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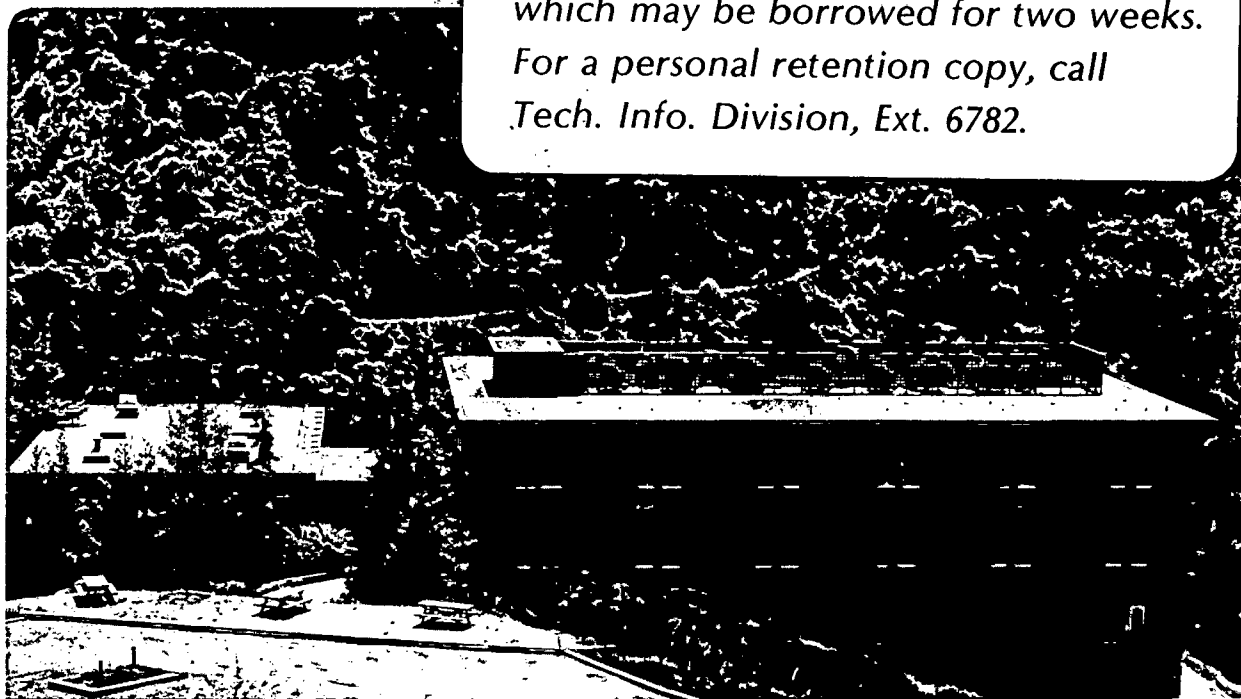
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U. Bardi, G.A. Somorjai, and P.N. Ross

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LIGAND EFFECTS FOR CO AND H<sub>2</sub> CHEMISORPTION  
ON A POLYCRYSTALLINE Pt<sub>3</sub>Ti SURFACE

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The Pt-Ti bimetallic system is interesting for several reasons, but most particularly as an example of an "Engel-Brewer" type intermetallic (1). The highly exothermic enthalpy of formation of these alloys has been interpreted in terms of strong bonding interaction of electrons in the d bands of both metals. In principle, such a strong interaction is likely to modify the electronic properties of the metals and cause changes in the chemical properties that are often called ligand effects. Ligand effects have been considered as a possible cause for the increased catalytic activity, as compared to pure Pt, of the Pt<sub>3</sub>Ti intermetallic in the electrolytic reduction of oxygen to water in acid fuel cells (2). Also a ligand effect caused by the Pt-Ti bond is considered to be related to the strong metal-support interaction (SMSI) which is observed when Pt supported on TiO<sub>2</sub> is reduced in hydrogen at elevated temperature (3,4). Because of these changes in the catalytic properties of platinum in the presence of Ti, we have undertaken a study of the surface properties of the ordered Pt<sub>3</sub>Ti intermetallic compound, which has the most exothermic heat of formation in the Pt-Ti system (5). In this paper we report the results of a study of carbon monoxide and hydrogen chemisorption, which we used as chemical probes to test the presence of ligand effects.

The Pt<sub>3</sub>Ti compound was prepared by arc melting the metals in an argon atmosphere. The Pt/Ti atomic ratio was checked after melting by x-ray emission spectroscopy. X-ray diffraction indicated that the alloy bulk structure was the fcc AuCu<sub>3</sub> type (Pt<sub>3</sub>Ti can also exist in the cubic β-W and hexagonal TiNi<sub>3</sub> type structures (5)) with lattice parameter 3.906 Å. Disk shaped samples about 1 mm thick and 5 mm diameter were mounted in a UHV system equipped with a single pass CMA with grazing

incidence electron gun for Auger electron spectroscopy (AES), a mass spectrometer for thermal desorption spectroscopy of adsorbates (TDS), and a sputter gun for surface cleaning. The sample could be annealed up to about 1200 K by resistive heating through the supporting Ta wires. The system was also equipped with an electron beam evaporator located in a separate chamber. The purpose of this evaporator was to coat the sample with a pure Pt film in order to be able to compare the alloy and pure metal properties in TDS experiments. In this way we insured that the surface area, geometry, and heating rate were exactly the same.

The AES spectrum after argon ion bombardment of the sample is shown in Fig. 1. A quantitative analysis of the spectrum using the elemental sensitivity factors reported in (6) indicates that a Ti(387 eV)/Pt(237 eV) Auger peak ratio of 3.8 corresponds to a Pt/Ti atomic ratio of 3.5. The difference between 3.8 and 3.0, the bulk stoichiometry, may not be significant in terms of this type of calculated composition. The residual carbon and oxygen in the AES spectrum were apparently bulk impurities, since they could not be eliminated by ion bombardment alone. To investigate that problem further, some samples were analyzed using spatially resolved AES, i.e. scanning Auger electron microscopy (SAM). This analysis indicated that arc-melting the pure elements results in a grainy structure with substantial  $\text{TiO}_2$  inclusions in the grain boundaries. Such inclusions would not be removed even by continuous ion bombardment. It was nevertheless possible to obtain a nearly oxygen-free surface by means of a thermal treatment. As shown in Fig. 1, annealing the sample at 923 K in vacuum was sufficient to remove all the carbon and most of the oxygen. We determined by mass spectrometry that carbon and oxygen were desorbed from the surface as  $\text{CO}_2$  during annealing. Samples prepared from different

melts had different amounts of bulk carbon and oxygen and for some samples the residual after annealing was carbon rather than oxygen. In every case, however, it was possible to obtain a clean surface, as residual carbon could be eliminated by exposing the surface to oxygen at 600-700 K. If the oxygen dosing was controlled carefully, no oxygen was left on the surface after this procedure. As shown in Fig. 2, the effect of the annealing was also to reduce the value of the Ti(387 eV)/Pt(237 eV) AES ratio from 3.8 to 1.9, indicating that surface of Pt segregation occurred. The Ti/Pt AES ratio after annealing remained unchanged upon cooling and showed very little dependency on the annealing temperature. All the AES results reported in this paper are for the clean surface obtained after annealing. Once the surface was cleaned and annealed, reaction with oxygen was observed only at high temperature and/or high oxygen pressure. At room temperature the surface did not react detectably with oxygen for pressures up to  $10^{-5}$  torr. In contrast, the bombarded surface reacted with oxygen in the  $10^{-8}$  torr range.

Figure 2 shows the AES results after room temperature CO adsorption on the clean  $Pt_3Ti$  surface. The carbon AES peak after CO saturation on the surface shows the double peak characteristic of the undissociated molecule (7). No residual carbon was detectable after CO flash desorption, indicating that dissociation did not occur during desorption. If the alloy surface was oxidized by 100L dosing with  $O_2$  at 573 K, CO adsorption was completely suppressed, as the residual amount seen in curve 3 could be attributed to desorption from the crystal holder.

Figure 3, curve 2 shows the result for CO thermal desorption from the Pt<sub>3</sub>Ti clean surface and curve 1 the result with a pure Pt surface. The surface was cleaned as described above, saturated with CO at room temperature (10L dose) and flashed at a rate of 44 Ks<sup>-1</sup>. For the pure Pt result, the Pt<sub>3</sub>Ti surface was covered with Pt by evaporation until the Ti AES peaks were undetectable and then annealed at 700 K (higher temperatures caused Ti diffusion through the Pt film). After a 10L dose of CO at room temperature, the TDS peak was recorded in the same manner as for the clean Pt<sub>3</sub>Ti surface. In curve 3 we show the CO TDS peak after Pt<sub>3</sub>Ti had been superficially oxidized by exposure to 5x10<sup>-6</sup> O<sub>2</sub> at 1000 K. The results on the clean polycrystalline Pt surface found here are comparable to those reported in the literature (8-10). Two desorption states were observed, which are usually interpreted as adsorption on the two different low index facets, (111) and (100), that normally occur on annealed polycrystalline Pt. CO on the Pt(111) facet has the lower desorption temperature, and according to work on single crystals (11), the saturation coverages on the two facets would differ only slightly.

In comparison with the pure Pt, the CO TDS curve for Pt<sub>3</sub>Ti shows two important differences: smaller area, indicating lower total CO coverage; a shift of the peak toward lower temperatures. The suppression of the high binding energy state has also been observed with a Au rich Pt/Au alloy, but no shift in the peak temperature for the low binding energy state was reported (12). Since the x-ray diffraction analysis of the Pt<sub>3</sub>Ti did not indicate any preferred orientation in this crystal, the peak shift probably did not arise just from the absence of (100) facets in the



intermetallic surface, but rather represents a real difference in adsorption energy. Furthermore, we have conducted a few CO adsorption experiments on Pt<sub>3</sub>Ti (100) and (111) single crystals, and these gave single TDS peaks displaced to lower temperatures than for either Pt (100) or (111) surfaces. If we estimate the adsorption energy from the temperature at which the first-order desorption rate is maximum (13), the two adsorption states on Pt correspond to 32 and 25 kcal/mole, and the state on Pt<sub>3</sub>Ti to 21 kcal/mole, at least a 4 kcal/mole decrease in adsorption energy.

In Fig. 4, we report the thermal desorption of hydrogen following room temperature dosing at 10<sup>-6</sup> torr. As in the CO desorption experiments, the results for the Pt<sub>3</sub>Ti surface were compared to those on a pure Pt surface obtained by evaporation onto the intermetallic crystal. In comparison with pure Pt, the very small hydrogen signal observed from the intermetallic surface can be taken as indicative of essentially no chemisorption of hydrogen on this surface at room temperature. Unfortunately, our holder was not equipped with any cooling capability, so we could not look for retention of hydrogen by the surface at lower temperature. The absence of hydrogen chemisorption could not be attributed to artefacts like surface contamination, as AES indicated the surface was clean, or CO competitive adsorption (no significant CO signal seen by mass spectrometer during the flash) or oxygen "clean-off" (no significant oxygen signal in mass spectrometer during or following hydrogen dosing). Also, the same surface was observed to chemisorb CO, as shown in Fig. 3, and artefacts like contamination and oxygen "clean-off" would have suppressed CO adsorption as well. The suppression of hydrogen chemisorption and the reduced bond energy for adsorbed carbon monoxide appear to be genuine effects of the presence of Ti in the Pt surface.

An interpretation of these results must first consider the bimetallic surface structure and composition. The AES signal reflects contributions from several surface layers and therefore the value of the Ti/Pt AES ratio alone cannot provide an unambiguous determination of the outermost layer composition. However, use of the elemental sensitivity factors (6), inelastic mean-free paths (14), and the usual relations for escape depths of Auger electrons (15) enable certain extreme cases of surface composition to be eliminated. In analogy with the Pt/Sn exothermic alloy (16,17), we assume, for this approximate calculation, that enrichment would occur through an exchange of atoms in the first two atomic layers (17). If we define an enrichment factor  $f$ , as

$$f = (\text{Ti/Pt})_{\text{surf}} / (\text{Ti/Pt})_{\text{bulk}}$$

so that  $f > 1$  is enrichment by Ti, and  $f < 1$  is enrichment by Pt, then it can be shown that the observed Ti/Pt AES ratio indicate that  $0.5 < f < 1.5$ , i.e. pure Pt or pure Ti overlayers are totally inconsistent with the AES data. Beyond these extreme cases of enrichment that do not seem to occur, it is possible to draw definitive conclusions about the surface composition from just the AES data. The chemistry of this system and general concepts (17) of surface segregation permit us to make qualitative arguments concerning the most likely surface composition. It seems unlikely that the bombarded bimetallic surface had the bulk composition, since the reactivity of this surface with oxygen at room temperature suggest a Ti rich surface. This would mean that the Pt segregation observed on annealing probably represents restoration of the bombarded surface to the bulk composition. Theoretical considerations (17) of the driving forces for surface enrichment indicate that in very exothermic alloy systems, where there is strong

intermetallic bonding, the strong bulk-type bonding predominates over surface-specific forces and termination at the surface in the bulk composition and structure is to be expected. While not definitive, the present AES data are at least consistent with this expectation.

The data presented here indicate the effect of Ti on CO adsorption is most probably a ligand effect, i.e. a modification of the Pt chemical properties caused by charge redistribution upon forming the Pt-Ti bonds. The CO-metal bond is very sensitive to variations in the electron distribution on the metal atoms. This bond has been described in terms of both a  $\sigma$  type bond, where the  $5\sigma$  molecular orbital donates electrons to the empty metal orbitals, and a  $\pi$ -type bond, where the metal donates electrons to the  $\pi^*$  antibonding orbitals of the CO molecule (18) which weakens the C=O bond but strengthens the metal-C bond. In the Engel-Brewer intermetallic bonding concept (1), the Pt rehybridizes from the metallic electronic configuration ( $d^9s + d^{10}s^0$ ) in order to maximize the number of d-bonds it can form with Ti. The Pt-Ti bonding maximizes use of the Pt d-orbitals for the intermetallic bond, and would leave only sp orbitals available for adsorbate bonding. One would expect then from the Engel-Brewer model that CO bonded to Pt in  $Pt_3Ti$  would have less bonding to the CO  $\pi^*$  orbitals than in the case of pure Pt, resulting in a weaker Pt-carbon adsorptive bond.

The SMSI effect for Pt dispersed on titanium oxide that was subsequently heated in hydrogen involved complete suppression of  $H_2$  and CO adsorption at room temperature. Tauster, Fung and Garten (3) considered the possibility of  $Pt_3Ti$  formation and showed that under their conditions of reduction at  $500^\circ C$  it was at least thermodynamically possible. However,

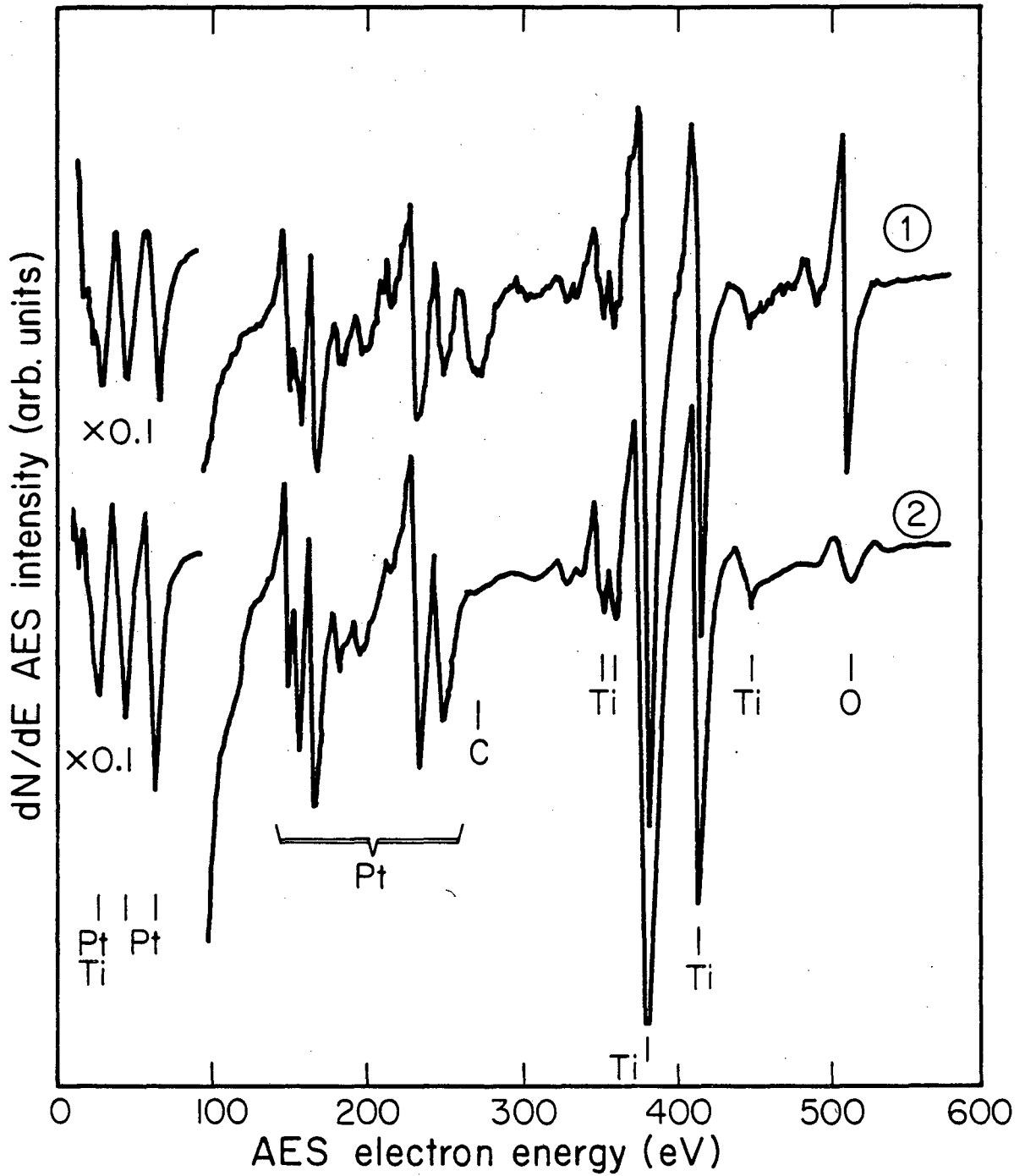
our results indicate that intermetallic formation would not account entirely for the SMSI effect described by these workers. In our experiments, hydrogen adsorption was absent on the intermetallic but CO adsorption was completely suppressed only when  $\text{TiO}_2$  segregated to the surface upon heating the  $\text{Pt}_3\text{Ti}$  in oxygen at elevated temperature. However, the trends of the effect of Pt-Ti intermetallic bonding on  $\text{H}_2$  and CO chemisorption are clearly the same as the effect of strong reduction of  $\text{Pt/TiO}_2$ , and it would seem that strong intermetallic bonding is implicated in the SMSI effect. It may be that the  $\text{Pt/TiO}_2$  system has structural constraints or anomalies that complement the intermetallic bonding effect. Further studies are in progress in order to elucidate the characteristics of the Pt-Ti bond by electron spectroscopy (XPS, UPS), and to make definitive determinations of the composition and structure of the intermetallic surface using LEED and single crystals.

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Figure Captions

- 1.) AES spectrum of the Pt<sub>3</sub>Ti surface. 2Vpp modulation  
Curve 1: surface after ion bombardment  
Curve 2: surface after annealing at 923 K
- 2.) AES of the Pt<sub>3</sub>Ti surface showing the carbon (CO) features for the clean surface, the clean surface after SA turnover with CO and the oxidized surface after saturation with CO, 2Vpp modulation.
- 3.) CO thermal desorption from  
Curve 1: polycrystalline Pt  
Curve 2: polycrystalline Pt<sub>3</sub>Ti (clean)  
Curve 3: polycrystalline Pt<sub>3</sub>Ti (oxidized)
- 4.) H<sub>2</sub> thermal desorption from  
Curve 1: polycrystalline Pt  
Curve 2: polycrystalline Pt<sub>3</sub>Ti



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Fig. 1

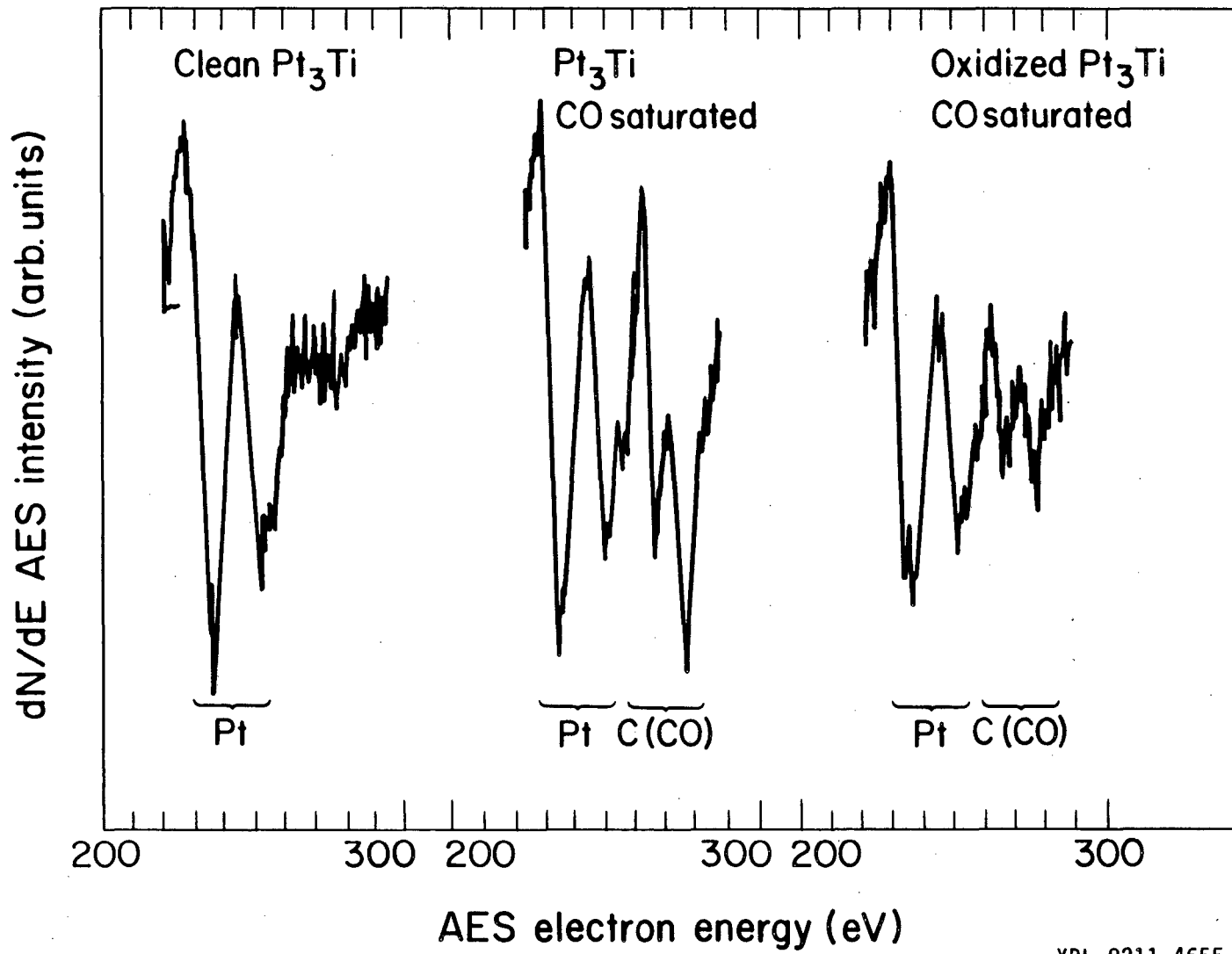
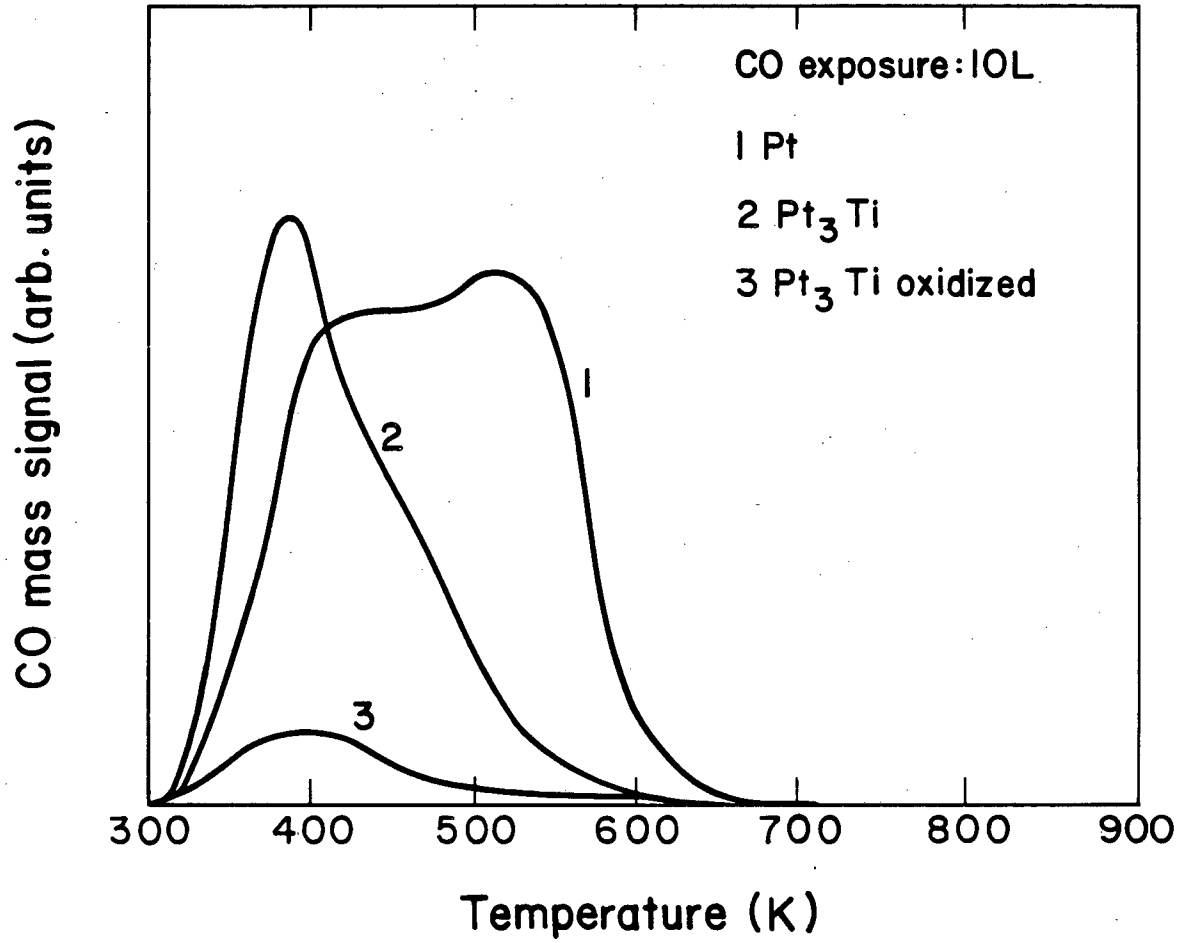


Fig. 2

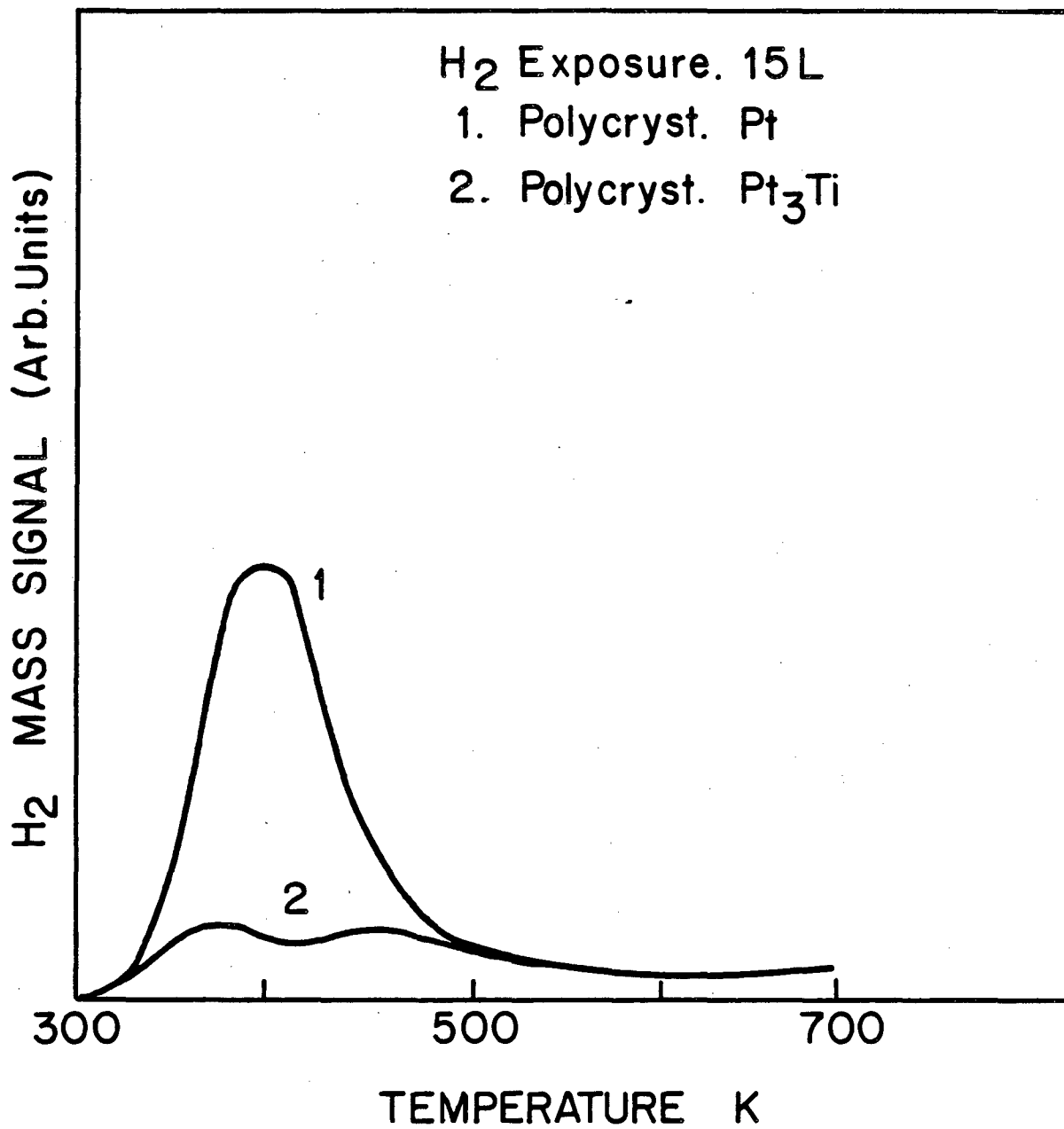
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Fig. 3





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Fig. 4

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