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OF Pt₃M ALLOYS (M = Ti, Co, and Sn)

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Abstract

Studies of the surface composition and CO chemisorption on the [111] and [100] oriented single crystals of the isostructural (fcc) alloys of bulk stoichiometry Pt_3M (M = Ti, Co and Sn) are reviewed. In principle, the study of these alloys is ideal for separating ensemble effects from electronic effects in adsorbate bonding, since the surfaces of these ordered alloys formed by bulk truncation have the M atoms in fixed positions without any M-M pair sites. Also by varying M from Ti to Co to Sn one can examine the effect of the d and s-p orbital contributions to the intermetallic bond on the binding energy of CO. In practice, one must account for surface segregation, and the formation of surfaces that do not have the ideal structure and composition. The strength of the intermetallic bond is found to play a major role in determining the composition of the surface. In the very exothermic alloys Pt_3Ti and Pt_3Sn, the thermodynamic tendency for the atom with the lower surface energy to be at the surface determines which of the two bulk planes forms the surface plane in the [100] orientation, either pure Pt ($TiPt_3$) or 50% M ($SnPt_3$). In $CoPt_3$ where the intermetallic bonding is relatively weak, the lower surface energy of Pt produces pure Pt planes on both the [111] and [100] orientations. Photoemission and thermal desorption studies show that the intermetallic bonding in all three alloys has only a small effect on the binding energy of CO, a decrease in adsorption energy of 20 kJ/mol. The surprising invariance of adsorption energy on Pt_3M surfaces having such a large variation in the d-orbital configuration of the M atom is attributed to the predominance of s-p orbital contributions to the intermetallic bond in these alloys.

1. Introduction

The relationship between catalytic activity and the electronic structure of a metal or multimetallic compound in a long standing problem in catalysis. The earliest attempts to examine this problem [1-4] focussed on the role of d-electrons, typically using Group VIII-Group IB bimetallic-alloys in an attempt to vary in a continuous and controlled fashion the

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d-band occupancy. The basic concepts of band filling in these alloys came from Mott and Jones [5]. Although many studies of this type were conducted, the approach was not very fruitful in elucidating the so-called electronic factor in catalysis. There were a number of unanticipated phenomena that undermined this approach. First there was the problem of surface segregation [6], which turned out to be a far more common phenomenon than anticipated, which produced surface compositions far different from the bulk composition. There was the further complication of surface clustering [7], where an ensemble or cluster of one element forms in a "sea" of the other element, i.e. a surface miscibility gap. Then there was realization of the fundamental deficiency in the concept that the catalytic activity of a metal is determined by the electronic structure of the crystal as a whole.

At present, the electronic factor in catalysis by metals is generally viewed in terms of localized chemical bonding similar to the "ligand" bonds in organometallics [8]. Modern computational methods permit very accurate calculations of the local (site-specific) electronic configurations in alloys, e.g. [9], and the use of the modern "alphabet soup" of surface science techniques has made it possible to identify and compensate for surface segregation phenomena. In short, one is in a much better situation today to examine the electronic factor in catalysis by the study of alloys than when this was first attempted. The purpose of this paper is to summarize a series of recent studies in our laboratory directed towards the question of the electronic factor in catalysis' specifically the role of d-electrons as evidenced by the nature of the chemical bond formed between carbon monoxide and the metal surface. The chemical bonding of CO to transition metal surfaces is perhaps the best understood surface bond of any molecular adsorbate. The basic concepts for the bonding originated with the semi-emperial molecular orbital theory of Blyholder [10], and have been refined by modern

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treatments [11-13]. The trends in metal-CO bonding in transition metals are dominated by mixing of occupied d-states of the metal with the unoccupied $2\pi^*$ anti-bonding orbitals of the CO molecule, so-called 2π "back-bonding". This back-bonding plays an extremely important role in the reactivity of the adsorbed CO molecule, as it weakens the C-O bond, and explains why CO dissociates on Ta at room temperature but not on Ni or Pt. The strength of the metal-CO bond then is a very sensitive measure of perturbations to the d-states of the metal due to the intermetallic bond formed by alloying.

In our studies, we sought to control the surface composition and avoid the ensemble (clustering) problem of solid-solution alloys by using highly ordered exothermic alloys having the bulk stoichiometry Pt_3M, with M = Ti, Co and Sn, having the fcc $AuCu_3$ ($L1_2$) crystal structure. ‡ In principle, these alloys form low index surfaces with the M atoms in well-defined positions completely surrounded by Pt atoms. Further, we used single crystal surfaces so that the local electronic configuration of every site on the surface is same all over the surface. Because of the very strong intermetallic bonding in two of these alloys, Pt_3Ti and Pt_3Sn, bond-breaking models [14] suggested that surface planes should have the same composition as bulk planes, with the thermodynamic tendency of one component to be at the surface (Pt in the case of Pt_3Ti, Sn in the case of Pt_3Sn) resulting in preferential termination of either (100) or (110) surfaces in the plane containing the higher concentration of the surface active element, e.g. either the "PtSn" plane (Pt_3Sn) on the pure Pt plane (Pt_3Ti). If this turned out to be the case, such surfaces are ideal for chemisorption studies, since the local site geometries would be well known and homogeneously distributed on the surface. By varying M from Ti to Co to Sn, we have three isostructural alloys with a large variation in d-occupancy, from d^2

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‡ The publications cited in this paper as related to the properties of "Pt3Co" are actually for the alloy $Pt_{80}Co_{20}$ which was not ordered in the bulk. However, recent work in our laboratory with a stoichiometric Pt_3Co crystal which is ordered has shown the same surface structures and properties as the $Pt_{80}Co_{20}$ crystal.

in Ti, to d^7 in Co to d^{10} in Sn, the latter being a completely filled 4d shell 25 eV below the Fermi level. Thus, in principle, one can compare the effect of p-p state intermetallic bonding (Pt-Sn) to direct d-d state and/or spd $^{-spd}$ hybrid (Pt-Ti and Pt-Co) bonding on the way CO bonds to the surface without the complication of widely varying surface structures and site geometries.

2. Results and Discussion

2.1 Surface composition

The structure of the three low index surfaces of Pt_3Sn [15] and Pt_3Co [16,17] were in complete accord with the thermodynamic models [14,18]. The Pt_3Sn (111) surface has the bulk termination structure with 25% Sn in the surface, while the Pt_3Sn (100) and (110) surfaces have the bulk termination structures formed by the "PtSn" planes with 50% Sn in the surface. The Pt_3Co surfaces, both (111) and (100), are terminated in reconstructed surfaces of pure Pt outermost planes [16]. In Pt_3Co(100), the Pt surface plane is even reconstructed into a quasi-hexagonal structure similar to the quasi-hexagonal structure of the pure Pt (100) surface [17]. The second atomic layer in Pt_3Co (100) is a bulk lattice plane containing 50% Co. In Pt_3Co (111), the pure Pt surface layer can only be produced by interchange of Co surface atoms with Pt atoms in the second plane forming a layer containing 50% Co, which means neither of the first two atomic layers are bulk lattice planes of $L1_2$ structure. The 50% concentration in {111} planes causes the formation of Co-Co bonds which have a slightly lower bond energy that Pt-Co bonds. However, the difference in surface energy between Pt and Co more than compensates for the energy penalty of forming Co-Co bonds in the second layer. In Pt_3Ti, the relative surface energies are similar to those in Pt_3Co (i.e. there is a thermodynamic preference for Pt to be at the surface), but the energy penalty for forming

bulk Ti-Ti bonds at the expense of Pt-Ti bonds is very large, e.g. 80 kJ /g-atom. Thus, thermodynamic models [19] predict preferential termination of Pt_3Ti (100) in the pure Pt planes, as in Pt_3Co, but the Pt_3Ti (111) surface should have the bulk termination structure, like Pt_3Sn (111). Unfortunately, the experimental results are equivocal. Ross and co-workers [20] found bulk termination structure with mixed layers on both Pt_3Ti (111) and (100) crystals, while Dwyer and co-workers [21] reported finding a pure Pt surface on Pt_3Ti (111), i.e. a "sandwich" structure similar to that on Pt_3Co (111). Dwyer and co-workers did not study Pt_3Ti (100). Possibly the different surface preparation procedures used by the two groups would explain the different results, considering the reactivity of Ti and the difficulty of preparing clean surfaces containing such reactive metals. Fortunately for my purposes here, the properties of the Pt_3Ti (111) reported by Dwyer and co-workers and our group are in complete agreement, e.g. XPS chemical shifts, UPS valence band spectra and even the CO thermal desorption curves.

2.2 Carbon monoxide chemisorption

On all the low index surfaces of all three Pt_3M alloys, the thermal desorption (TDS) curves look surprisingly similar. This is shown by the comparison of the TDS curves for the (111) surfaces in Figure 1. The TDS curve shows a rigid shift towards lower temperature versus a pure Pt (111) surface (obtained in the same apparatus under the same conditions) of about 50 K in each case. Using the same frequency factor as for Pt(111), this converts to a decrease in adsorption energy of 20 kJ/mol. There are few other manifestations of changes in the bonding of CO to the alloy surface versus the pure Pt surface, e.g. no shifts in 01s XPS, or new valence bond features in UPS. In the case of Pt_3Ti (111), Paul et. al. [21] reported a 30 cm^{-1} decrease in the metal-carbon vibration and a 40 cm^{-1} decrease in the carbon-oxygen

vibrations compared to Pt(111). There are no vibrational spectra reported for CO on either Pt3Co or Pt3Sn bulk alloy surfaces. The vibrational spectra for CO/Pt3Ti(111) indicate a weakening of <u>both</u> the metal-carbon-bond and the carbon-oxygen bond upon formation of the Pt-Ti intermetallic bond.

2.3 Electronic structure

Wertheim et. al. [22] used a Born-Haber cycle analysis to show how core-electron binding energy shifts of the constituent elements in Pt3Hf are directly related to the enthalpy of formation. Hf is isoelectronic with Ti, and one might expect a very similar electronic structure in Pt3Hf versus Pt3Ti. Table 1 summarizes the enthalpies of formation and core-level binding energies for the Pt3M series in our studies. Qualitatively, the magnitude of the M atom core-level shifts does correlate with the enthalpy of formation. The direction of the charge transfer is clearly from the M atom to Pt, in accord with the expectations based on electronegativity differences and with the semi-empirical model of Miedema et. al. [23], and the amount of charge transfer (uncorrected for final state screening) appears to correlate (qualitatively) with the enthalpy of formation. It is interesting to note an *apparently* similar strength of intermetallic bonding from d-electrons (Ti) as from p-electrons (Sn), a surprising result. As discussed below, the similarity in bond strength between Pt3Ti and Pt3Sn is actually due to a similarity in bonding electrons, that the intermetallic bond is actually formed from p-electrons from *both* Ti and Sn.

The valence band spectra of all three Pt3M compounds have qualitatively similar valence band structures as seen either from x-ray or UV photoemission. A typical result is shown in Figure 2, which compares the UPS energy distribution curves (EDC) of Pt3Ti(111) with Pt(111) in the same spectrometer. Also shown is the EDC for polycrystalline Pt3Hf from the

work of Wertheim et. al. [22]. As pointed out before, Pt_3Ti and Pt_3Hf are isoelectronic, and it is not surprising that the EDC's for the two curves are very similar. Compared to Pt, there is a lower density of states near E_F, between E_F and (E_F-2 eV), and a much larger and narrower state at the bottom of the valence band, near E_F-6 eV. The EDC for $Pt_3Sn(111)$ is shown in Figure 3, with a direct comparison with the calculated DOS of Skriver [24]; for purposes of this comparison the secondary electron background has been subtracted using the Shirley method [25]. The major features of the theoretical DOS for Pt_3Sn are reproduced in the EDC. The band structure of Pt_3Sn has a unique 5d band positioned near the Fermi level in a common sp band formed by Pt 6s and 6p states as well as Sn 5p states. As expected, the bonding in Pt_3Sn is primarily via the partially occupied Sn 5p and the unoccupied Pt 6p orbitals. The effect of this donation of p electrons to the unoccupied Pt 6p states is to shift the d-states down in energy and narrow the band. In the Shustorovich and Baetzold model [26], this shift of the Pt 5d states results in less overlap with the $2\pi^*$ states of CO and decreases the bond energy of CO on the Pt sites in the Pt_3Sn surface.

I am not aware of a comparable full band calculation for Pt_3Ti or Pt_3Co, but there is a comparable calculation for Pt_3Hf by Watson et. al [27]. What is surprising and particularly significant in this calculation is the hybridization of the Hf d-states into p-states and the strong p-character to the intermetallic bond. The Pt site d transfer is essentially zero valued despite the fact that the alloy bands that are distinctly Pt d-like are filled by the intermetallic bond formation. This band filling by ~1/2 electron per Pt is caused by hybridization of other wave-function character into the nearly filled Pt d bands. Thus, the intermetallic bonding in Pt_3Hf is actually quite similar to the bonding in Pt_3Sn in spite of the fact that Hf and Sn have completely different d-electron configurations. Alloys like Pt_3Hf and Pt_3Ti appear to

represent the most dramatic departure from the rigid band model of Mott and Jones [5], which predicted that Hf (or Ti), with the greater number of d holes than Pt, would gain in d count by hybridization of those d holes into the nearly occupied Pt d bands.

The strong p-character of the intermetallic bond in this family of alloys thus has only an indirect effect on the d-states localized on the Pt sites, and therefore a relatively subtle effect on the chemisorption of organic molecules that bond via the Pt d-orbitals, like CO. It is interesting to compare the present results with Pt bulk alloys with qualitatively similar results with Pt monolayer films on Ta [28] and related systems like Pd films on Ta and W, and Ni on W and Mo [29]. In the case of the (100) and (110) surfaces of Pt_3Ti and Pt_3Co, one actually has a structure similar to these pseudomorphic monolayers, a monolayer on-top-of a dissimilar metal substrate, but in the alloy case the substrate is a 50% PtTi or PtCo alloy layer versus say a pure Ti or Co layer. Nevertheless, one sees qualitatively similar behavior, the EDC's for Pt/Ta(110) reported by Ruckman et. al. [28] is similar to that in Figure 1 for Pt_3Ti or Pt_3Hf, and the CO is also more weakly bonded to the Pt monolayer, with an even bigger shift in desorption peak temperature to below 300^oK. Goodman and co-workers [29] have put forward a general correlation for interpreting the CO TDS from a variety of metal monolayer systems, based on the molecular orbital theory of Shostorovich and Baetzold [26]. The strength of the CO bond, as measured by the TDS peak temperature, was found to be proportional to the energy separation between the centroid of the valence band EDC and the CO $2\pi^*$ orbital, and both the stronger and weaker bonding cases are reported. This "correlation" is also consistent with the results for the Pt_3M bulk alloys of this paper. Interestingly, the magnitude of the effects of metal-substrate bonding on CO adsorption are even stronger in the case of Pt/Ta(110) monolayers than in these bulk Pt alloys. To my knowledge CO adsorption on

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Pt$_3$Ta has not yet been studied. If one assumes that CO on Pt$_3$Ta surfaces would be similar to CO on Pt$_3$Ti, then the larger effect of the metal-substrate intermetallic bond in the Pt/Ta(110) monolayer versus a Pt$_3$Ta bulk alloy could simply be due to the greater coordination of Ta with Pt in the former case, e.g. Pt surface atoms are bonded to four Ta atoms of the substrate in Pt/Ta(110), but only to two Ta atoms in the second layer of the Pt$_3$Ta(100) alloy (assuming the same surface structure as the Pt$_3$Ti(100) surface). Another factor would be localization of the d-orbitals in the purely 2D monolayer in Pt/Ta(110) due to the complete absence of Pt in the second layer, which would cause even more narrowing of d-band than in the alloy.

Acknowledgment

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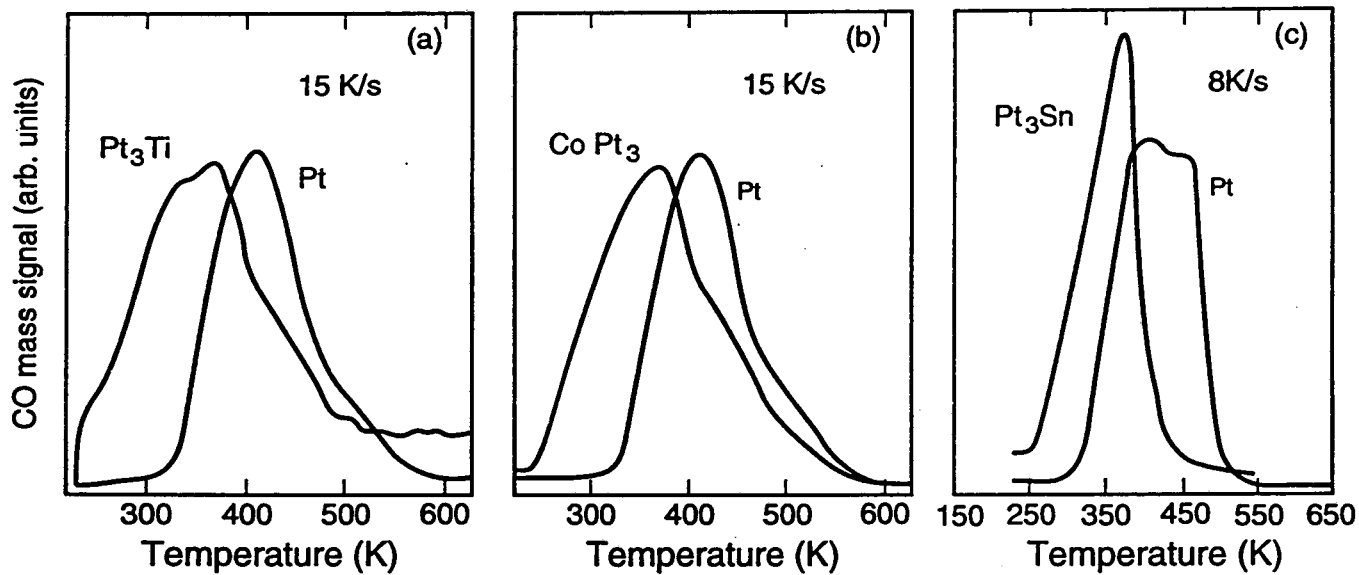36.   A. Haner, P. Ross, U. Bardi and A. Atrei, submitted to J. Vac. Sci. and Technol. A.

Figure Captions

Figure 1.   Thermal desorption spectra (TDS) for CO adsorbed to saturation at $225^{O}K$ on the (111) faces of Pt_3Ti [20c], Pt_3Co [16b] and Pt_3Sn [36] versus a Pt (111) crystal in the same apparatus.

Figure 2.   UPS energy distribution curves (EDC's) comparing Pt (111) with Pt_3Ti (111) and polycrystalline Pt_3Hf. The Pt (111) and Pt_3Ti (111) are angle-resolved spectra taken at normal emission, 0.3 eV resolution (from [20c]). EDC of Pt_3Hf from Wertheim et. al. [22] was obtained with a similar spectrometer (hemispherical) but unspecified resolution.

Figure 3.   Comparison of experimental EDC for Pt_3Sn (111) (with background subtracted) and theoretical total DOS of Skriver [24]. The EDC is angle-integrated at 0.3 eV resolution (previously unpublished spectrum).
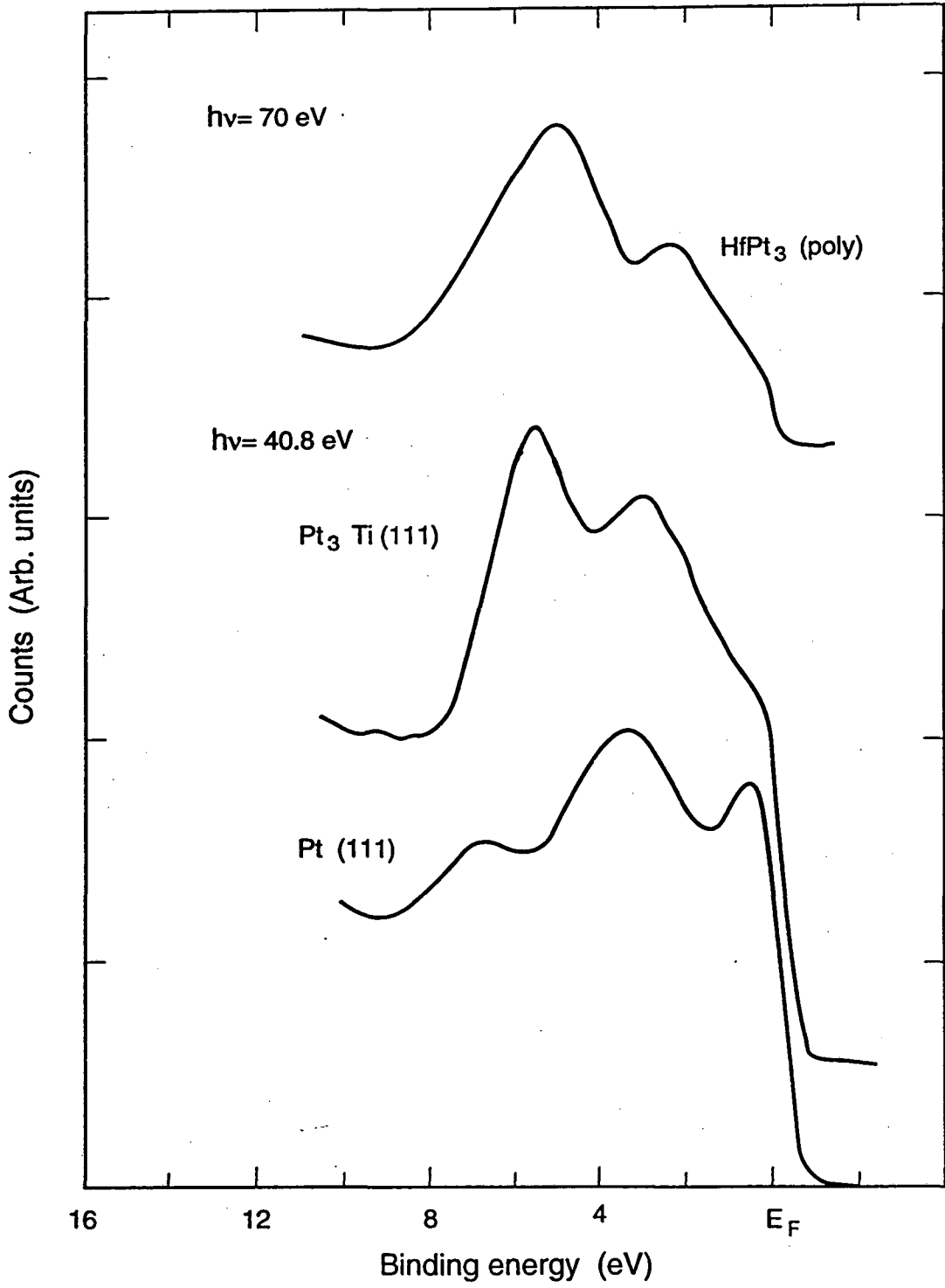
Table 1

M	Atomic Configuration	Enthalpy of formation of Pt_3M (kJ/g-atom)	Ref.	Chemical shift‡ (vs. M^0) in eV	Ref.	Apparent charge transfer
Ti	$3d^2\,4s^2$	-85.4	31	+1.3	20a	$-2e^-$
(TiO)	(+II)	-	-	+0.8	34	
(TiO_2)	(+IV)	-	-	+4.7	34	
Co	$3d^7\,4s^2$	-3.0	32	+0.5	16	$-0.5e^-$
(CoO)	(+II)	-	-	+2.1	35	
Sn	$4d^{10}\,5s^2\,5p^2$	-50.2	33	+0.6	36	$-1e^-$
(SnO)	(+II)	-	-	+1.7	35	

Correlation between the electronic structure and the intermetallic bond energy in Pt_3M ordered $(L1_2)$ alloys

‡ Chemical shifts are not surface resolved and are representative of bulk atom states

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Fig. 1

XBL919-7055

hν= 70 eV

HfPt$_3$ (poly)

hν= 40.8 eV

Pt$_3$ Ti (111)

Pt (111)

Counts (Arb. units)

16   12   8   4   E$_F$

Binding energy (eV)

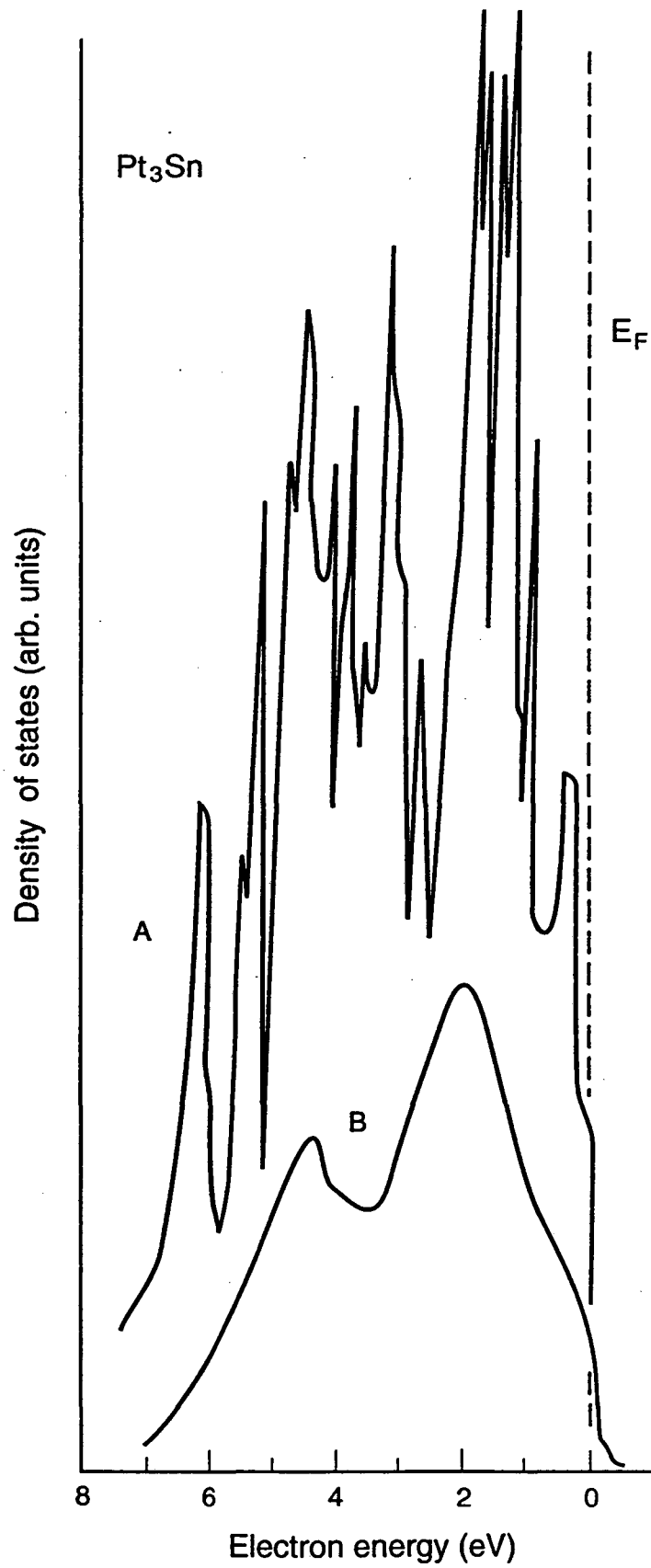XBL919-7054

Fig. 2

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Fig. 3

16   XBL919-7056

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