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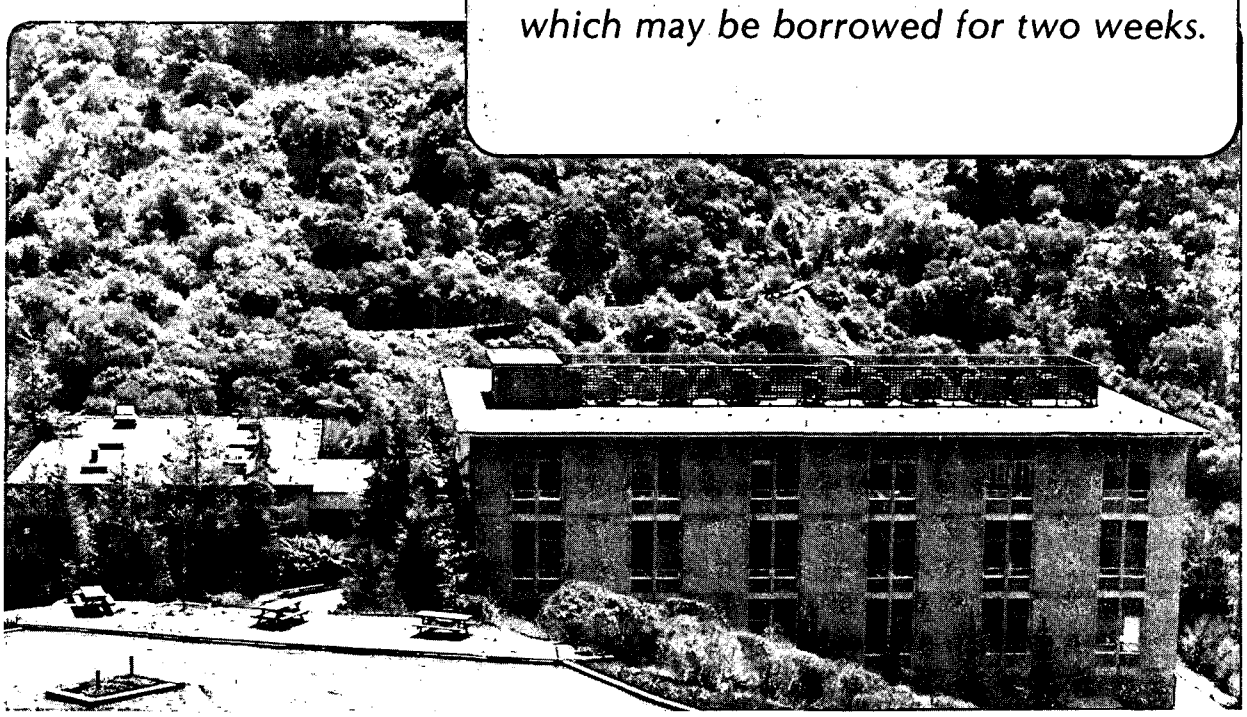

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SURFACE OXIDATION OF A PT-20% CO ALLOY, AN XPS AND LEED STUDY ON THE [100] AND [111] ORIENTED SINGLE CRYSTAL SURFACES

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ABSTRACT

The interaction of oxygen with the surface of a Pt alloy containing ca. 20 at % of cobalt was studied by LEED and XPS. At this composition, cobalt was found to be randomly substituted in the Pt fcc lattice both in the bulk and at the surface. [111] and [100] oriented single crystal surfaces as well as polycrystalline surfaces were studied. Dosing these surfaces with oxygen at room temperature at pressures lower than ca. $1x10^{-5}$ torr resulted in the formation of a chemisorbed oxygen layer. At temperatures over ca. $700^{o}K$ dosing with oxygen in the same range of pressures led to the formation of a sequence of ordered oxide overlayers. XPS and LEED data showed that the first layer to form was an epitaxial monolayer structurally equivalent to either the (111) or (100) plane of cobalt monoxide (CoO). Under conditions of controlled oxygen dosing, CoO islands of monoatomic thickness nucleated and randomly decorated a nearly pure Pt surface. This surface-decoration structure was meta-stable over a narrow range of oxygen partial pressures and surface temperature. At higher temperatures and pressures, the oxide islands first coalesced, forming a compact monolayer that completely blocked the surface for chemisorption, then changed in stoichiometry and structure to form a structural precurser to Co_3O_4.

1. INTRODUCTION

In general, the chemical environment is among the most important factors in determining the surface composition of a binary alloy. In the presence of oxygen, the oxidation of the more electropositive component may lead to extensive surface segregation, even though in vacuum the surface composition may be close to that of the bulk. In the case of platinum alloys, platinum does not form stable oxides, so that in most binary platinum alloys, oxidation is expected to cause the surface precipitation of an oxide of the metal alloyed with platinum. The surface resulting from this process is formed of oxide moieties which cover, fully or in part, the alloy surface. Such a surface may have the same type of structure which is obtained upon reducing platinum (and other metals) supported on certain ceramic oxides at high temperature, the so-called SMSI state.[1] Special catalytic properties exist for this state which are believed to result from interaction of the oxide and the platinum at the edges of the oxide moieties. Our interest in the present work was to determine whether we could produce cobalt oxide "decorated" platinum surfaces by controlled oxidation of the alloy thereby creating a surface with potentially interesting catalytic properties. In this study we examined the surface oxidation and oxide precipitation phenomena of a $CoPt_4$ single crystal using a combination of XPS and LEED in a manner analogous to our previous studies of the oxidation of Pt-Ti[2,3] and Pt-Zr[4] alloys. In both of the latter alloys, we observed that treatment with oxygen at high temperature led to the surface precipitation of titanium or zirconium oxides of variable stoichiometry. In the present work we report that for the Co-Pt alloy, treatment with oxygen at high temperature led to the precipitation of cobalt oxide on the alloy surface. However, in contrast to the behavior of the Pt-Ti and Pt-Zr alloys, we found that the cobalt oxide overlayer was easily

reduced by moderate thermal annealing in UHV to reform the metallic (oxygen-free) alloy surface.

2. EXPERIMENTAL

Polycrystalline platinum-cobalt alloy material was prepared by arc melting the base metals in inert atmosphere starting from a 3:1 atomic ratio of platinum to cobalt. A single crystal bar was obtained from the polycrystalline material by the floating zone technique. Disk shaped samples oriented along the [100] and [111] axes were prepared from the single crystal bar. Polycrystalline Co-Pt samples were cut from the original polycrystalline rod. Some Co loss took place in processing so that the bulk composition of the three different crystals were, therefore, slightly different (20 $\pm$ 2 at. %), but these differences did not appear to affect the surface chemistry observed. X-ray examination showed that the bulk structure was a fcc solid solution (random substitution) of Co in Pt, which is consistent with the bulk phase diagram for Co-Pt[5].

Before examination in UHV conditions, one of the surfaces of the sample was mechanically polished and the opposite face was gold brazed onto a tantalum foil. The sample was held in the vacuum chamber on a sample manipulator by Ta wires spotwelded to the supporting Ta foil. Annealing was accomplished by resistive heating from current passed through the supporting Ta wires. Temperatures were measured by a chromel-alumel thermocouple spotwelded to the supporting foil. Exposure to oxygen was performed by introducing oxygen directly into the vacuum chamber by means of a leak valve. The highest oxygen pressure which could be maintained in the chamber was of the order of 1×10^{-5} torr.

X-ray photoelectron spectroscopy measurements were performed using a hemispherical electron energy analyzer with a position sensitive detector[7] and

a Mg x-ray source. A unique feature of this analyzer is its very small acceptance angle (ca.0.5^{o}) which makes it especially useful for angle-resolved and variable take-off angle photoemission measurements. The spectrometer was mounted in a vacuum chamber equipped with facilities for ion bombardment and mass spectrometry. This chamber was not equipped with a LEED optics. LEED measurements were performed in two other vacuum chambers. The (111) sample was mounted in a chamber equipped with a 4-grid LEED optics and a single pass CMA electron analyzer for AES. The (100) sample was mounted in a chamber equipped with a 3-grid LEED optics, also used in RFA mode for AES. Both of these chambers were also equipped with facilities for ion bombardment and gas introduction.

3. RESULTS

3.1 XPS Results

3.1.1 Composition of the Clean Surface

In contrast to our previous experience with Pt_3Ti,[2,3] annealed surfaces having O or C levels below the detection limit by XPS or AES were obtained relatively easily. In the study of any alloy surface, extended ion bombardment is undesirable, as preferential sputtering can lead to depletion of one component from the near surface region which may be difficult to anneal out. Chemical cleaning is preferable when possible, as by oxidation-reduction dosing cycles with oxygen and carbon monoxide, hydrogen or ethylene. On the CoPt study, we found that, after a brief ion bombardment upon introduction of an air exposed crystal to a UHV system, simple oxygen dosing ($5x10^{-7}$ torr, 473°K) followed by flashing to 1073°K produced a clean (O,C free) surface.

The compositions of the clean, annealed surfaces were calculated from the integral areas under the Co $2p_{3/2}$ and Pt $4p_{3/2}$ XPS peaks using the Scofield cross-sections[16] together with the analyzer transmission function. A second

calculation was made applying the simpler method of using the relative integral intensities of the Co $2p_{3/2}$ emission in the alloy and the pure metal for the same counting time and analyzer geometry. The results were nearly identical, e.g. for the [111] alloy (18.8 at. % Co) the surface composition of 19.5 at. % Co by the first and 18.5 at. % by the second method. There was no evidence from the XPS analysis of enrichment of the surface in either constituent in the clean state.

3.1.2. Composition of Oxidized Surfaces

The XPS results e.g. chemical shifts, peak ratios etc., obtained after treatment in oxygen in the same conditions were essentially the same for all three types of surfaces studied (e.g. polycrystalline, [111] and [100] oriented). In the following, therefore, the experimental results will be described without referring to a specific sample.

Oxygen chemisorption at room temperature on the alloy surface could be detected by XPS from the appearance of the O(1s) peak (Fig. 1). That the oxygen was chemisorbed, as opposed to absorbed into an "oxide" state, was indicated both by the O(1s) binding energy and by the invariance of the Co $(2p_{3/2})$/Pt$(4p_{3/2})$ XPS peak area ratios (Fig. 2a). We observed that any shift in the O(1s) binding energy was directly coordinated with a change in the Co/Pt XPS peak area ratio. As we will discuss in detail in Sec. 4, these shifts in binding energy and changes in Co/Pt XPS area ratios are indicative of the onset of cobalt oxidation accompanied by nucleation of cobalt oxide on-top-of the surface. Oxygen chemisorption was found to be completely reversible, with complete disappearance of the O(1s) signal upon heating to 773°K. Also, all of the oxygen put on the surface at near room temperature could be titrated from the surface with CO. When the oxygen dosing was carried out at moderately elevated temperature (300-700°K), the Co/Pt ratio did not

change significantly, but a higher annealing temperature and/or a longer annealing time was necessary to remove the adsorbed oxygen.

High temperature (over about 700°K) exposure to oxygen caused the surface nucleation of oxidized cobalt, as shown by the relative increase of the intensity of the cobalt and oxygen XPS peaks with respect to the platinum peak (Fig. 2b). The surface nucleation of cobalt oxide was also confirmed by measuring the ratio of the area of the Co and Pt peaks as a function of the take-off angle, i.e. the angle formed by the electron analyzer with respect to the surface. On the clean alloy surface the variation of the Co/Pt XPS ratio as a function of the angle was too small to be detectable. On the oxidized surface, the Co/Pt XPS ratio was found to increase with increasing take-off angle in exactly the same manner as the O/Pt ratio for CO chemisorbed on Pt.[7]. This result clearly indicates that oxidized cobalt formed an overlayer on the surface, as opposed to forming subsurface oxide nuclei.[7]

A consequence of the growth of cobalt oxide nuclei on-top-of the alloy surface was the loss of metallic surface sites which could chemisorb gas molecules. This could be seen from the decrease in the amount of CO desorbing from the surfaces (Fig. 3) as a function of Co segregation to the surface after oxygen dosing. The amount of carbon monoxide adsorbed (to saturation) on the surface, determined by TDS, was gradually suppressed as oxidation progressed, indicating that the cobalt oxide layer blocked the surface adsorbing sites. The reduction of the amount of adsorbed CO was found to be approximately a linear function of the intensity of the Co XPS signal, suggesting that the cobalt oxide formed an expanding layer of constant thickness, i.e. patchwise growth. From this measurement it was possible to obtain a value of the Co/Pt XPS intensity ratio corresponding to the formation of a compact "monolayer" of cobalt oxide (CoO), i.e. that ratio resulting in

complete suppression of CO adsorption.

Although the position of the Pt(4f) peaks were not affected by Co oxide formation, the Co(2p) peaks showed distinct chemical shifts. In Fig. 4, we show a comparison of the Co(2p) peaks relative to a) polycrystalline Co foil; b) clean alloy surface; c) oxidized alloy surface after exposure to $1x10^{-5}$ x 5 min at $773^{o}K$ (e.g. 3000 Langmuirs) of oxygen. The XPS Co spectrum of the oxidized surface is typical of "CoO" formation. The width of the peaks and the presence of a low binding energy shoulder suggests, however, that some of the cobalt was in the metallic state, presumably representing photoemission from metallic cobalt atoms under the surface. (Note that the peaks at 799 eV and 803 eV for the clean alloy surface are Pt Auger transitions.)

High temperature treatment in vacuum of the oxidized alloy surface led to a reduction of the relative intensity of the cobalt and oxygen XPS signals. In most cases, we found that annealing at ca. 1100 K in UHV resulted in the complete elimination of oxygen from the surface, restoring the original clean alloy surface. The temperature at which the sample had been exposed to oxygen and the length of the exposure appeared to be the most important factor in determining the conditions for eliminating the surface oxide by heat treating, i.e. dosing at higher temperature and for longer times led to a longer time needed to eliminate the oxygen from the surface.

3.2 LEED Results

A detailed discussion of the LEED analyses are reported elsewhere.[6] Only a brief restatement of these observations is given here. The pattern of the clean annealed [111] oriented surface was fcc(111)-1x1 with a surface lattice parameter nearly the same as that of a pure Pt(111) surface. On the [100] oriented surface we observed a more complex pattern which could be interpreted in terms of a "quasi-hexagonal" surface reconstruction similar to

that exhibited by a pure Pt(100) surface, but with a lattice parameter contracted by 4% from the "hex" reconstruction on Pt(100). The bulk lattice parameter in Pt-20 % Co alloy is contracted by 2.5% relative to pure Pt.[5]

The LEED pattern of the clean surfaces remained unaltered upon exposure to oxygen at conditions which did not lead to the formation of oxide overlayers, (using the criteria for defining the oxide described in the previous section). Superlattice reflections appeared in the LEED pattern only after exposure to oxygen under conditions leading to an increase of the relative intensity of the Co XPS signals. The LEED pattern observed after exposure to oxygen at 5×10^{-6} torr at $873^{o}K$ of the [111] oriented surface can be described in matrix notation as a $\begin{vmatrix} 1.15 & 0 \\ 0 & 1.15 \end{vmatrix}$. This primitive cell may in fact correspond to a 7x7 (7/6=1.17) or a 8x8 (8/7=1.142) coincidence cell. This pattern was the only superlattice pattern observed upon oxidation of the [111] surface. Many of the superlattice spots detectable in the pattern were interpreted as multiple diffraction spots; such spots can be detected only if the overlayer is uniform and of a thickness on the order of a single atomic layer.

On the (100) face, several different LEED patterns due to distinct phases of oxidized cobalt overlayers were detected (Table 1). For oxide coverages smaller than a monolayer, the superlattice patterns coexisted with the "quasi-hexagonal" substrate reconstruction characteristic of the clean $CoPt_4$ (100) surface. The substrate reconstructed pattern, however, disappeared when the oxide coverage approached the monolayer, leaving only "1x1" type substrate spots. The pattern appearing after exposure to oxygen at 2×10^{-6} torr at $873^{o}K$ can be described in matrix notation as $\begin{vmatrix} 10/9 & 0 \\ \bar{5}/9 & 1 \end{vmatrix}$. The coincidence for this phase can be described as c(2x10). The primitive unit cell area for this phase is approximately the same as that of the (8x8) phase observed on the

(111) face. Two equivalent domains were observed, as well as multiple diffraction spots, the latter indicating a single layer thickness.

After further treatment in oxygen at the same pressure, but at the higher temperature of $1073^{o}K$, the $\begin{vmatrix} 10/9 & 0 \\ \bar{5}/9 & 1 \end{vmatrix}$ phase disappeared, to be replaced by a different superstructure pattern. This new pattern can be described as a c(3/2x3/2), using the Wood notation. Multiple diffraction features were also evident in this pattern. A third superlattice pattern was observed either to coexist with the c(3/2x3/2) pattern or to be formed exclusively after further oxygen dosing of the c(3/2x3/2) structure. In matrix notation the pattern can be described as $\begin{vmatrix} 2 & 0 \\ \bar{1} & 12/7 \end{vmatrix}$. Multiple order features relative to this phase appear to be weak or absent, indicating that the pattern may correspond to a multilayer phase.

4. DISCUSSION

The stoichiometric, ordered $CoPt_3$ alloy has a heat of formation equal to approximately -3.0 Kcal/mole at $914^{o}K$.[8] The disordered alloy of the same composition has a heat of formation of -2 Kcal/mole at the same temperature. Since the heat of formation of cobalt monoxide is considerably more negative (-56.9 Kcal/mole at $298^{o}K$), simple thermodynamic considerations show that, in the presence of any measurable oxygen pressure, the oxidation of the cobalt in the alloy is thermodynamically favored. Similar thermodynamic considerations were made for the Pt_3Ti alloy in a previous study.[2] In that case it was shown that the formation of an overlayer of titanium oxide, although thermodynamically favored at all temperatures (H = -124 Kcal/mole for TiO), was observed only at high temperature. Kinetic factors related to the activation energy necessary to transport an atom from below the surface to an overlayer on the surface appeared to slow the oxidation process at low temperature on Pt_3Ti. The same kinetic factors were expected to play a role

in the oxidation of the Pt-Co alloy, and indeed surface oxidation was observed here only at high temperature, whereas the low temperature interaction of oxygen with the surface was chemisorption.

In general, one would expect that the oxide overlayer might adopt a structure similar to that of a bulk oxide at some stage in the growth process. However, the substrate/overlayer interaction may cause a considerable structural and/or electronic perturbation when the overlayer forms a flat layer of single atomic thickness. Oxide layers having a structure close to TiO(111) were observed to form in the initial stage of oxidation of the Pt_3Ti alloy.[2] Similarly, in the case of Pt-20% Co, LEED and XPS data are in good agreement in identifying the cobalt oxide layer which segregates in the initial stage of the oxidation process as cobalt monoxide (CoO). The shift towards higher binding energy of the Co(3p) XPS peaks and the presence of satellite features permit the identification of CoO on the surface from a comparison with the XPS spectra reported[9-13] for bulk cobalt oxides. CoO has the fcc, NaCl type structure and the LEED data are interpretable in terms of the formation of layers similar in structure to the CoO (111) plane (on both the [111] and [100] oriented alloy surfaces) and to the CoO (100) plane (on the [100] oriented alloy surface), as summarized by the data in Table 2. Proposed real-space structural models for these phases are shown in Figs. 5 and 6.

In all these "CoO-type" surface oxide phases, some variation in the interatomic distances occurs between the surface oxides and the bulk CoO. There is an apparent contraction of the in-plane Co-Co bond distance in both the CoO(111)-type and Co(100)-type surface phases relative to the distances in the bulk CoO oxide. We found a similar contraction of the Ti-Ti bond length in the formation of TiO-(111)-type (TiO also has the NaCl structure) planes

upon oxidation of the ordered alloy Pt_3Ti.[2] We have interpreted these contractions as a buckling of the metal-oxygen planes in order to maximize the number of overlayer metal atoms occupying "on-site" positions with respect to the metal atoms below, i.e. the 4-fold hollow, bridge and A-top positions, in order to satisfy the intermetallic bonding that still exists in these monatomic overlayer structures.

Considerations based on the number of on-site overlayer Co atoms also provides a rationalization for the observed transition in symmetry of the CoO overlayer on the [100] oriented alloy surface between the quasi-hexagonal (c(2x10) and the square (c(3/2x3/2)). If both phases form a single atomic layer, the coverage in terms of Co atoms per unit surface area is approximately the same, consistent with the XPS data that indicated little change in coverage during this transition. However, the two structures differ in the number of overlayer Co atoms that can be located on the same type of substrate site. For the c(2x10) coincidence cell, half the Co atoms can occupy 4-fold hollow sites and half the bridge sites on the layer below. For the c(3/2x3/2) cell, for every eight Co atoms on the surface, only one can occupy a 4-fold hollow site, two on a bridge site, and one on an A-top site, i.e. only half the atoms are in bonding sites. The Co_3O_4-type phase is totally incommensurate with the metal substrate, and thus has no Co atoms in on-site positions. This progressive loss of Co-Pt metallic bonding coordination suggested in these structures is consistent with the progressively more oxidizing conditions used for the formation of these structures.

There were three sets of observations that independently support the conclusion that the oxide layers grown on the alloy surface under the oxidizing conditions used here were all of monatomic thickness: 1.) the

linear suppression of CO chemisorption with the surface concentration of Co; 2.) the functional variation of the Co/Pt XPS ratio with take-off angle; 3.) the appearance of double-diffraction spots in LEED. The exception to this was the oxide forming under the moxt oxidizing conditions we could use in our UHV systems, the incommensurate $\begin{vmatrix} 2 & 0 \\ \bar{1} & 12/7 \end{vmatrix}$ phase that appears to be related structurally to Co_3O_4. This structure formed at higher Co/Pt XPS ratios than the other phases, did not exhibit the same variation in XPS ratio with take-off angle, and the double-diffraction spots were weak or absent. The sequence of oxide structures observed here for the Pt- 20 % Co alloy is remarkably similar to the sequence we observed previously with the ordered alloy Pt_3Ti_2, i.e. the formation of a monatomic layer of "MO" followed by multilayer formation of the higher oxide (Co_3O_4 or TiO_2). This was somewhat surprising in that the thermochemistry of the Co-O system[14,15] is much more favorable for the formation of "MO" multilayers than is the case in the Ti-O system.[2] Apparently kinetic and/or structural effects dictate the transition to the growth of multilayers of the higher valent cobalt oxide.

5. CONCLUSION

Our results show that oxygen can exist on the Pt-20 % Co alloy surface in two different states: a) as a chemisorbed layer; and b) as a cobalt oxide overlayer. The properties of chemisorbed oxygen appeared to be very similar to those reported for oxygen chemisorbed on pure platinum surfaces.[10,11] The oxidized overlayer grew as expanding nuclei of monatomic thickness with composition CoO and structure similar to that of the bulk CoO phase. The oxidation mechanism for the Pt-Co alloy was qualitatively similar to those of the Pt-Ti and Pt-Zr alloys studied previously.[2-4] The result is nucleation of "MO" islands of monoatomic thickness that randomly "decorate" a nearly pure Pt surface. This surface-decoration structure was meta-stable over a narrow range

of oxygen partial pressure and surface temperature. At higher temperatures and pressures, the islands first coalesced to form a compact monolayer that completely blocked the surface for chemisorption, then changed in stoichiometry and structure to form a precursor to Co_3O_4. The principal difference we found in the behavior of the Pt-Co alloy in comparison to the other alloys was the complete decomposition of the surface cobalt oxide by means of thermal annealing in UHV at relatively moderate temperatures. The role of "MO" islands on the catalytic properties of platinum is at present still unclear, although several models have been proposed involving electronic intermetallic interaction at the edges of the oxide islands.[1] Our results for three different Pt alloy systems show that the formation of these oxide islands appears to be a general process which occurs for binary alloy where one of the two metals is substantially more electropositive than the other.

ACKNOWLEDGMENT

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Table 1. LEED results for oxidation of [100] alloy crystal.

Phase	Unit Cell Dimensions (Å)	Angle	Area Primitive Cell ($Å^2$)	Notes
Pt(100)(1x1)	2.77, 2.77	90	7.7	Pt(100) bulk termination
$CoPt_4$(100)(1x1)	2.72, 2.72	90	7.4	Bulk data
$\begin{vmatrix} 10/9 & 0 \\ \bar{5}/9 & 1 \end{vmatrix}$ or c(2x10)	3.02, 3.11	119.05	8.22	Oxidized at $2x10^{-6}$ torr O_2 873°K.
c(3/2x3/2)	2.88, 2.88	90	8.29	Oxidized at $2x10^{-6}$ torr O_2 1073°K
$\begin{vmatrix} 2 & 0 \\ \bar{1} & 12/7 \end{vmatrix}$	5.44, 5.40	120.2	25.3	Further oxidation of c(3/2 x 3/2)

Table 2. Comparison of bulk cobalt oxides data and LEED results for oxidized Pt-20% Co alloy.

Phase		Unit Cell Dimensions (Å)	angle (degrees)
Bulk CoO (111)		3.11, 3.11	120
Alloy (111)-(8x8)		3.02, 3.02	120
Alloy (100)	$\begin{vmatrix} \overline{10}/9 & 0 \\ \overline{5}/9 & 1 \end{vmatrix}$	3.02, 3.11	119
Bulk CoO(100)		4.27, 4.27	90
Alloy (100)-c(3/2x3/2)		4.1 , 4.1	90
Bulk Co_3O_4(111)		5.68, 5.68	120
Alloy (100)	$\begin{vmatrix} 2 & 0 \\ \overline{1} & 12/7 \end{vmatrix}$	5.44, 5.40	120

FIGURE CAPTIONS

Fig. 1. XPS spectrum of the alloy surface showing the Pt(4p3/2) and O(1s) peaks. From top to bottom: a.) 10^3L exposure of O_2 at 700^oK, b.) exposure to 30 L of O_2 at 288^oK, c.) clean surface.

Fig. 2. XPS area ratios as a function of progressively increasing oxygen exposure of polycrystalline alloy: a.) at room temperature; b.) at 773^oK. Open circles: Co(2p3/2)/Pt(2p3/2) area ratio; full circles: O(1s)/Co(2p3/2) area ratio.

Fig. 3. Amount of carbon monoxide desorbing from the oxidized alloy surface as a function of extent of segregation of cobalt (as oxide) to the surface.

Fig. 4. Co(2p1/2 and 2p3/2) peaks for a.) polycrystalline cobalt, b.) [100] oriented clean alloy surface and c.) oxidized [100] alloy surface. In the bottom spectrum the position of the main Co peaks and the presence of satellite peaks are typical of CoO, cobalt monoxide.

Fig. 5. Model for the "quasi-hexagonal" CoO layer which forms the [100] oriented alloy surface. The structure model has been built assuming a structure similar to the CoO (111) plane of the bulk fcc-NaCl compound. A similar structure forms on the alloy (111) surface.

Fig. 6. Model for the structure of the c(3/2x3/2) phase of cobalt monoxide forming on the alloy (100) surface.

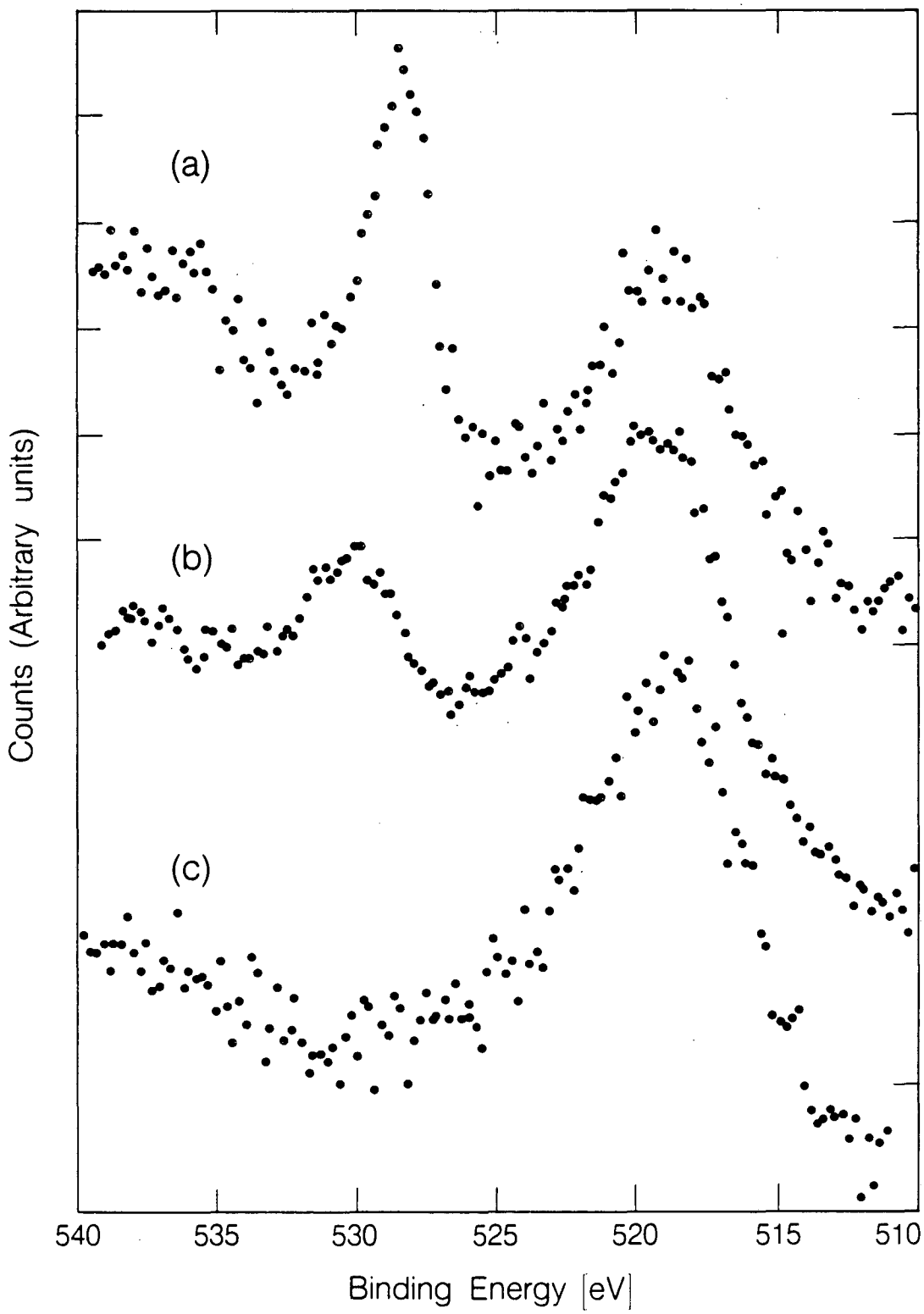

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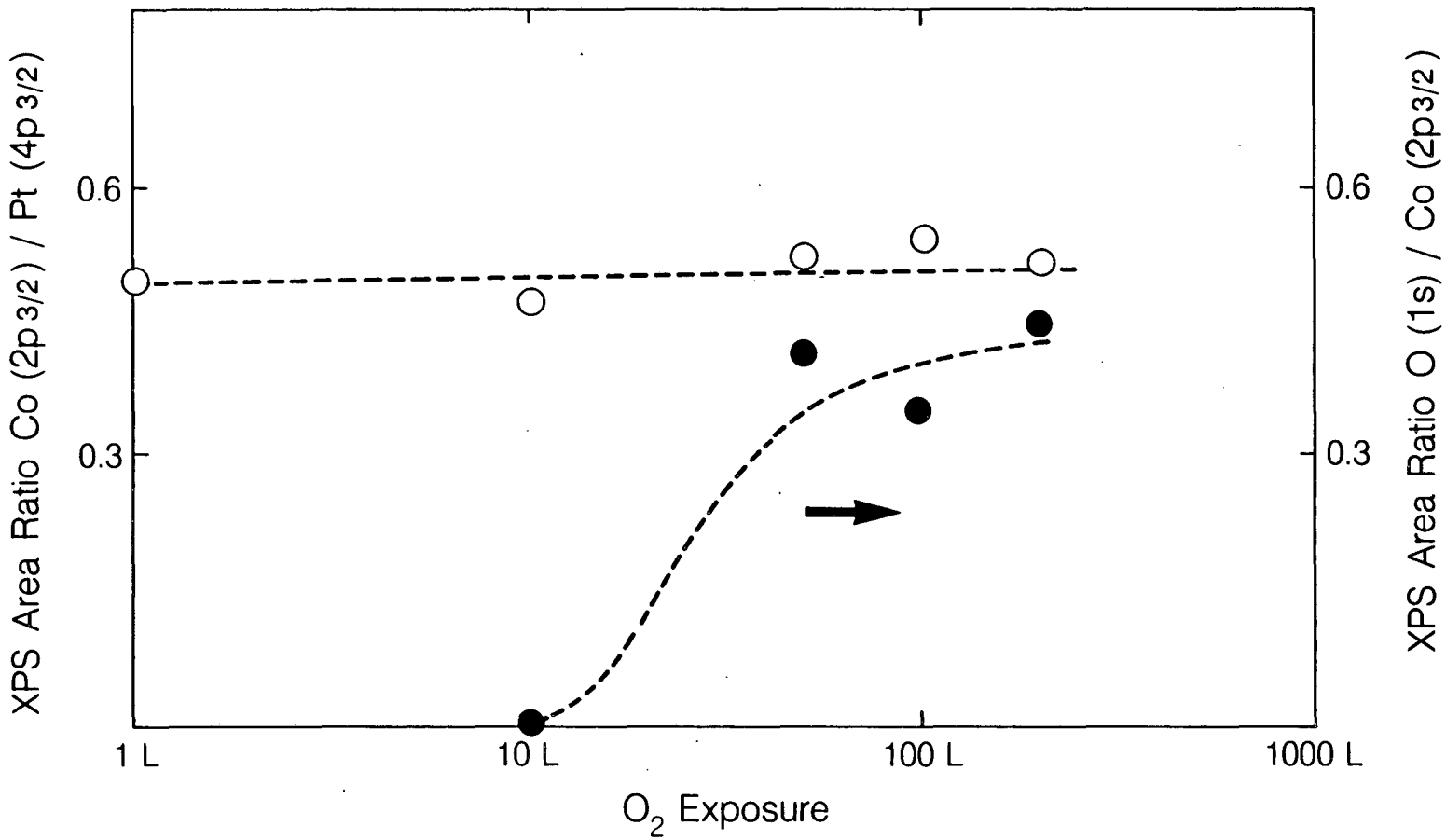
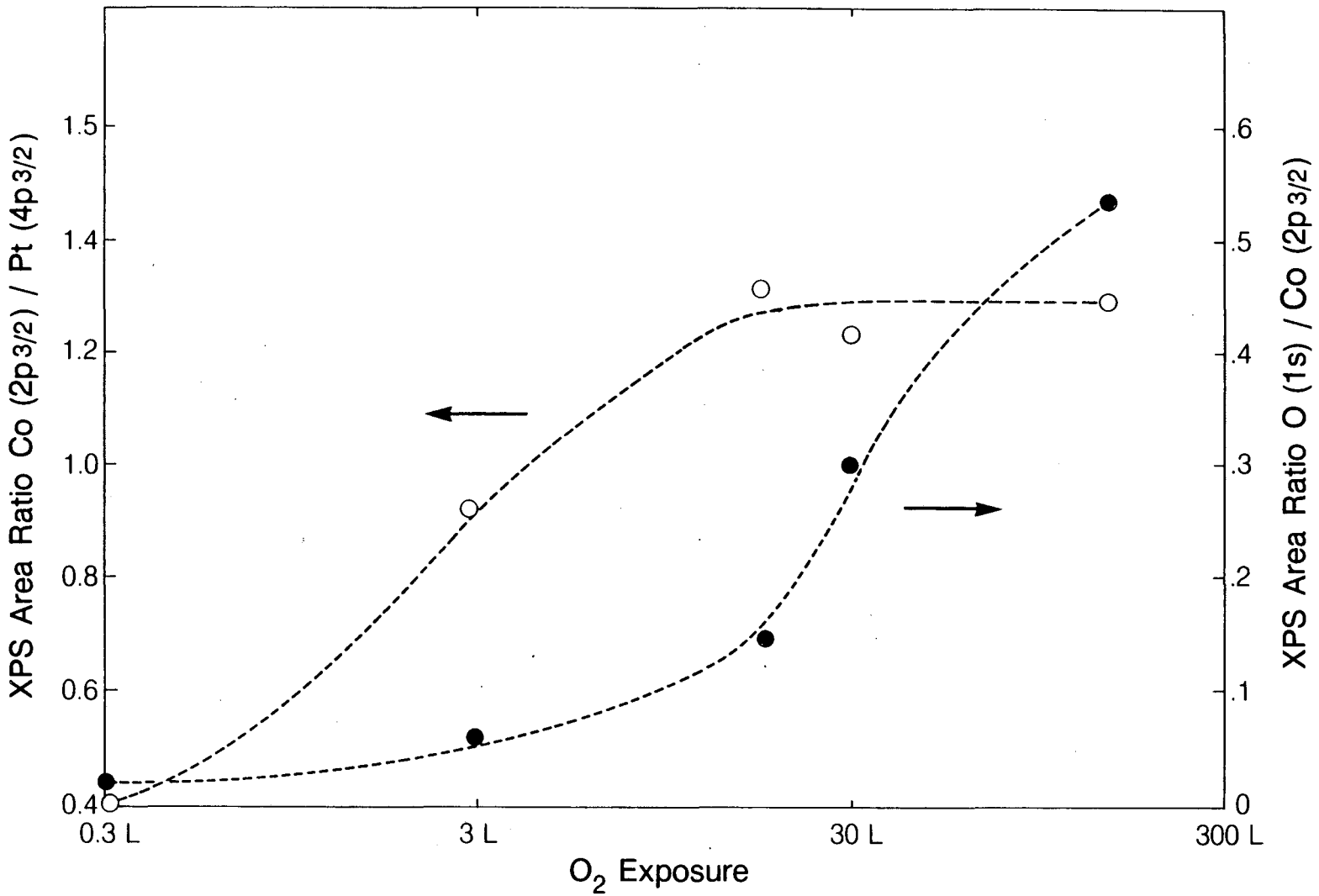
Fig. 1



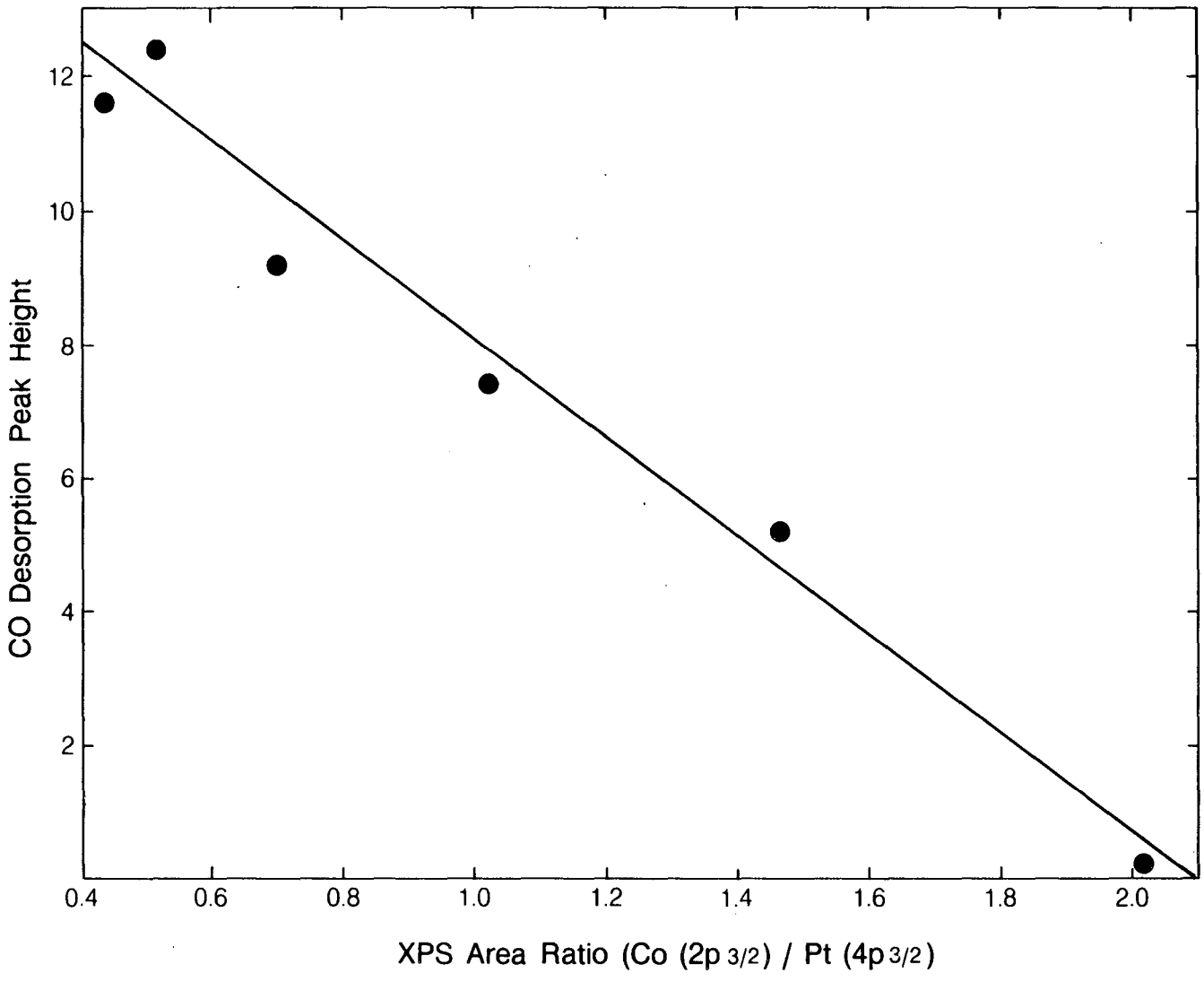
XBL 862-531 A

Fig. 2a



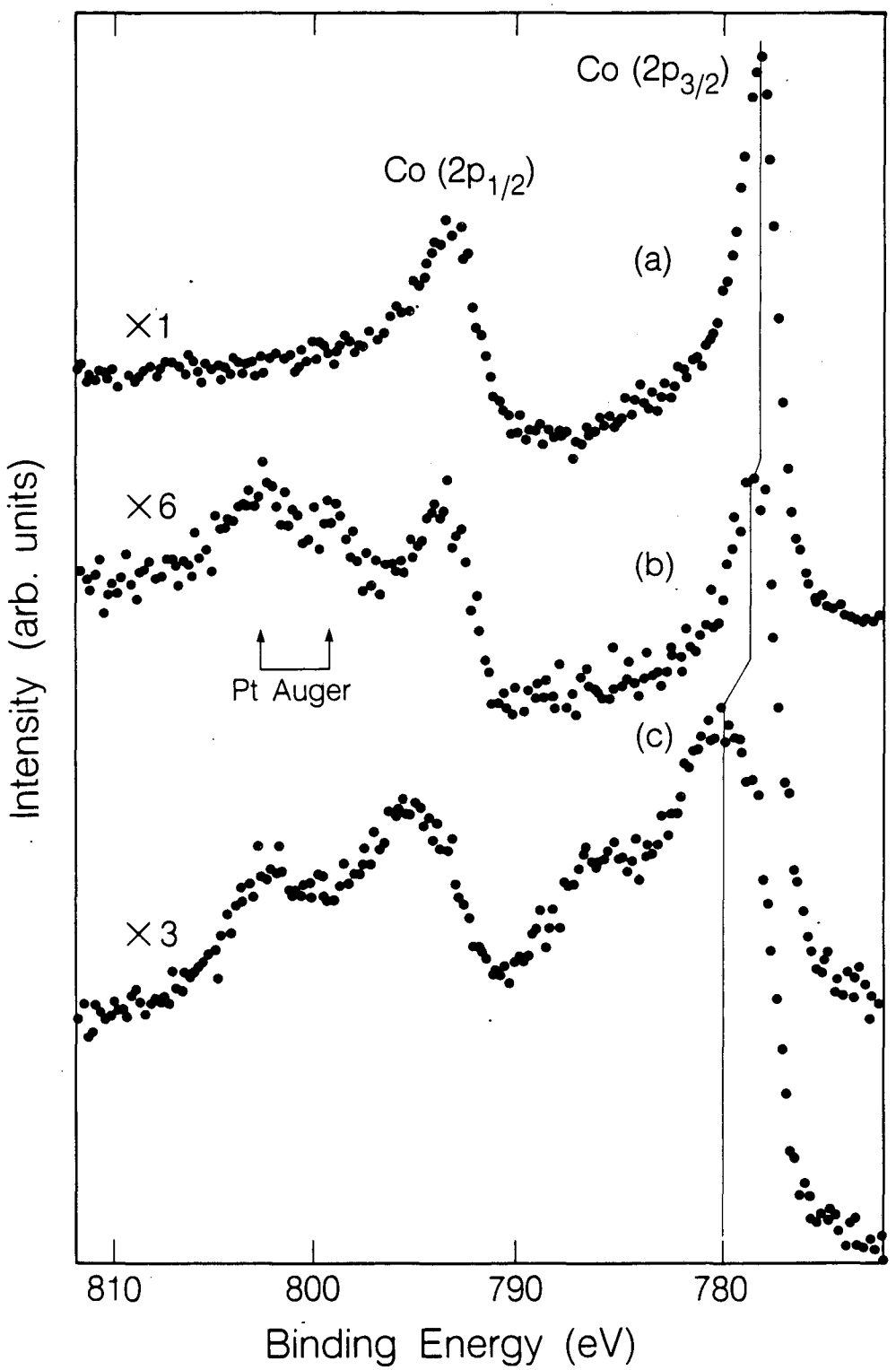
XBL 862-532 A

Fig. 2b



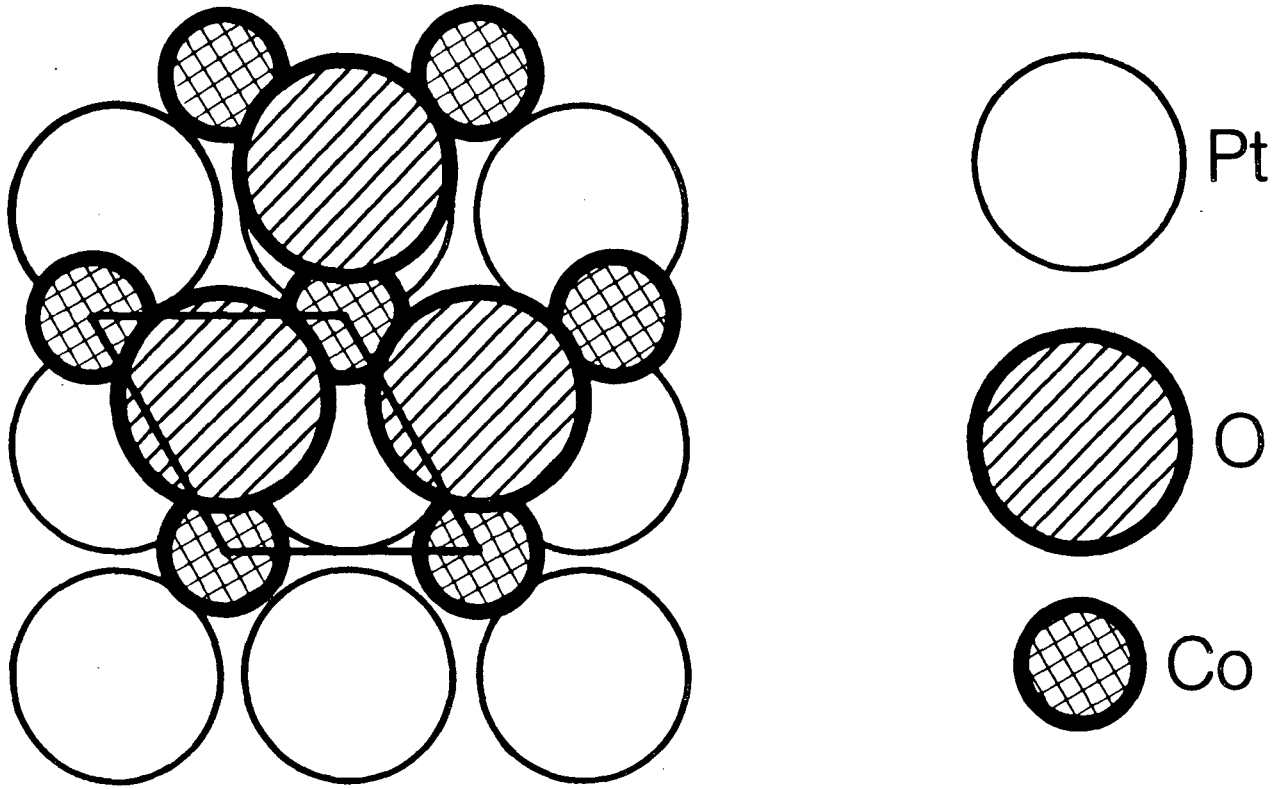
XBL 862-530 A

Fig. 3



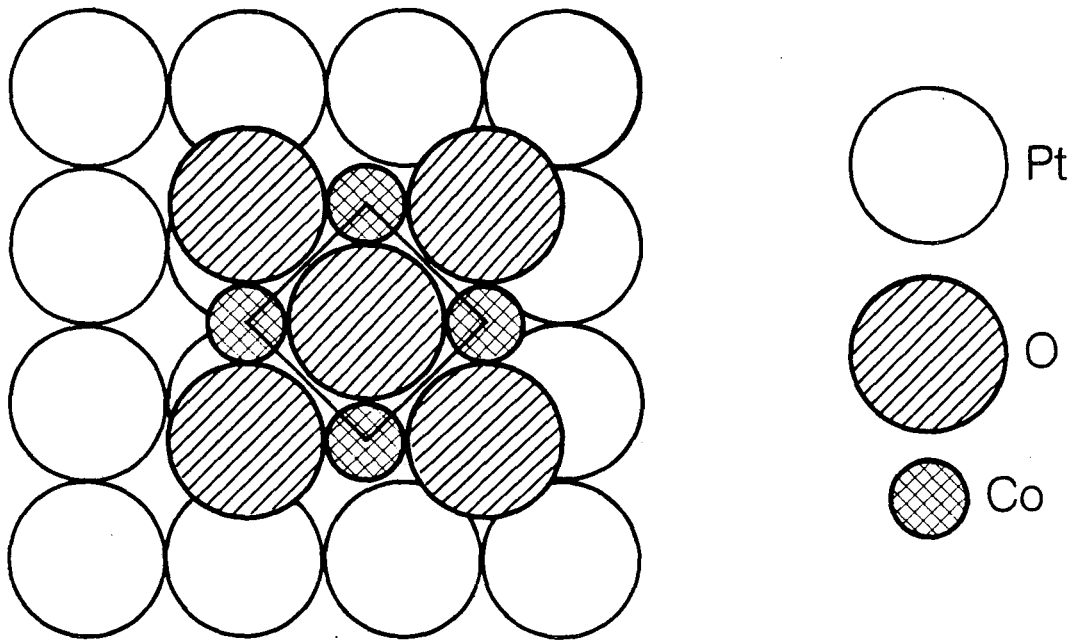
XBL 874-8123

Fig. 4



XBL 8610-10184

Fig. 5



XBL 8610-10185

Fig. 6

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