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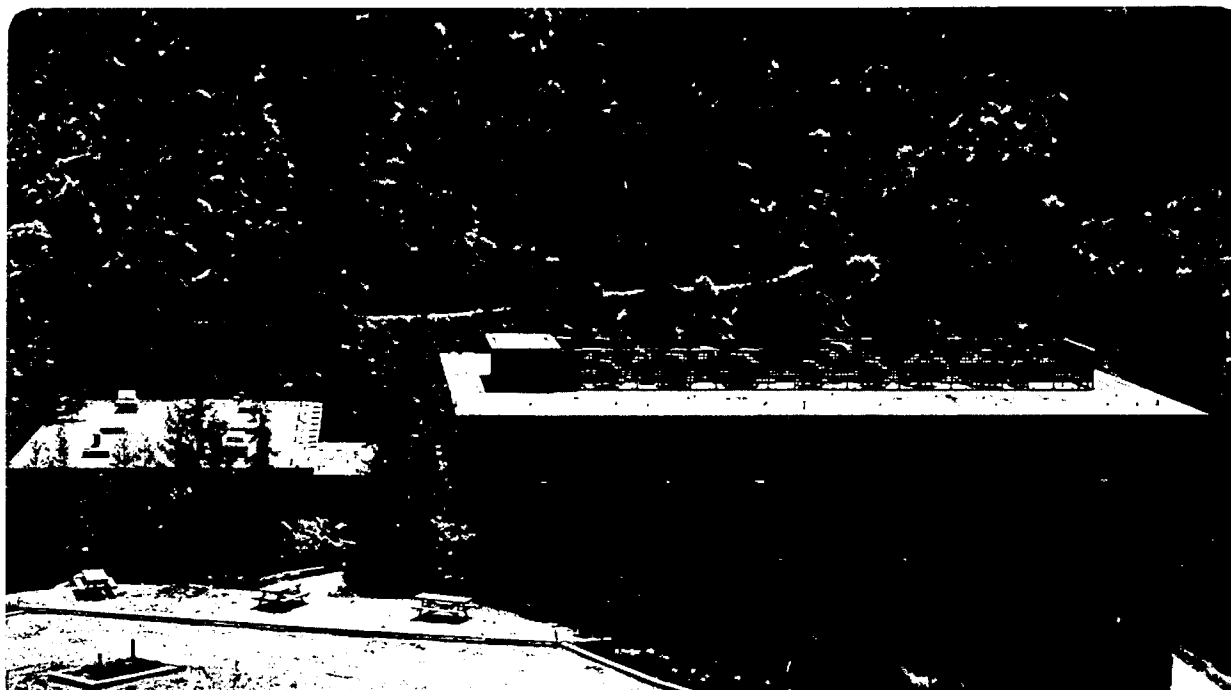
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CO CHEMISORPTION ON THE [111] and [100]
ORIENTED SURFACES OF THE CoPt_3 ALLOY

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ABSTRACT

In a previous study, it was shown that surfaces of both the [111] and [100] oriented single crystals of CoPt_3 have a "sandwich" structure having an outermost atomic layer that is essentially pure Pt and a second layer enriched in Co (with respect to the bulk). In the present work, we report a study of the energetics of carbon monoxide chemisorption on these surfaces, and compare the results with our previous study of carbon monoxide adsorption on TiPt_3 surfaces, which have surfaces that are compositionally mixed, i.e. ordered substitution of Ti for Pt as in the bulk. A surprising similarity in the activation energy for desorption of carbon monoxide from Pt sites on both the CoPt_3 and TiPt_3 surfaces was found, with the adsorption energy being substantially lower on the alloy surfaces than for pure Pt surfaces of the same orientation. Since the CoPt_3 surfaces have a pure Pt top layer, it appears that the intermetallic bonding between Co in the second layer and Pt in the top layer changes the electronic states available for the bonding of carbon monoxide to the surface.

1. INTRODUCTION

Alloy surfaces have been the object of numerous surface science studies investigating the structural and adsorptive properties in order to develop a better understanding of catalysis by alloys. Binary alloys composed of platinum and one electropositive metal are of interest from a fundamental point of view, since they often form intermetallic compounds with highly negative enthalpies of formation¹ and with ordered structures at characteristic bulk compositions, and may have ordered surface structures with unique catalytic properties. When both metals are present in the surface, the catalytic and adsorptive properties may be affected both by the formation of intermetallic bonds,^{2,3} and by the dispersion on the solute metal in the surface.^{4,5}

Of particular interest to us is the trend in surface chemistry for the binary alloys of nominal composition $M Pt_3$ when M changes across the 3d transition metals, e.g. $M = Ti(d^3s)$ to $Cu(d^{10}s)$. The trend in the bulk structure of these alloys indicates that as the 3d occupation increases, i.e. as the admetal becomes more electronegative, the heat of formation of the alloy decreases,^{1,9} the order-disorder transition temperature decreases,¹⁰ and the composition range for the formation of ordered phases narrows.^{9,10} We have reported previously⁶⁻⁸ detailed studies of the surface chemistry of the alloy $TiPt_3$, which has a very negative enthalpy of formation (- 82 kcal/mol) and has an ordered bulk phase with the $L1_2$ structure with a critical temperature above $1500^{\circ}K$. These studies

have shown that TiPt_3 forms clean annealed low index surfaces that are ordered and are simple truncations of the bulk L1_2 structure. The chemistry of carbon monoxide adsorption was found to be more complicated than on either the pure Pt or pure Ti surfaces, but some of the bonding character of each metal is preserved in the alloy, i.e. the adsorption is dissociative at Ti sites and molecular at Pt sites.

In the present work, we report the study of the surface chemistry of the alloy CoPt_3 , and compare the chemistry to that observed on TiPt_3 . Cobalt is not as electropositive a metal as Ti, the heat of formation of the CoPt_3 alloy is much lower (- 3 kcal/mol versus - 82) and the alloy as we used it was not ordered in the bulk. Using a combination of LEED and low energy ion-scattering spectroscopy (LEISS), we found¹² that the clean annealed alloy surfaces of both the [111] and [100] orientations are essentially pure Pt, e.g. less than 2 at% Co. In this respect, CoPt_3 is very different from TiPt_3 , where both the [111] and [100] surfaces have mixed compositions, i.e. both Pt and Ti are in the top layer. We found here that the chemistry of carbon monoxide adsorption on CoPt_3 appeared to have some similarities to that on TiPt_3 , and to be energetically quite different from that on either pure metal surface.

2. EXPERIMENTAL

The Co-Pt alloy was prepared by arc melting the pure elements in inert atmosphere in the proportion of 3Co:1Pt. Single crystal samples were obtained by repeated zone refining in vacuum. Elemental analysis of the single crystal samples by x-ray fluorescence indicated some

loss of Co occurred during the zone refining. Thus, the notation of CoPt_3 for this alloy is primarily for convenience, the alloy being slightly substoichiometric. X-ray examination of the single crystal samples before performing surface studies showed that the bulk alloy was ordered, with the fcc AuCu_3 type ($L1_2$) structure and a lattice constant of 3.85 \AA , corresponding to a 1.8% contraction with respect to pure platinum ($a=3.924 \text{ \AA}$). This value is in agreement with the value reported¹¹ for the lattice parameter of stoichiometric CoPt_3 (3.831 \AA). However, x-ray diffraction analyses performed after the samples underwent thermal treatments during the UHV study showed that the alloy was disordered (disordered meaning a random substitution of Co for Pt in the fcc lattice versus an ordered substitution of Co for Pt at the corners of the unit cell), but the interatomic distance was not significantly changed. The critical temperature for the order-disorder transition in CoPt_3 is a relatively low 850°K ,¹⁰ lower than the annealing temperature we used to obtain clean surfaces with sharp LEED patterns, e.g. 1000°K . Apparently, the high temperature disordered structure was quenched when the crystals cooled from the annealing conditions typically used in our UHV chamber.

Disk shaped single crystal samples oriented along the $[111]$ and $[100]$ were cut from the single crystal rod and mechanically polished. The disks were gold brazed to tantalum foil. The foil was held to a sample manipulator by spotwelded tantalum wires which were also used to anneal the sample by resistive heating. A chromel-alumel thermocouple was spotwelded to the tantalum foil for temperature measurements. Cleaning of the sample surface could usually be

obtained by means of cycles of Ar ion bombardment and annealing in UHV at or over 900⁰K. This treatment was not always sufficient for the complete removal of the carbon surface contamination, which could be obtained by annealing the ion bombarded surface in presence of a low (ca. 1×10^{-8} torr) pressure of oxygen.

Surface analysis by LEED, AES, ARXPS and LEISS were performed as described previously.¹² Carbon monoxide desorption spectroscopy was done by dosing the clean annealed surfaces with CO (Matheson Research Grade) at room temperature and at a pressure of 1×10^7 torr for $10 - 10^3$ sec (1 - 100 Langmuirs), then heating the crystals at a rate of 14 degs/sec (the [100] sample) or 16 degs/sec (the [111] sample). The quantity of CO desorbed as a function of time/temperature was determined with a quadrupole mass spectrometer (Leybold-Hereus Model IQ-200).

3. RESULTS AND DISCUSSION

3.1 LEED

The LEED pattern exhibited by the clean, annealed [111] oriented surface had simple hexagonal symmetry with no "superlattice" reflections due to ordered cobalt substitution in the surface, in contrast to the superlattice pattern we observed for $\text{TiPt}_3(111)$.⁸

A schematic for the LEED pattern for the clean, annealed [100] oriented surface is shown in Fig. 1. The spots at the vertices of the "square" in this pattern are those of a unit cell which has the same structural parameters as those of an unreconstructed Pt(100) surface. The rows of "extra spots" which appear along the sides of the

unit cell are due to surface reconstruction. Since the surface does not appear to be perfectly ordered, a totally unambiguous indexing of the pattern was not possible. The spot separation in the doublets was found to be approximately $1/24$ of the cell side, so that the pattern can be described as a (non-centered) "5x24", but is in an approximation and does not account for all the features observed. As we reported previously,¹² LEISS analysis indicated the composition of the surface associated with this "5x24" reconstruction was essentially pure Pt. It is clear, therefore, that this structure is related to the "(1x5)" family of reconstructions observed on the (100) surfaces of Ir, Pt and Au.¹³ It suggests that the surface of $\text{CoPt}_3(100)$ has top layer of Pt atoms arranged in a "quasi-hexagonal" structure similar to the (111) surface of Pt. Angle-resolved XPS analysis¹² also indicated that the second layer of atoms at this surface is enriched in Co relative to the bulk, e.g. 50-60 at% versus the bulk 25 at%. A surface structure consisting of a top layer of pure Pt with a second layer of 50 at% Co is a possible bulk termination structure of the [100] orientation of the L1_2 ordered structure.⁸ Thus, this surface structure does not necessarily represent surface enrichment in the classical sense,⁵ but may perhaps be more correctly viewed as a rare instance of an ordered alloy surface region forming from a disordered alloy bulk lattice.

On the other hand, the (1x1) LEED pattern for the [111] oriented crystal and LEISS data indicating little or no (< 2 at% Co) Co in the top layer indicate surface enrichment of Pt to the surface in the classical sense. A similar enrichment of Pt was observed by Gauthier, et al.¹⁴ for the [111] orientation of $\text{Pt}_{78}\text{Ni}_{22}$ crystal.

Treglia and Zagrand¹⁵ have proposed a mean-field theory incorporating lattice strain (the size effect), surface tension, and intermetallic bonding that predicts surface enrichment in Pt in the Pt-Ni system, but not to the extent of a 100% Pt surface.

The adsorption of CO at room temperature produced no ordered superstructures detectable by LEED. On the CoPt₃(100) surface, prolonged exposure to CO caused the ("5x24") reconstruction to disappear, to be replaced by a simple (1x1) pattern. The lifting of the surface reconstruction by CO chemisorption is also a characteristic of the pure Pt(100) surface.²⁴

3.2 XPS

In Fig. 2 we show the Co2P_{3/2} peak for the clean annealed (oxygen free) alloy surfaces compared with the same peak for a clean polycrystalline Co foil. There was clearly a shift of 0.5 eV towards higher binding energy for Co in CoPt₃ versus the pure metal. The Co2P_{1/2} peak showed a similar shift. Platinum core level (4f) photoemission from the alloy was essentially unshifted with respect to the pure platinum surface. The +0.5 eV binding energy shift for Co in the CoPt₃ alloy is qualitatively similar to the +1.3 eV shift observed for Ti in the PtTi₃ alloy,¹⁶ but not as large. In the case of Ti in TiPt₃, the shift for the alloy was as large as the shift for Ti in the cubic monoxide TiO, but here for Co in CoPt₃ the shift is about 0.8 eV less than the shift for the cubic monoxide CoO¹⁷. It appears that the intermetallic bonding in CoPt₃ has some similarity to the bonding in TiPt₃, e.g. the solute atom in the alloy state has a lower electron density about its nucleus than does the same atom in the

lattice of like solute atom, but the change from the state as the pure metal is not as dramatic for Co as the solute atom.

Another qualitative similarity in the intermetallic bonding can be seen in the (bulk) valence band structures, shown in Fig. 3. These should be compared with the spectra for TiPt_3 given in Ref. 7. For both the CoPt_3 and TiPt_3 alloys, there is an increase in the density of states at the bottom of the valence band (about 6 eV below the Fermi level), this increase being more pronounced in TiPt_3 than in CoPt_3 . If we combine both the core level shifts with the changes in the valence band density of states, an elementary interpretation is that in forming the intermetallic bonds in these alloys, there is a rehybridization of d-orbitals of the solute atom that are non-binding (atomic -like) in the pure solute metal to form bonding orbitals in the alloy, which results in a shift in electron density from about the solute atom to the interatomic region.

The adsorption of carbon monoxide on the clean alloy surface could be detected in XPS by the appearance of the oxygen and carbon 1s peaks. The O1s peak resulting from adsorbed CO was shifted by 1.8 eV towards higher binding energy with respect to the oxygen peak for oxygen chemisorbed on the surface (Fig. 4). This is the same shift we observed for the chemisorption of CO on pure Pt surfaces. The asymmetric shape of the O1s peak, with the shoulder on the high energy side, is identical to the spectrum reported by Norton, et al.¹⁸ for CO on Pt(111), and quite different from the doublet spectrum we reported previously⁷ for $\text{TiPt}_3(111)$. We attributed the doublet structure as arising from the distinctly different bonding geometries predicted for

CO at Pt and Ti sites² in the $\text{TiPt}_3(111)$ surface. Flashing the crystal to $>900^\circ\text{K}$ completely removed all oxygen and carbon detectable by XPS, showing that no detectable decomposition of CO took place during desorption. This result indicates a substantial difference in the interaction of CO with the CoPt_3 alloy in comparison to the TiPt_3 alloy, where ca. 25% of CO molecules adsorbed were dissociated even at low temperature ($<330^\circ\text{K}$).⁷

3.3 TDS

In Fig. 5 we show the thermal desorption spectra recorded from the $[111]$ and $[100]$ oriented alloy surfaces after adsorption to saturation with CO. The CO TDS peak for a polycrystalline CoPt_3 surface was similar to that of the $[111]$ surface. The shape of the CO TDS spectrum from the $\text{CoPt}_3(111)$ surface is qualitatively similar to the spectrum observed on the $\text{Pt}(111)$ surface by various authors,¹⁹⁻²⁴ although it occurs at a significantly lower temperature. Also, the maximum in the broad spectrum for the $\text{CoPt}_3(100)$ surface occurred at a considerably lower temperature than the main peak from pure $\text{Pt}(100)$.^{22,23} For exposure to CO to lower than saturation coverages, we found the same behavior that has been reported for pure platinum surfaces,¹⁹⁻²³ i.e. a shift of the maximum of the CO TDS peak towards higher temperatures for lower coverages. On both the $[111]$ and $[100]$ oriented surfaces of CoPt_3 , saturation coverage by CO was somewhat lower than that found on the pure Pt surface of the same orientation, e.g. 60-70%.

The observation of purely molecular CO desorption from the CoPt_3 surfaces is not surprising, considering that the surface composition of

these surfaces is essentially pure Pt, and it is well known that CO does not dissociate on clean Pt surfaces. On the TiPt_3 surfaces, approximately 25% of the CO adsorbed at low temperature is dissociated during thermal desorption, the dissociation occurring for the CO adsorbed at Ti sites.⁷ For the CO desorbing molecularly from the Pt sites, the spectrum from the $\text{TiPt}_3(111)$ surface⁷ was very similar to the result here for $\text{CoPt}_3(111)$, with a peak temperature of 360-370⁰K. Using the Redhead²⁵ analysis for TDS, the 50⁰K difference between the peak temperatures from the two alloy (111) surfaces and the Pt(111) surface means an activation energy for desorption that is ca. 15% lower on the alloy surfaces. For the $\text{CoPt}_3(100)$ surface, the difference is even larger, corresponding to an activation energy that is 22% lower than for the Pt(111) surface.

It is well known that CO is a useful molecule for probing electronic effects in alloy surfaces due to the sensitivity of the CO-metal bond to the d-orbital configuration of the metal. However, it is also well known that one must consider structural effects (so-called "ensemble" effects) in addition to electronic effects when interpreting the effect on adsorbate bonding of dispersing a solute metal atom in the surface of another metal. In our analysis of CO bonding to TiPt_3 surfaces,² we used a quantum chemical treatment to examine both ensemble effects, e.g. the elimination of some Pt-Pt bridge sites and Pt 4-fold hollows, as well as the effect of intermetallic bonding on the kind and number of orbitals available for bonding CO to Pt sites. The AESD-MO calculations² showed that even for CO bound to a-top Pt sites (i.e. no ensemble effect), the use of Pt d-

electrons to form intermetallic bonds with Ti reduces the back-bonding contribution to the total CO - Pt bond energy. In the case of the CoPt₃ surfaces, the clean annealed surfaces are essentially pure Pt, so there can be no ensemble effect due to Co dispersed in the topmost layer. There is, nonetheless, a pronounced difference in CO bonding to this pure Pt surface layer, presumably due to intermetallic-bonding of Pt surface atoms with the Co atoms in the second layer. We have presented core level and valence band spectroscopy which indicate that there are qualitative similarities in the bulk electronic properties of CoPt₃ and TiPt₃, and now suggest that the general features of the AESD- MO bond model for TiPt₃ applies to CoPt₃. It is surprising, however, that the effects of intermetallic bonding are so significant, given that the Co - Pt bond energy is so much lower than the Ti - Pt bond energy.

ACKNOWLEDGMENT

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REFERENCES

1. L. Brewer in "Phase Stability in Metals and Alloys"
(P. Rudman and R.I. Jaffee, eds.), McGraw-
Hill, New York 1967, p.39, p. 39ff.
2. S.P. Mehandru, A.B. Anderson and P.N. Ross, J.
Catal., 100, 210 (1986).
3. J.A. Horsley, J. Am. Chem. Soc., 101, 2870 (1979).
4. M.J. Kelley and V. Ponc, Prog. Surf. Sci., 11, 139
(1981).
5. W.M.H. Sachtler and R.A. Van Santen, Appl. Surf.
Sci., 11, 139 (1981); Adv. Catal. 26, 69
(1977).
6. U. Bardi, P.N. Ross and G.A. Somorjai, J. Vac. Sci.
Technol., A 2, 1467 (1984).
7. U. Bardi, D. Dahlgran and P.N. Ross, J. Catalysis,
100, 196 (1986).
8. U. Bardi and P.N. Ross, Surf. Sci., 146, L555
(1984).
9. "Selected values of Thermodynamic Properties of
Metals and Alloys," R. Hultgren, R.L. Orr, P.P.
Anderson and K.K. Kelley eds., New York and London
1962, p. 647ff.
10. W. Moffatt, "The Handbook of Binary Phase Diagrams,"
Genium Publishing, Schenectady, NY, 1984.
11. E. Gebhardt and W. Koster, Z. Metallkunde, 32, 253
(1940).

12. U. Bardi, A. Atrei, P. Ross, E. Zanazzi and G. Rovida, Surf. Sci., 211/212, 441 (1989).
13. M.A. Van Hove, R.J. Koestner, P.C. Stair, J.P., Biberian, L.L. Kesmodel, I. Bartos and G.A. Somorjai, Surf. Sci., 103, 189 (1981).
14. Y. Gauthier, Y. Joly, R. Baudoing, and J. Rundgren, Phys. Rev. B, 31 6216 (1985).
15. G. Treglia and B. Legrand, Phys. Rev. B, 35 4338 (1987).
16. B. Beard and P. Ross, J. Phys. Chem., 90, 6811 (1986).
17. U. Bardi, B. Beard and P. Ross, J. Vac. Sci. Technol. A, 6, 665 (1988).
18. P. Norton, J. Goodale and E. Selkirk, Surf. Sci., 83, 189 (1979).
19. G. Ertl, M. Neumann and K.M. Streit, Surf. Sci., 64, 393 (1977).
20. R.W. McCabe and L.D. Schmidt, Surf. Sci., 66, 101 (1977).
21. D.N. Collins and W.E. Spicer, Surf. Sci., 69, 85 (1977).
22. M.A. Barteau, E.I. Ko and R.J. Madix, Surf. Sci., 102, 99 (1981).
23. A. Crossley and D.A. King, Surf. Sci., 95, 131 (1980).

24. P. Thiel, R. Behm, P. Norton, and G. Ertl, J. Chem. Phys., 78, 7448 (1983).
25. P. Redhead, Vacuum, 12, (1962).

FIGURE CAPTIONS

Fig. 1. Schematic of LEED pattern for the clean annealed surface of $\text{CoPt}_3(100)$.

Fig. 2. Comparison of the $\text{Co}2P_{3/2}$ peak for a clean polycrystalline cobalt foil (upper curve) and for the clean, $[100]$ oriented alloy surface. A similar result was obtained for the $[111]$ oriented surface.

Fig. 3. Comparison of the valence band structure for clean (100) platinum (top curve), clean polycrystalline Co (middle curve), and the clean $[100]$ oriented CoPt_3 surface (bottom curve).

Fig. 4. Comparison of $01s$ peak for (a) carbon monoxide and (b) oxygen chemisorbed to saturation at 298 K on $[111]$ oriented CoPt_3 .

Fig. 5. CO thermal desorption after 10 Langmuir exposure at 300°K from the $[100]$ and $[111]$ oriented CoPt_3 surfaces. Heating rate: 14 deg/sec $[111]$ and 16 deg/sec $[100]$. The position where the main CO TDS peaks occur for Pure Pt(111) and Pt(100) surfaces is also marked in the figure.

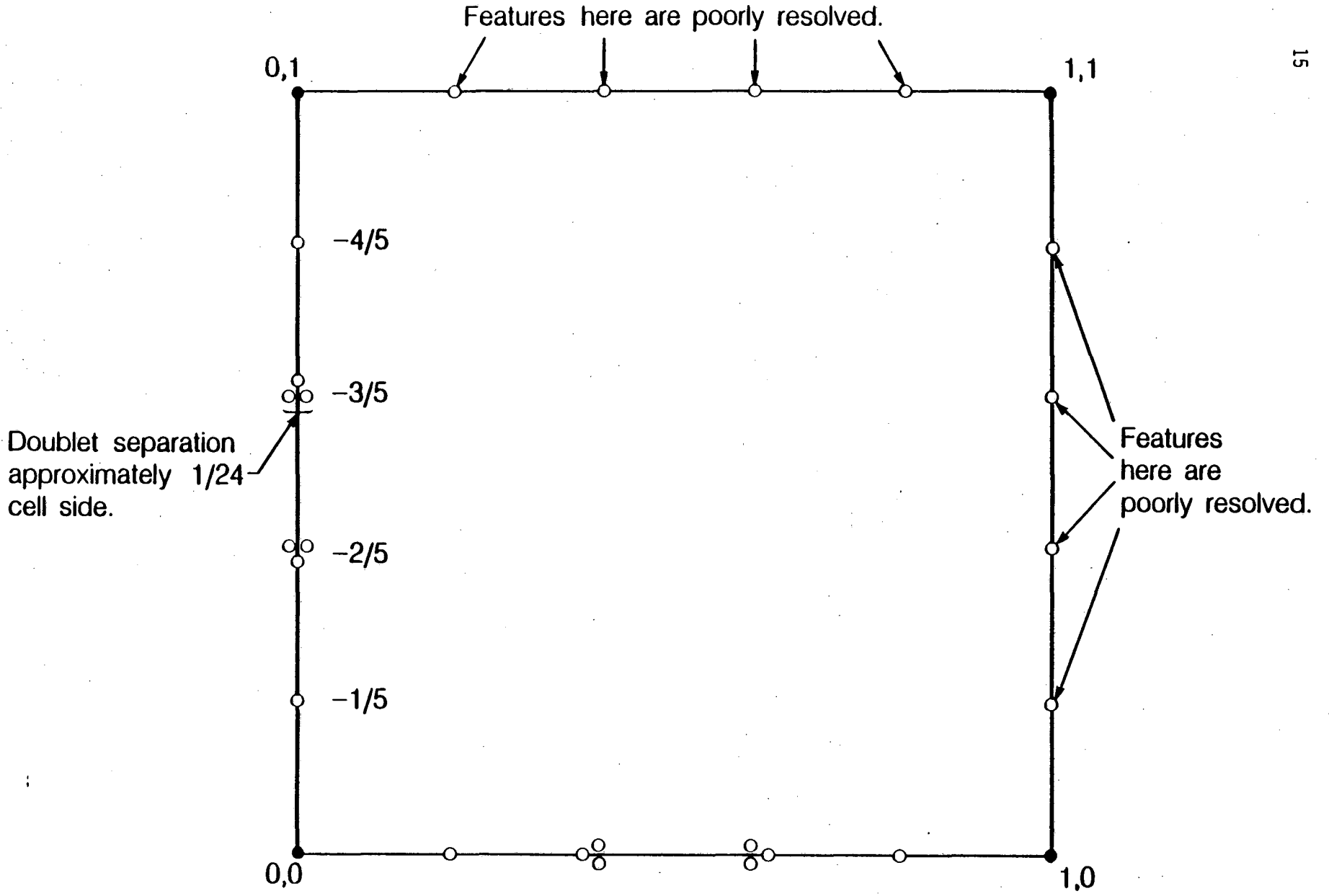


Fig. 1

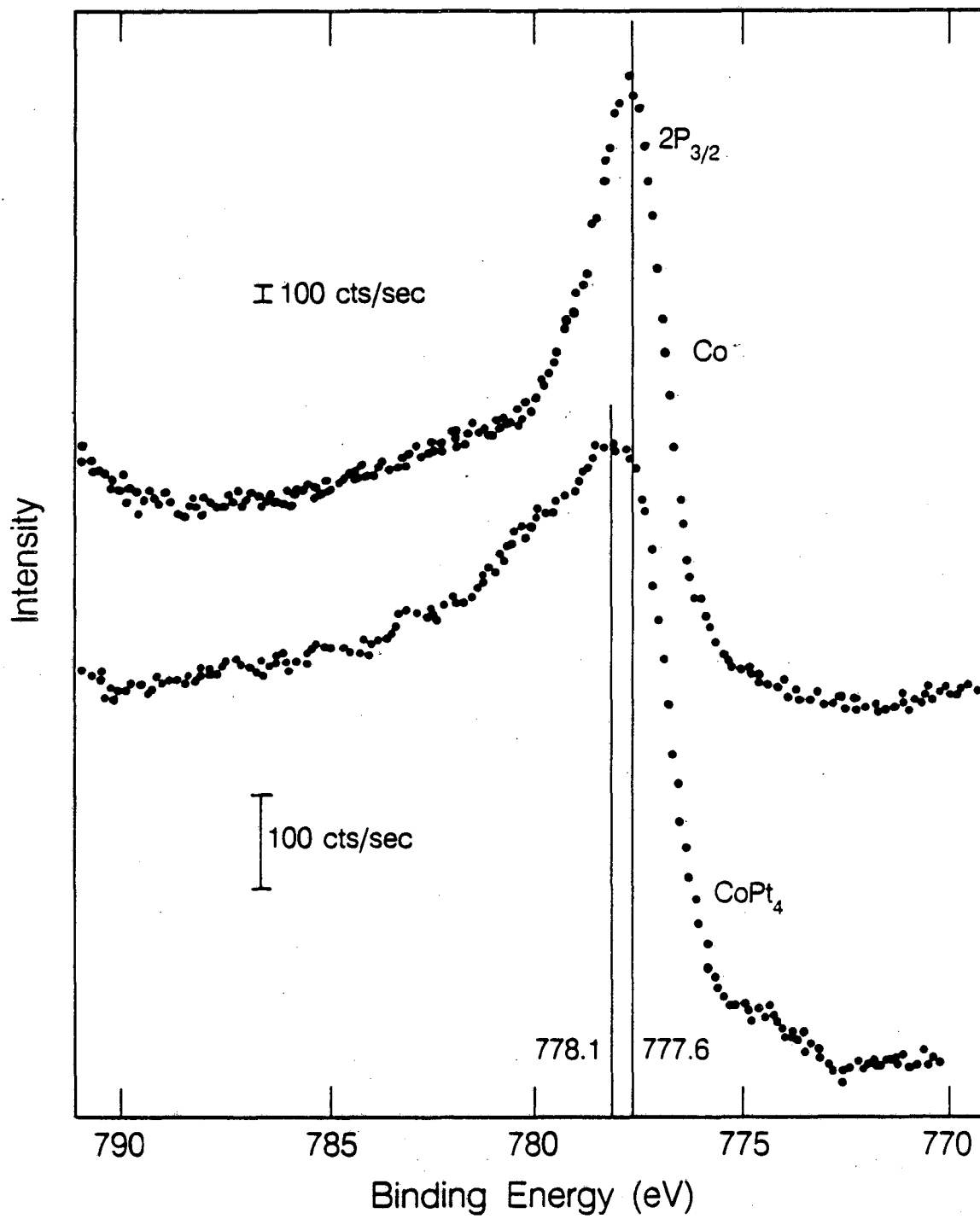


Fig. 2

XBL 8610-10187

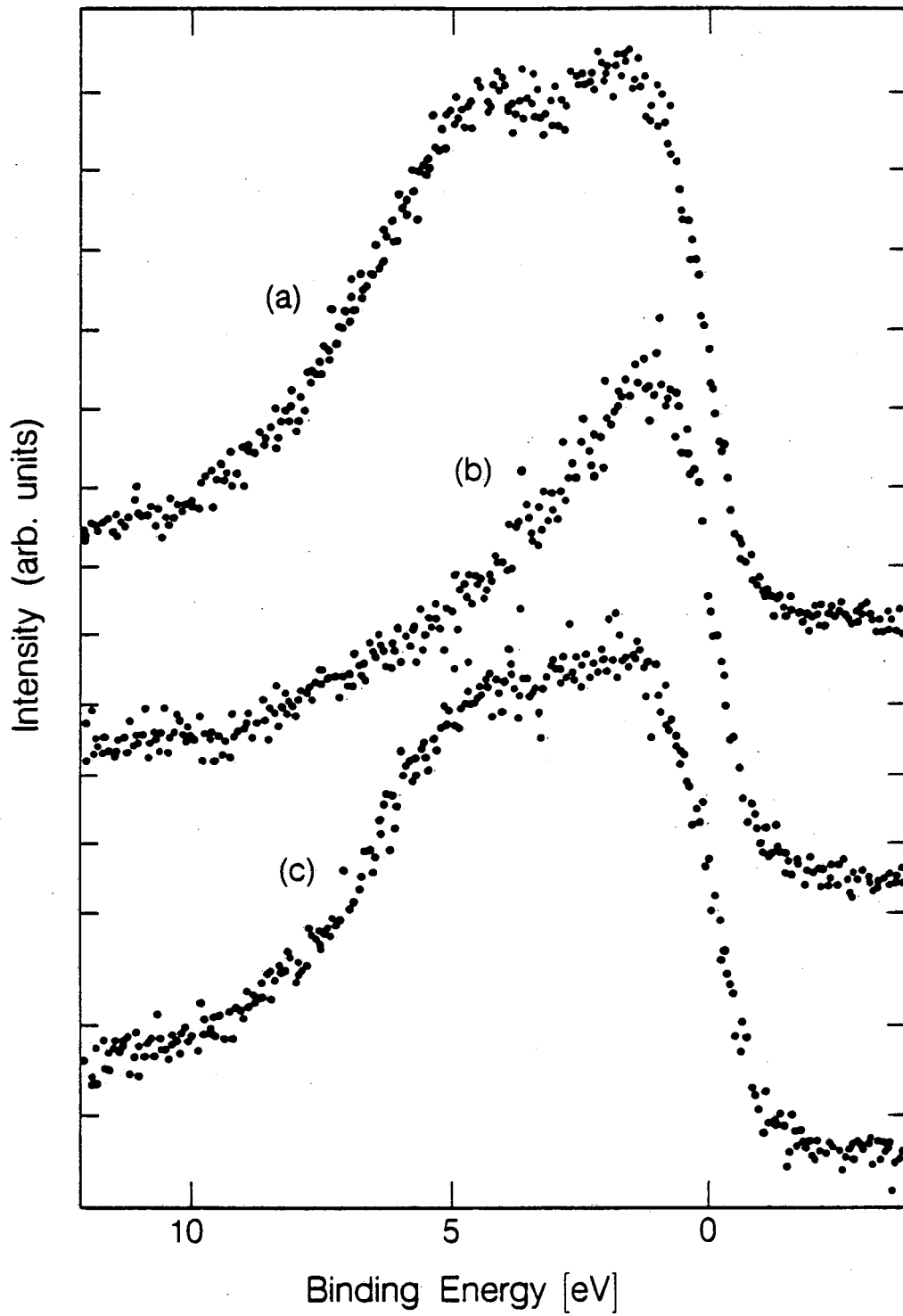


Fig. 3

XBL 8610-10186

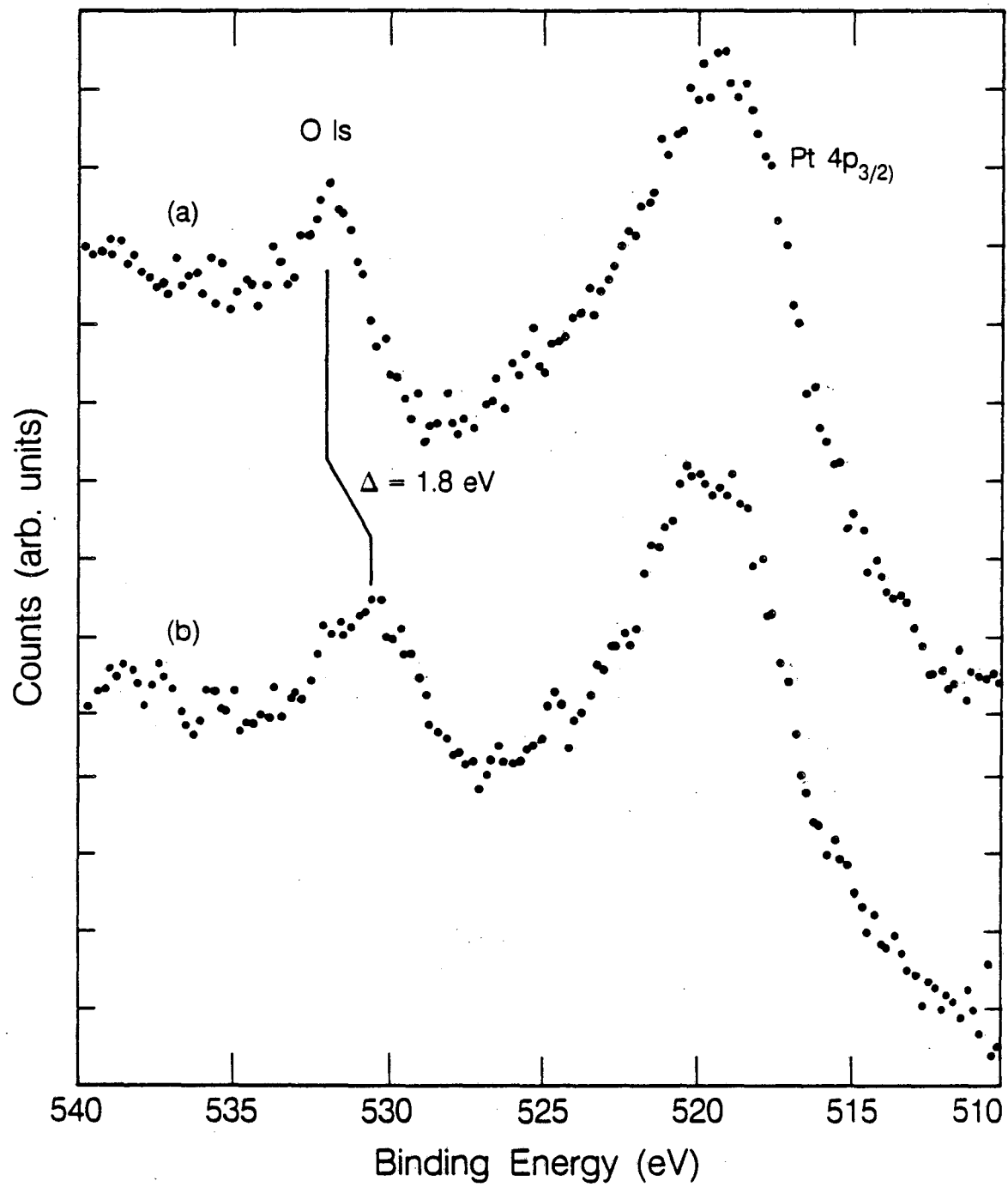


Fig. 4

XBL 869-10140A

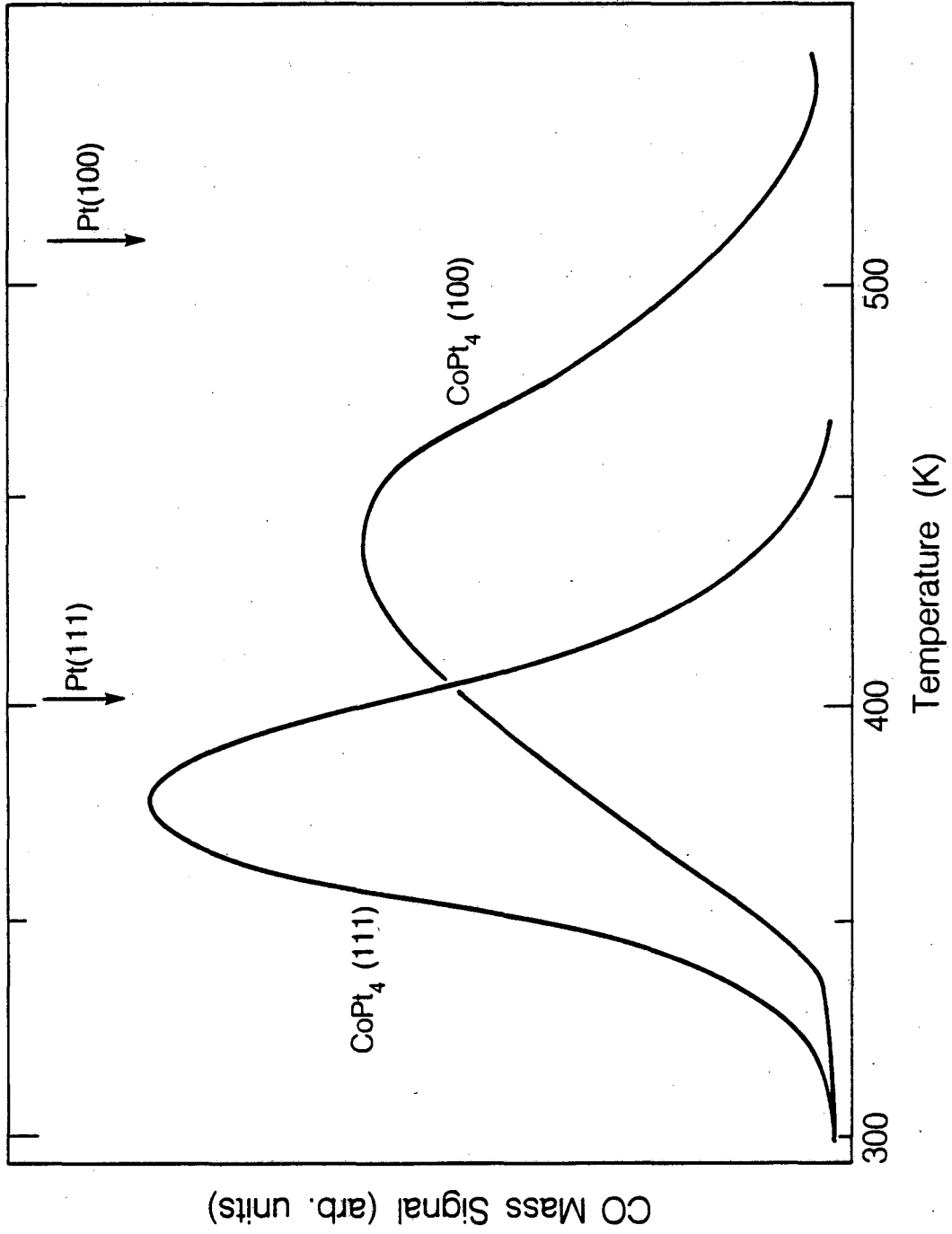


Fig. 5

XBL 8610-10188

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