HO SN=.10820
 HO DELTA=.09710
 HO ZETA=.13540
 LAMBDA 71= 4.0
 LAMBDA 241= 8.0
 LAMBDA 2024=30.0
 LAMBDA 431= 8.0

DAJ =2.3540
 DSN =2.9098
 DDELTA=2.1570
 DZETA=2.3800

XB	XC(71)	XC(241)	XC(2024)	XC(431)	71/431	241/431	2024/431	71/241	71/2024
.500	.370	.375	.380	.571	.649	.658	.665	.987	.976
.550	.435	.440	.443	.522	.835	.843	.849	.991	.983
.500	.501	.504	.506	.472	1.060	1.066	1.072	.994	.989
.650	.566	.568	.570	.423	1.337	1.342	1.346	.996	.993
.700	.631	.632	.633	.374	1.687	1.690	1.693	.998	.997
.750	.696	.696	.697	.325	2.143	2.144	2.144	1.000	.999
.800	.761	.761	.760	.276	2.761	2.759	2.757	1.001	1.002
.867	.838	.837	.836	.195	4.294	4.287	4.281	1.002	1.003

HO AU=.13900
 HO SN=.10820
 HO DELTA=.09710
 HO ZETA=.13540
 LAMBDA 71= 4.0
 LAMBDA 241= 8.0
 LAMBDA 2024=30.0
 LAMBDA 431= 10.0

DAU =2.3540
 DSN =2.9098
 DDELTA=2.1570
 DZETA=2.3800

XB	XC(71)	XC(241)	XC(2024)	XC(431)	71/431	241/431	2024/431	71/241	71/2024
.500	.370	.375	.380	.577	.642	.650	.658	.987	.976
.550	.435	.440	.443	.527	.826	.834	.840	.991	.983
.500	.501	.504	.506	.477	1.049	1.055	1.061	.994	.989
.650	.566	.568	.570	.428	1.323	1.328	1.333	.996	.993
.700	.631	.632	.633	.378	1.670	1.674	1.676	.998	.997
.750	.696	.696	.697	.328	2.123	2.124	2.124	1.000	.999
.800	.761	.761	.760	.278	2.738	2.735	2.733	1.001	1.002
.867	.838	.837	.836	.197	4.261	4.254	4.248	1.002	1.003

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