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THE SURFACE STRUCTURE AND COMPOSITION OF <111> AND <100> ORIENTED SINGLE CRYSTALS OF THE ORDERED ALLOY Pt_3Sn

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The surface composition and structure of <111> and <100> oriented single crystals of the ordered alloy Pt_3Sn ($L1_2$ or Cu_3Au-type) were determined using a combination of low energy electron diffraction (LEED) and low energy ion scattering spectroscopy (LEISS). The clean annealed surfaces displayed p(2x2) and c(2x2) LEED patterns, respectively, and the Sn/Pt LEISS intensity ratios at normal incidence were consistent with the surface compositions expected for bulk termination surface structures. In the case of the <100> crystal, preferential termination in the mixed (50% Sn) layer was indicated, which appears to be the consequence of the thermodynamic tendency for Sn to be at the surface. A strong variation in Sn/Pt LEISS intensity ratios with incidence angle was observed on both surfaces, indicating an outward displacement of Sn atoms from the plane of Pt atoms.

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1. Introduction

Pt-Sn alloys are of considerable commercial interest as both heterogeneous catalysts for hydrocarbon conversion [1-2] and as electrocatalysts for the direct electro-oxidation of methanol in fuel cells [3-4]. Because surface composition is critical to the behavior of alloys in these applications, there has been considerable study of the surface segregation phenomena in this system, both experimentally and theoretically. Of particular fundamental interest is the behavior of the highly ordered exothermic alloy Pt_3Sn, the alloy treated in one of the first theoretical analyses of segregation in ordered alloys [5]. Experimental studies of polycrystalline Pt_3Sn by Biloen and co-workers [6-8] found surface enrichment in Sn by LEISS, with surface compositions as high as 50-60 at.% Sn. However, in the theoretical analysis of Pt_3Sn by Van Santen and Sachtler [5], <u>no</u> segregation was predicted on the (111) face of the ordered alloy, and segregation was predicted on the (200) face by interchange of Pt atoms in the surface with Sn atoms in the layer below to form a 50% Sn surface. To date we are not aware of any experimental study of the surface structure and composition of a Pt_3Sn single crystal, which would provide a more rigorous test of this segregation theory.

The ordered Pt_3Sn alloy has the Cu_3Au ($L1_2$) structure with tin atoms on the corners of the face centered cubic unit cell and platinum atoms on the center of the faces. The <111> and <100> single crystal faces of other members of the $L1_2$ family, such as Cu_3Au [9-11], Ni_3Al [12-13], and Pt_3Ti [14], have bulk termination surface structures. One might, therefore, expect bulk termination of <111> and <100> Pt_3Sn, but because of the surface enrichment of Sn observed on polycrystalline

Pt_3Sn and the relatively large difference in surface energy between Sn and Pt [5], it is not immediately obvious that Pt_3Sn will behave like Cu_3Au or Ni_3Al. In this paper, we report the results of the first study of the surface structure and composition of the <111> and <100> oriented single crystals of Pt_3Sn using a combination of low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and low energy ion scattering spectroscopy (LEISS).

2. Experimental

Single crystal Pt_3Sn was prepared by combining high purity platinum and tin in stoichiometric amounts and then refining the alloy using the Bridgeman-Stockberger technique under a helium atomosphere and in high purity alumina crucibles. The formation of a single crystal, single phase ordered alloy was confirmed by x-ray diffraction analysis of powders ground from the crystal. The bulk composition of the alloy was confirmed by quantitative analysis using wet-chemical methods and emission spectroscopy (Galbraith Laboratories) to be 24.3 ± 0.5 at.% Sn. Single crystal slices (1mm x 10mm diameter) oriented along the <111> and <100> were spark cut and mechanically polished down to 0.05 μm. All single crystal faces were within 0.5° of their respective crystal planes as determined by Laue back-reflection x-ray diffraction. LEED patterns were observed with 4-grid LEED optics (Varian) and AES spectra were recorded with a single-pass CMA (Varian). LEISS was conducted in another vacuum chamber equipped with a hemispherical analyzer (Leybold Heraeus). One keV Ne^+ ions were used for LEISS ($\varphi = 135^\circ$) with variation of incidence angle from normal to 15° glancing. The beam current was 70 nA and the beam was rastered over a 3mm x 3mm area. Due to experimental constraints, no LEISS experiments were conducted with a variable azimuthal angle. The surfaces were prepared with cycles of Ar^+ sputtering, heating to 1023 K for 10 mins., approximately 10L dosing of O_2 (at 5×10^{-8} torr) at 623 K to remove carbon, followed by another vacuum anneal at temperatures up to 1023 K.

3. Results and Discussion

In the $L1_2$ structure, the {111} planes are all equivalent and have the bulk composition, while the {100} and {110} planes alternate between 50% Sn:50% Pt and 100% Pt, resulting in two inequivalent regular terminations of the bulk crystal. These two terminations will be designated the (100) and (200) planes or (110) and (220) planes, respectively. From our powder x-ray diffraction analysis, we obtained a value of 3.998 Å for the bulk lattice parameter of our Pt_3Sn crystal, very close to the value of 4.0015 Å reported in the JCPDS [15]. Since the Pt_3Sn lattice is expanded only by 2% from the Pt lattice (3.9231 Å), the fundamental beams from the alloy crystal are expected to be located on the LEED screen close to those of a pure Pt crystal of the same orientation, making it easy to recognize superlattice beams arising from ordered substitution of Sn for Pt in the surface.

3.1 Pt_3Sn <111>

A poorly ordered (1x1) pattern (Fig. 1a) was observed immediately after the initial ion bombardment. The Auger spectrum for this surface (Fig. 2) shows that ion bombardment selectively sputtered tin from the surface, so that the bombarded surface has very little tin left in it. Subsequent thermal annealing restored tin to the surface and concurrently produced half-order spots in the LEED pattern, eventually forming a well-contrasted p(2x2) pattern (Fig. 1b). Auger analysis showed that the Sn/Pt signal ratio stabilized when the annealing temperature was greater than 900 K. Carbon appeared on the surface during the initial anneal and was easily removed by oxygen dosing. Thereafter, the surface remained clean at all temperatures for extended periods of time. Once the clean annealed surface was formed, neither the LEED pattern nor the AES spectrum changed with temperature cycling between 300 - 973 K. The observed p(2x2) LEED pattern is similar to that observed on the <111> orientations of Cu_3Au [9-10], Pt_3Ti [14], and Ni_3Al [12], all three alloys having the same $L1_2$ structure as Pt_3Sn.† It has also been observed on Sn vapor deposited on Pt (111) at a substrate temperature above 450 K [16].

The LEIS spectra for the clean annealed <111> oriented single crystal are shown in Figure 3a. Using the theoretical ion-scattering cross-sections [17] for Sn and Pt, the normal incidence spectrum clearly indicates the surface composition is between 25-50 at.%, consistent with the p(2x2) LEED pattern and bulk truncation structure. However, the strong variation of the Sn/Pt LEIS intensity ratio with incidence angle indicates that Sn atoms are shadowing Pt atoms at grazing incidence. A more quantitative analysis of this shadowing, such as that used by Buck and co-workers [18] for Cu_3Au, was not possible in this study, since we could not control the azimuthal angle of the ion beam on the crystal.

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† What we term the 1/2-order beam is referenced to the pure Pt (111) unit mesh. This beam is also an integer-order beam of the Pt_3Sn (111) unit mesh. However, because the {100} planes of the $L1_2$ structure of Pt_3Sn can have either of two unit meshes, we prefer to reference the beams to the pure Pt unit mesh of the same crystal orientation.

However, qualitatively the strong variation with incidence angle (at an arbitrary azimuth) clearly indicates that the Sn atoms are displaced outward from the plane of Pt atoms, similar to the displacement of Al atoms from the plane of Ni atoms in Ni_3Al [12,13].

3.2 Pt_3Sn <100>

The LEED patterns for Pt3Sn <100> following Ar+ ion bombardment and annealing is shown in Fig. 1 (c-d). Initially, the pattern was a poorly ordered (1x1), again associated with a low Sn/Pt AES ratio due to preferential sputtering of tin. Upon annealing, the Sn/Pt AES ratio increased, eventually stabilizing to approximately the same ratio shown in Figure 2 for the <111> crystal, and a c(2x2) LEED pattern appeared with characteristic streaking (actually fine structure) around the fundamental beams. Further annealing to 1023 K reduced the streaking. However, due to sample heater limitations, the maximum temperature that could be achieved was 1023 K. With further heating, we assume that all streaking along the fundamentals would disappear.

The streaks in the LEED pattern are due to the presence of ordered step arrays on this apparently incompletely annealed surface, with the steps running preferentially along the diagonal rows of the surface. The fact that the LEED beams are streaked rather than split means that the step arrays are randomly up-and-down rather than periodically up-and-down, as occurs with a facetted surface [19]. The dependance of the streaking on beam energy [19,20] can be used to determine the step height, while the length of the streak can be used to determine the distance between steps, i.e. the terrace length. Figure 4 shows the LEED patterns for the c(2x2) surface annealed at 1023 K at three beam energies, 60, 70 and 80 eV. The (01) spot is sharp at the 60 and 80 eV, but streaked at 70 eV. The alternation in sharp and streaked spots continued to higher energy, with a frequency of ca. 20 - 25 eV. Using the kinematic theory for step-arrays [19], we calculated that for a monatomic step height the frequency would be much larger than 20 eV, sharp spots would alternate with streaks about every 60 eV. On the other hand, for diatomic step heights the kinematic theory predicts sharp (01) spots at 59, 81 and 108 eV, with the most intense streaking at 69 and 95 eV, in nearly perfect agreement with the LEED patterns we observed. The length of the streaks indicates the mean terrace length was ca. 20 - 25 Å. This means that the <100> crystal, in this partially annealed state, was preferentially terminated in c(2x2) terraces connected by randomly up-and-down diatomic steps. It was clear from the LEED patterns that annealing at successively higher temperatures decreased the step density and increased the terrace length, and that the temperature limitation in our sample holder prevented us from obtaining an atomically flat surface with c(2x2) symmetry. A c(2x2) pattern (without streaking) was observed on the <100> crystals of Cu_3Au [9-11], Pt_3Ti [14], and Ni_3Al [13], all three alloys having the same $L1_2$ structure as Pt_3Sn.

The LEIS spectra for the clean annealed <100> crystal surface are shown in Figure 3b. Again using the theoretical ion-scattering cross-sections [17] for Sn and Pt, the normal incidence spectrum clearly indicates a surface composition of at least 50 at.% Sn, consistent with the termination in the compositionally mixed (100)-c(2x2) layer. As with the <111> surface, there was a strong angular dependance on the Sn/Pt LEIS intensity ratios below 45°, again indicating an outward displacement of Sn atoms from the plane of Pt atoms.

4. Conclusions

The <111> and <100> oriented single crystals have clean annealed surface structures that are closely related to the ideal bulk truncation structures. Some buckling in both surfaces is indicated by the angular dependance of the LEIS spectra, qualitatively similar to the buckling observed on Ni_3Al [12,13]. There is no evidence from the result with the <111> Pt_3Sn single crystal of surface segregation of Sn. The preferential termination of the <100> crystal in the compositionally mixed (100) layer is the result of surface segregation constrained by strong ordering energies [5] that prevent the formation of either surface or subsurface layers not having the bulk substitution of the solute atom. Thus, it appears likely that the surface enrichment observed with polycrystalline Pt_3Sn [6-8] was due entirely to preferential termination in (100) and (110) planes (50% Sn) and not to the interchange of atoms between layers.

The <100> orientations of Cu_3Au, Ni_3Al and Pt_3Sn are all preferentially terminated in the compositionally mixed (100) layer. These three $L1_2$ ordered alloys have in common the property that the minority atom has the lower surface energy [21], and thus has the tendency to segregate to the surface. On the other hand, in the case of Pt_3Ti, the majority atom has the lower surface energy and the tendency to segregate to the surface [22], and the <100> crystal is preferentially terminated in the (200) pure Pt plane [23]. It would appear that in these $L1_2$ systems the segregation tendency of <u>either atom</u> results in the preferential termination either in the (200) (majority atom segregating) or (100) (minority atom segregating) plane, with both the surface and subsurface planes retaining bulk substitution of the minority atom. Thus, the consequence of segregation in ordered fcc alloys appears to be fundamentally different than in disordered fcc alloys like $Pt_{80}Ni_{20}$ [24] or $Pt_{80}Co_{20}$ [25], where surface segregation drives an interchange of atoms between atomic layers and the formation of subsurface planes that are compositionally very different from planes in the bulk [26].

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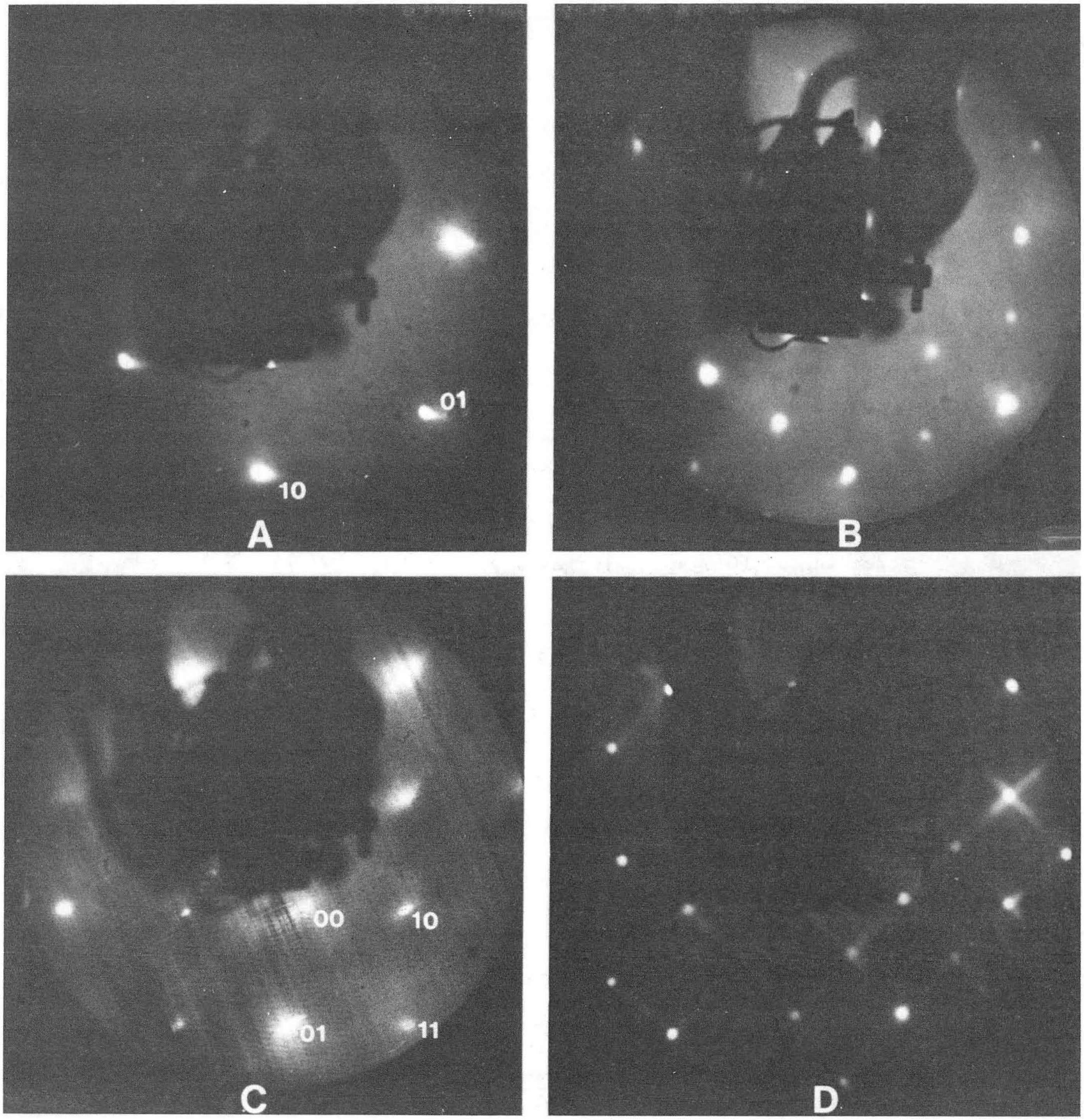
FIGURE CAPTIONS

1. LEED patterns of Pt_3Sn <111> at 70 eV after ion bombardment (a) and annealing 1073 K (b). LEED patterns of Pt_3Sn <100> at 135 eV after ion bombardment (c) and annealing 1023 K (d).

2. Auger electron spectra for Pt_3Sn <111>: a) immediately after argon ion bombardment and b) after successive oxygen dosing/annealing cycles.

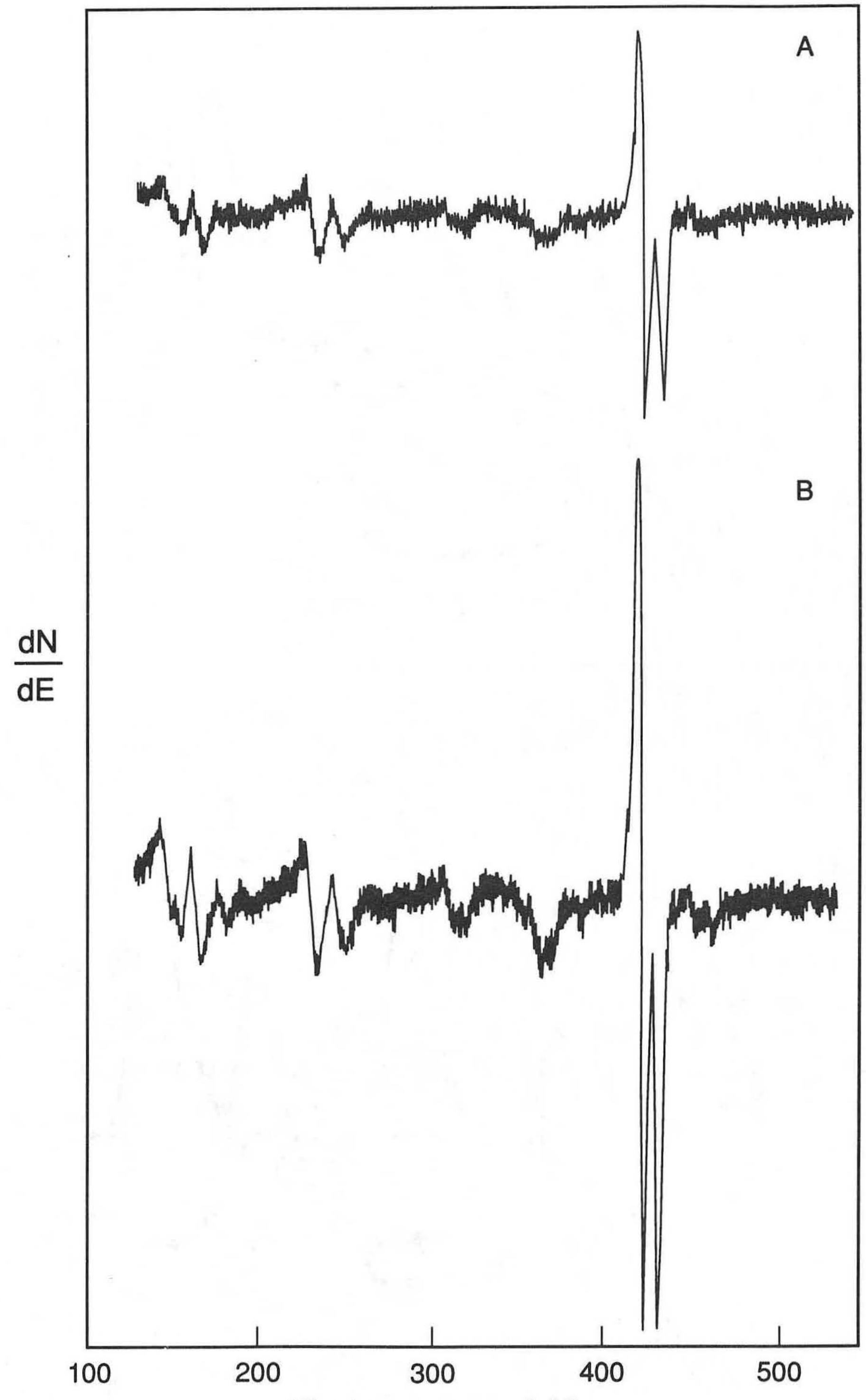
3. Ne^+ ion scattering spectrum for clean, annealed Pt_3Sn <111> (a) Pt_3Sn <100> (b) at different incident angles (1 keV, scattering angle $\varphi = 135^o$). Peak for scattering from Pt atoms is at 670 eV, that for Sn at 540 eV.

4. LEED patterns of the same Pt_3Sn <100> crystal as in 1(d) at three different beam energies showing alternation in streaking of (01) spot with energy.



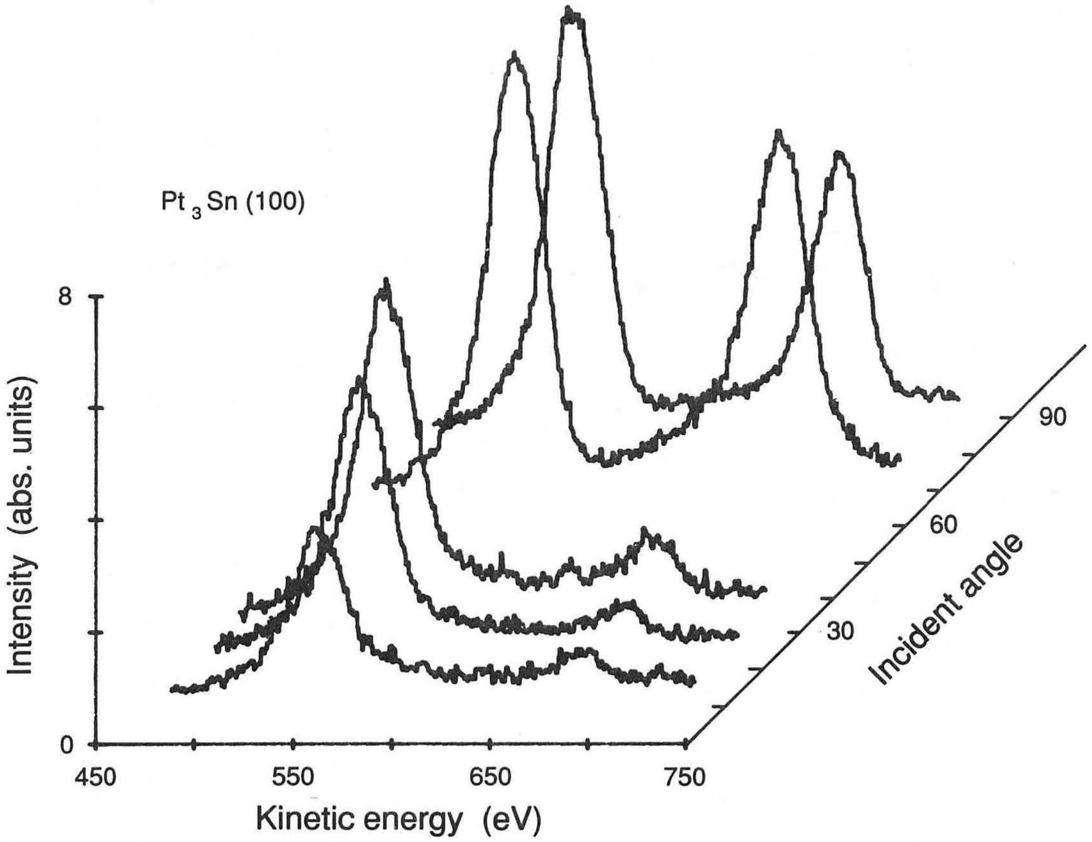
XBB907-5930-A

Fig. 1



XBL908-6730

Fig. 2


Pt $_3$ Sn (100)
8
0
Intensity (abs. units)
450
550
650
750
Kinetic energy (eV)
30
60
90
Incident angle

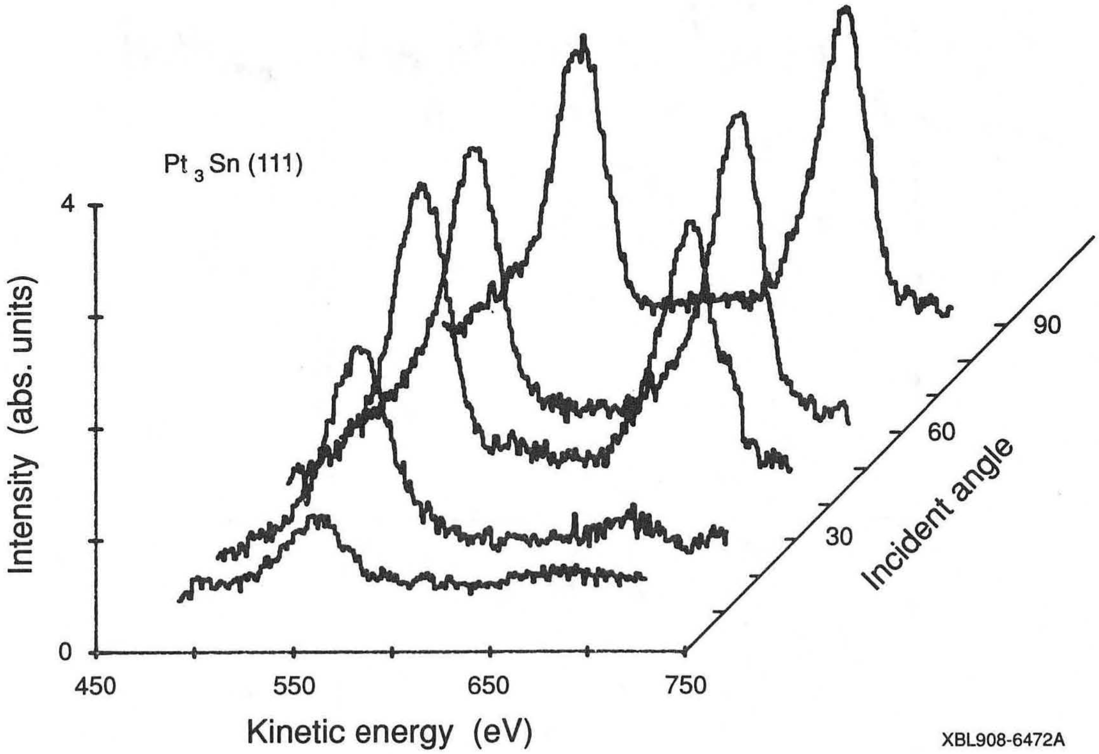

Pt $_3$ Sn (111)
4
0
Intensity (abs. units)
450
550
650
750
Kinetic energy (eV)
30
60
90
Incident angle
XBL908-6472A

Fig. 3

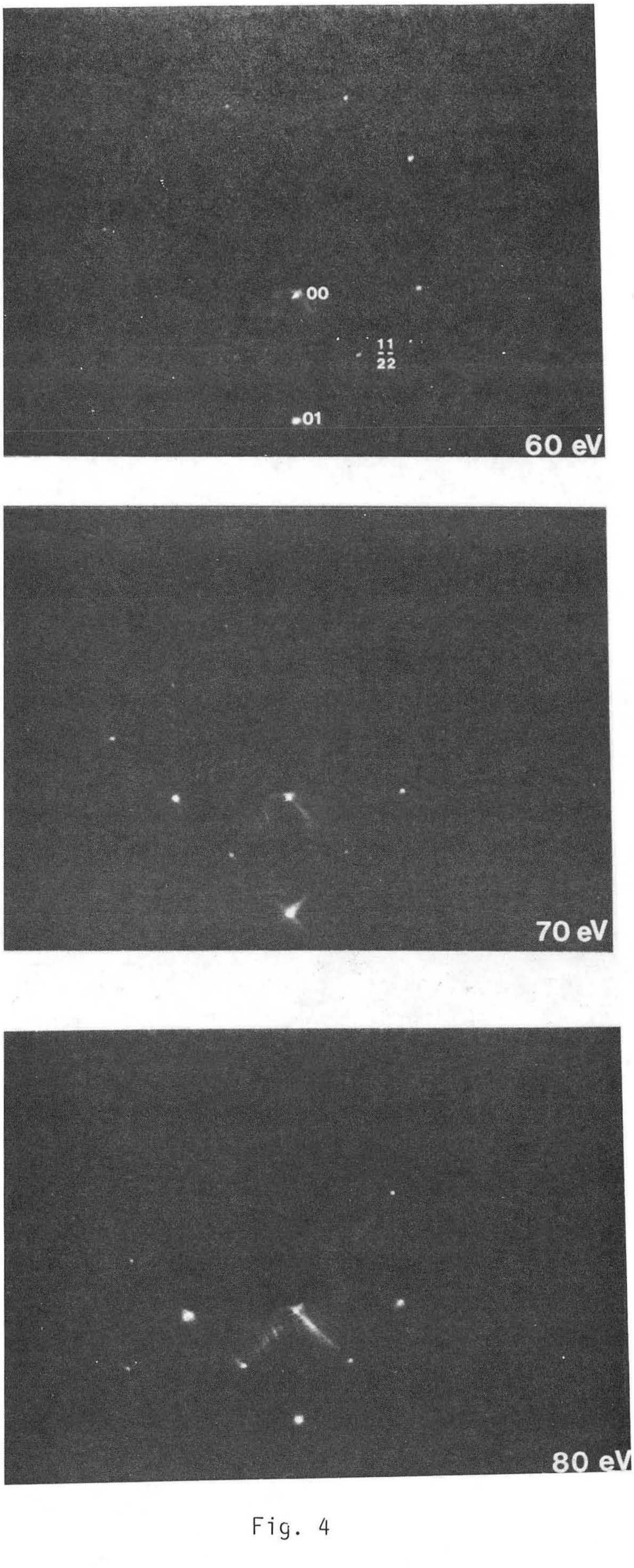


Fig. 4

XBB 899-7807A