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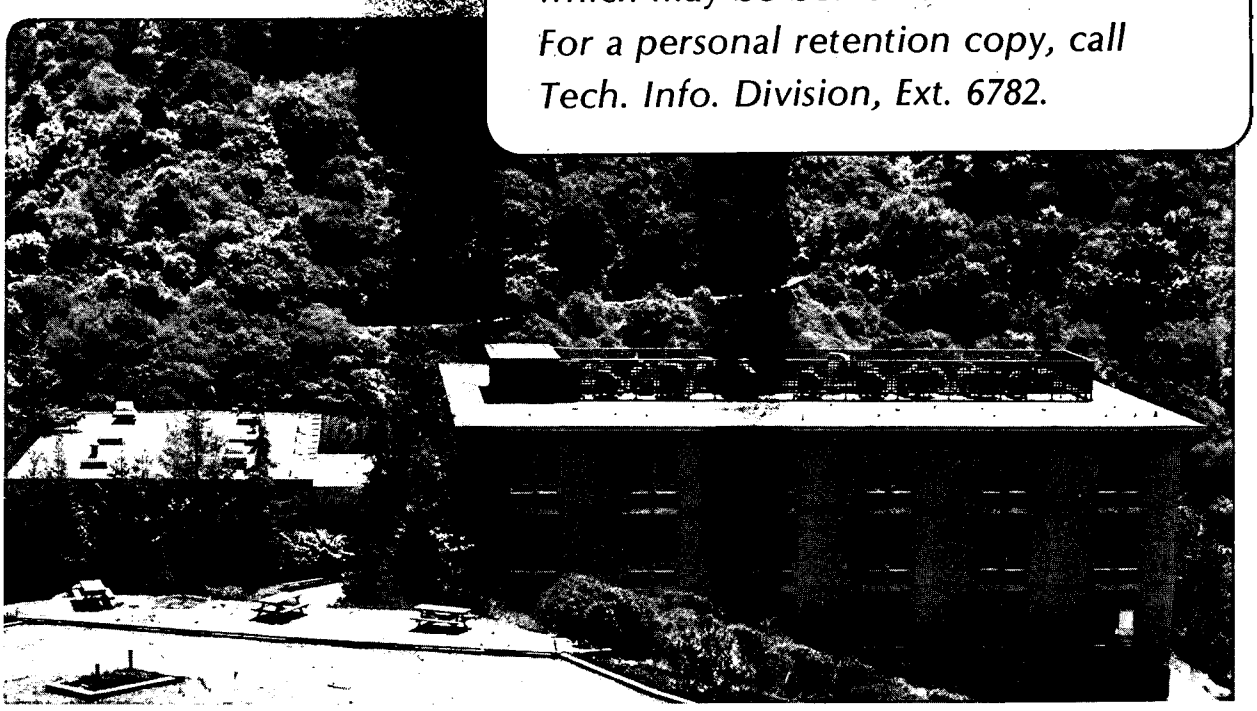

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VALENCE BAND AND CORE-LEVEL ELECTRONIC STATES IN Pt_3Ti

G. N. Derry[§] and P. N. Ross
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720

ABSTRACT

XPS data for the valence band, the Pt4f states, and the Ti2p states are presented for the intermetallic Pt_3Ti. Relative to the Pt valence band, the Pt_3Ti band shows a decrease in the density of states just below the Fermi level and a shift of the centroid to higher (binding) energy. Ti2p and Pt4f binding energies showed relatively large shifts with respect to the pure metals. These changes in the valence band density of states and core level binding energies are shown to arise from hybridization of the d-orbitals in both metals to form strong intermetallic bonds. Bond formation is accompanied by charge transfer from Ti → Pt leaving the Ti atoms in ca. +1 valence state.

[§]Present address: Department of Physics, University of North Carolina, Chapel Hill, North Carolina.

Intermetallics formed by combining metals from the left side of the transition series with metals from the right side have very interesting properties. They tend to be highly stable and unreactive, exhibit a variety of ordered phases, and have extremely high heats of formation.[1] It was recently discovered that they can show very high catalytic activity for the electrolytic reduction of oxygen to water in fuel cells.[2] The high stability of these intermetallics has been qualitatively interpreted in terms of the Engel-Brewer picture,[1] and a semi-empirical explanation has been presented by Miedema, et al.[3] More recently, the electronic structure of such materials has been studied by photoemission in conjunction with SCF-Xα-SW cluster calculations,[4] and with Augmented Spherical Wave (ASW) band calculations.[5] In this communication, we present x-ray photoemission spectra of the valence band, the Pt4f states, and the Ti2p states for a single-crystal sample of Pt_3Ti.

The experiments were performed in an ultrahigh vacuum chamber ($P \simeq 1 \times 10^{-8}$ Pa) equipped with a MgKα x-ray source (h = 1253.6 eV) and a hemispherical analyzer with multichannel counting capability. The apparatus is described in detail elsewhere.[6] The hemispherical analyzer has an intrinsic kinetic energy resolution of ca. 1.5% of the pass energy. Pt4f core level spectra and valence band spectra were taken at pass energy of 64 eV, while the Ti2p spectra were taken at pass energy of 128 eV. The sample was a single crystal of Pt_3Ti cut to expose the (111) surface. The surface was cleaned <u>in vacuo</u> by numerous cycles of heating in oxygen, Ar ion sputtering, and high temperature annealing. The surface was difficult to clean due to the affinity of the titanium for oxygen at elevated temperatures. Eventually, however, the above procedure yielded a surface with less than

5% monolayer contamination from carbon and oxygen as determined by XPS. The sample was oriented to maximize bulk emission (i.e. near normal take-off) making the influence of any residual contaminants negligible.

Data for the valence band emission is presented in Fig. 1. At these energies the final state is in the continuum and the data should be a reasonable representation of the density of states. Relative to the Pt valence band, also shown in the figure, two striking differences are clearly seen: a dip in the density of states ca. 1 eV below E_F; a shift in the valence band centroid to higher binding energy with an increase in the density of states at the bottom of the valence band (at ca. 6 eV below E_F). It is also clear that the Pt_3Ti valence band is poorly approximated by a superposition of the elemental valence bands.[7,8] These features of the valence band suggest strong rehybridization occurs to form the intermetallic bonds.

Similar behavior was seen by Fischer, et al.[4] for polycrystalline Ni_3Ti and interpreted by comparison with 4-atom cluster calculations. The calculations showed a lowering of electron occupancy in states near the highest occupied molecular orbital, in accordance with the experimental result. They also found moderate charge transfer (0.38 e/Ni atom), yielding ~+1 charge at the Ti site. In an extensive study of Ni and Pd alloyed with about twenty metals, Fuggle, et al.[5] also found valence band results similar to Fig. 1 for Ni and Pd alloyed with early transition metals. The decrease in the density of states at E_F is accompanied by d-band narrowing and movement of the centroid to higher binding energy. Fuggle, et al. were able to observe similar trends in the density of states results from ASW band calculations. Their interpretation of these results is that the

valence band modifications are due to d-d hybridization with little (~0.3e) transfer of charge.

These results provide a qualitative basis for understanding the properties of intermetallics. The high binding energy for example can be interpreted as the result of higher electronic density in the metal-metal bonding orbitals, seen in both the valence band data and in the ASW calculations as movement of the d-band centroid to higher binding energy. This has implications for the surface chemistry of these substances; the density of the states near the Fermi level, which generally play an important role in the chemisorption bond, is significantly lower. Moreover, these states were found by Fischer, et al.[4] to be delocalized and s-like in Ni_3Ti. From these considerations one would expect weaker chemisorption for adsorbates that require a high d-electron density of states at the Fermi level, e.g. carbon monoxide and hydrogen.[9] Weaker chemisorption was, in fact, observed by Bardi, et al.[10] for CO and H_2 based on thermal desorption experiments with both polycrystalline Pt_3Ti and with the same (111) surface used in this work. Higher catalytic activity with Pt/Ti alloys might then be expected from the greater mobility and reactivity of adsorbed species.

The theoretical interpretations discussed above[4,5] involved only modes charge transfer, whereas the semi-empirical formulations[1,3] employ charge transfer as the basis of bond formation. The direction of charge transfer in the picture used by Miedema, et al. is consistent with the classical electronegativities of the constituent species. The direction and extent of charge transfer in bond formation can be investigated by measuring binding energy shifts in the core levels, although interpretation is often difficult due to ambiguities in the reference level and to the

small magnitude of the shifts.[11]

In Fig. 2 we present data for the Pt4f levels in Pt_3Ti. The energy scale is the same as in Fig. 1, i.e. the reference zero is the sample Fermi energy. Data for the Ti2p levels is shown in Fig. 3, again with the same energy zero. The binding energy data is summarized in Table 1 along with values from the literature for the pure metals and the binding energy shifts. Note, however, that for each sample the energy zero (Fermi level) is different on an absolute (vacuum) reference basis so the meaning of these shifts is ambiguous.

A method to calculate core level shifts which employs the sample Fermi energy as a natural reference has recently been formulated.[12] The basis of the method is to assume complete screening of the core-hole and then to approximate the screened core-hole site as a (Z+1) impurity embedded in a (Z) metallic matrix. The level shift is calculated from a Born-Haber cycle. This method has been extended to the treatment of alloys[13] and applied to several alloy systems.[14,15] Using the calculational techniques outlined in these references, which employ the Miedema scheme as a computational tool, we find the values to be $\Delta E_c(Pt) = 0.26$ eV and $\Delta E_c(Ti) = 1.0$ eV. Comparison with the shifts in Table 1 shows the agreement to be rather poor. Although the method generally works well,[13,14,15] there have been some other cases where it disagreed with experiment.[14] Steiner, et al.[14] tentatively ascribe these exceptions to changes in the screening caused by large scale rehybridization of the atomic orbitals, which is indicated in the present case by the valence band data for Pt_3Ti.

We propose here another method for interpreting the observed binding energy shifts in alloys which enables one to estimate the direction and

magnitude of charge transfer. The key element in the interpretation is the definition of a common reference electron energy applicable to all three metals (the two pure metals and the alloy). The electron energy with respect to the vacuum level is given by

$$E_V = E_C + \Phi \tag{1a}$$

where E_C is the measured (Fermi referenced) binding energy and Φ is the sample work function. The vacuum level reference is not a suitable common reference because it neglects the surface dipole; we define a true binding energy referenced to the zero of energy for the crystal as

$$E_B = E_C + \Phi - \Phi_b \tag{1b}$$

where Φ_b is the barrier height from the surface dipole. Then we define two new quantities,

$$\delta E_v \equiv E_v(\mathrm{Ti2p}) - E_v(\mathrm{Pt4f}) \tag{2}$$

$$\delta E_B \equiv E_B(\mathrm{Ti2p}) - E_B(\mathrm{Pt4f}) \tag{3}$$

which represents the difference between the titanium and platinum core level energies using the reference level specified by the subscript. It is clear from these definitions that for two dissimilar pure metals we have

$$\delta E_v(\mathrm{Pt,Ti}) = \delta E_B(\mathrm{Pt,Ti}) + \Delta\Phi_b \tag{4}$$

where the $\Delta\Phi_b$ term is the difference between the dipole barrier potentials in platinum and titanium. For the two metals in the intermetallic, however,

$$\delta E_v(\mathrm{Pt_3Ti}) = \delta E_c(\mathrm{Pt_3Ti}) = \delta E_B(\mathrm{Pt_3Ti}) \tag{5}$$

because all reference terms are identical and thus cancel. Finally, we define one more quantity, the shift

$$S \equiv \delta E_c(Pt_3Ti) - \delta E_v(Pt,Ti) \tag{6}$$

which represents the change upon alloying of the difference between the two atomic core levels. From equations 4 and 5 we see that

$$S = \Delta(\delta E_B) - \Delta\Phi_b \tag{7}$$

where the term $\Delta(\delta E_B)$ is the shift measured with respect to a common reference level for all three metals that occur as a result of Pt-Ti bond formation. We can evaluate equation 6 directly from the binding energy data for pure metals and for the intermetallic in Table 1 along with work function data from the literature.[17] The result of these calculations is S = 3.5 eV. Since the term $\Delta\Phi_b$ is the difference of two quantities which are not very large, we would argue that $\Delta\Phi_b$ is almost certainly less than ~2 eV. We therefore conclude that $\Delta(\delta E_B) > +1.5$ eV, and that there is significant charge transfer in Pt-Ti bond formation. Reference spectra for Ti and Pt compounds[16] indicates that a 1 eV shift in binding energy of either Ti2p or Pt4f corresponds to approximately 1 eV^- of charge transfer. The direction of the charge transfer conforms to the classical electronegativity predictions and the magnitude, which cannot be calculated accurately, is approximately consistent with the results (~ + 1e on the Ti site) of the SCF-Xα-SW[4] and ASW[5] calculations.

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Table 1. Core level energies and shifts (in eV), each referenced to the sample's Fermi energy.

	Pt[a]	Ti[a]	Pt_3Ti	Δ
$Pt4f_{7/2}$	70.9		71.7	0.8
$Pt4f_{5/2}$	74.1		75.0	0.9
$Ti2p_{3/2}$		453.8	456.9	3.1
$Ti2p_{1/2}$		459.8	462.9	3.1

[a]from ref. 16

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FIGURE CAPTIONS

Fig. 1. XPS spectrum of the Pt_3Ti valence band. Pass energy 64 eV.

Fig. 2. XPS spectrum of the Pt4f lines for Pt_3Ti. Pass energy 64 eV.

Fig. 3. XPS spectrum of the Ti2p lines for Pt_3Ti. Pass energy 128 eV.

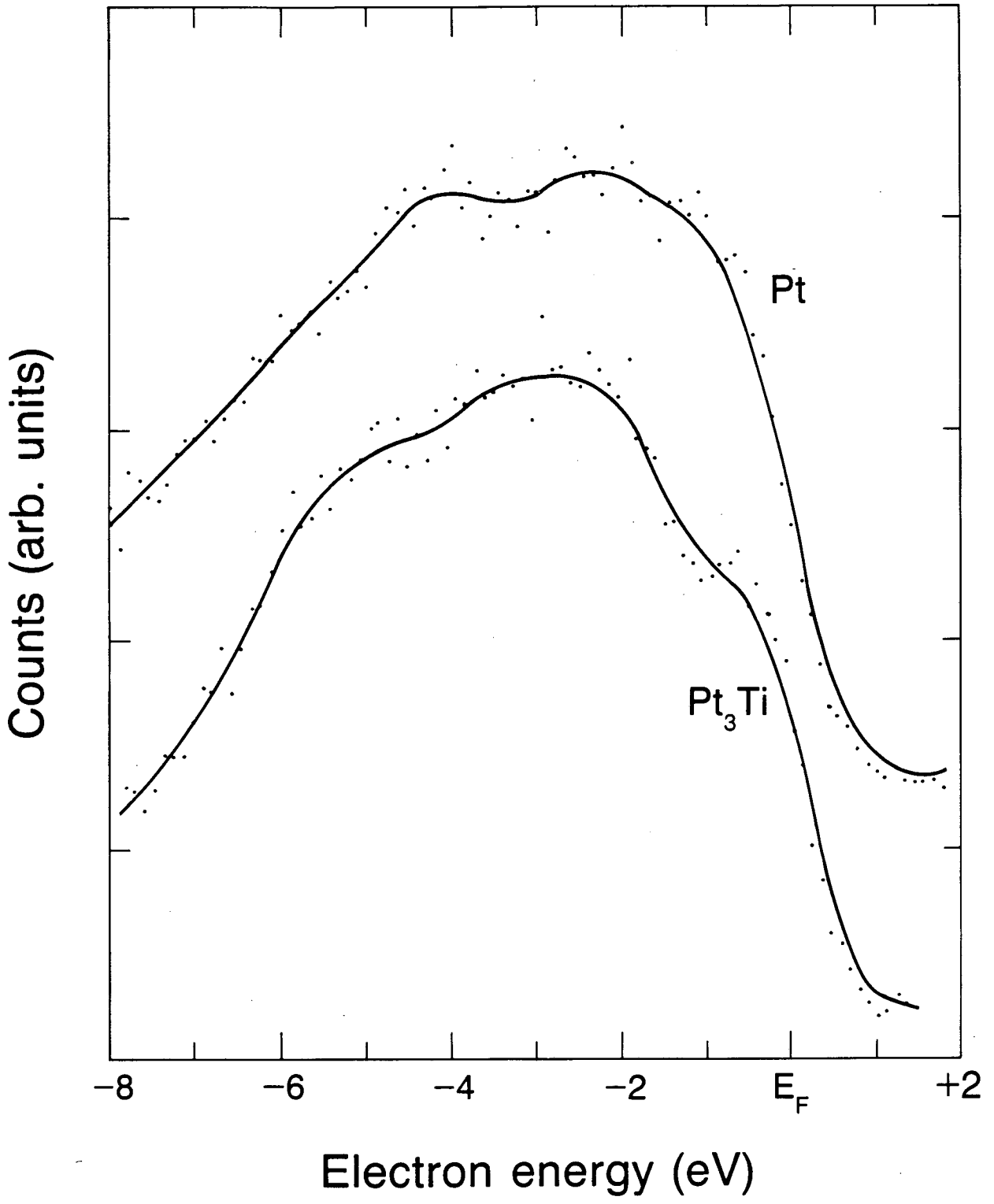

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Fig. 1

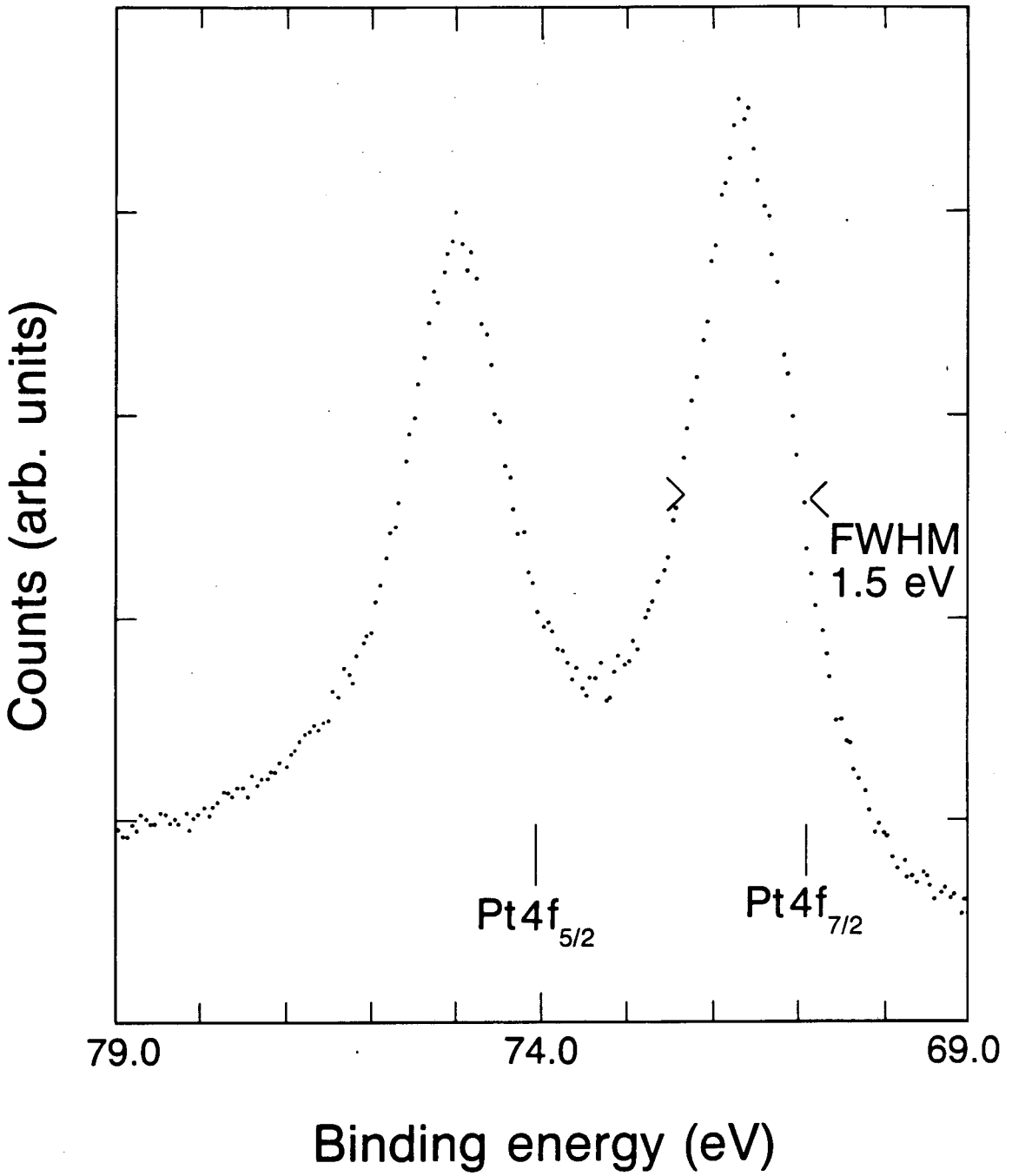

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Fig. 2

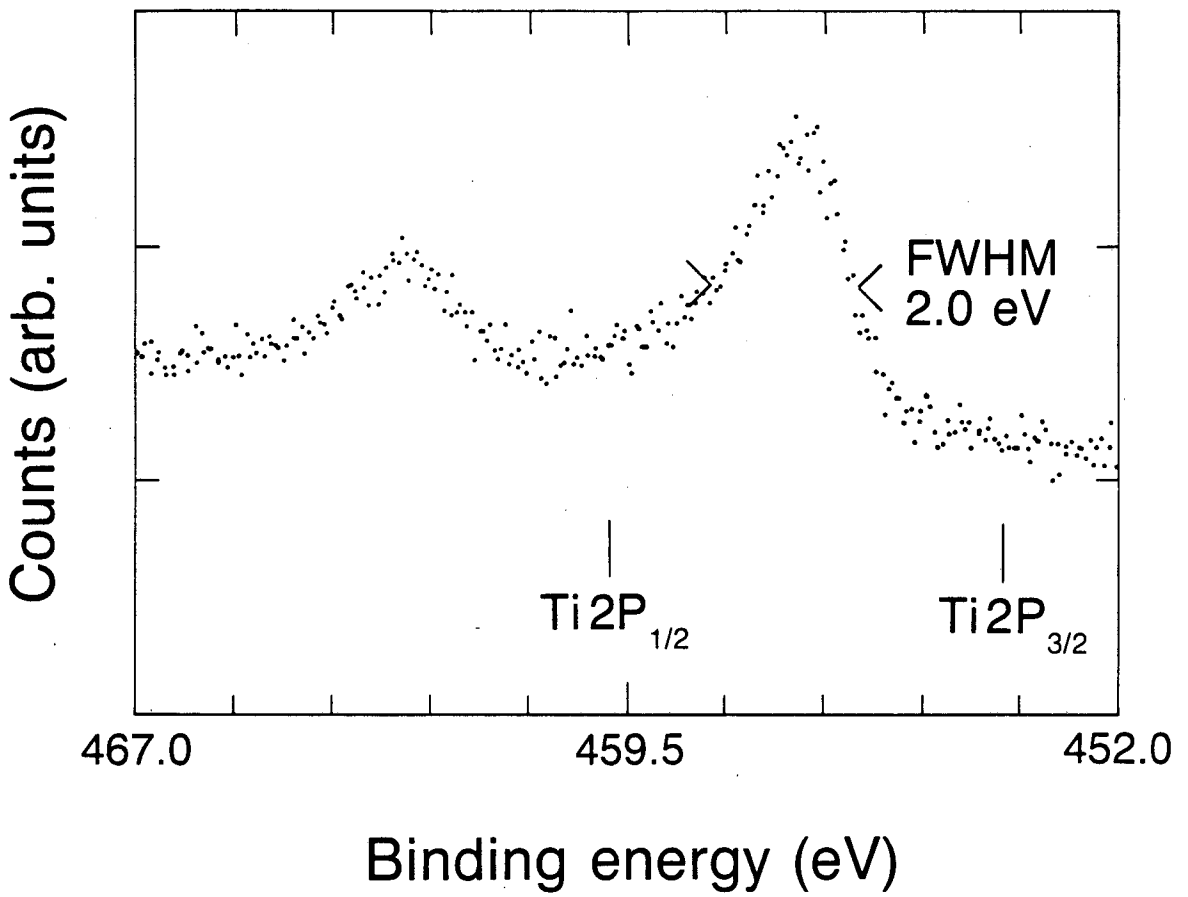

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Fig. 3

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