LBL-29435
Preprint

Lawrence Berkeley Laboratory
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Materials & Chemical Sciences Division

Submitted to Electrochemica Acta

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P.N. Ross

August 1990

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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CHARACTERIZATION OF ALLOY ELECTROCATALYSTS FOR DIRECT OXIDATION OF METHANOL

Philip N. Ross

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

I. Introduction

Platinum catalysts promoted by the addition of one or more admetals either to the platinum (e.g. alloying) or to the electrolyte (e.g. underpotential deposition) are the most active catalysts known for methanol oxidation [1]. In spite of the significant strides in understanding the mechanism of oxidation on pure Pt surfaces [2], our understanding of why one metal is more active than another, or how admetals promote the reaction remains relatively primitive. One of the limitations of our understanding has been the absence of a systematic methodology to characterize the surface composition and structure of multimetallic catalysts. However, in the last decade there has been an explosion of new techniques for catalyst characterization that can easily be applied to electrocatalysts in the "dry" state, and some even that can be applied in-situ. The purpose of this paper is to review new characterization methodologies that have been developed in recent years and to show how these techniques enable one to couple the study

This work was supported by the Assistant Secretary for Fossil Energy, Office of Fuel Cells, Advanced Concepts Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

of model catalysts, e.g. bimetallic alloys of known surface composition, with the study of practical catalysts, e.g. supported bimetallics, in order to understand and even to anticipate the behavior of the practical catalysts under reaction conditions.

The analytical techniques we have used in these characterization studies reviewed here will not be described in detail, but the interested reader will be referred to detailed treatments of each technique. The examples chosen to illustrate the application of these techniques will emphasize two particular bimetallic systems, Pt-Ti and Pt-Co. While these catalysts do not have enhanced activity for methanol oxidation, and in fact are much less active than pure Pt, they are of fundamental interest in relation to electronic theories of catalysis. Further, the characterization methodologies that have been used in the study of these two systems can be applied to any multimetallic system of interest for methanol oxidation.

II. Model Catalysts

Model catalysts are those that have a well-controlled bulk structure and are prepared in such a form that surface analytical methods can be applied for definitive determination of surface composition. One cannot over-emphasize the importance of determining and controlling the surface composition of the model catalysts, since catalysis occurs via interaction of surface atoms of the catalyst with the reactants. One of the objectives of characterization of

model catalysts should also be the determination of how the surface composition changes with time under reaction conditions.

It is now generally agreed that Auger electron spectroscopy (AES) by itself is not a reliable method for determining the composition of the surface of an alloy due to the finite escape depth of Auger electrons [3]. However, the combination of AES with low energy ion scattering (LEISS) is probably the most reliable method for surface composition analysis available in "standard" commercial UHV instrumentation [4]. AES does permit fast and reliable determination of surface cleanliness, and is much better in this regard than LEISS alone because of the relatively small ion-scattering cross-section of low-Z contaminants like C and O [5]. Because of the strong neutralization cross-section of low energy (a few keV) ions in metals [6], the penetration depth of the ions is limited to only the outermost atomic layer. However, rough surfaces are a problem for LEISS, as the scattering angle becomes indeterminate and the elemental resolution is lose, i.e. the method is not applicable to powders.

In our experience, the ideal model multimetallic catalyst is a non-porous solid produced either by bulk fusion of the pure metals or by the sequential deposition of one metal on another with vacuum annealing. There are advantages in both approaches, and for completness both should be used. For example, in the synthesis of a

supported alloy, the two metals are usually added to the support as separate phases, then heat treated to produce the alloy, requiring a reaction between the two phases. The chemistry of these reactions is crucial to producing the desired alloy composition and dispersion, and this chemistry can be observed directly using UHV surface analytical systems. We have used this approach in the study of alloy formation chemistry in both the Pt-Zr and Ti systems [7,8]. By depositing $Zr(Ti)O_x$ layers on top of Pt single crystals and heating in vacuum, one can follow the reduction of the oxide layer and the formation of the alloy phase by the various electron spectroscopies, e.g. AES and XPS. What we found, which was unexpected and important, was that the oxide layer dissolved completely, producing a dilute Pt-Zr(Ti) alloy in the bulk and an essentially pure Pt surface. Subsequently, Spencer [9] produced a surface enrichment theory that predicts surface enrichment by Pt at any bulk composition less than 25 at % Ti(Zr), which is consistent with these observations.

Another example of the study of alloy formation chemistry with UHV surface analytical techniques is that by Paffett and Windham [10], with the Pt-Sn system. They deposited metallic Sn layers on a Pt(111) single crystal surface, annealed in UHV, and observed the change in surface composition with LEISS and the surface structure with low energy electron diffraction (LEED). Because of the very high solubility of Sn in Pt, heating the Sn overlayer in

vacuum causes dissolution of Sn into the bulk, but unlike the Pt-Ti system, Sn did not disappear entirely from the surface, but rather formed a surface alloy containing 33 at% Sn in a $\sqrt{3} \times \sqrt{3}$ - R30 structure. The thermodynamic driving force to form this surface alloy is surface enrichment by Sn, which has a lower surface tension than Pt and its presence at the surface lowers the total surface energy [11]. This observation of surface alloying in the Pt-Sn system is of considerable importance in preparing a practical Pt-Sn alloy catalyst. The surface composition of the alloy will be essentially independent of the bulk composition in a Pt-rich mixture, and only a very small quantity of Sn, e.g. 1-5 at%, is necessary to produce a 33% Sn alloy surface on all the Pt particles present!

Bulk alloys made by fusion of the elements are also model catalyst systems of interest that should be studies in parallel to the metal-metal or metal-oxide overlayers. For methanol oxidation, we are usually interested in Pt-rich alloys. It is particularly advantageous in fundamental studies to use bulk alloys that form ordered substitutional structures, since the admetal substitutes for Pt at specific sites in the unit cell, enabling the experimenter to control the ligand geometry of the (hopefully) active site. The fcc Ll_2 [12] structure shown in Figure 1, occurs at the stoichiometry Pt_3M for many M metals, including Ti (Zr, Hf), V, Cr, Fe, Co and Sn. Regular terminations of the bulk Ll_2 crystal structure normal to the three major zone axes

produces a variety of surface compositions, from pure Pt (the (200) and (220) planes), 25% M (the (111) plane), to 50% M (the (100) and (110) planes). Thus, it is possible to have a surface with a higher concentration of M than in the bulk, i.e. enrichment, but without segregation, i.e. without interchange of atoms between the first atomic layers (non-bulk substitution). For example, in our laboratory, we have studied the equilibrium surface compositions of three Pt_3M systems, Ti [13-16], Co [17-19] and Sn [20,21] using the combination of LEED and LEISS. Both Pt_3Ti and Pt_3Sn have bulk termination of both the <111> and <100> oriented crystals with preferential formation of the compositionally mixed plane, (111) and (100) respectively. On the other hand, Pt_3Co is terminated normal to all three major zone axes in pure Pt surfaces, a clear example of a system exhibiting <u>both</u> enrichment and segregation.

Once the structures and compositions of the bulk alloy surfaces are determined, one can study chemisorption and reactivity of the surface to determine the effect of the admetal positioned in the surface in a specific way. As might be expected, there is a very strong electronic interaction between the Pt and the admetal in these ordered alloys, and this has an effect on the chemisorption properties (and reactivity). Figure 2 shows the He(II) photoemission from $Pt_3Ti(111)$ compared to pure Pt. Bonding of Pt to Ti produces a dramatic decrease in the density of states (DOS) near the Fermi-level, and an increase in the

DOS near the bottom of d-band. A Extended-Huckel calculation of the Pt-Ti bonding [16] showed that these changes in DOS represent filling of the Pt d-band by donation of d-electrons from Ti to unfilled Pt d-orbitals. Because of its sensitivity to d-orbital bonding [22], carbon monoxide makes an excellent probe molecule to examine the effect of the intermetallic bonding on adsorption. The thermal desorption spectra (TDS) for CO desorbing from $Pt_3Ti(111)$ and Pt(111) are compared in Figure 3. For adsorption at room temperature, only about 3/4 of the CO adsorbed desorbs intact, the other 1/4 is dissociated on the surface, i.e. every CO molecule adsorbing on a Ti atom is dissociated. For the CO molecules desorbing from Pt sites, the shift in desorbtion temperature at constant coverage corresponds to a decrease in average binding energy of ca. 4 kcal/mol, about a 20% decrease. The decrease in binding of CO to Pt is attributed to the reduction of back-bonding to the CO- π^* orbital due to filling of the Pt d-orbitals by donation from Ti (this donation occurs even with an oxygen bound to the Ti site). Clean Ti surfaces dissociate CO at room temperature [16], so that these experiments do not reflect any change in the character of the Ti atoms due to intermetallic bonding. However, electron donation should make Ti even more electropositive, binding oxygen even more strongly than the pure metal.

Interestingly, a similar effect of intermetallic bonding is observed on Pt_3Co surfaces, as shown by the TDS

curves in Figure 3, even though they have pure Pt outer surfaces [19]. Photoemission spectra also show [19] a qualitatively similar valence band structure, indicating that d-band filling occurs in Pt_3Co as in Pt_3Ti.

The behavior of Pt_3Sn surfaces towards CO is qualitatively similar, and the valence band spectra are also very similar to those described above for Pt_3Ti and Pt_3Co. This was unexpected and is not understood, since the electronic configuration of Sn is quite different from that of either Ti or Co, i.e. the d-orbitals are completely full (25 eV below E_F). However, none of these alloys is a better catalyst for methanol oxidation than pure Pt. The inactivity of these alloys appears to be due to the effects of intermetallic bonding on the adsorptive properties of the surface.

Another function of the study of model catalysts is the use of surface analytical techniques to determine what happens to the catalyst during use. Analyses of this type can take various forms, depending on the nature of the effect one is looking for and the type of spectroscopy being used. To use very surface sensitive techniques like AES, LEISS or LEED, one needs a special apparatus for transferring the sample under clean conditions between the electrochemical cell and the UHV analytical system [24]. We have used such a system in our laboratory to study the stability of Pt_3Ti [25], Pt_3Co [26], and Pt_3Sn [21] surfaces under simulated fuel cell operating conditions. It was

determined that neither the Pt-Ti nor the Pt-Co surfaces are stable in acid electrolyte, even as hydrogen anodes, becoming essentially pure Pt surfaces by dissolution of the base metal. On the other hand, Pt_3Sn surfaces have a reasonable window of stability when used in acid electrolyte as either hydrogen or methanol anodes.

In one of the few in-situ studies of alloy catalysts, and the only one of its kind known to me, Gottesfeld and co-workers [27] used ellipsometry to determine the stability of Pt-Cr alloys when used as oxygen cathodes in acid electrolyte. As one might expect from the Pourbaix diagram for Cr, they found the surfaces to be unstable, with dissolution of Cr leaving a roughened pure Pt surface, and an apparent enhancement of activity due to the roughness. These studies of the behavior of the surfaces of bulk alloy metals clearly indicate the need for such studies in order to interpret the observed behavior of real catalysts, which can often produce "apparent" enhancements that are not truly interesting or of practical value.

III. Real Catalysts

Because catalysis is a surface effect, we try to achieve the highest possible surface area when we prepare the catalyst. Usually, this means the active phase is dispersed on a support, the most common example being Pt clusters dispersed on a conductive carbon black [23]. In the case of an alloy catalyst, by direct analogy, one would achieve the highest surface area by dispersing the alloy on

a conductive support such as carbon. There are many examples of supported bimetallic electrocatalysts that have been used in fuel cells, in both anodes [1] and cathodes [24]. It is now well-established practice in the literature of gas-phase heterogeneous catalysis to distinguish "supported bimetallic" catalysts from "supported alloy" catalysts, since two metals may be present on the same support and not be alloyed [28]. If it is our intention to prepare a supported alloy of a given bulk/surface composition, as opposed to just a supported bimetallic catalyst, then we face the challenge of developing a characterization procedure for determining: i.) what fraction of the mass of the two or metals present are alloyed; ii.) how many alloy phases are present; iii.) what is the particle size distribution of each alloy phase; iv.) what are the surface compositions of the different alloy phases.

A. Identification of Alloy Phases

The review chapter by Kinoshita and Stonehart [29] provides an excellent background on procedures for preparing and characterizing supported metal catalysts. My purpose here is to extend that review to cover specifically multi-metallic systems, and to do so by example of the study of the Pt-Ti and Pt-Co bimetallic systems, for which we have the advantage of having conducted the study of the surface chemistry of the bulk alloys in parallel to the study of the supported catalysts. We have used three techniques in

combination to identify the chemical state (including alloy phases) of the metals present on the support. These are x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and extended x-ray absorption fine structure spectroscopy (EXAFS). The use of XRD and XPS in these studies is well covered in the review by Kinoshita and Stonehart, while the more recent technique of EXAFS applied to bimetallic catalyst characterization is described in the excellent monograph by Sinfelt [28]. Normally, one thinks of XPS as a surface sensitive technique, and that is true for non-porous solids, but for porous solids like supported metal catalysts, the XPS spectra come from the whole crystallite, since the crystallite size is typically of the same order of magnitude as the escape depth of the photoelectrons [3]. Both the x-ray techniques of XRD and EXAFS are bulk methods, except when used in the grazing incidence mode with optically flat solid surfaces [30]. Thus, in the context of supported metal catalysts, all three techniques examine bulk structure of the phases present on the support surface.

Figure 4 shows the Ti(2p) XPS spectra for a typical Pt fuel cell catalyst impregnated with TiO_x and heated in-vacuum. Using reference spectra of the pure compounds (Table I), one can easily see the conversion of Ti from a "TiO_2-like" state into a "Pt_3Ti-like" state, although some of the Ti clearly remains in the oxide state even after treatment at 1200°C. Because the chemical shift between

these states is relatively large, the peaks are easily deconvoluted and the peak areas give a quantitative measure of the relative fraction of "alloy" versus oxide state as a function of temperature (Table II). Although the chemical shift of Ti in the "alloy" state is the same as it is in Pt_3Ti, that does not mean that the alloy phase present is Pt_3Ti, since more dilute phases of Pt-Ti also have the same chemical shift. Phase identification was provided by XRD. Figure 5 shows the XRD patterns for the 1200°C treated sample, with the presence of superlattice lines apparent. Superlattice reflections come only from ordered alloy phases, and the lattice parameter calculated from the 2θ values of the reflections indicates the ordered phase is Pt_3Ti, as opposed to the more dilute ordered phases Pt_5Ti or Pt_8Ti [31]. The shape of the diffraction peaks indicated there were only two metallic phases present - Pt_3Ti and pure Pt. The oxide phase is essentially invisible, probably because it is amorphous, and also because of the lower scattering power of the oxide versus the Pt containing phases. It was difficult to quantify the ratio of the two metallic phases, since the intensity of the superlattice reflections is a function of the order parameter [32] for the crystallites, which was unknown. However, since the XPS had given us the quantification between "alloy" and oxide (e.g. about equal amounts of each phase are present at 1200°C), and the XRD patterns had identified Pt_3Ti as the only alloy phase, the combination of the two analyses tells

us what fraction is Pt_3Ti and what is still pure Pt. In the case of the catalyst in Figures 4-6, the total amount of Ti present was exactly twice the stoichiometric amount to convert all the Pt to Pt_3Ti. Therefore, the combined analyses showed that at 1200°C, all the Pt was converted to Pt_3Ti, but at the expense of significant coarsening and substantial loss of surface area, e.g. the average crystallite size determined by x-ray line broadening was 30 - 50 nm an impractical result. At 900°C, the analyses showed that about 2/3 of the Pt had been converted to Pt_3Ti, and 1/3 remained as pure Pt, but the average crystallite size remained at a practical level of 5 - 10 nm. Below 900°C, the amount of alloy formation was impractical, if the intention was to make a supported Pt_3Ti catalyst.

In the particular case of the Pt-Ti system, the large chemical shift of the alloy state and the formation of a highly ordered phase were intrinsic chemical properties of this system that were particularly advantageous for the two techniques used, XPS and XRD. Not all multi-metallic systems have such chemical properties, and these two techniques in themselves will not necessarily provide as clear a characterization as we saw in the Pt-Ti system above. However, EXAFS is as powerful as these two methods taken together, and has the advantage of providing structural information from amorphous phases as well as crystalline phases. The radial distribution functions determined from EXAFS spectra for the same Pt-Ti catalyst as

discussed above is shown in Figure 6. Again using various Ti compounds as standards, one can follow the evolution of atomic coordination around the Ti atoms as a function of heating: the short bonds (< 2Å) are O nearest neighbors, the two neighbors at 2.7 and 4.5Å are Pt atoms in the first and second coordination sphere, respectively. The relatively high intensity of the second neighbor peak clearly identified the Ti-Pt phase as a highly ordered phase, since the backscattered intensity from second and third shells is extremely sensitive to disorder. The relative intensities of the backscattering from the O and Pt atoms, corrected for the differential cross-sections, indicates that in the 1200°C sample approximately the same number of Ti atoms have O environments and Pt environments, and in the 900°C sample the distribution is approximately 2/3 - O and 1/3 - Pt. These ratios are consistent with the XRD/XPS determinations described above.

All three of the techniques described above are volume integrating methods, and it is very difficult to extract information about the distribution of alloy composition among different crystallites on the support from these methods alone. In the previous examples with the Pt_3M ordering alloys, this was not a problem, since the Pt_3M phase is the thermodynamically most favored Pt- rich phase, and only alloy phase is expected to form. However, more generally, alloy systems of interest for methanol oxidation, such as Pt-Ru, are not strongly ordering alloys, and the

thermodynamics may not drive the system to form only one alloy phase. It would be extremely difficult to extract alloy composition distribution from either XPS or EXAFS. XRD can give such information, but the information would be skewed by the very strong dependance of x-ray diffraction intensity on crystallite size, which weights large crystallites (> 5 nm) relative to small ones. However, alloy composition distribution and crystallite size information can be obtained directly from electron microscopy, either in a transmission (TEM) or in a scanning (STEM) microscope.Because most supported electrocatalysts use carbon as the support material, high Z-element phases appear in high contrast relative to the support, making crystallite size determination of supported metals relatively easy by TEM [23,29]. It is also possible to use weak beam methods [33] in a TEM to determine particle shape even for crystallites on the order of 10 nm in size. We have used the atomic resolution microscopy to follow the growth of Pt crystallites on a carbon black support during vacuum annealing, and used the weak beam technique to determine the change in particle shape with size [34]. Examples from this study are shown in Figures 7 and 8. In as- prepared form, Pt in the standard Pt fuel cell catalyst [35] is in the form of clusters of near- sphere shape with a narrow size distribution of 2 - 3 nm diameter. Upon heating in-vacuum (10^{-6} torr), particle growth can be observed in-situ occurring either by vapor phase transport or surface

diffusion of atoms, i.e. no motion of crystallites, resulting in the formation of nearly perfect cubo-octahedral microcrystallites. This shape-size relation would cause a catalytic reaction to exhibit size dependent kinetics if the reaction were structure sensitive as appears to be the case of oxygen reduction [36].

The problem of determining composition distribution among metal clusters dispersed on a support can be addressed using STEM, although there are relatively few examples of this in the literature. One from our laboratory is shown in Figure 8. This catalyst is Pt-Co-Ni tri-metallic system [37] on a carbon black support. We heat-treated the material in vacuum and used STEM analysis with elemental detection by x-ray fluorescence to map the elemental distribution as a function of heating. The figure shows the secondary electron image, along with the Pt, Co and Ni elemental maps from x-ray fluorescence. It is clear that there is a one-to-one correspondence between all four images, and that every particle appears to contain all three elements, i.e. a supported ternary alloy! Through the use of standards, the analysis can be made reasonably quantitative, and enables the composition of each crystallite to be determined.

As was the case for the study of model catalysts, most of the characterization studies of real catalysts have been carried out ex-situ. The techniques that utilize x-rays can be used in-situ, and O'Grady and co-workers [44] have

pioneered the use of EXAFS in-situ to examine the chemistry of a variety of electrode materials during electrolysis, including supported Pt. However, I am not aware of any in-situ EXAFS studies of supported alloy catalysts, although they are certainly possible and in-situ EXAFS will be an important technique for the future. For the present, one can conduct the ex-situ EXAFS analyses before and after use in cells, and determine the effect of electrolysis on the alloy structure. Examples of such studies may be found in the reports by Beard and Ross [25,26].

Finally, there is the question of determining the surface composition of supported alloy crystallites/clusters, which is the most difficult, but most relevant, information to obtain. For gas phase catalysts, the technique used most frequently is quantitative volumetric chemisorption [38]. The method is based on the selective chemisorption of a probe molecule on one of the constituent atoms of the surface. A classic example is carbon monoxide as the probe molecule, which is selectively chemisorbed by Pt in many Pt alloys, e.g. Pt-Sn [39]. Assuming that there is one CO molecule adsorbed on every surface Pt atom, the surface composition can be determined by measuring the volume of CO adsorbed, if the total number of surface atoms is known. The total number of surface atoms (the dispersion) has to be measured independently, e.g. by adsorption of a probe molecule that adsorbs on all surface atoms. In the case of unsupported alloys, e.g.

powders, the total number of surface atoms can be measured using nitrogen physisorption and the BET analysis [29]. For supported alloys, one needs two selectively adsorbing probe molecules, one that adsorbs on the alloy atoms but not the support atoms, and one that adsorbs only on one of the alloy atoms. Examples of such pairs of molecules are H_2/CO and O_2/CO. Changing the adsorption temperature can also be used to create selective adsorption, which is frequently the case when using CO. For example, with supported Pt-Ru [40,41], the heat of adsorption of CO on Pt is ca. 10 kcal/mol higher than for Ru, so that adsorption of CO at a temperature just above the temperature for desorption of CO from Ru produces selective adsorption on Pt atoms. Hydrogen atoms are adsorbed on both Pt and Ru surface atoms at room temperature, and at any temperature above ca. 100°K there is insignificant adsorption of either H_2 or CO onto the carbon support. Hence, the H_2/CO chemisorption method can be used to determine both the degree of dispersion of the alloy phase and the average surface composition of all the phases present [41]. The chemisorption method does not, however, distinguish between alloyed and unalloyed metal surfaces, it is simply a method of counting atoms at surfaces, and must be used in conjunction with the techniques described above to be certain one is measuring <u>alloy</u> surface compositions. There are examples of a comparable use of electrochemical adsorption to determine surface composition of alloys in-situ, e.g. the selective adsorption of hydrogen on Pt

surface atoms observed by the cyclic voltammetry [42] of Pt-Au alloy foils. But the examples are relatively rare, and this is clearly not a well developed technique in electrocatalysis. Furthermore, cyclic voltammetry can itself alter the composition of the surface by extending the potential beyond the region of stability of the alloy, which is often not known.

IV. Future Developments

The most active catalysts for methanol oxidation are multimetallic materials which may or may not be alloys. Most of these materials were developed and tested in a time period before surface analysis and the new x-ray techniques like EXAFS were widely available. Also, researchers in electrocatalysis did not adopt methods for characterizing their catalysts even in the "dry" state as quickly as did their counterparts in gas-phase catalysis. As a result, it is difficult to assess the fundamental implications of activity trends for multimetallic catalysts reported in the electrocatalysis literature [1,2], and to use these trends to predict directions to seek new materials. Some of the most active catalysts now known should be re-examined using the variety of characterization methods described in this paper in order to determine <u>what surface</u> is actually catalyzing the methanol oxidation reaction. An example of such a re-examination is the study in my laboratory of Pt_3Sn and Pt modified by electrosorbed Sn [20,21]. Contrary to the assertion by some groups [1], we did not find the Pt-Sn

alloy to be a more active catalyst than pure Pt. This result was independent of the bulk alloy composition, since surface enrichment of Sn produces the same surface on all the alloys. However, Sn added to the acid electrolyte enhanced the activity of Pt(111) several- fold, apparently via a direct interaction between the Sn ion in solution and methanol adsorbed on the surface. These results suggest a new direction for catalytic materials might be sought by a marriage of homogeneous and heterogeneous concepts.

Another example of a catalytic system which deserves re-examination is Pt-Ru. It is possible that this system has not been optimized, since it is only recently known [41,43] that Pt enrichment occurs in this system, and that in supported Pt-Ru bimetallic catalysts [41] a significant concentration of Ru is on the surface only for Ru- rich compositions (> 50%), which were not examined in the previous methanol fuel cell work [1]. Catalyst characterization can and probably will in the future play an extremely important role in the process of optimization of a given material as well as in the search for new materials.

Acknowledgments

The work described here on the characterization of Pt-Ti and Pt-Co catalysts was supported by the Assistant Secretary for Fossil Energy, Office of Fuel Cells, Advanced Concepts Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The ongoing study of methanol electrocatalysis by alloys and the author's participation in

this workshop was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution, Electrochemical Energy Systems Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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TABLE I: Binding Energies[a] for Pt and Ti in Standard Compounds and Chemical Shifts

	$Pt(4f_{7/2})$	$Ti(2p_{3/2})$	ΔBE
Pt foil	70.9		ref[b]
Pt_3Ti	71.2		+0.3
Ti foil		453.8	ref[b]
TiO		454.6	+0.8
TiC		454.7	+0.9
$TiPt_3$		455.1	+1.3
TiO_2		458.5	+4.7
$TiCl_3$		459.4	+5.6

[a] Binding energy scale referenced to $Au(4f_{7/2})$ at 83.8 eV
[b] Reference state for chemical shifts.

TABLE II: Integrated XPS Intensity Ratios of $Ti(2p_{3/2})$ to $Pt(4f_{7/2})$ Signals for Heat-Treated Catalysts

chemical state of Ti	as-prepared	700 °C	900 °C	1200 °C
as TiO_2	1.89	0.49	0.48	0.47
as "alloy"	0	0.09	0.22	0.55
total Ti	1.89	0.58	0.70	1.02

Figure Captions

1. Configurations of the three low index faces of an alloy having the $L1_2$ crystal structure. Example shown is the alloy Pt_3Sn.

2. He(II) photoemission spectra for Pt(111) compared to Pt_3Ti(111). Ref. [14].

3. TDS spectra for CO at saturation coverage on (1) Pt_3Ti(111) compared to (2) Pt(111). Adsorption on Pt_3Ti was at a lower temperature to achieve same coverage as on pure Pt. Ref. [14].

4. XPS spectra in Ti(2p) region for TiO_2-impregnated Pt on carbon catalyst as a function of heat treatment temperature. Ref. [15].

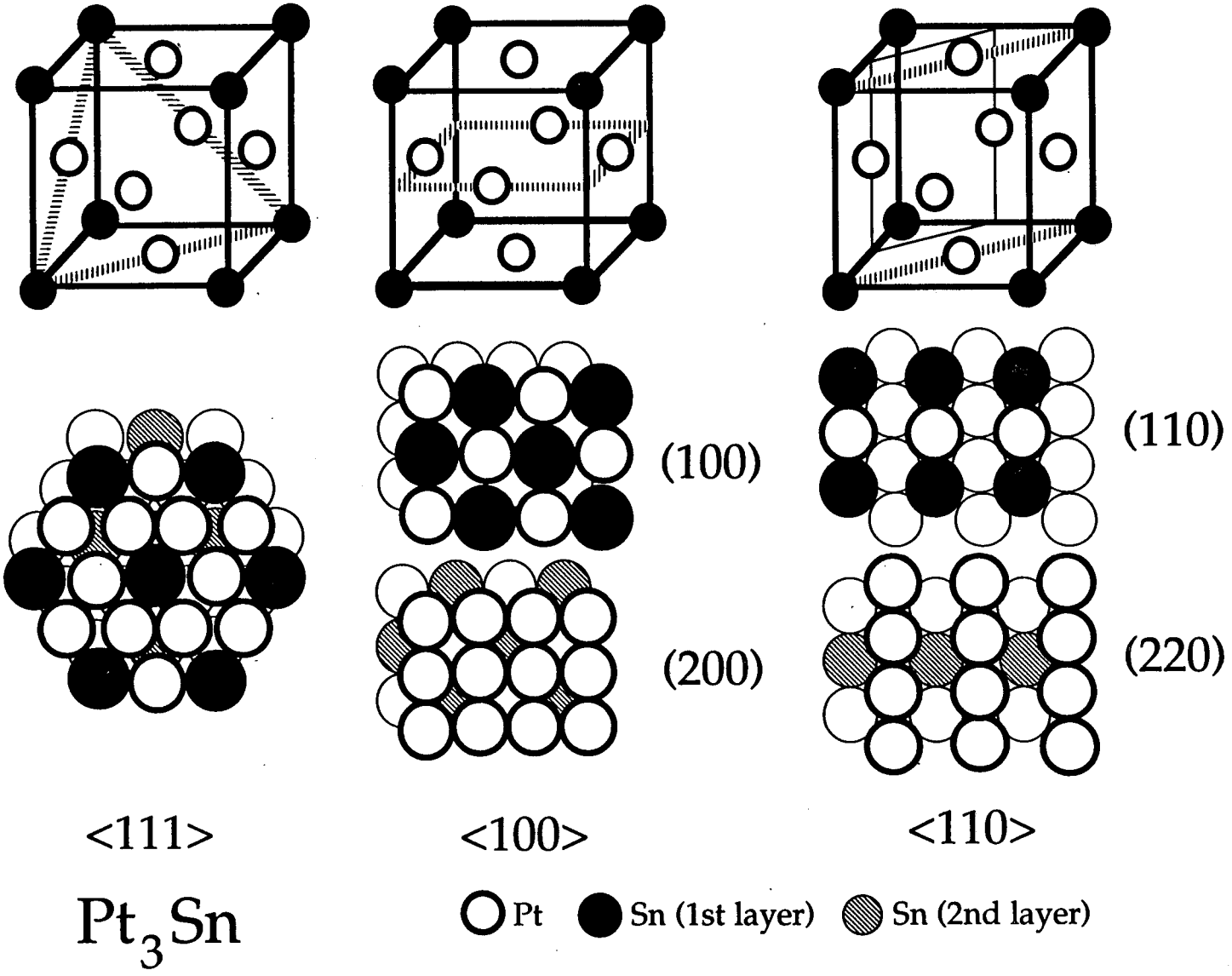
5. (a.) X-ray diffraction scan of the TiO_2-impregnated standard Pt on carbon catalyst in the as-prepared state. Ref. [15]. (b.) XRD scan for the 1200°C heat-treated catalyst. Graphite (002) and (10) reflections are at ca. 25° and 43°, respectively. Super-lattice lines are indicated by arrows. Cu-Kα radiation was used.

6. Magnitude of Fourier transform of $k^3\chi(k)$ spectra for the TiO_2-impregnated Pt catalyst as a function of heat treatment temperature. Ref. [15].

7. Transmission electron micrographs of Prototech Pt on carbon fuel cell catalyst as a function of heat-treatment: top - left as-received; top - right after 900°C; lower - left after 1200°C; lower - right is drawing of a cubo-octahedron in orientation of crystallite in image at left. All images at same magnification. Ref. [34].

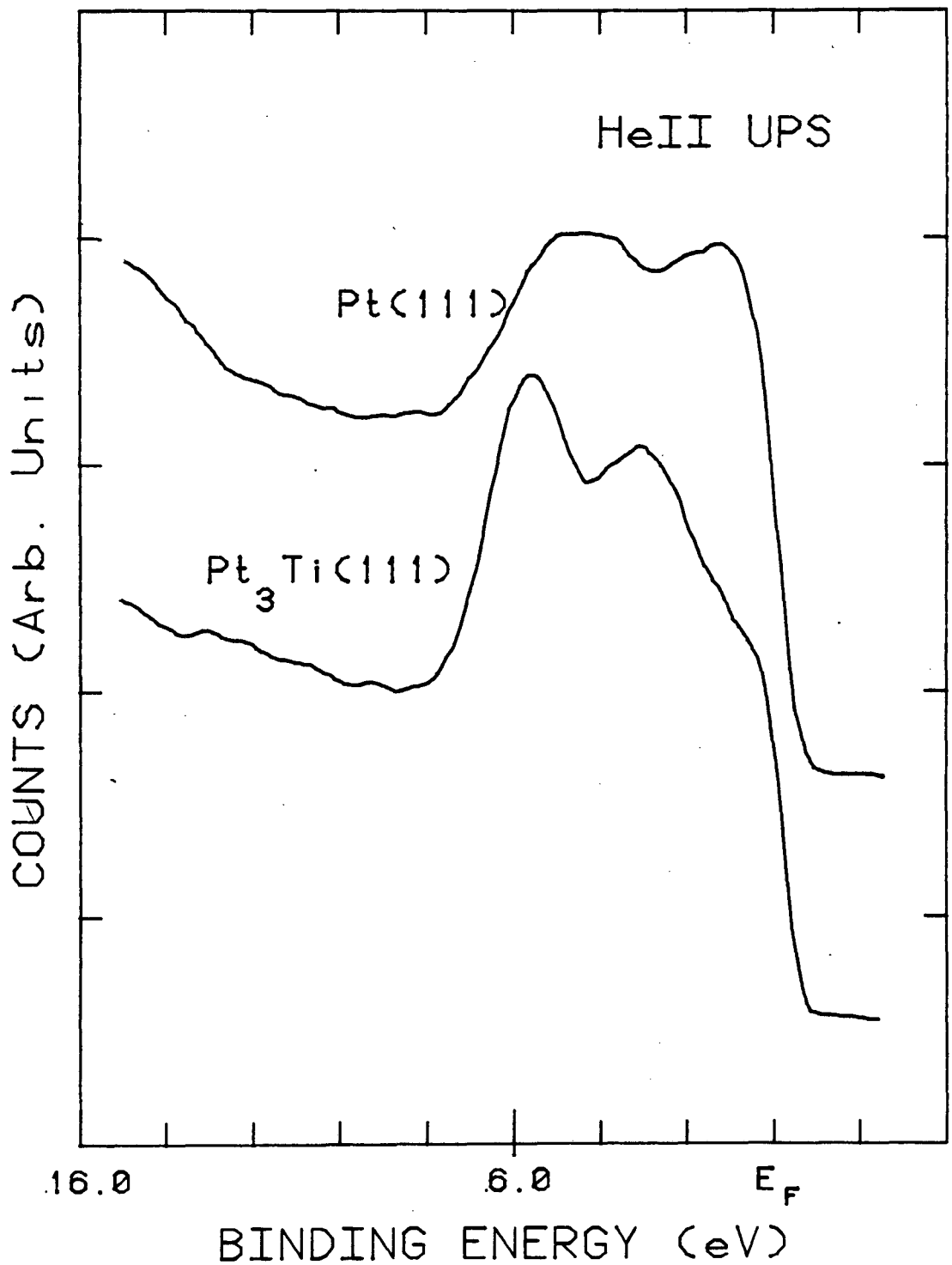
8. (left panel) Weak-beam image of the 1200°C heat-treated Pt fuel cell catalyst. (right panel) Drawings of cubo-octahedra in orientations matching weak-beam images. Ref. [34].

9. (lower left) Secondary electron image of a Pt-Co-Ni catalyst on a carbon black support. Pt:Co:Ni loadings in atomic ratios of 3:1:1. (upper left) and (lower right) X-ray mapping images formed from Pt, Co, and Ni characteristic x-ray emission. 30 nm beam at 200 KeV.



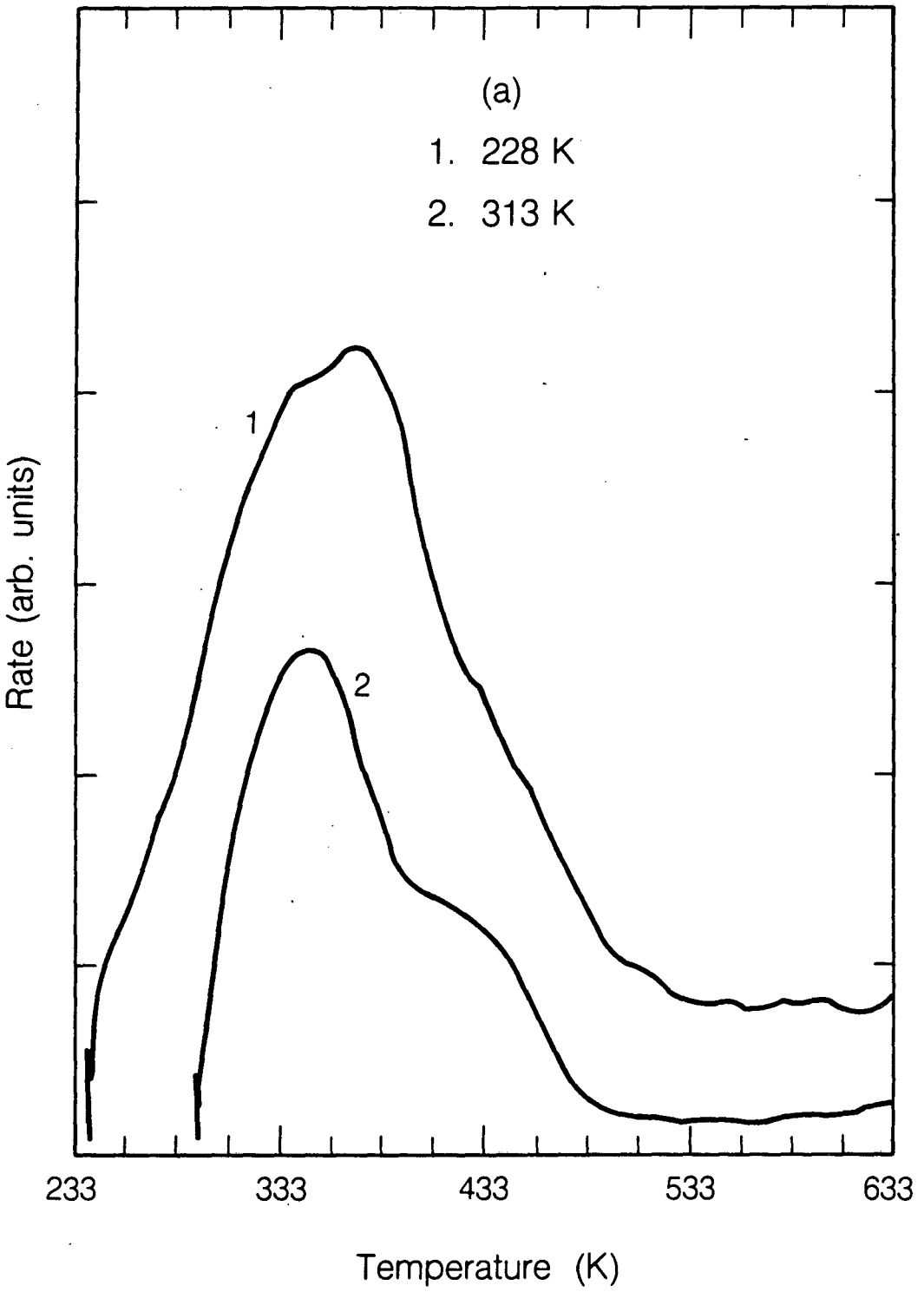
XBL 902-651

Fig. 1



XBL 844-1327

Fig. 2



XBL 862-10611

Fig. 3a

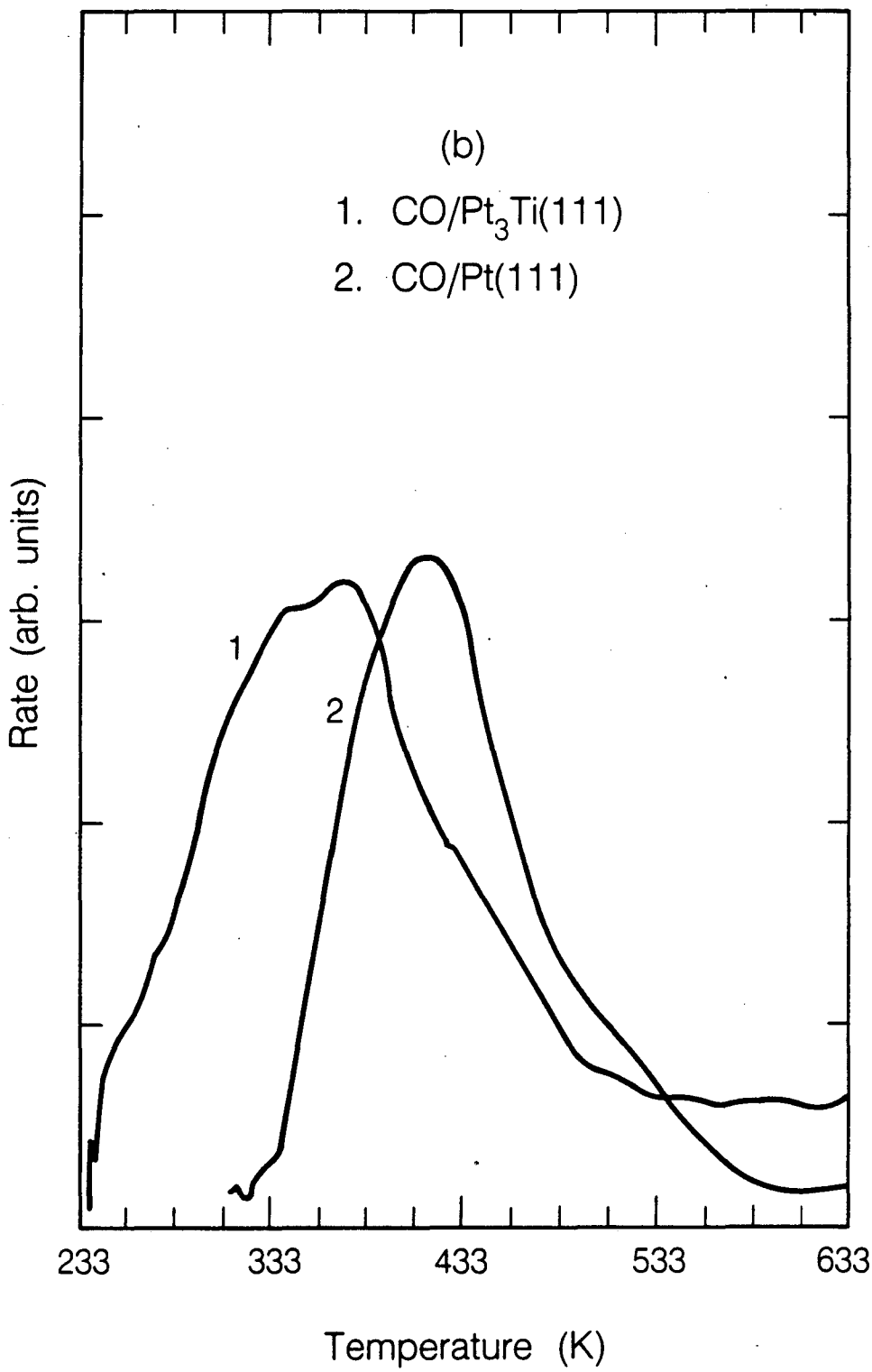


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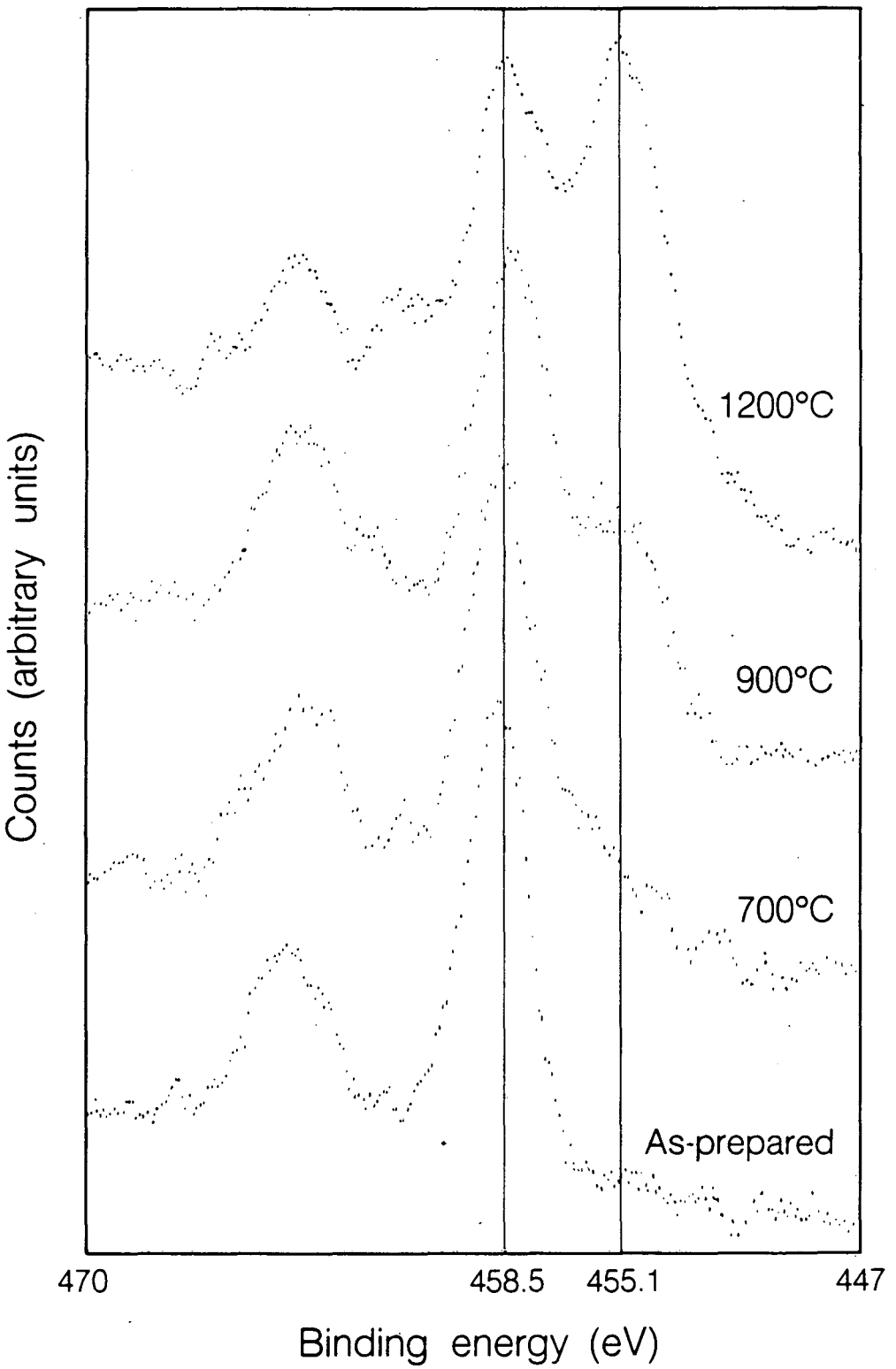
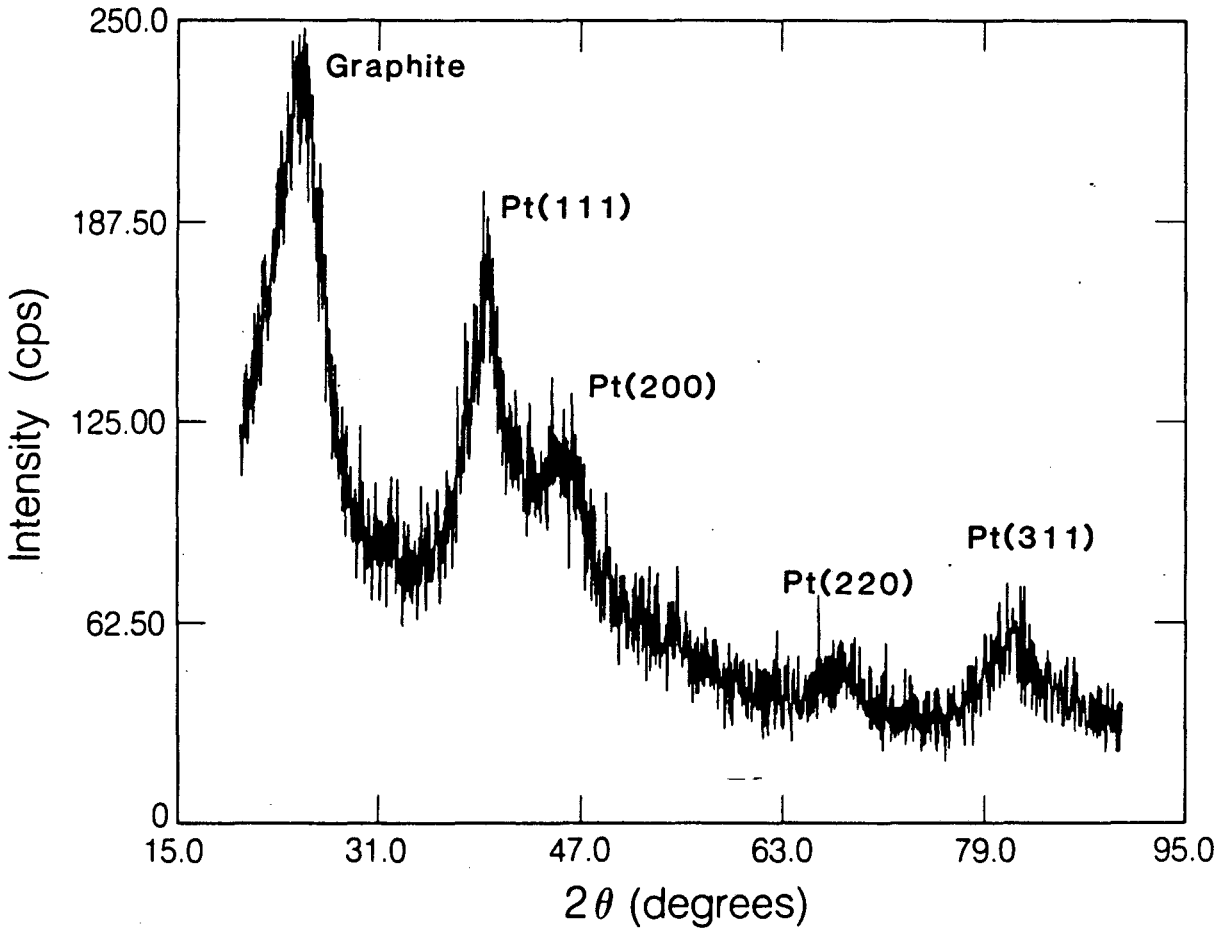
Fig. 3b



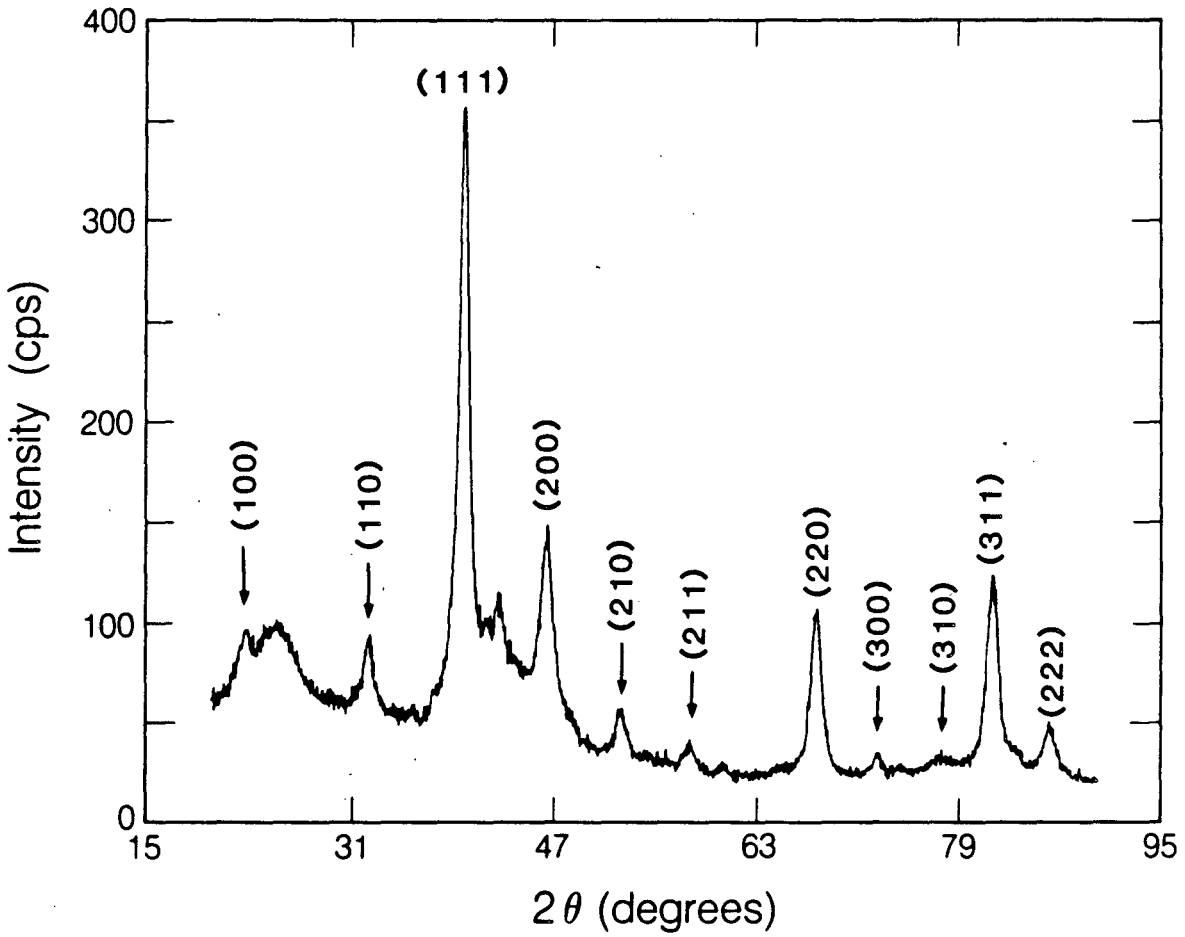
XBL 855-8896

Fig. 4



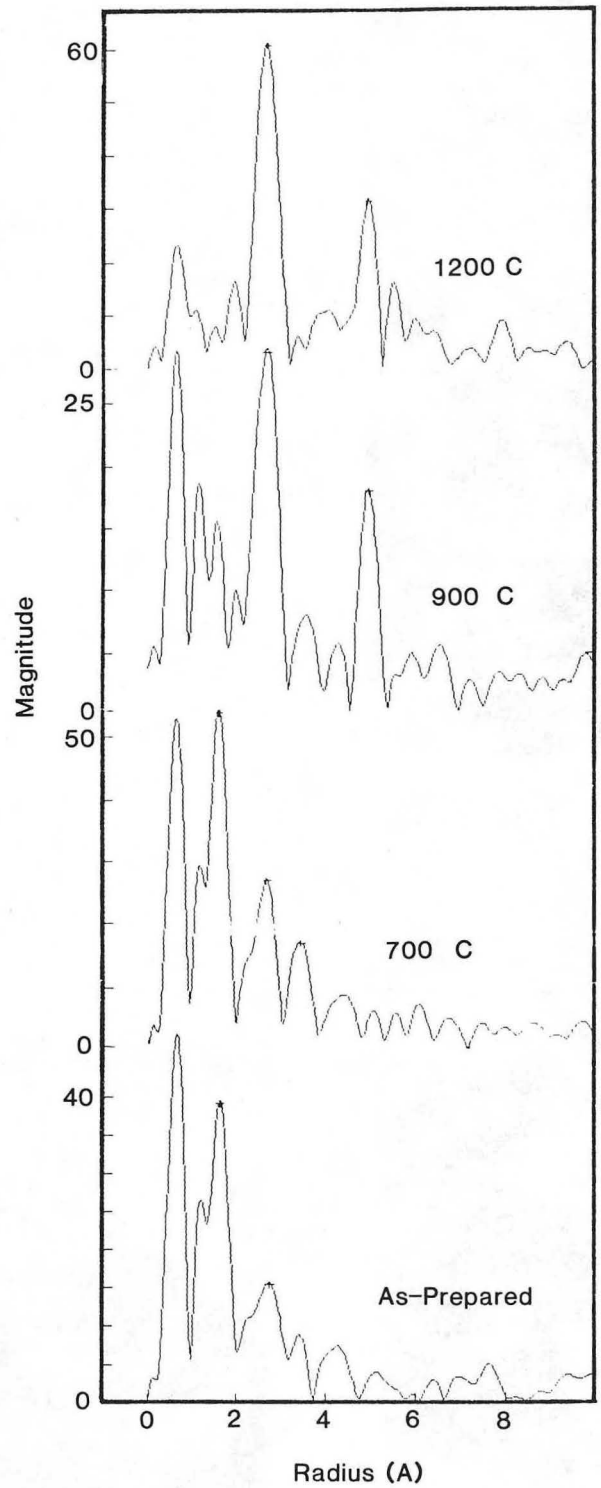
XBL 855-8894 A

Fig. 5a



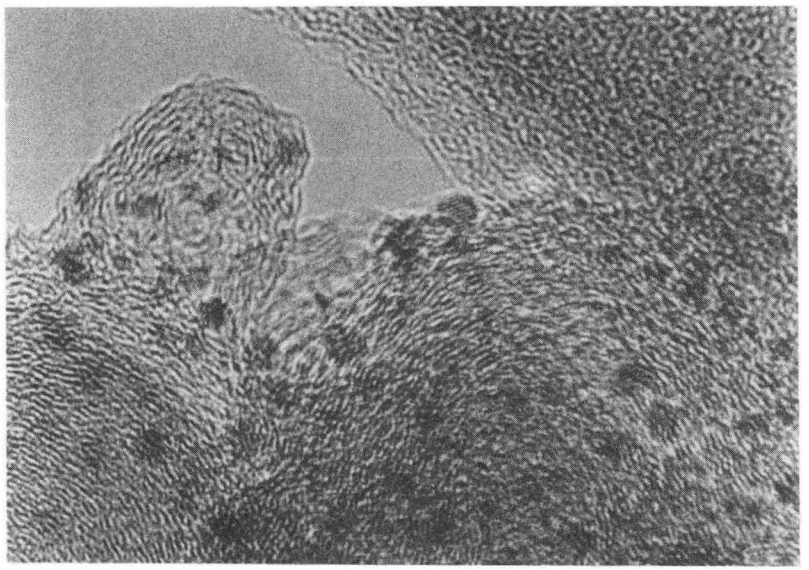
XBL 855-8895 A

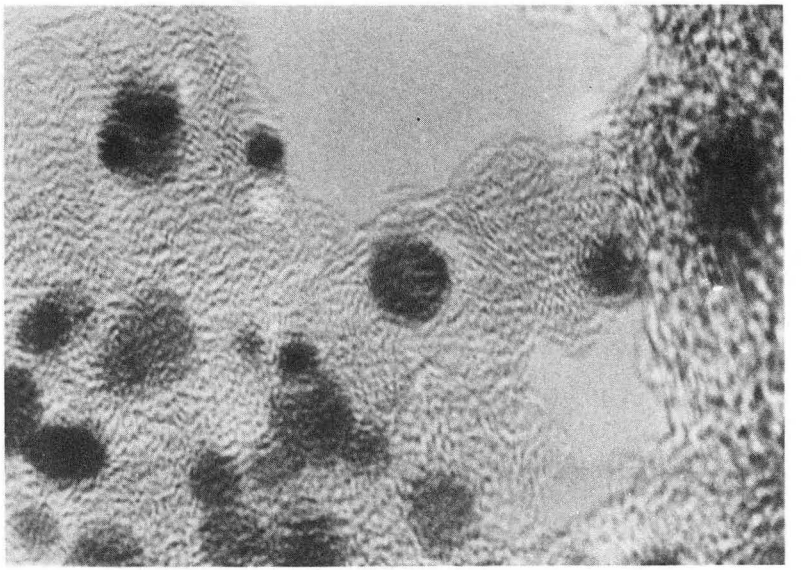
Fig. 5b

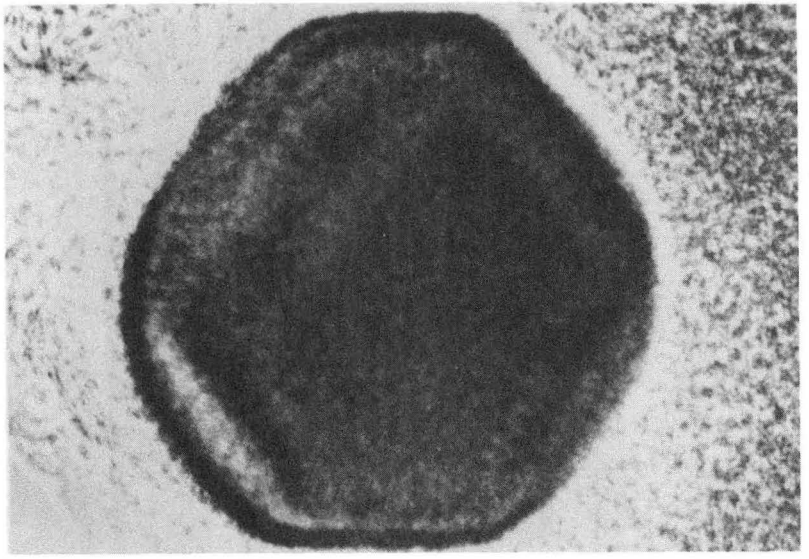


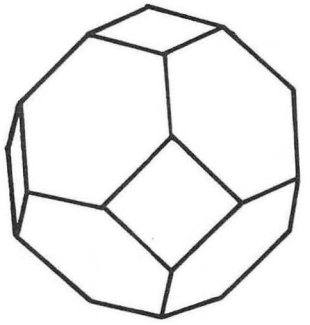
XBL 857-3117

Fig. 6





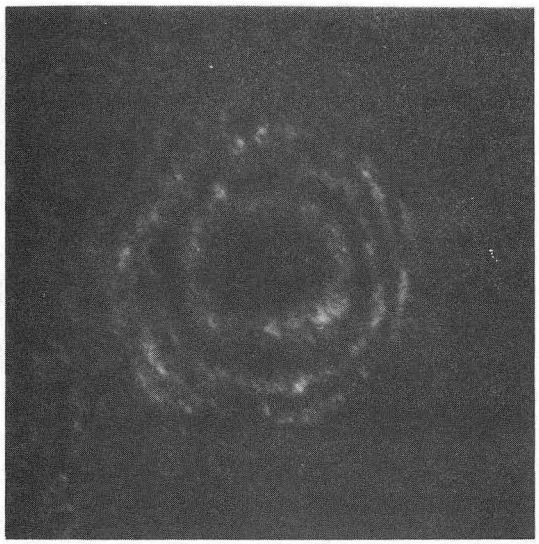




0.01 μm

Fig. 7

XBB 858-6702



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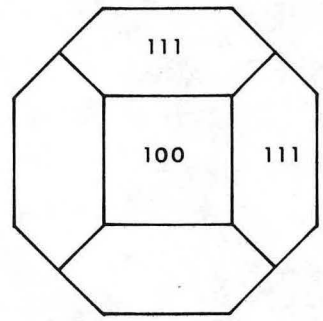
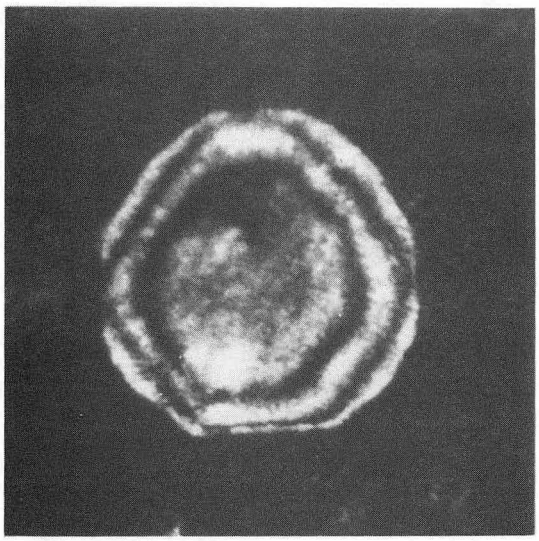
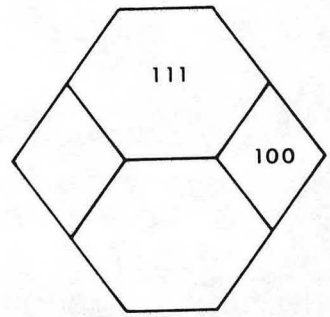
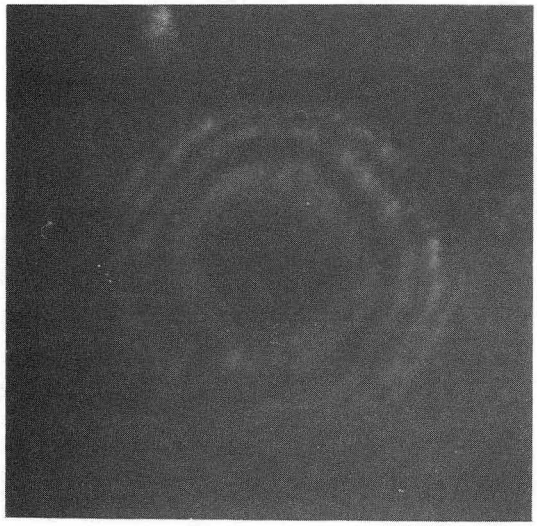


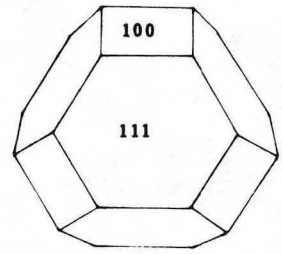
⟨100⟩ orientation





⟨110⟩ orientation





⟨111⟩ orientation

Fig. 8 XBB 858-6699

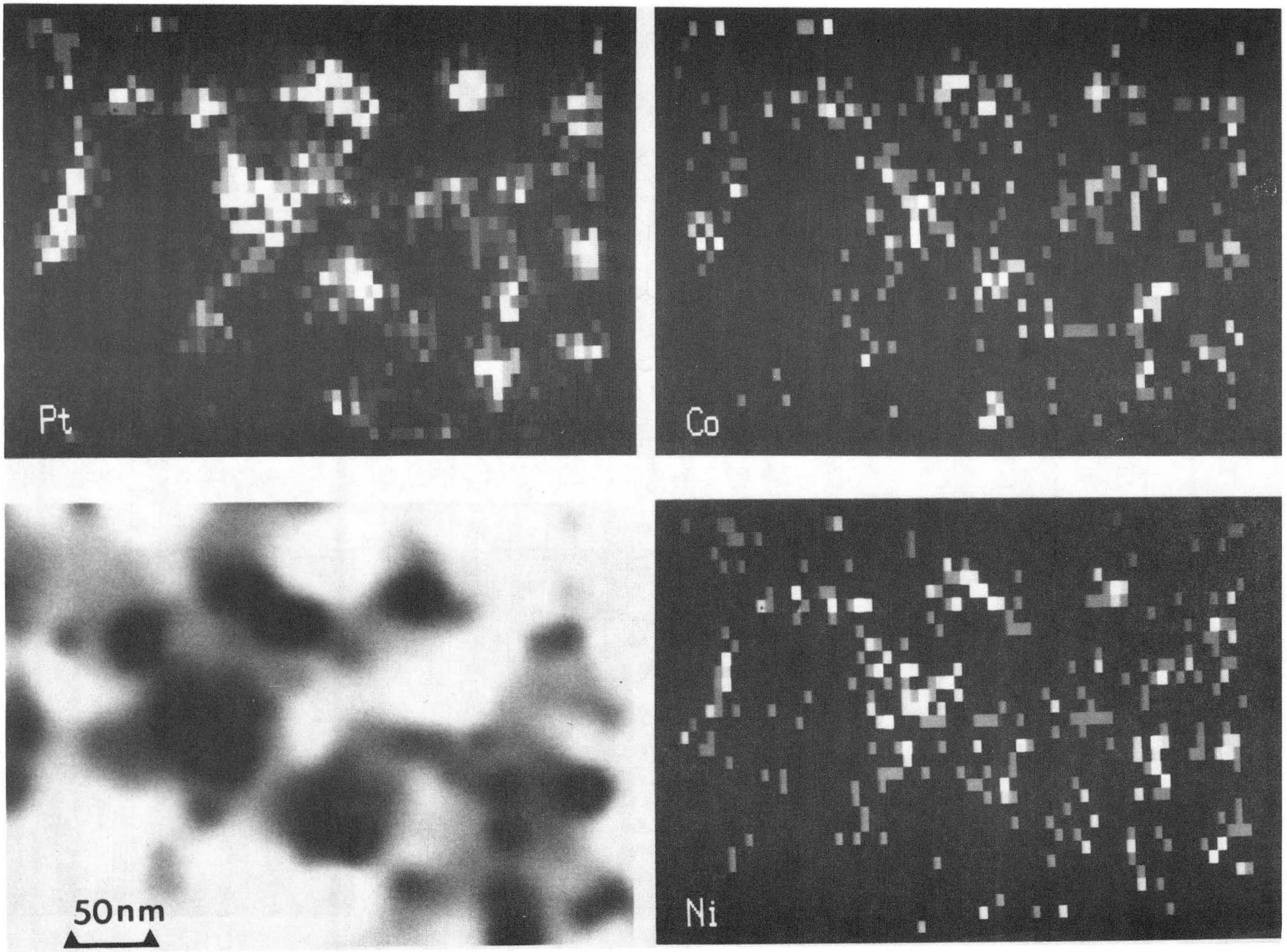


Fig. 9

XBB 871-1

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720