LBL-31199
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Submitted to Journal of Vacuum Science and Technology A

Surface Composition Determination of Pt-Sn Alloys by Chemical Titration with Carbon Monoxide

A.H. Haner, P.N. Ross, U. Bardi, and A. Atrei

November 1991

| LOAN COPY |
|Circulates |
|for 4 weeks|
Bldg. 50 Library.
Copy 2
LBL-31199

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

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

LBL-31199

SURFACE COMPOSITION DETERMINATION OF Pt-Sn ALLOYS BY CHEMICAL TITRATION WITH CARBON MONOXIDE

A.H. Haner and P.N. Ross
Materials Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720, USA

and

U. Bardi and A. Atrei
Dipartimento di Chimica
Universita' di Firenze
50121 Firenze, Italy

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

LBL-31199

SURFACE COMPOSITION DETERMINATION OF Pt-Sn ALLOYS BY CHEMICAL TITRATION WITH CARBON MONOXIDE

A.H. Haner and P.N. Ross
Materials Science Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720, USA

and

U. Bardi and A. Atrei
Dipartimento di Chimica
Universita' di Firenze
50121 Firenze, Italy

Abstract

The use of chemical titration with carbon monoxide to determine the surface composition of Pt-Sn alloys was studied using Pt_3Sn single crystals of known surface composition. The surface composition of the (111) and (100) faces were determined independently by the combination of LEED crystallography and low energy ion scattering (LEIS). CO was adsorbed on these surfaces to saturation at 250 K and thermally desorbed into a mass spectrometer. The area under the TDS curve for the alloy surface was compared to the area under the curve for the pure Pt surface of the same orientation. The ratios were 0.5 +/- 0.05 for $Pt_3Sn(100)$ and 0.7 +/- 0.05 for $Pt_3Sn(111)$, in excellent agreement with the 50% Pt and 75% Pt surface compositions derived from LEED and LEIS. The success of the titration method in this case appears to be due to: a) selective adsorption of CO on Pt atoms; b) the relatively weak effect of the Pt-Sn intermetallic bond on the Pt-CO bonding.

1. Introduction

The composition of the outermost layer of an alloy is a fundamental parameter in determining the adsorptive and catalytic properties of the surface. A method often used for the quantitative determination of the surface composition of alloy catalysts is chemical titration by selective adsorption [1]. This method requires a gas which is selectively adsorbed on just one of the components, or which is adsorbed in a known ratio on each component. Another assumption of the method is that the number of adsorbed molecules per surface atom does not change when the element is diluted in the surface. Finally, one must also assume that chemisorption does not induce surface segregation, thus changing the surface composition.

If the above assumptions are satisfied, chemical titration provides a fast, simple, and reasonably accurate method for the determination of the surface composition of an alloy. A further advantage of the method is that it can be applied to dispersed samples as well as to massive ones. However, the results of the method can be accepted with confidence only as long as the foregoing assumptions can be verified. Such a verification can only be obtained by independent methods, such as by surface analytical methods like electron spectroscopy (AES, XPS) or low energy ion-scattering (LEIS).

Previously, chemical titration by carbon monoxide was used by Verbeek and Sachtler [2] to determine the surface composition of polycrystalline Pt_3Sn powders. Van Santen and co-workers [3] appeared to confirm the assumptions of the titration method for this material by comparison of the surface composition determined independently by LEIS with that determined by CO titration. Both methods indicated the surface composition of vacuum annealed samples was 40+/-3 a/o Pt. However, use of polycrystalline samples made it

impossible to compare the results with theory [4], which predicts a different surface composition for the (111) (25% Pt) vs. the (100) or (110) surfaces (50% Pt). In the present paper, we report a study of single crystal Pt_3Sn surfaces and show that indeed it is possible and reasonable to use CO as a selective titrating molecule. The result of comparative thermal desorption on single crystal Pt and Pt_3Sn samples shows that the amount of CO desorbed is proportional to the fraction of Pt in the surface as determined independently by LEED crystallographic analysis and LEIS.

2. Experimental

Pt_3Sn and pure Pt single crystal samples with a surface oriented along the (001) and (111) planes were prepared as described in [5]. All samples were cut to discs of the same diameter to permit a direct comparison of the results of thermal desorption measurements. The samples were introduced in vacuum systems with base pressure in the 10^{-8} Pa range. LEISS and XPS measurements were performed in the same system equipped with a hemispheric electron energy analyzer with multichannel detector. For XPS, we used a conventional, non-monochromatized Mg/Al Kα source. For LEISS we used a 1KeV beam of Ne^+ ions. The scattering angle was 135 degrees.

Thermal desorption and Auger electron spectroscopy measurements were performed in a different vacuum system equipped with a single pass CMA with coaxial electron gun and quadrupole mass spectrometer. This mass spectrometer was equipped with a "cone" formed from Ta sheet that shielded the ionizer from gases not line-of-sight from the crystals including the edges of the crystals. The ionizer was ca. 2 cm from the aperature, which was ca. 0.5 cm in diameter. This UHV system also has a fast-introduction sample transfer mechanism [19],

which permitted one sample to be "parked" in vacuum while the other was analyzed by LEED/AES/TDS. Thus, Pt_3Sn crystals and pure Pt crystals could be interchanged without breaking vacuum. CO thermal desorption spectra were obtained after saturating the sample with CO at 250 K. The sample temperature was then raised at a linear rate, variable in the range of 7 to 12 K/sec. TDS spectra were recorded at the same ionizer emission current and electron multiplier voltage. Because pure Pt and Pt_3Sn surfaces could be interchanged without breaking vacuum, and TDS curves from each obtained within a few hours, the mass spectrometer gain could be reasonably assumed to be constant. Both UHV systems described above were also equipped with LEED optics. The procedure for the crystallographic LEED analysis followed that of Van Hove et. al. [6a]. Application of the procedure to the particular case of Pt_3Sn surfaces is described in another paper [6b].

3. Results and Discussion

Cleaning of the Pt_3Sn surface was obtained by cycles of Ar^+ ion bombardment and annealing, until XPS or AES showed no significant amounts of surface contamination. The LEED patterns for the clean Pt_3Sn surfaces have been described in detail previously [5], but for completeness we show them again here (Fig. 1). In brief, the low index surfaces were found to have a periodicity corresponding to bulk truncation. For the (110) crystal, we also observed features in the LEED patterns that could not be explained in terms of bulk truncation, but which may be attributed to surface reconstructions [7]. Further study showed however that these anomalous features can be eliminated, or at least strongly reduced, after repeated cycles of ion bombardment and annealing.

Quantitative LEED crystallographic analysis of the Pt_3Sn (100) and (111) surfaces [6] confirmed this qualitative interpretation of the LEED patterns. In the case of the (001) surface, the stable termination is the "PtSn" plane, that is the surface contains 50% of Pt atoms (Fig. 2). For the (111) surface, the bulk termination is a plane of composition "Pt_3Sn", that is the surface contains 75% Pt atoms (Fig. 2). A comparison of the calculated and experimental I-V curves for the various possible structures is shown for the (100) surface in Fig. 3. The LEED calculations were also performed for models involving random enrichment of either component in the outermost plane, but no improvement in the agreement between the calculated and experimental intensities could be obtained in this way. The dynamical LEED analysis cannot, however, rule out a minor amount of surface enrichment, e.g. the accuracy of the composition may be estimated as of the order of +/- 5% taking into account LEED measurements performed on other Pt alloys [18, 19].

LEIS measurements were consistent with the LEED results by clearly indicating that both Pt and Sn are present in the outermost surface layer [5]. Characteristic LEIS spectra are shown in Fig. 4. A quantitative determination of the surface composition from LEIS depends on the availability of accurate sensitivity factors for the elements involved. It is also dependent on the assumption that the scattering and the neutralization cross sections remain unvaried when the elements are alloyed. The latter is an especially important factor in the case of Sn, which exhibits a strong oscillation in ion yield (as a function of energy) due to quasi-resonant charge exchange [10] that also produces a significant matrix effect in the sensitivity factor. If the Pt and Sn sensitivity factors reported by Biloen et. al. [3] are used, a significant surface enrichment in Sn is obtained in comparison to the expected value for a

bulk truncation model, e.g. for (100) 60-65% Sn vs. 50%. However, composition closer to the expected bulk truncation values are obtained from the LEIS data if the sensitivity factors reported by Heiland and Taglauer [11] are used.

Thermal desorption spectra for CO at saturation coverage are shown in Figs. 5 and 6. The TDS curves for pure platinum are in good agreement with the literature results [12-14]. In the case of the alloy surfaces, for both crystallographic orientations the peak is significantly shifted towards lower temperatures, indicating a lower adsorption energy (ca. -20 kJ/mol). The lower adsorption energy for CO on Pt_3Sn is characteristic of certain Pt bimetallic alloys and certain metallic overlayers on Pt [15], and is usually attributed to a change in the electronic properties of the Pt surface atoms due to the Pt-Sn bond, i.e. a "ligand effect" [1].

Measuring the area under the TDS curves for the alloy and pure Pt surfaces, we obtain ratios of 0.5 + /-0.05 the Pt_3Sn/Pt(001) surface and 0.7 + /-0.05 for the Pt_3Sn/Pt (111) oriented surfaces. The error limits on these area ratios were derived from repeating exactly the same measurement and by repeating the measurement with different heating rates (from 7-12 K/s). These results appear in good agreement with the surface structural model derived from LEED, i.e. substitution of Sn for Pt in the surface eliminates 50% of the Pt sites on the (100) surface and 25% of the Pt sites on the (111) surface. It appears therefore that on this surface the CO molecules are selectively adsorbed on the Pt atoms only (as expected) and that the CO/Pt ratio does not change going from pure Pt to the alloy surface in these conditions of exposure and adsorption temperature.

The absolute coverage of CO on the pure Pt surfaces under the dosing conditions used was determined from the O1s/Pt4p XPS peak areas and the calibration by Norton et. al. [16]. The values were 0.62 +/-0.05 for (111) and 0.74 +/-0.05 for (100). Note that the calculation of surface composition from the TDS curves does not involve the assumption that there is one CO molecule adsorbed per Pt atom, which is clearly not the case in these UHV experiments, whereas it may be so under the conditions (much higher CO pressure) used originally by Verbeek and Sachtler [2]. What is assumed here (and by Verbeek and Sachtler) is that the CO/Pt ratio at saturation is the <u>same</u> for the alloy surface as for the pure Pt surface which can only be rigorously true if the Sn atoms do not alter the fraction of CO adsorbed in the a-top position versus the bridge-bonded positions. From purely geometric considerations, one can see from Figure 2 that Sn atoms in the (111) surface eliminate the same number (1/3) of a-top sites and Pt-Pt bridge bonding sites, and thus no change in the CO/Pt stoichiometry would be expected between Pt_3Sn(111) and Pt(111). Paffett et. al. [17a] have reported HREELS vibrational spectra for CO adsorbed on a Pt(111) surface modified by Sn adatoms, which indicated Sn atoms had only a small effect on the ratio of bridge-bonded to a-top CO at saturation coverage (0.34 versus 0.43 for Pt(111)), in agreement with these geometric considerations. On the other hand, Sn atoms in the (100) plane (the 50% Sn termination) of Pt_3Sn eliminate all of the Pt-Pt bridge bonding sites, and 1/2 the a-top sites. From purely geometric considerations, therefore, one might expect a slightly greater than 50% reduction in the amount of CO adsorbed on the Pt_3Sn (001) surface versus the Pt(100). However, since

the ratio of bridged to linear CO on Pt(100) is only 0.2 - 0.3, according to the HREELS spectra of Behm et. al. [17b], the effect appears to be smaller than the uncertainty in our measurement of the total amount of CO adsorbed on each crystal.

We have therefore demonstrated that chemical titration by CO adsorption is a quantitative method suitable for the determination of the surface composition of Pt-Sn alloys, and probably for Pt surfaces with Sn overlayers as well [18]. This method appears to be more reliable than LEIS, in this particular case, since LEIS results are critically dependent on the accuracy of the relative sensitivity factors and the effect of the matrix on the ion yield from Sn atoms leads to considerable uncertainty in the sensitivity factor.

Acknowledgment

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. W. Sachtler and R. Van Santen, Adv. in Catal. 26, 69 (1977).

2. H. Verbeek and W. Sachtler, J. Catal. 42, 257 (1976).

3. P.Biloen, R. Bouwman, R. Van Santen and H.Brongersma, Appl. Surface Science 2, 532 (1979).

4. R. Van Santen and W. Sachtler, J. Catal. 33, 202 (1974).

5. A.H. Haner, P.N. Ross and U. Bardi, Surface Science 249, 15 (1991).

6a. M. Van Hove, W. Weinberg and M. Chan, "Low Energy Electron Diffraction", Springer Verlag (Berlin), 1986.

6b. A. Atrei, U.Bardi, G.Rovida, M.Torrini and P.N. Ross, submitted to Surf. Sci.

7. A. Haner, P. Ross and U. Bardi, in: Structure of Surfaces III (ICOSS-III),, eds. M. Van Hove, K. Takayanagi and X. Xide (Springer-Verlag, Berlin) in press.

8. Y. Gauthier, Y. Joly, R. Baudoing and J. Rundgren, Phys Rev. B31, 6216 (1985).

9. Y.Gauthier, R. Baudoing, M. Lundberg and J. Rundgren, Phys Rev. B35, 7867 (1987).

10. R. Erickson and D. Smith, Phys. Rev. Lett. 34, 297 (1975).

11. W. Heiland and E. Taglauer, Nucl. Instr. Methods 132, 535 (1976).

12. D. Collins and W. Spicer, Surf. Sci. 69, 85 (1977).

13. H. Steininger, S. Lehwald and H. Ibach, Surf. Sci. 123, 264 (1982).

14. G. Poelsema, R.L. Palmer and G. Comsa Surf. Sci. 136, 1 (1984).

15. C. Campbell, Ann. Rev. Phys. Chem. 41, 775 (1990) and references therein.

16. P. Norton, J. Goodale and E. Selkirk, Surf. Sci. 83, 189 (1979).

17a. M. Paffett, S. Gebhard, R. Windham and B. Koel, J. Phys. Chem. 94, 6831 (1990).

17b. R. Behm, P. Thiel, P. Norton and G. Ertl, J. Chem. Phys. 78, 7437 (1983).

18. M. Paffett and R. Windham, Surf. Sci. 208, 34 (1989).

19. F. Wagner and P. Ross, Adv. Electrochem. and Electrochem. Engr., Wiley-Interscience (New York), Vol. 13, 1984, pp. 69-113.

Figure Captions

1. LEED patterns observed for the clean Pt_3Sn alloy surfaces: a) (111) face after sputtering and b) after annealing; c) (001) face after sputtering and d) after annealing. In both cases the symmetry of the unit mesh corresponded to what was expected for a surface formed by bulk truncation.

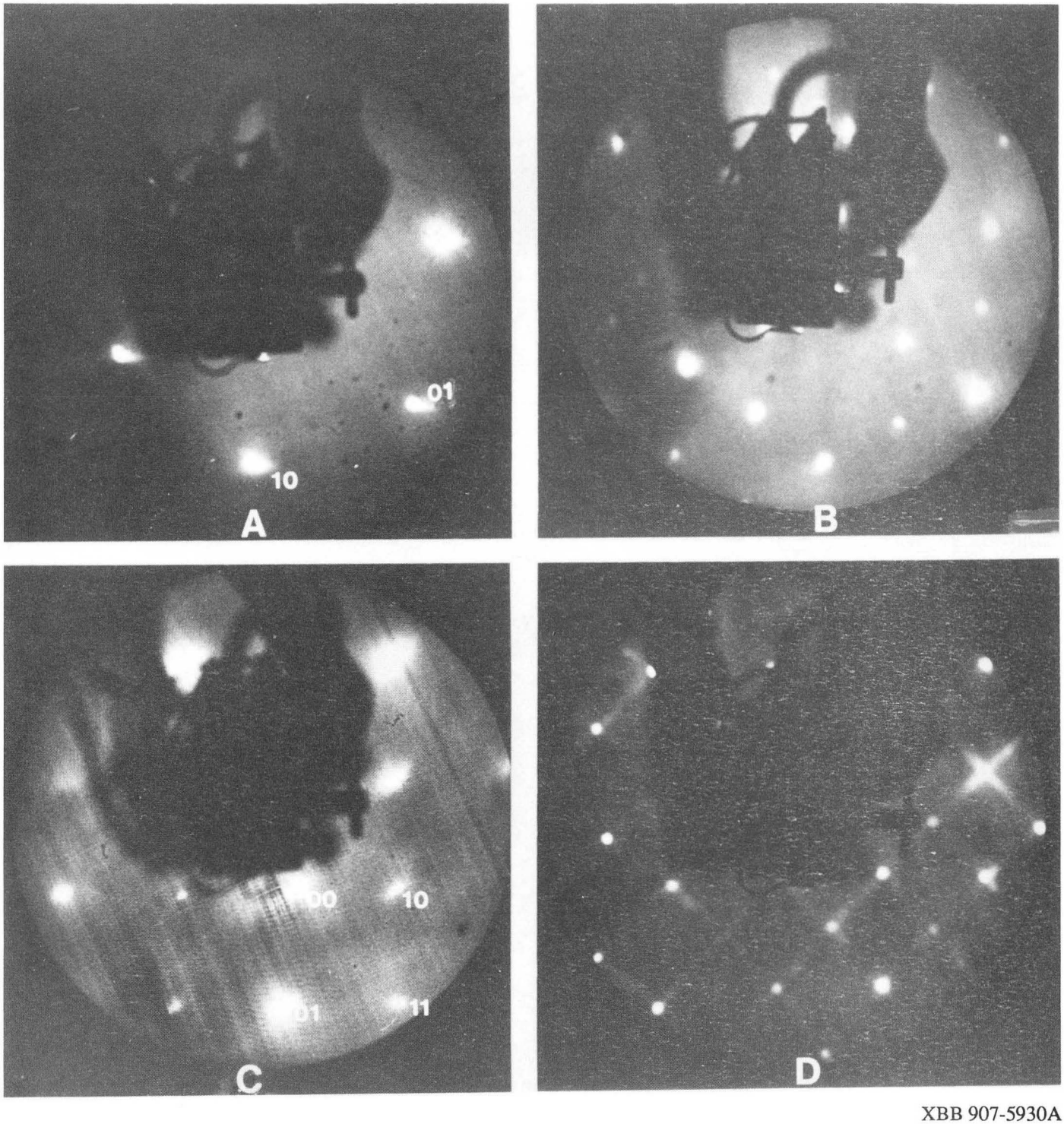
2. Crystal structure of Pt_3Sn and the bulk truncation surface structures of the three low index planes.

3. Results of the LEED crystallographic analysis for the $Pt_3Sn(001)$ surface: EXP - experimental data; A - theory for bulk truncation in pure Pt plane, all atoms in bulk lattice positions; B - theory for bulk truncation in "PtSn" plane with $0.2 Å$ upward displacement of Sn atoms from bulk lattice positions. From [6].

4. LEIS spectra for the clean low index Pt_3Sn surfaces. 1 keV Ne^+ ions at normal incidence with $\theta = 135^o$. Peak at 670 eV is for scattering for Pt atoms while that at 540 eV if - from Sn atoms. From [5].

5. CO TDS curves for the clean Pt and Pt_3Sn (111) surfaces.

6. CO TDS curves for the clean Pt and Pt_3Sn (001) surfaces.



XBB 907-5930A

Figure 1

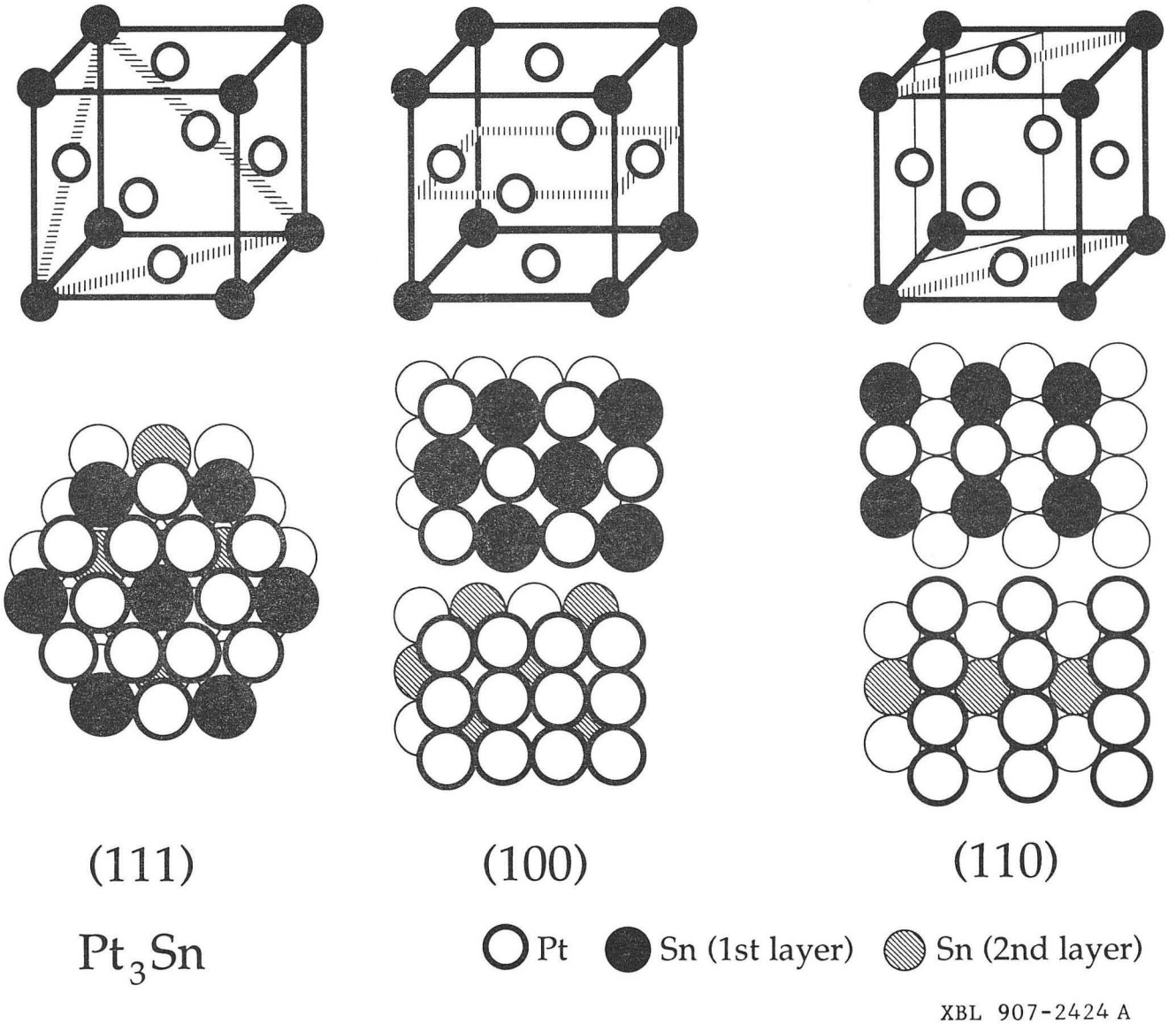
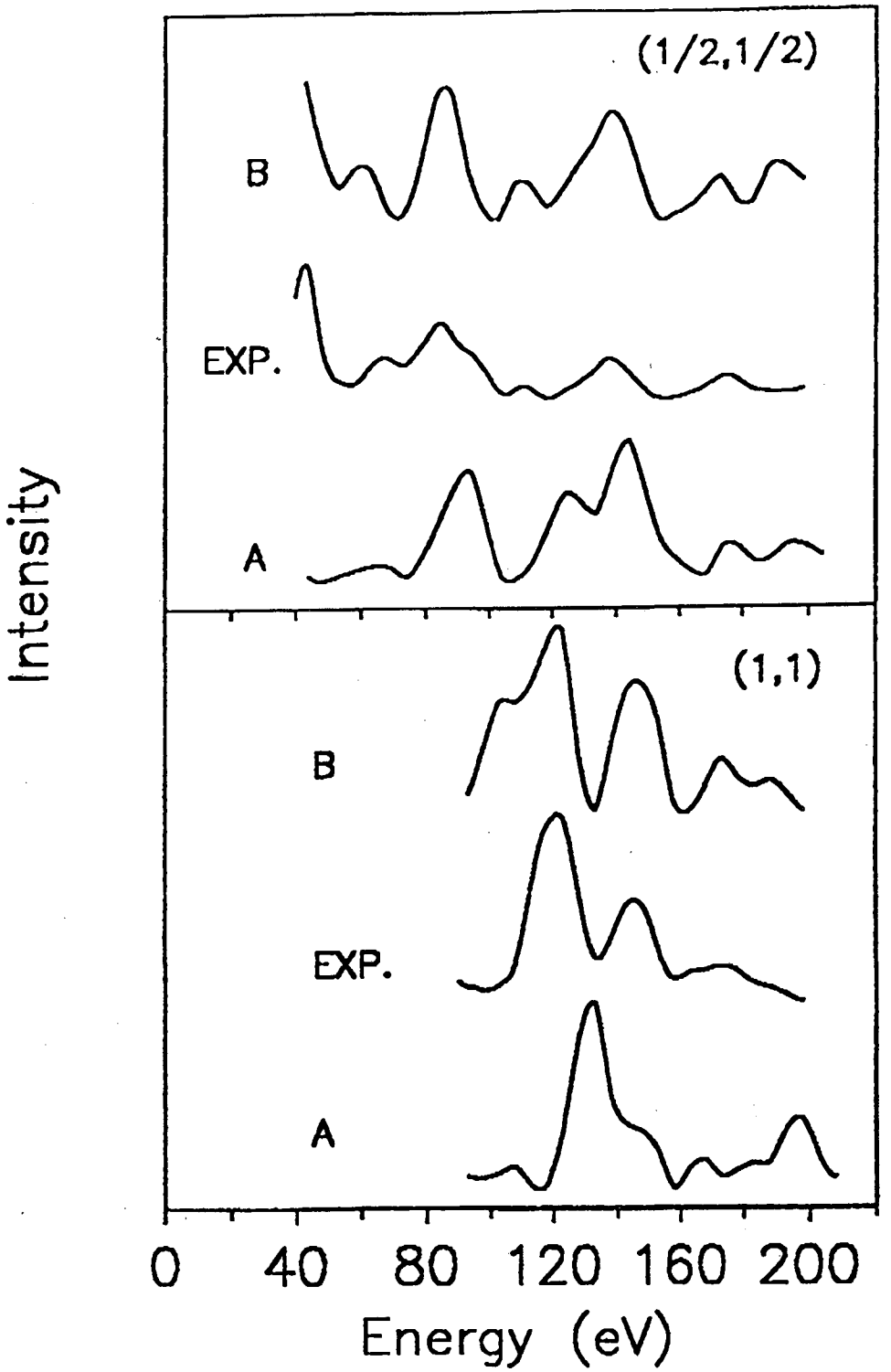
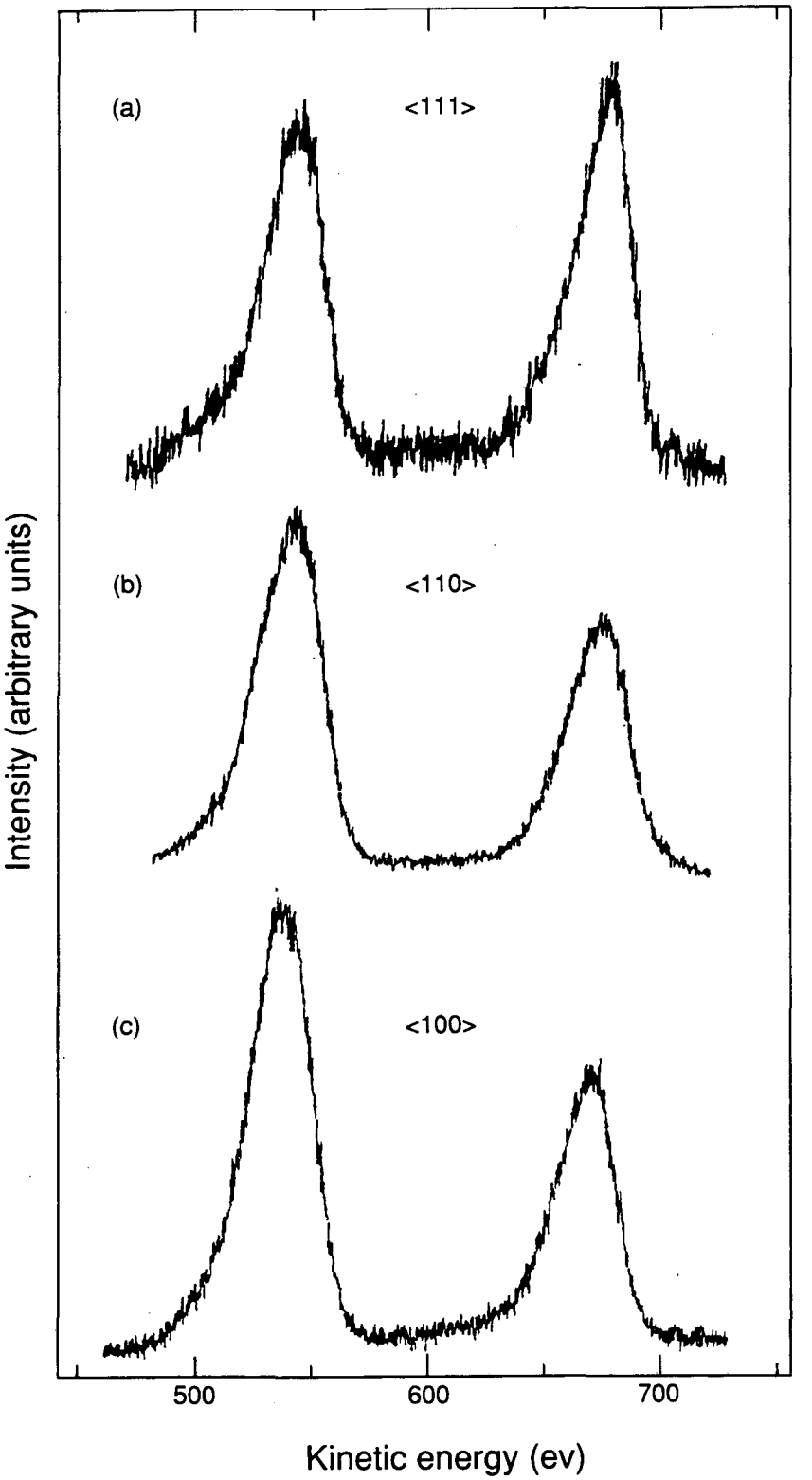


Figure 2



XBL 9111-2471

Figure 3



XBL 905 – 6400

Figure 4

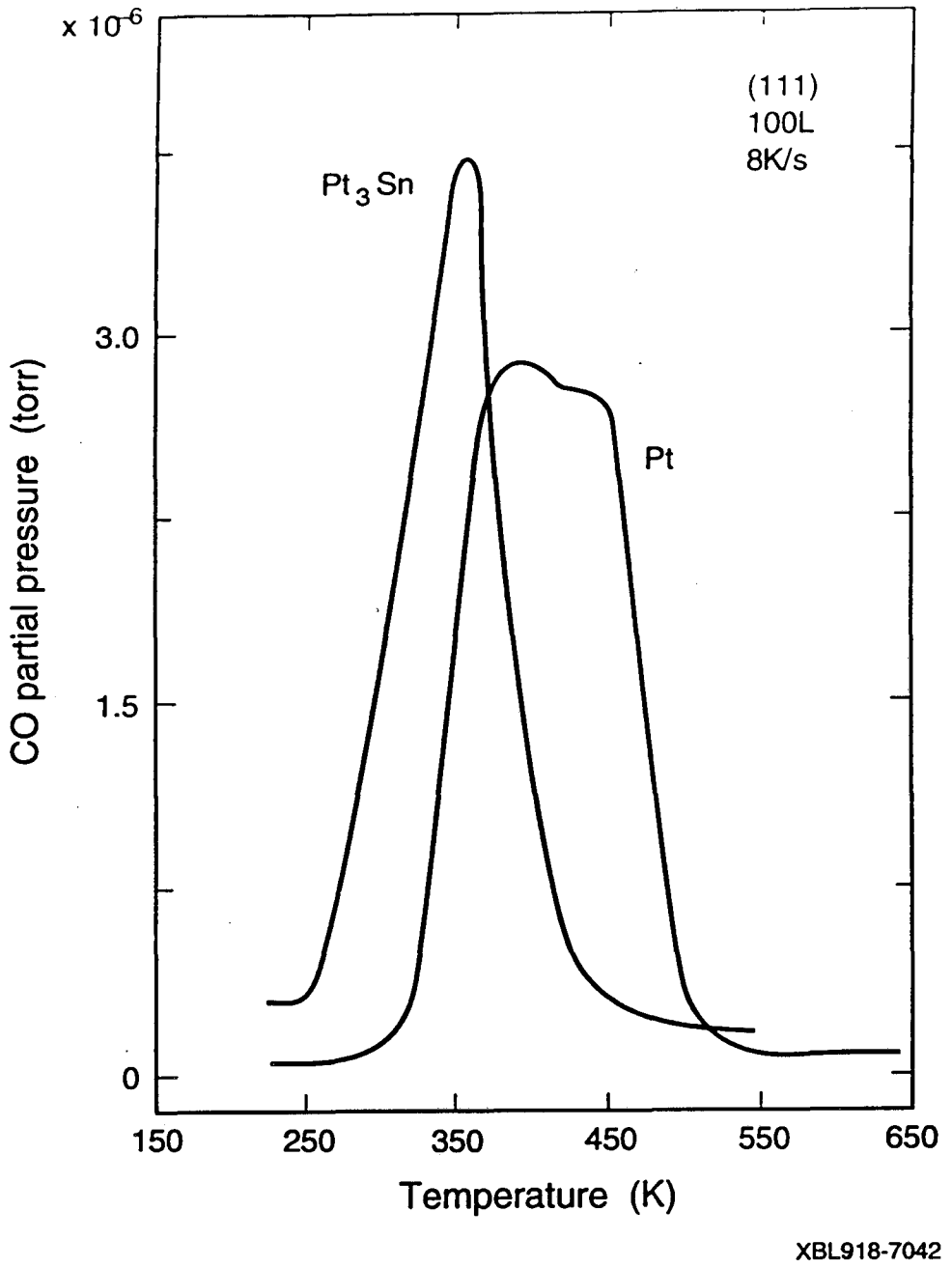

x 10-6
(111)
100L
8K/s
Pt3Sn
Pt
3.0
1.5
0
CO partial pressure (torr)
150
250
350
450
550
650
Temperature (K)
XBL918-7042

Figure 5

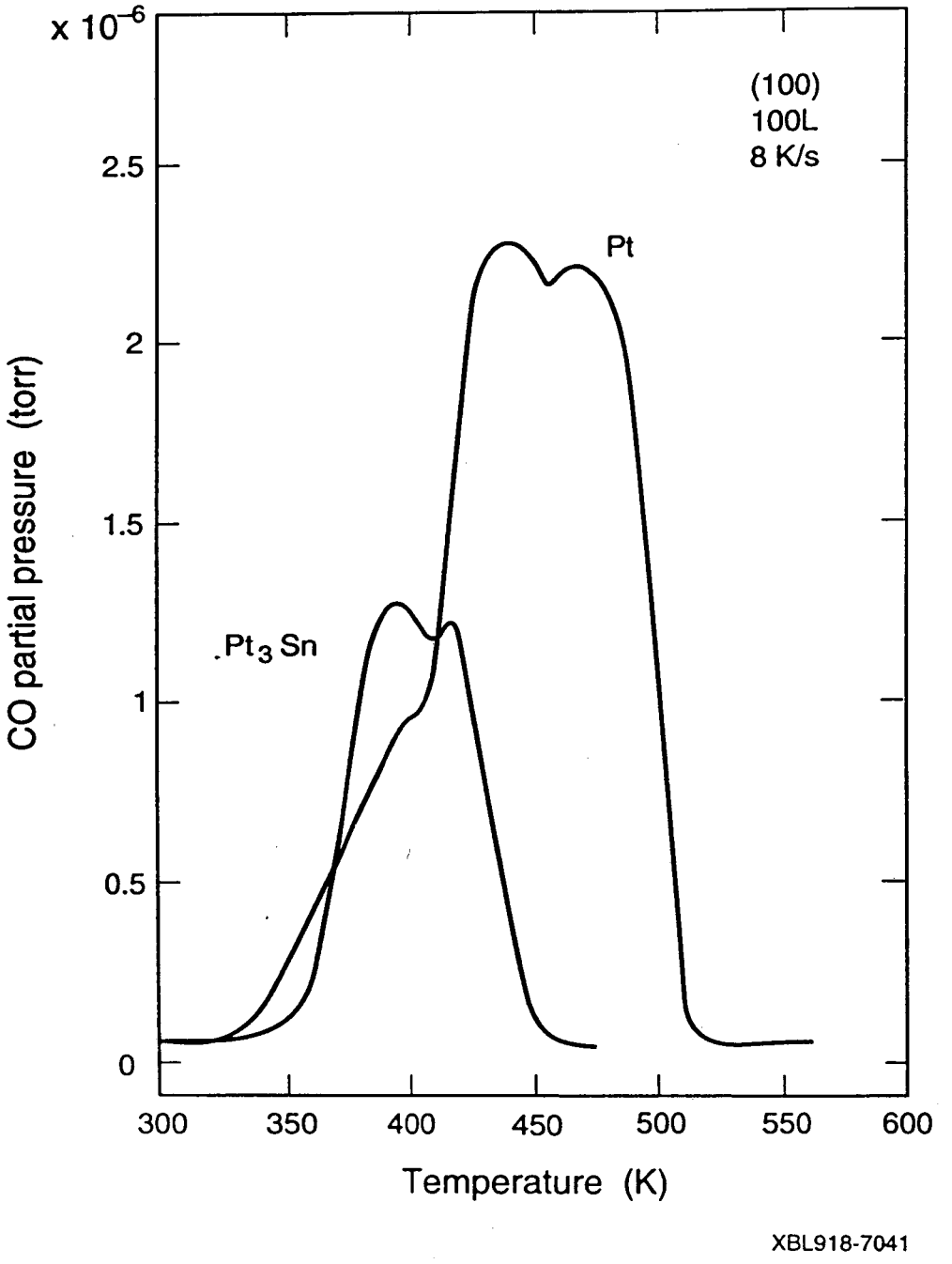

x 10^-6
(100)
100L
8 K/s
Pt
Pt3 Sn
CO partial pressure (torr)
2.5
2
1.5
1
0.5
0
300
350
400
450
500
550
600
Temperature (K)
XBL918-7041

Figure 6

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720