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AUGER ELECTRON SPECTROSCOPY STUDY OF THE SURFACE COMPOSITION OF THE LEAD-INDIUM SYSTEM

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Abstract

The Auger spectra of lead-indium alloys (4.53, 9.08, 28.63, 44.62 and 60.49 atom% lead) and of pure lead and indium were monitored in the liquid and solid states. The relative intensities of the lead 92 eV and the indium 403 eV Auger peaks were used to determine the surface composition. The peak intensity ratio proved to be a sensitive detector of the change of surface composition with respect to temperature and bulk composition. The surface layers of the alloys were richer in lead than the bulk, and the surface composition exhibits a temperature dependence similar to that predicted by the ideal monolayer model. However, the surface lead excess was smaller and the temperature dependence of the surface composition weaker than predicted. This can best be explained by the presence of a concentration gradient extending over one or more atomic layers between the bulk and the surface layer. Oxygen decreased while carbon increased the surface excess lead concentration. Ion bombardment at 300°K caused appreciable solid state diffusion. This effect was considerably reduced by lowering the temperature to 78°K;however, selective removal of Pb then took place. Auger electron spectroscopy, when coupled with suitable calibration of the peak intensities, should be an excellent technique to study the surface thermodynamics of multicomponent systems.

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Introduction

The application of surface thermodynamic principles to multi-component systems readily shows that, in equilibrium, the surface composition may be markedly different from the bulk composition. Assuming that the surface consists of only the topmost atomic layer[1] (monolayer model), the surface composition of an ideal binary solution is related to the bulk composition according to the equation[2]

$$x_1^s/x_2^s = (x_1^b/x_2^b)\exp\,(\gamma_2 - \gamma_1)a/kT \qquad (1)$$

where x_1^s, x_2^s and x_1^b, x_2^b are the surface and bulk atom fractions, respectively, for the two constituents 1 and 2, γ_1 and γ_2 are the surface tensions of the pure components, a is the average surface area occupied per atom, and the other symbols have their usual meanings. According to Equation 1, the component that has the smaller surface tension will accumulate on the surface. The exponential dependence of the surface atom fraction ratio on the surface tension difference ensures that, if this model has any validity, the surface composition will always be quite different from the bulk composition. The surface tensions of most liquid metals are in the range 0.5 to 1.2 Nm^{-1}. Assuming a surface tension difference as small as 0.05 Nm^{-1} one obtains(at 1000°K and a mean surface area of 10^{-19} m^2 per atom) $x_1^s/x_2^s = (x_1^b/x_2^b)\cdot 1.44$, a considerable surface excess of component 1, which was assumed to have the lower surface tension. However, for most real systems, it is more reasonable to expect a concentration gradient between the surface

monolayer that is enriched in one of the constituents of a binary system and the bulk phase. This gradient may extend over several atomic layers.[3]

Auger electron spectroscopy (AES) provides a means to measure directly the surface composition by experiment. This nondestructive technique detects the Auger electrons emitted from atoms of the condensed phase (liquid or solid). As long as low energy Auger peaks are studied, the Auger electrons detected are emitted primarily by the atoms of the topmost atomic layer. It has been shown[4] that the Auger peak heights are proportional to the concentrations of the corresponding atomic species. Auger spectroscopy thus offers a means to analyze this layer with respect to all its constituents.

The purpose of this work was to determine the surface composition of a binary system that is fairly ideal (i.e., shows complete miscibility and has a low heat of mixing) as a function of bulk composition, temperature and surface contaminants. In this type of work, it is of course imperative that equilibrium be established between the surface and the bulk. Since this is often difficult to achieve in the solid state, it was decided to work with liquid samples. The lead-indium system melts at a low temperature and has vapor pressures that are negligibly low below 800K. The surface composition can thus be monitored by AES in ultra-high vacuum.

Selected Properties of the Lead-Indium System

The phase diagram[5] of the Pb-In system is shown in Figure 1. In the liquid state, there is complete miscibility and ideal behavior, except near

the indium-rich end of the diagram. The vapor pressure of lead is less than 10^{-8} torr at its melting point (600°K), that of indium less than 10^{-11} torr at its melting point (425°K).[6] A great deal of surface tension data is available both on the pure liquid metals and on the binary system. The most reliable determination of the surface tensions of the pure metals appears to be that by Lazarev,[7] who obtained

$$\gamma_{In}(Nm^{-1}) = 0.5592 - 8.9(t-t_f)\cdot 10^{-5}$$

$$\gamma_{Pb}(Nm^{-1}) = 0.4603 - 12(t-t_f)\cdot 10^{-5}$$

The experimental results of Pokrovski et al.[8] agree well with those of Lazarev. The surface tension of the pure components as well as that of various Pb-In alloys has been measured by Hoar and Melford.[9] Using the surface tensions of Lazarev and the monolayer model, we have calculated the surface indium atom fraction as a function of the bulk atom fraction at 773°K. The results are displayed in Figure 2. The straight line indicates the bulk composition. The surface indium atom fraction is markedly lower than in the bulk. (In evaluating the surface atom fractions, we have estimated the atomic areas from the known densities, using the formula $a = 1.09V^{2/3}N^{-2/3}$, where V is the molar volume and N is Avogadro's number. The average value for the Pb-In system is 1.0×10^{-19} m^2.)

In Table I, the surface to bulk atom fraction ratio $(x^s_{Pb}/x^s_{In})/(x^b_{Pb}/x^b_{In})$ is given at various temperatures. It can be seen that the predicted enrichment of lead is very large. The surface atom fraction ratio is

50 times the bulk value at 773°K and increases with decreasing temperature. The values of Table I can be directly compared with those obtained in our experimental work and discussed below.

Experimental

A. Apparatus

The Auger electron spectroscopy studies were carried out in a 15 liter stainless steel vacuum chamber pumped by means of a water-cooled titanium sublimation pump and a 6-in. oil diffusion pump filled with silicon fluid (Dow-Corning 704). The system was protected against pump vapor backflow by an efficient liquid-N_2 cooled trap. After bakeout at 200°C, the ambient pressure in the vacuum chamber was of the order of 10^{-9} torr. The chamber was separated from the diffusion pump by a gate valve. The pressure was measured by an ionization gauge. A leak valve permitted the admission of gases at low pressures in a controlled manner. There was also an ion bombardment gun for sputter cleaning the sample surface.

The samples were supported against gravity by a tantalum spoon mounted on a manipulator equipped with linear and rotary motion controls and with a liquid-N_2 cooling system. The spoon was indirectly heated by means of a tungsten filament mounted just below it, the power being supplied by a SCR controller that provided highly filtered DC current. The sample temperature was monitored by a chromel-alumel thermocouple spot-welded to the spoon; the constancy and reproducibility were better than 1°.

The electron optics were of the four grid retarding potential LEED

type. Additional screening was provided to prevent stray electron pickup. The first and fourth grids were grounded, the second and third being strapped together and swept with a ramp voltage. The sweep voltage was modulated with a 450 Hz 4V amplitude AC signal. The collector plate was held at +90V, being connected to a battery through a 2 megohm resistor. The AC Auger signal was detected by means of a PAR HR-8 lock-in amplifier connected across the latter. To reduce the noise level, the preamplifier plug-in module was removed from the amplifier and mounted on the optics flange. The working principles and the electronics of the retarding field energy analyzer in AES have been described in detail elsewhere.[4]

The second derivative technique yields a d^2I/dV^2 vs. V plot, where I is the collector current at the retarding grid voltage V. The output was recorded on an X-Y recorder. To permit glancing angle electron bombardment of a horizontal sample surface, the whole chamber was tilted in such a way that the axis of the optics was 22° angle off vertical. The electron beam was provided by a CRT type electron gun (Superior electronics type 3WP) mounted in such a way as to give a bombardment angle of 11° with respect to the horizontal.

B. Samples and Sample Cleaning Procedures

The starting materials were lead metal and indium metal, both 99.999% purity from Cominco Products, Inc. Five alloy samples were prepared by melting weighed amounts of the two metals in a pyrex test tube. Since oxide layers were already present on the metals, no particular precautions

were taken to avoid oxidation, which was quite insignificant in all cases. After thorough mixing, the melt was poured onto a cold glass surface, producing a sample of silver-like appearance. The major contaminants as indicated by the Auger spectra were carbon and sulfur. In no case were silicon peaks observed, indicating that pump fluid contamination was negligible. With a new sample holder increased carbon and especially sulfur levels were obtained on heating to temperatures around 800°K indicating diffusion of these elements from the sample holder (tantalum) to the sample surface. However, after cleanup as described below, these effects were no longer observed, and contaminants present on the surface probably originated in the bulk of the sample (with the possible exception of some carbon formed by thermal cracking of ambient hydrocarbons at temperatures above 800°K).

Attempts were made to clean the sample by vaporization in vacuum. However, although at 973°K there was an appreciable rate of evaporation of the sample (as indicated by metal films formed on the viewing ports of the vacuum chamber) the carbon and sulfur concentrations at the surface remained constant or even increased. Ion bombardment was an efficient way to remove sulfur, indicating that this contaminant was confined to the surface by surface segregation. The ion bombardment was carried out *in situ* with 300V Ar ions (5-10 μA for 30 min or longer). Generally, most of the carbon also disappeared during ion bombardment, but, on melting the sample, the carbon peak reappeared due to diffusion from the bulk. Ion bombardment of the liquid sample gradually removed all the carbon, but

on melting the sample, the carbon peak reappeared due to diffusion from the bulk. Ion bombardment of the liquid sample gradually removed all the carbon, but this cleaning procedure was inconveniently slow. The most efficient sample cleaning procedure proved to be oxygen treatment. The standard procedure adopted was a 24-hour heat treatment in O_2 of pressure 2×10^{-7} torr at 773°K, which removed all, or almost all, of the carbon. If needed, raising the temperature or pressure would bring about a further reduction of the carbon concentration. Temperatures above 873°K were avoided, since vaporization of lead might change the sample composition. The efficiency of carbon removal was strongly dependent on the sample composition, samples high in lead being far more difficult to clean, possibly because lead oxide formation competed with carbon removal. (Judging from thermodynamic data, PbO is far more likely to form than In_2O_3.)

C. Measurement Technique

The sample was centered by shining a light beam along the central axis of the optics where the LEED gun would normally have been located, creating a light spot in the middle of the well-centered sample. The electron beam was centered by electrostatic focusing. This can be readily monitored since there is appreciable fluorescence of the sample on electron impact. A properly focused beam had a diameter of about 1 mm, but the glancing angle geometry made it difficult to keep all of the electrons in the beam on the sample. The beam sometimes had to be repositioned

because strong tantalum peaks from the sample holder appeared in the spectrum. It was found that the Auger signal amplitude was considerably increased by tilting the sample holder slightly toward the gun, then increasing the angle of incidence. Since the sample surface was curved because of the surface tension of the liquid, the angle varied somewhat, the average value being about 20°. The energy distribution spectra (dI/dV vs. V), as obtained by tuning the lock-in amplifier to the modulation frequency, ω, proved too indistinct for quantitative work. Instead, the differentiated spectra (d^2I/dV^2 vs. V) were obtained by tuning to the second harmonic, 2ω, using a frequency doubler for the reference frequency. The excitation voltage was 1200V at a total beam current of about 1 mA. The sweep range was 0 to 600 eV and the sweep speed was 50 V/min at a time constant of 1s. On a few occasions, high noise levels forced high time constants, the sweep speed being lowered in proportion. For each sample, Auger spectra were recorded over a range of temperatures from 298°K to 773°K.

Results

A. Auger Spectra

The spectra of the pure elements, lead and indium were first examined and are shown in Figures 3a and 3b. These studies were aimed at locating the strongest Auger peaks that could be readily monitored in the alloy systems rather than at a quantitative investigation of the complete spectra data. In the indium spectrum (Figure 3a) the most prominent peaks are

those involving excitations from the M_5 level, the $M_5N_1N_{4,5}$ (293 eV), the $M_5N_{2,3}N_{4,5}$ (340 eV) and the $M_5N_{4,5}N_{4,5}$ (403 eV).[10] The Auger spectrum of In was found to be independent of temperature and did not change upon solidification or on melting. In the Auger spectrum of liquid lead (Figure 3b), the only strong peak was at 92 eV, which can be associated with an NOO Auger transition. Thus, it was decided to monitor the peak-to-peak intensity of the lead 92 eV and the indium 403 eV transitions and to use changes in the intensity ratios to detect variation of alloy surface composition. The relative intensities of the Pb-92 eV and In-403 eV peaks for the pure liquid samples under similar experimental conditions was 2.5:1, which may be taken as a rough estimate of the factor to be used in comparing the intensity ratios with Pb:In atomic ratios.

In the Auger spectrum of solid lead, however, several Auger peaks appear in the region below 100 eV that are not present in the spectrum of molten lead. Just below the melting point (593°K) a broad peak appears in the 36-55 eV range and another peak at 72 eV, both several orders of magnitude stronger than the 92 eV peak, the only one present from liquid lead. At 473°K the 92 eV peak became strong again, about 1/2 of the intensity of a single broad peak in the 45-75 eV rang (the two Auger peaks previously present at higher temperatures having merged into one). While segregation of impurities upon solidification might seem a reasonable explanation to fit these data, no plausible combination of impurities will fit the observed Auger spectra. It is also unlikely that the same impurities that would cause the appearance of the extra features

in the Auger spectrum below the melting point would be entirely absent on the liquid lead surface or decreased in surface concentration as the temperature is lowered to 200°C or below. On the other hand, the calculated lead spectrum[10] contains several closely spaced peaks in the 36-52 eV, 58-65.5 eV and 70.5 eV ranges. Thus, it would seem likely that the change in the Auger spectrum reflects structural changes associated with the liquid-solid transition. This phenomenon requires further scrutiny that will be attempted in the future. These observations are surprising in view of the behavior of the In Auger spectrum which did not show changes upon melting or solidification.

The Auger spectra of five Pb-In alloys were then examined. These samples contained 4.53, 9.08, 28.63, 44.52, and 60.49 atom% lead. It should be mentioned that due to the experimental difficulties encountered with the sample with the lowest lead concentration, only the last four samples yielded useful and reliable data. A typical Auger spectrum of a liquid Pb-In alloy taken at 773°K (the 44.62 atom % lead sample) is shown in Figure 4. In addition to the prominent lead and indium Auger peaks, there is a peak due to carbon at 270 eV indicating that the surface was not yet fully cleaned. The set of peaks at 160-170 eV is due to the tantalum holder and the oxygen Auger peaks around 500 eV are caused by the oxide layer on the tantalum metal (on account of the oxygen treatment of the samples to remove carbon). The 9.80, 28.63 atom% lead and the 60.49 atom% lead samples yield Auger spectra very similar to that shown in Figure 4, but with different Pb:In Auger peak intensity ratios. It was more

difficult to remove the carbon from the 9.08 and 60.49 atom% lead alloy samples than from the others, and therefore the intensity data showed more scatter than in the case of the other two samples. The ratio of the peak-to-peak intensities of the lead 92 eV and In 403 eV Auger transitions as measured from the molten alloy samples at 773°K in vacuum is plotted as a function of the bulk lead:indium atom ratio in Figure 5 for the various alloy samples. The experimental points can be fitted to a straight line with a slope of 12.

Perhaps a more sensitive probe of the concentration changes in the surface phase is the measurement of the temperature dependence of the Auger peak intensities. In the bulk phase the composition remains unchanged as a function of temperature, for a given sample; in the surface phase, however, the composition should change as a function of temperature as indicated by Equation 1. Substituting the lead and indium surface tension values into Equation 1 and plotting the logarithm of the atom fraction ratio against the reciprocal temperature, log X^s_{Pb}/X^s_{In} vs. 1/T yields a straight line with positive slope of 965. We have plotted the logarithm of the Pb:In Auger peak intensity ratio as a function of the reciprocal temperature for the 28.63 atom% lead sample in Figure 6. The data fall on a straight line with a positive slope of 330. In Figure 7 the logarithm of the Pb:In Auger peak intensity ratio is plotted as a function of T^{-1} for the 44.62 atom% lead sample. For this sample, data were also taken in the presence of various partial pressures of CO and 2×10^{-7} torr oxygen. The experimental points follow straight lines with a positive slope of 300.

While the presence of CO has no affect on the lead:indium Auger peak intensity ratios, the presence of oxygen reduces the ratio appreciably. Traces of carbon, as indicated by the Auger spectra, had little affect on the Pb:In intensity ratio. However, the massive carbon contamination that was detectable in the 60.49 atom% lead sample markedly increased the lead concentration at the surface. The presence of carbon in this sample produced changes in the lead to indium intensity ratio of a factor of 2-5. Upon purging the sample of carbon by the oxygen heat treatment, the Pb:In ratio returned to its expected lower value.

The 4.53 atom% lead sample exhibited Auger spectrum changes very different from the samples richer in lead. No lead was detected on its surface above 493°K. Below 493°K the spectrum changed drastically, the previously featureless 0-100 eV region being filled with strongly temperature dependent structures resembling those that appeared just below the melting point of pure lead. The transition was very sharp as a function of temperature, and reproducible. There was no change in the visual appearance of the sample at this transition that was detected in the Auger spectra. As the temperature was lowered further the spectrum became simpler, exhibiting a broad peak at 80 eV. This spectrum remained unchanged until the melting point (433°K) was reached. Below the melting point the 80 eV peak shifted to a higher energy with decreasing temperature and reached 110 eV at 25°C, while a new peak appeared at 43 eV. The series of indium peaks that was observed on all of the samples remained at approximately constant intensities throughout the entire temperature range

(773-298°K) which indicates that the spectral changes did not originate in drastic surface composition changes.

B. Effect of Ion Bombardment on the Surface Composition

The effect of ion bombardment on the surface composition of alloy samples was studied at various temperatures. Our purpose was to establish a surface composition identical to the bulk composition and to use the Auger spectra of the ion bombarded samples as a reference to study subsequent variations of the surface composition. The 4.53 and 28.63 atom% samples were Ar ion bombarded (0.1 Am^{-1} at 300V) after being cooled to temperatures near the boiling point of liquid nitrogen (78°K) to minimize the possibility of surface composition changes by diffusion. For both samples, Auger spectra identical to that of pure In were obtained after 5-16 hours of bombardment. On heating the samples, the previously described structures reappeared in the Auger spectrum of the 4.53 atom% sample at around 393°K, while lead was detected on the surface of the 28.63 atom% sample only above the melting point. The same samples were also ion bombarded at room temperature. In this case, the features associated with lead in the Auger spectra of both samples were considerably more prominent than when the samples had merely been cooled from temperatures above the melting point. Thus, neither condition of ion bombardment yields a surface with a composition identical to that of the bulk.

Discussion

Unlike most previous work in this field, this is a study of the surface composition in equilibrium between bulk and surface. For this reason we focused our attention on liquid alloy surfaces, since it is expected that equilibration between bulk and surface occurs readily in the liquid phase, and far more so than in the solid state. This has been confirmed by our results. A complete quantitative interpretation of the Pb-In alloy Auger spectra in terms of surface concentrations would require knowledge of the ejection depth distribution of the detected Auger electrons. This implies data on the mean free paths of both the electrons of the incident beam and the Auger electrons and also on the cross sections of the Auger process for both elements and of all competing processes, all as a function of energy. However, theory has not yet reached a stage where this complex problem can be handled, and experimental data is not available. Thus, one has to depend on fairly rough estimates of the surface compositions using the Auger peak intensities. Judging from the inelastic damping of electrons in LEED studies, the lead 92 eV Auger electrons are likely to originate in the first two atomic layers of the surface, while the indium 403 eV Auger electrons would be expected to come from the first 4-6 layers. These values are applicable in a situation where the incident beam penetrates so deeply that the escape probabilities of the Auger electrons are the only factors that determine the escape depth distributions. This, however, is probably not the case in a glancing angle geometry like the one used in the present work. An indication that most of the In 403 eV

electrons are backscattered from the surface layer can be found in the relative peak heights of the three indium peaks. If these peaks originate at different depths, one might expect their intensities to change differently as more lead is added to the surface, replacing indium atoms that contribute more to a low than to a high energy peak. However, the relative peak heights have been found to be the same for all samples.

A rough value of the conversion factor to be used when calculating atomic ratios from intensity ratios can be obtained from the spectra of the pure metals. Under similar conditions, the intensity of the 92 eV lead peak was 2.5 times that of the 403 eV indium peak. Applying this to the slope of the straight line in Figure 5, the Pb:In ratio on the surface is found to be about five times that in the bulk. Even though the calibration is not very accurate, it is apparent that the surface is considerably richer in lead than the bulk but not as rich as expected from the mono-layer model (which indicates a factor of 50).

Further proof that the surface is enriched in lead comes from the temperature dependence of intensity ratios as shown in Figures 6 and 7. Since this temperature dependence is independent of calibration, it has more quantitative significance than the estimate of the absolute atomic ratio. There is a strong temperature dependence of the type expected from the monolayer model, the lead excess increasing with decreasing temperature. The slopes of the two curves are less steep than those predicted by the monolayer model. (When extrapolated to infinite temperature, where surface and bulk should have the same composition, the two straight

lines give intensity ratio to atomic ratio conversion factors of 2.8 and 4.5, respectively, in reasonable agreement with that previously obtained.)

What are the reasons for the discrepancies between the experimental values and the monolayer model? First of all, the surface as defined by Auger spectroscopy is not a monolayer but includes contributions from lower layers. Since these (in the monolayer approximation) are bulk material, both the lead excess and its temperature dependence will be less than predicted. In fact, if the bulk contribution to the Auger spectrum is too large, the temperature dependence of the intensity ratio will disappear. Unfortunately, there is no way to find the depth distribution of the excess lead in the "Auger surface" from available data, but any simple multilayer model (for example, one layer of lead concentration intermediate between surface and bulk) will more closely predict the experimental values. Also, the monolayer model is primarily concerned with activities rather than concentrations. A Gibbs law treatment of available surface tension data indicates that the total adsorbed lead is insufficient to form the almost complete lead monolayer required by the monolayer model. The surface phase would thus appear to be quite non-ideal.

The effect of oxygen in lowering the Pb:In ratio was striking. This observation can be readily explained since the vapor pressure of PbO is sufficiently high that the samples could be depleted of lead by selective vaporization. The effect of carbon in increasing the Pb:In ratio is equally marked. While traces of carbon that were detectable in many Auger spectra seem to have little effect, carbon peaks comparable to the In peak intensities had the effect of increasing the Pb:In ratio by a factor of 2-5. It appears that the strong Pb-C bond provides a driving force for bringing

more lead to the surface. The wetting angles of lead and indium on graphite at 400°C are $\theta_{Pb-C} = 138°$ and $\theta_{In-C} = 142°$. If the surface tension is replaced by an interfacial tension, the ideal monolayer model, the Pb:In atomic ratio would be increased by a factor of 1.2. The observed increase in the Pb:In Auger peak intensity ratio was much larger, however. The Pb-C interaction must be stronger then as indicated by the wetting angle.

It is apparent that gas molecules adsorbed on the surface or dissolved impurities that show partial segregation on the surface in certain temperature ranges, are additional components of the multi-component surface phase components that can drastically change the surface composition. It has been shown by Bouwman and Sachtler[13] that the surface of a gold-platinum alloy becomes enriched in platinum and the surface of a silver-palladium alloy becomes enriched in palladium in the presence of CO. The formation of the strong carbonyl bonds with platinum and palladium provides the driving force for the migration of these metal atoms to the surface and changes of the surface composition. The nickel-copper alloy system has been studied by many.[14,15,16,17]

Some of the researchers find the surface composition rich in nickel as expected from its lower surface tension, while others find the surface composition identical to the bulk composition. Christmann and Ertl[18] find the silver-palladium alloy system surface composition the same as the bulk composition, although the enrichment of the surface layer in silver would be expected. Some of the causes of the discrepancies between the various studies can be assigned to the absence of equilibration between the surface

and the bulk phases (solid and not liquids were used) or to the analysis of high energy Auger transitions to obtain the data that are only marginally sensitive to changes of surface composition having large bulk atom contributions. However, not all of the observations can be explained this way. The presence of an unwanted third component may stabilize the surface composition in a way very different from what is expected from the two-component systems. Minute amounts of carbon may enrich the surface of a silver-palladium alloy with palladium, thus counteracting the expected silver enrichment for the surface phase of the two-component system. The formation of a surface compound of well-defined stoichiometry which is the same as the stoichiometry in the bulk may also "fix" the surface composition and thus render any ideal solution model inapplicable.

We have hoped that ion bombardment at low temperatures will permit the determination of the bulk composition which can in turn be used as a reference to determine the change of concentration in the surface phase. However, we have found some experimental evidence for the selective removal of one component (lead) during low temperature sputtering. Although this technique may not be used with confidence for determining the bulk composition, the effect of selective sputtering is an interesting phenomenon itself, one that should be explored in the future. In the solid state, atomic diffusion to the surface was detected only near the melting point. However, diffusion would be induced by ion bombardment at considerably lower temperatures (25°C). This is not surprising since the ion energies used for sputtering (300 eV) are many times the activation energy of a

diffusion process. However, the fact that the surface had a composition further from that of the bulk after ion bombardment than before is somewhat unexpected. In short, our data indicate that results obtained from ion bombarded alloy surfaces should be treated with caution.

The 4.53 atom% Pb alloy sample behaved differently from the other four samples that were richer in lead. The lead disappeared from the surface at about 493°K altogether, for example. Although the differences are not easy to reconcile, it should be noted that the phase diagram of the lead-indium system, although it exhibits ideal behavior on the lead-rich side, becomes rather non-ideal on the indium-rich side. It may well be that the changes in the bulk phase diagram at this surface composition are the reasons for the strange variations of the surface composition as a function of temperature for this indium-rich sample.

It appears that Auger electron spectroscopy is an excellent technique to study surface equilibria of multi-component systems.[19] With improvements in the calibration procedures, Auger electron spectroscopy should become an important tool in surface thermodynamics. This field of surface thermodynamics although its great importance is well recognized, has not been developed as rapidly as many other fields of modern surface science. Auger electron spectroscopy should enable one to determine surface phase diagrams of multi-component systems to uncover new surface phases and compounds that exist only in the surface environment.

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Table I

Surface to bulk Pb-In atom fraction ratios as a function of temperature predicted by the monolayer model.

Temperature	0°C	200°C	300°C	400°C	500°C	600°C
$\frac{(X^s_{Pb}/X^s_{In})}{(X^b_{Pb}/X^b_{In})}$	9470	309	125	77	50	36

Figure Captions

Figure 1 Phase diagram of the Pb-In system.

Figure 2 Surface atom fraction of indium as a function of the bulk atom fraction at 773°K.

Figure 3 (a) The Auger spectrum of indium.

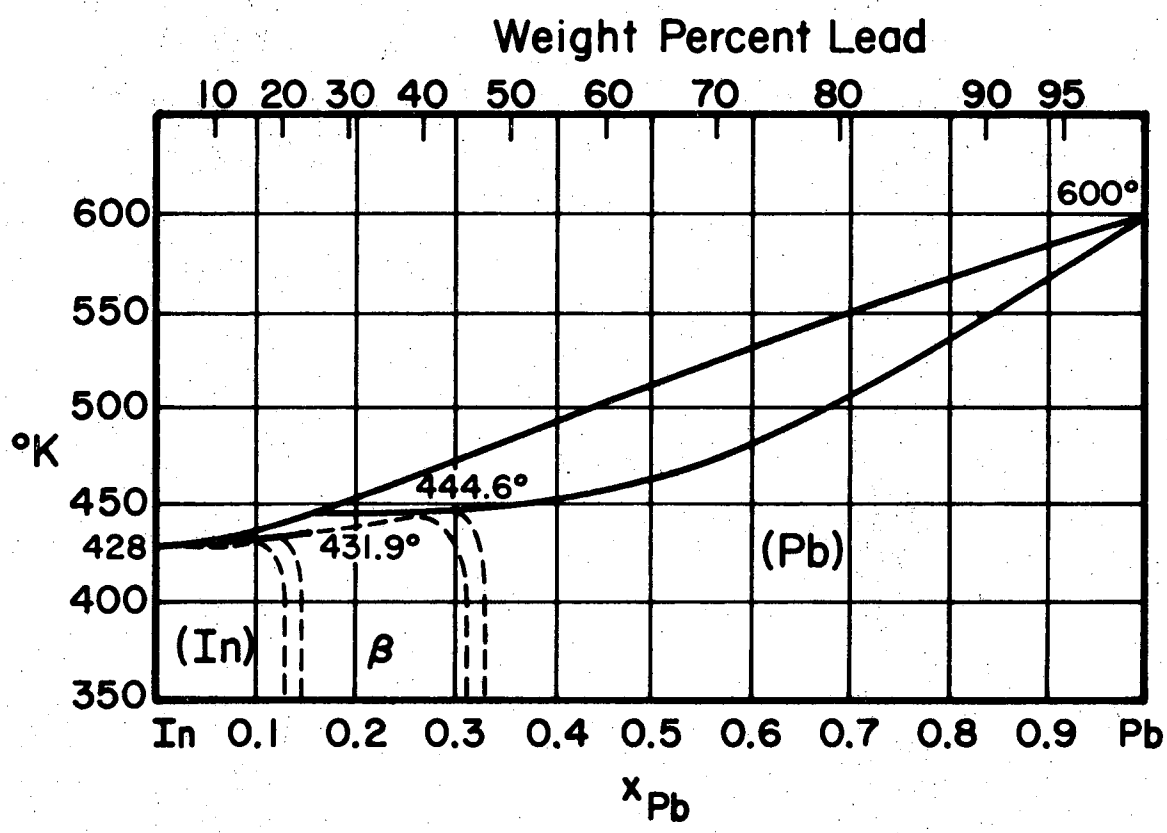
(b) The Auger spectra of molten lead.

Figure 4 Typical Auger spectrum of a molten Pb-In alloy taken at 500°C (44.62 atom % lead sample is shown).

Figure 5 The ratio of the Pb:In Auger peak intensities as a function of the bulk Pb:In atom ratio for the 28.63 atom % lead sample.

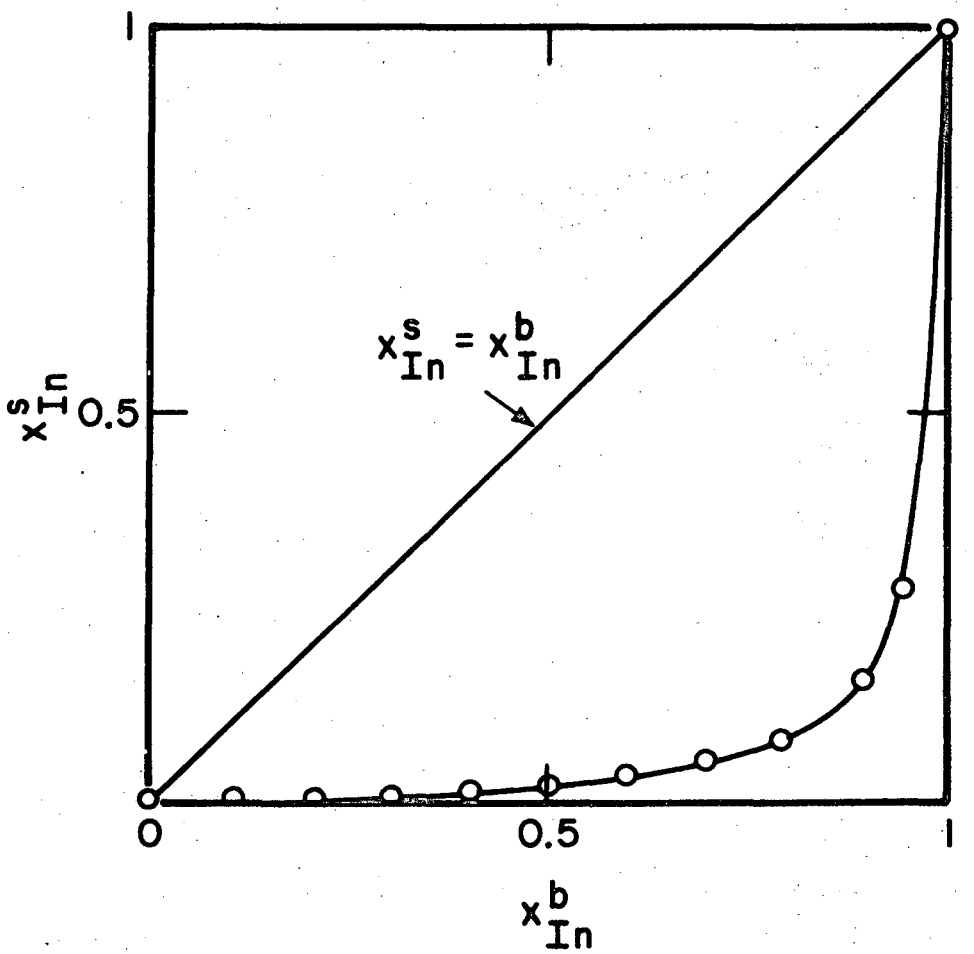
Figure 6 The logarithm of the Pb:In Auger peak intensity ratio as a function of the reciprocal temperature for the 28.63 atom % lead sample.

Figure 7 The logarithm of the Pb:In Auger peak intensity ratio as a function of the reciprocal temperature of the 44.62 atom % lead sample in the presence of (a) carbon monoxide and (b) oxygen. × — 3×10^{-9} torr CO; O — 2×10^{-7} torr CO; □ — 2×10^{-6} torr CO; + — 2×10^{-7} torr O_2.



XBL 737-6404

Fig. 1



XBL 737-6390

Fig. 2

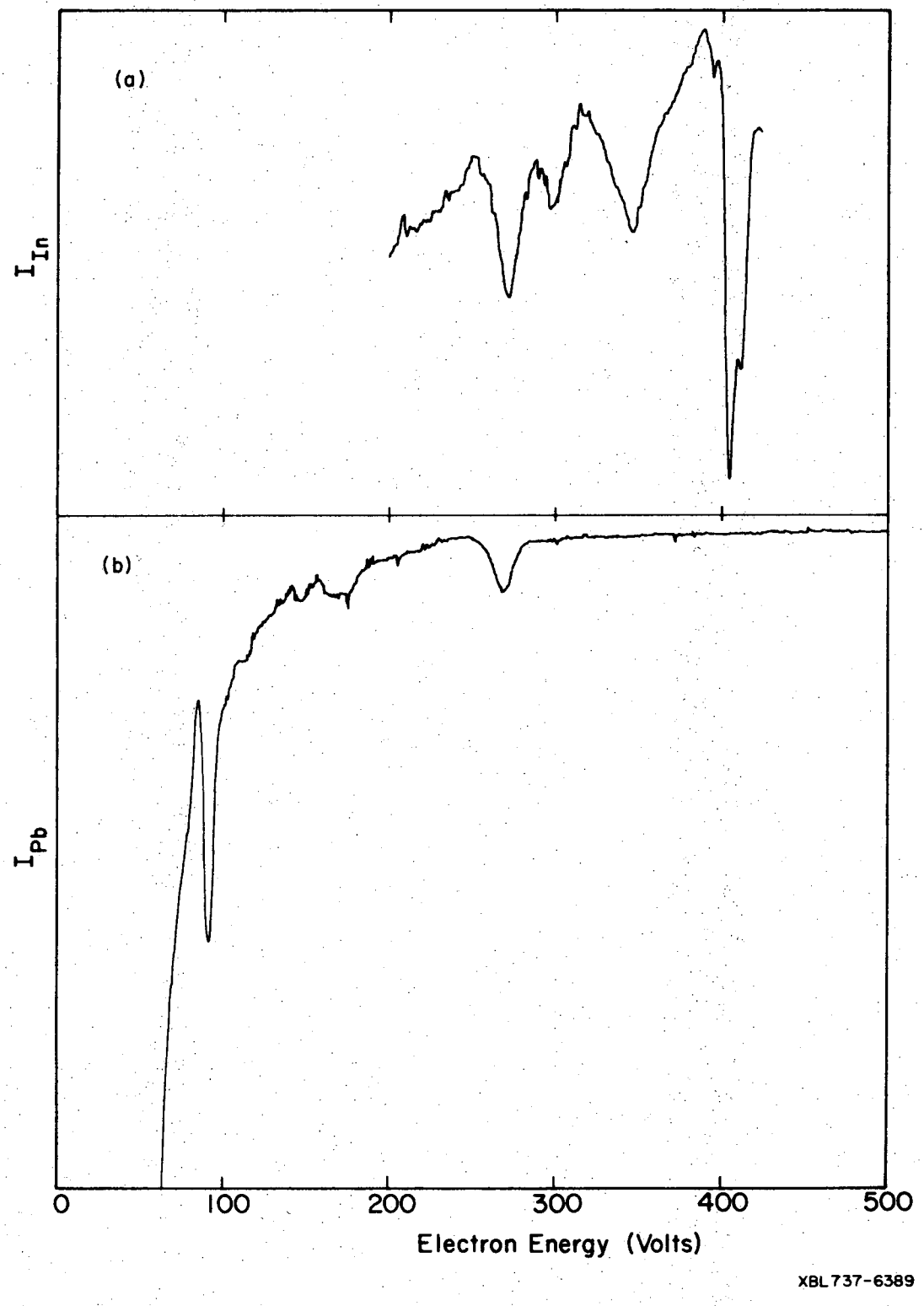

(a)
I_{In}
(b)
I_{Pb}
0
100
200
300
400
500
Electron Energy (Volts)
XBL 737-6389

Fig. 3

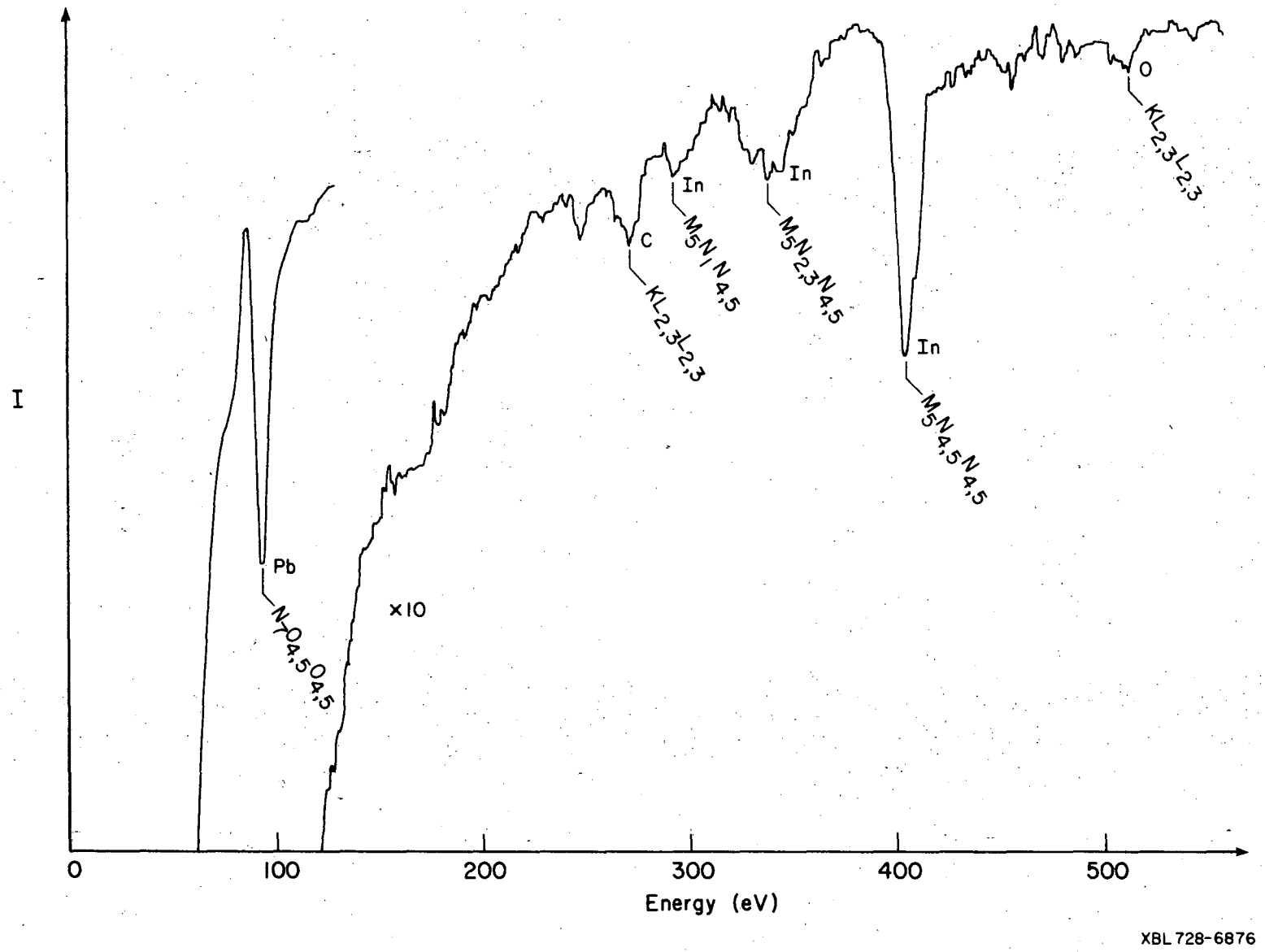
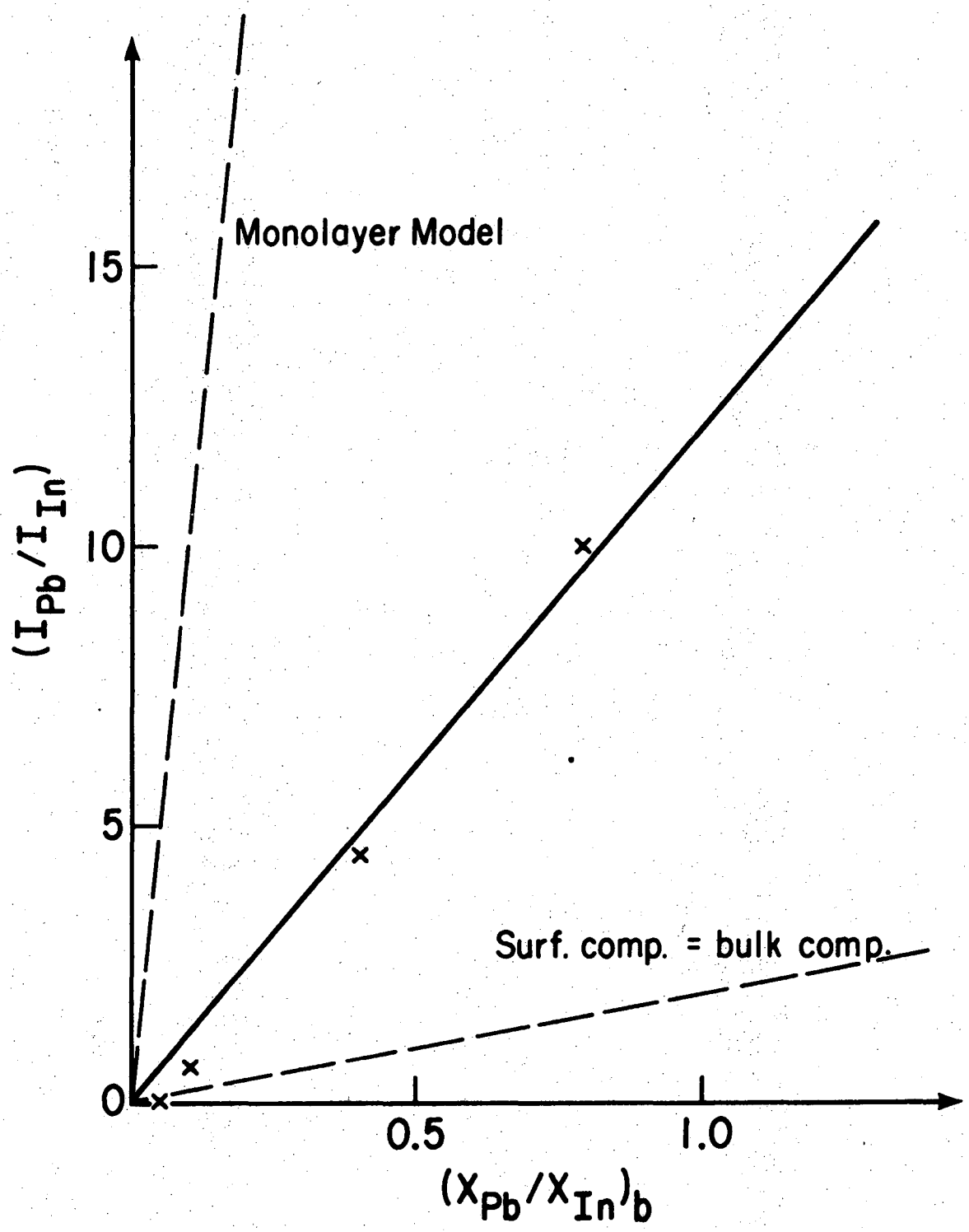

I
Pb
$N_{7}O_{4,5}O_{4,5}$
×10
C
$KL_{2,3}L_{2,3}$
In
$M_5N_{1}N_{4,5}$
In
$M_5N_{2,3}N_{4,5}$
In
$M_5N_{4,5}N_{4,5}$
O
$KL_{2,3}L_{2,3}$
0
100
200
300
400
500
Energy (eV)
XBL 728-6876

Fig. 4



XBL728-6874

Fig. 5

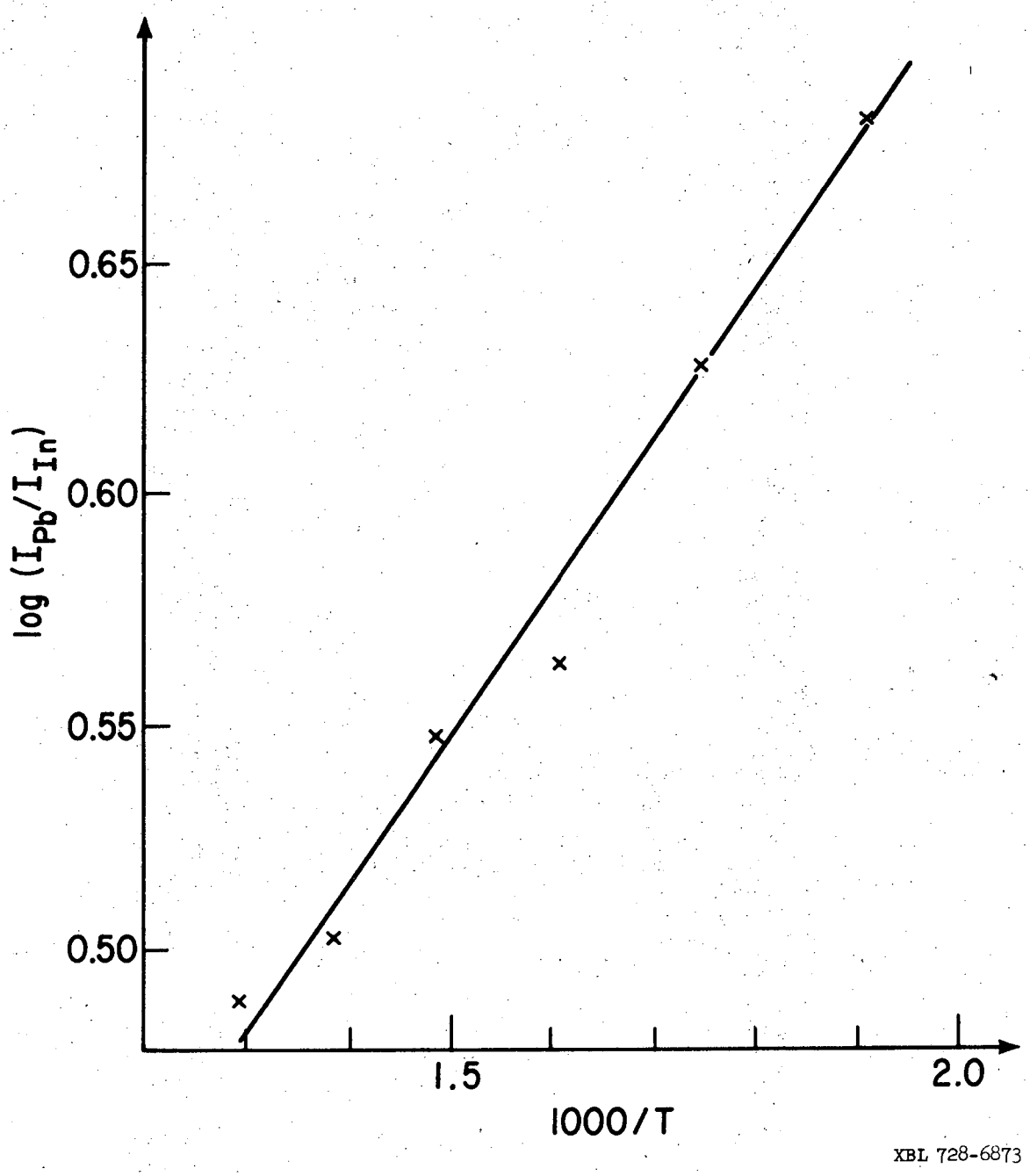


Fig. 6

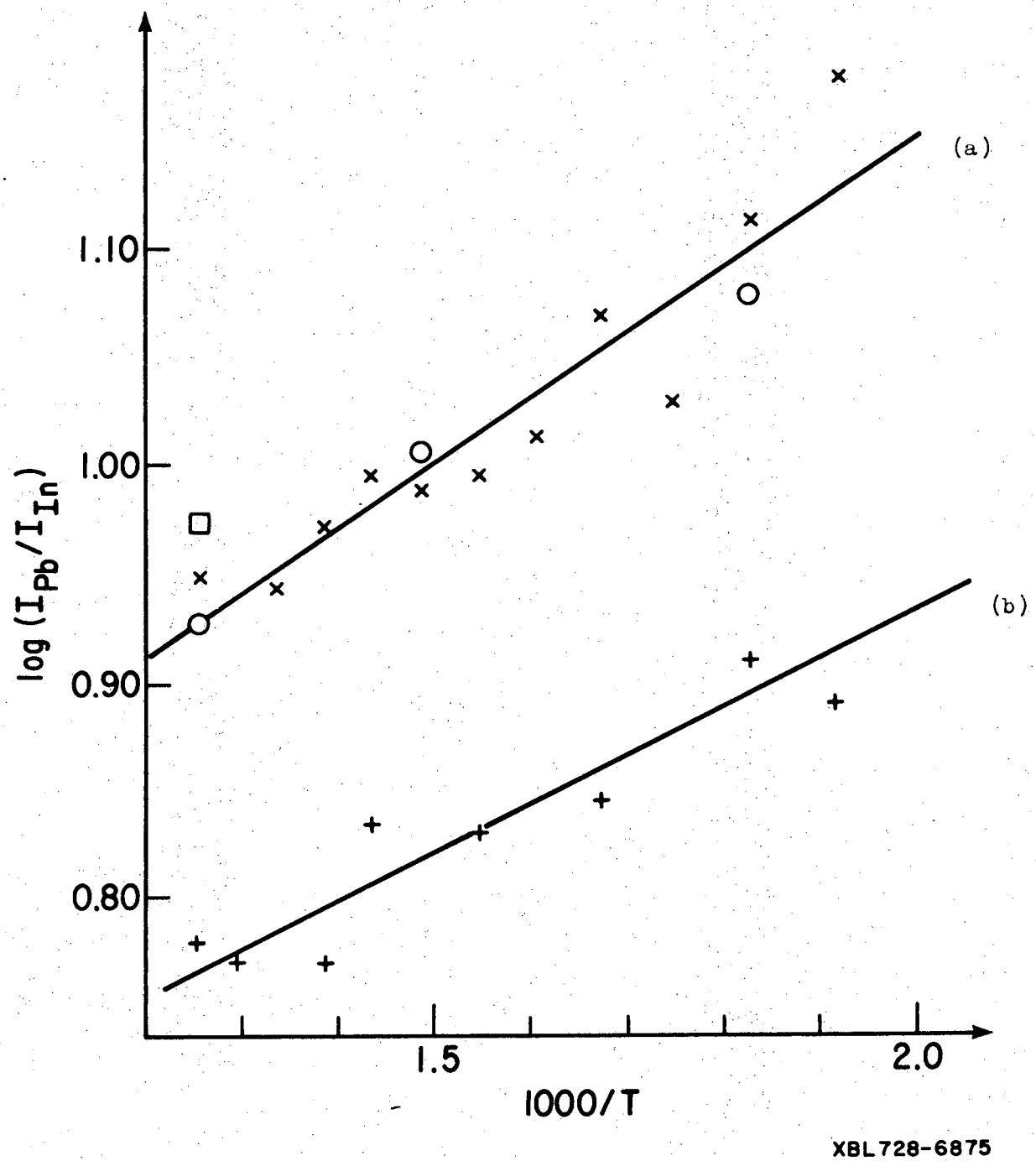


Fig. 7

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