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ABSTRACT

Using the high resolution transmission electron microscopy techniques of weak-multibeam dark-field and direct lattice imaging, platinum particles ranging in size from 0.8nm to 50nm were imaged and their surface structure characterized. The platinum crystallites were evaluated for specific catalytic activity with respect to crystallite size. It was found that the rate of electrochemical oxygen reduction decreased for catalysts having a particle size of less than 3.5nm. We suggest that the dominating (111) surfaces and rough (110) regions on these small particles are less active than (100) and (100) vicinal planes.

## 1. INTRODUCTION

The characterization of the structure of small, metallic, and crystalline particles contained in real catalysts has been very accurately achieved through the use of transmission electron microscopy (TEM) techniques [1-3]. With the development of electron microscopes having high resolution capabilities, the direct detailed investigation of microstructures of materials is possible, in particular the examination of the surfaces of very small particles contained in catalysts. These small crystallites are necessary in catalyst systems where a large surface area often increases the reaction rate of the catalyst. It becomes important to determine the particle shape since the specific catalytic activity may be expected to be dependent upon which crystal planes form the surface [4,5]. In particular, since the number and arrangement of the atoms at the surface of a metal crystallite are known to theoretically determine the equilibrium shape [6], then the direct observation of these surfaces would provide information that would allow correlation between catalytic activity and surface sites. To obtain this objective, the TEM technique of weak-beam dark-field can be utilized to determine particle shape in three-dimensions. Further, high resolution TEM observations can provide direct imaging of surface planes and atoms.

In earlier studies using high resolution dark-field microscopy, Yacamán and Ocaña [7] determined the shape of particles using a weak-multibeam method. Their calculations predicted Pendellösung fringes for crystallites as small as 2.5nm. This theory was applied to the small Pt particles, averaging 14nm in diameter, observed in a graphite supported catalyst [8] where the cubo-octahedral shape was verified. Other investigators have also confirmed particle

shapes using this weak-beam dark-field method [9]. The direct imaging of catalyst particle lattice structures has only recently been obtained [10-12]. The use of higher voltage TEMs has allowed further observations of lattice images in particles as demonstrated by the structural images of the Pt-C catalysts [13,14], of single crystalline and twinned Pt catalyst particles on alumina [15], of multiply-twinned particles (MTPs) of epitaxially grown Au and Ag [16] and of MTPs of epitaxially grown Ni-Cr fine particles [17]. In other large particle (diameter >15nm) high resolution imaging, (111) surface reconstructions of Au, Ag, and Pb surfaces were uniquely analyzed for monatomic structural information [18]. Most recently, excellent high resolution images from 2.0 to 4.0nm Au particles were obtained [19], and their growth patterns were dynamically followed.

The present TEM study uses weak-beam dark-field and high resolution TEM techniques to characterize an annealed catalyst consisting of platinum particles (10 to 50nm in diameter) supported on amorphous carbon black. This information is then helpful in interpreting weak-beam and high resolution data from smaller particles of the same catalyst. The microstructure characterization of the Pt particles of various sizes is then correlated with specific activity data from this catalyst.

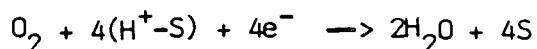
## 2. PLATINUM/CARBON ELECTROCATALYST

The platinum crystallite/amorphous carbon catalyst system is of interest in the development of more efficient fuel cells. Specifically, the reduction of oxygen by the platinum is affected by the change in size and/or shape of these crystallites. An excellent overview on the electrocatalysis of fuel cell reactions was recently written by Appleby [20] to which the interested reader is referred for more background.

In order to prepare standard specimens of commercial electrocatalyst for use in fuel cells, solutions containing a platinum sulfite colloid were introduced to a carbon black support (Cabot, Vulcan XC72) [21]. The colloidal platinum particles adsorbed on the vulcan were then reduced in H<sub>2</sub> to form metallic clusters having a size distribution of 0.8 to 4.0nm. Larger crystallites of this catalyst were formed by heating the standard specimens in a high purity He atmosphere for two hours at progressively higher temperatures, e.g., a 900°C anneal produced Pt particles with sizes from 2.0 to 10nm and at 1200°C the Pt crystallites ranged from 10 to 50nm in diameter.

The catalytic activity of platinum for oxygen reduction was obtained from these platinum catalysts having varying size distributions. In this study, the kinetics of oxygen reduction were measured in hot concentrated phosphoric acid (180°C, 98wt% H<sub>3</sub>PO<sub>4</sub>) using the procedures of Kunz and Gruver [22].

The stoichiometry of the reaction is



where H<sup>+</sup> - S is the solvated proton and S is the solvating species (in very concentrated acid the solvating species is not well-known). The conditions for kinetic measurement were chosen to correspond to those applicable to ambient pressure phosphoric acid fuel cell technology [23]. Following Kunz and Gruver [22], the measure of relative catalytic activity was determined by the current density per unit weight and/or per unit area of platinum at 0.9V versus a reversible hydrogen electrode in the same electrolyte. The specific platinum surface area was measured using the carbon monoxide chemisorption method [24]. Platinum crystallite size was measured using TEM as described in the following section.



The observed variation of catalytic activity with crystallite size is shown in Figure 1. The mass activity exhibited a maximum that occurred near a characteristic crystallite dimension (an equivalent diameter) of 3.5nm. The activity per unit area Pt on the surfaces of crystallites is approximately constant for "large" crystallites, then drops sharply as crystallite size decreases below 2nm. It is interesting to note that the activity appears to extrapolate to zero (!) at ca. 1nm, i.e. atomically dispersed Pt has near-zero activity.

### 3. EXPERIMENTAL PROCEDURES

Specimens were prepared for TEM examination by agitating a small amount of the crushed catalyst powder and some ethanol in an ultrasonic bath. The suspension was then dropped onto clean holey C grids. Stable specimens were also prepared by pressing the catalyst powder onto clean Cu grids; however, this method prevented tilting to high angles and also caused heating of the small metallic particles when using higher accelerating voltages. This second method of sample preparation was necessary, however, when determining an appropriate crystallite size. Fears that errors in size estimates would occur when samples were ultrasonically agitated were proven unfounded as average particle diameters were similar in samples prepared by both methods. Particle diameters were measured under bright field conditions.

Samples were examined by TEM using the JEOL 200CX at 200kV accelerating voltage and the JEOL Atomic Resolution Microscope (ARM) at 1000kV accelerating voltage. Particle shape was determined by examining the crystallites under weak-beam, dark-field conditions. For this technique, particles were tilted slightly off the zone axis and were illuminated using the (200) weakly dif-

fracting beam. If no diffracted beams were observed, as was the case for the smaller particles, then an area close to the (200) beam was chosen. This beam should lie just outside the first amorphous carbon ring. The specimen was canvassed in the dark-field mode to find the appropriately tilted small particle in a weak-beam condition. The weak-beam images of the particles at different orientations were compared to projected models of cubo-octahedra at these orientations.

The Pt particles were further characterized by high resolution TEM. To obtain lattice images, appropriately isolated particles were tilted toward the desired zone axis. Particles were first chosen from the characteristic shape outlines for  $\langle 110 \rangle$  and  $\langle 100 \rangle$  oriented particles corroborated during the dark-field work. It was necessary to choose a particle that was either close to the edge of the carbon black support or that was isolated on the holey carbon film so that scattering effects from the support or diffraction effects from other particles could be avoided.

#### 4. HIGH RESOLUTION TEM

##### 4.1 Crystallite Shape

Upon examining the Pt/C catalyst annealed at 1200°C in the weak-multibeam, dark-field condition, symmetric faceted particles were seen. Figure 2 shows three differently oriented particles imaged by this method. The Pendellösung fringes of the 18nm particles in this figure can be used to interpret the shape of the particle much as contour lines describe a topographic map. Sketches of the shape outlines for a cubo-octahedral crystallite for each of the 3 different orientations are shown for comparison with the TEM images.

The cubo-octahedral shape having hexagonal (111) surfaces shown in this figure is the theoretically predicted equilibrium shape [6] of large particles (>2,000,000 atoms) and is thus used in this study. Calculations were made [25] of the number of Pendellösung fringes allowed for the present diffraction conditions using a range of excitation errors. For 200kV accelerating voltage and the (200) weak diffracting beam, a maximum of 4 or 5 fringes was predicted for 18nm particles regardless of the specific bright-field or dark-field conditions if the tilt angle was not excessive. Since the weak-beam images of the Pt particles that were annealed at 1200°C approximately follow this predicted behavior, then the cubo-octahedron correctly defines the morphology of these crystallites.

The dark-field images of the Pt crystallites shown in Figure 2 are not perfect cubo-octahedral shapes, however, as certain surface planes appear to have grown larger in proportion to the rest of the crystal, or truncations of planes are observed. Also, the bright fringes of the image project a rather rough surface because of their wavy nature. Thus, it is clear that the surface planes of these particles are not atomically smooth and further high resolution imaging is necessary to define these surfaces.

Using the same techniques as for the larger crystallites, particles having diameters from 0.8 to 10nm were imaged in the dark-field condition with a weak (200) beam. The results are shown in Figure 3. Particles from specimens that were annealed at 900°C, Figure 3a, show regular 6-sided facets (as expected for the projection of the <110> or <112> orientations of the cubo-octahedron) in the weak-beam condition while exhibiting only a sphere-like image in bright-field, Figure 3b. This particle at 6.0nm diameter is also shown with

calculations made by Kilaas [25]. As particles decrease in size to less than 3.5nm, it becomes theoretically impossible to detect any contour lines in them and the image must be interpreted solely by its shape, as seen for the 2.5nm particle in Figure 3c. The square shape of this particle from the standard unannealed Pt/C catalyst sample suggests the  $\langle 100 \rangle$  cubo-octahedral orientation having triangular (111) faces rather than the hexagonal (111) faces as drawn schematically for the 1200°C annealed material of Figure 2. The high resolution bright-field image of the unannealed catalyst particle shows faint {111} lattice fringes in Figure 3d. Thus, observations of the Pt particles in this catalyst based solely upon the weak-beam dark-field images suggest that the cubo-octahedron is the general shape even for crystallite clusters in the standard material (the smallest crystallites observed).

#### 4.2. Surface Atomic Structure

Using the ARM which has a large angle ( $\pm 40^\circ$ ) biaxial goniometer stage [26], it was possible to orient some Pt particles that were annealed at 1200°C to give direct lattice information. Figure 4 shows one such particle isolated on the holey C support grid tilted to the  $\langle 100 \rangle$  zone axis. Although the basic shape is that of a square truncated at the edges typical for a cubo-octahedron in this orientation, it is apparent that the faces of the crystal are quite rough. The (100) surfaces at the corners of this square zig-zag to create steps; e.g., the enlarged inset of the particle in Figure 4b shows the {100} planes to be no wider than 9 atoms on the surface before a step is encountered. The (110) surfaces making up the sides of this square shape, on the other hand, are quite large and regular, consisting of 1 x 1 (100) planes.

When these particles are oriented so that the (111) surfaces are visible on the edges, then "rounded" (111) faces are observed. Figure 5 shows one edge of another particle of this same catalyst oriented toward the  $\{110\}$  zone axis. It appears that adatoms have attached themselves to these (111) planes with the result that a curvature rounds out the sides of the particle to form an approximate (110) surface. From the atomic observations of these two large catalyst particles, it appears that the rough surfaces of the cubo-octahedral crystals provide a variety of site geometries for catalysis.

Platinum particles from the catalyst specimens annealed at  $900^{\circ}\text{C}$  were also imaged under high resolution conditions using the 200CX EM. The results are shown in Figure 6 where the  $\{111\}$  lattice planes are visible in a small crystallite. The faces of the particles having a (111) surface are quite large and distinct compared to the other faces. These other faces tend to round themselves out so that the particles appear as flattened spheres. These incomplete cubo-octahedral surface structures are approximately  $1 \times 1$  (110) surfaces. This same particle shape was also observed for the even smaller crystallites contained in the standard non-annealed material.

## 5. DISCUSSION

The catalytic activity for electrochemical oxygen reduction of small Pt crystallites dispersed on carbon black was observed to decrease with crystallite size when the size was below ca. 3.5nm, with a projected near-zero activity for a monatomically dispersed state. This type of trend in activity with size is not unique in catalysis and has been observed previously with other Pt catalysts used in hydrocarbon oxidation reactions [27], particularly in reac-

tions with excess oxygen stoichiometry. As indicated by Bond [27], it has been suggested by numerous workers that this trend is related to the (unsubstantiated) property that oxygen dissolves more easily into small particles, essentially converting the crystallite into a metal oxide. We have tried to substantiate this property by studying the oxidation of these catalysts with x-ray photoelectron spectroscopy, but have not found evidence for preferential oxide formation in this size range. As a result of our TEM analysis of surface structure variation with crystallite size, we suggest that this general trend is related to the variation in adsorbed states of oxygen on various site geometries.

The surface structure of Pt particles in these catalysts was imaged by TEM high resolution techniques and a difference between particles less than 3.5nm and those greater than this size was observed. The (111) face is a smaller fraction of the surfaces of large particles but dominates all surfaces in the smaller particles. The large particles have rough surfaces with no two faces forming a uniform edge of the crystallite. On the other hand, the small particles show some fairly smooth (111) facets but the other regions are rounded by formation of (110) planes. Thus, it appears that there are more active sites for oxygen reactions at the surfaces of the larger particles for a given characteristic size. Also, the (111) surfaces and rough (110) surfaces may be considered to bind oxygen in a less active form leading to lower activity in smaller crystallites.

## ACKNOWLEDGEMENTS

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## REFERENCES

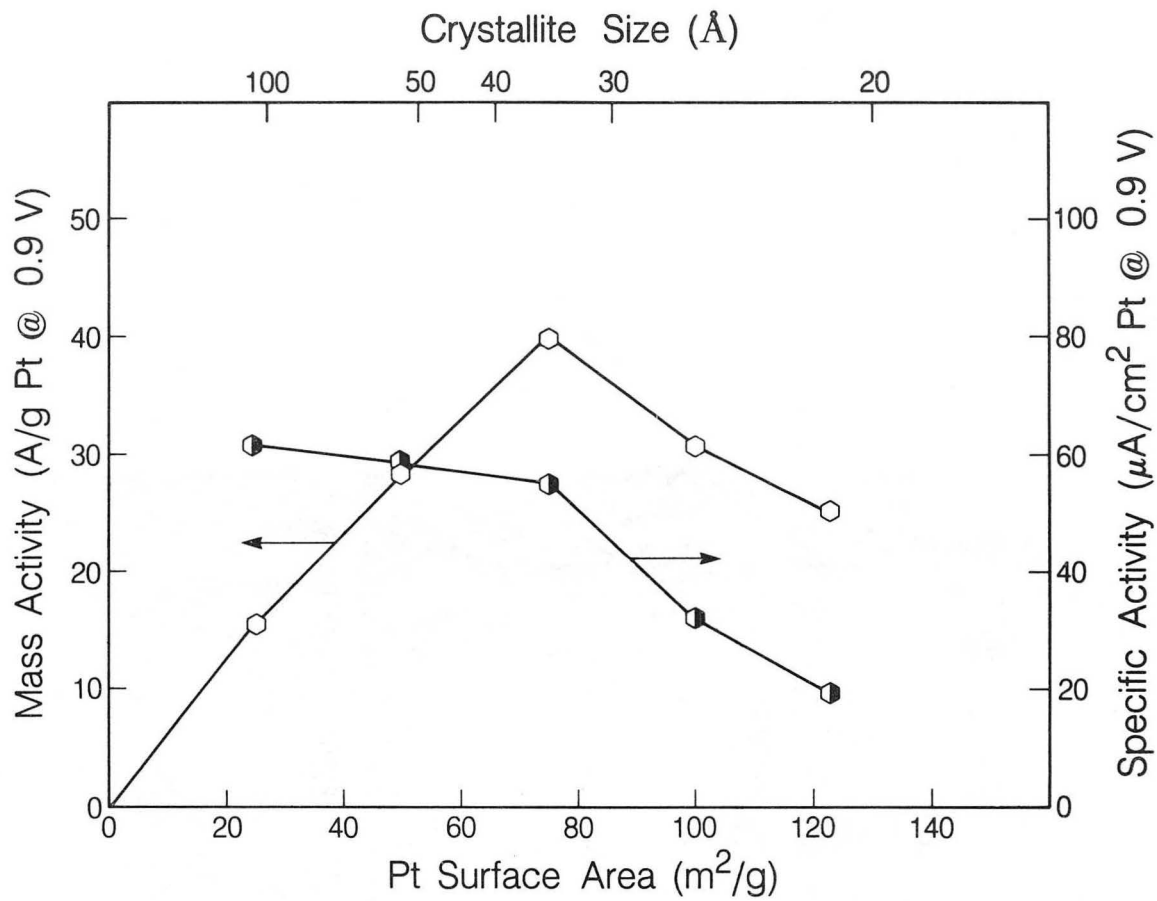
- [1] Howie, A., Marks, L. D. and Pennycook, S. J., *Ultramicro.* 8 (1982) 163.
- [2] Schmidt, L. D., Wang, T. and Vacquez, A., *Ultramicro.* 8 (1982) 175.
- [3] Yacamán, M. J., *Appl. Catal.* 13 (1984) 1.
- [4] Van Hardeveld, R. and Hartog, F., *Surf. Sci.* 15 (1969) 189.
- [5] Burton, J. J., *Cat. Rev.-Sci. Eng.* 9(2) (1974) 209.
- [6] Wang, S.-W., Falicov, L. M. and Searcy, A. W., *Surf. Sci.* 143 (1984) 609.
- [7] Yacamán, M. J. and Ocaña Z., T., *phys. stat. sol.(a)* 42 (1977) 571.
- [8] Yacamán, M. J. and Dominguez E., J. M., *J. Catal.* 64 (1980) 213.
- [9] Avalos-Borja, M. and Heinemann, K., in: *Proc. 39th Annual EMSA Meeting, Atlanta, GA, 1981, Ed. G.W. Bailey (Claitor's: Baton Rouge, LA, 1981) p. 222.*
- [10] Jefferson, D. A., Millward, G. R. and Thomas, J. M., *Acta Crystallogr.* A32 (1976) 823.
- [11] Cowley, J. M., Wheatley, J. C. and Kehl, W. L., *J. Catal.* 56 (1979) 185.
- [12] Sanders, J. V., *Chemica Scripta* 14 (1979) 141.
- [13] Jalan, V.M. and Stonehard, P., in: *Proc. ECS Meeting., Los Angeles, CA 1979.*
- [14] Smith, D. J., Fisher, R. M. and Freeman, L. A., *J. Catal.* 81 (1983) 107.
- [15] Smith, D.J., White, D., Baird, T. and Fryer, J.R., *J. Catal.* 81 (1983) 107; White, D., Baird, T., Fryer, J.R., Freeman, L.A., Smith, D.J. and Day, M., *J. Catal.* 81 (1983) 119.
- [16] See, e.g., Smith, D.J. and Marks, L.D., *Ultramicro* 16 (1985) 101.
- [17] Ishimasa, T. and Fukana, Y., *Surf. Sci.* 156 (1985) 241.
- [18] Takayanagi, K., *Ultramicro.* 8 (1982) 145.
- [19] Wallenberg, L. R., Bovin, J. O. and Schmid, G., *Surf. Sci.* 156 (1985) 256.



- [20] Appleby, A. J., Energy 11 (1986).
- [21] Petrow, H. G. and Allen, R. J., U. S. Patent 3,992,512, Nov. 16, 1976.
- [22] Kunz, H. R. and Gruver, G. A., J. Electrochem. Soc. 122 (1975) 1279.
- [23] "Advanced On-Site Power Plant Development Technology Program", DOE/NASA 0289-1, 1984.
- [24] Bett, J., Kinoshita, K., Rontsis, K. and Stonehart, P., J. Catal. 29 (1973) 160.
- [25] Kilaas, R. NCEM, unpublished data, 1985.
- [26] Gronsky, R., Mat. Res. Soc. Symp. Proc. Vol. 31 (1984) p. 1.
- [27] Bond, G. E., Surf. Sci. 156 (1985) 966.

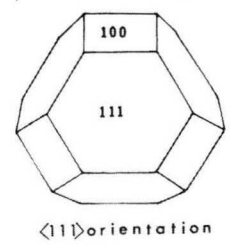
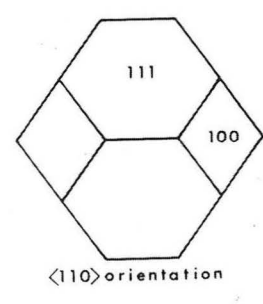
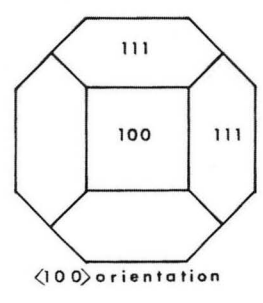
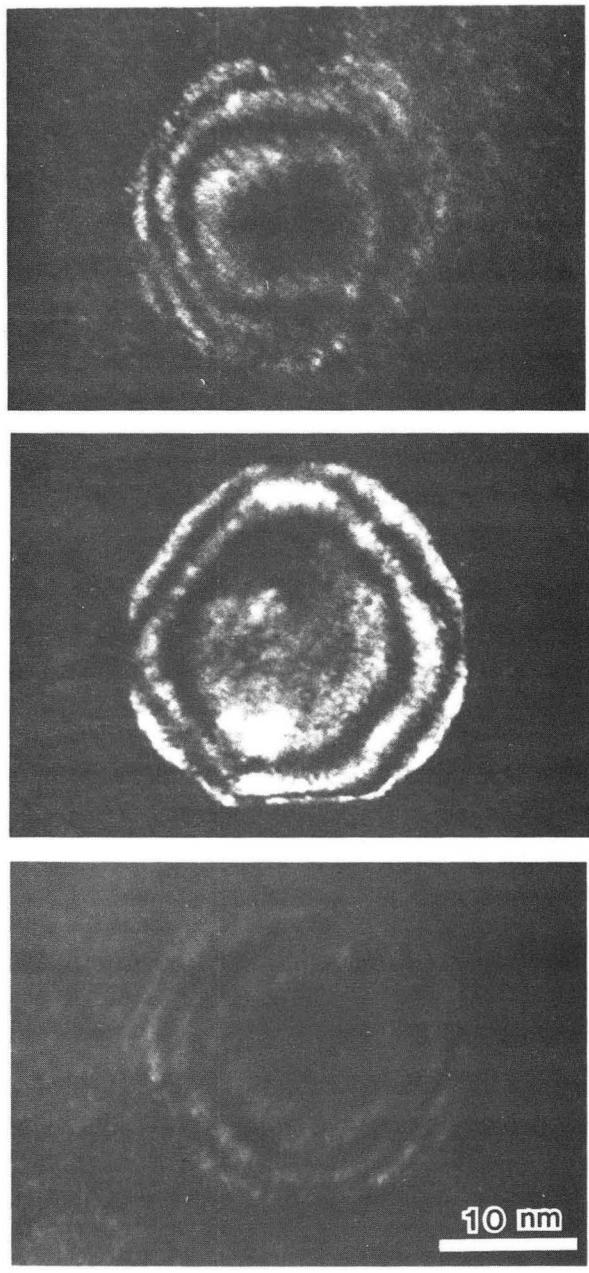
## FIGURE CAPTIONS

- Fig. 1 Graph showing variation of catalytic activity with platinum crystallite size.
- Fig. 2 Weak-multibeam dark-field images of platinum single crystal particles that were annealed at 1200°C oriented approximately toward  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  and the sketched shape outlines of similarly oriented cubo-octahedron.
- Fig. 3 Weak-beam dark-field (a) and bright field (b) images of the Pt/C catalyst annealed at 900°C. High resolution dark-field (c) and bright field (d) micrographs of the standard, non-annealed Pt/C catalyst.
- Fig. 4 (a) High-resolution (ARM) micrograph of a single Pt particle from the 1200 C annealed catalyst oriented along  $\langle 100 \rangle$  showing atomic surface microstructure. (b) Enlargement giving details of the  $(110)$  and the  $(100)$  faces. (c) Sketch of particle.
- Fig. 5 High resolution (ARM) micrograph of single crystalline Pt particle from the 1200°C annealed catalyst oriented along  $\langle 110 \rangle$  showing  $(111)$  and  $(110)$  faces.
- Fig. 6 High resolution (200CX EM) micrograph of a single Pt crystallite of the catalyst annealed at 900°C showing  $\{111\}$  lattice planes and rounded incomplete cubo-octahedral  $(110)$  surface structure.



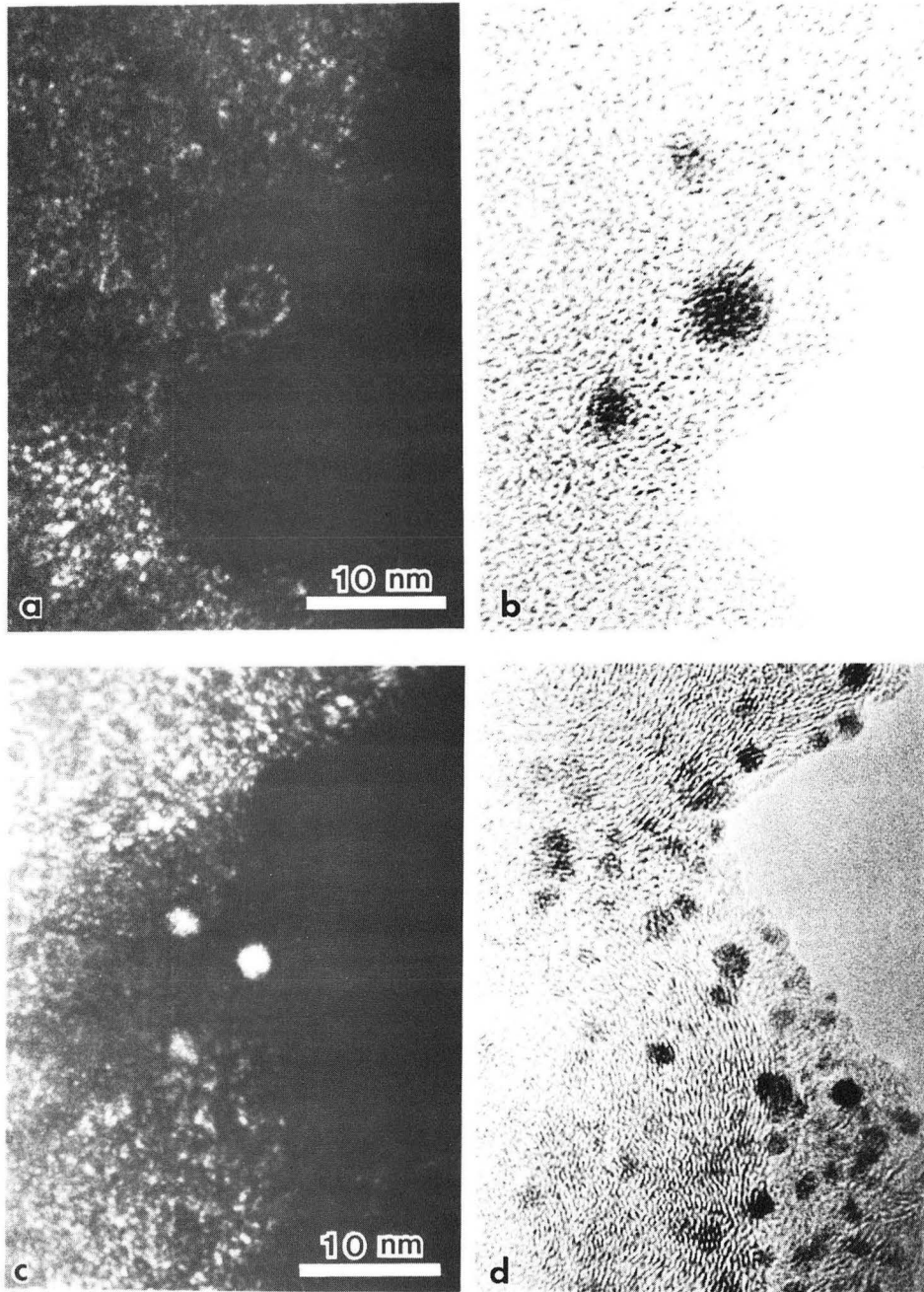
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Fig. 1



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Fig. 2



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Fig. 3

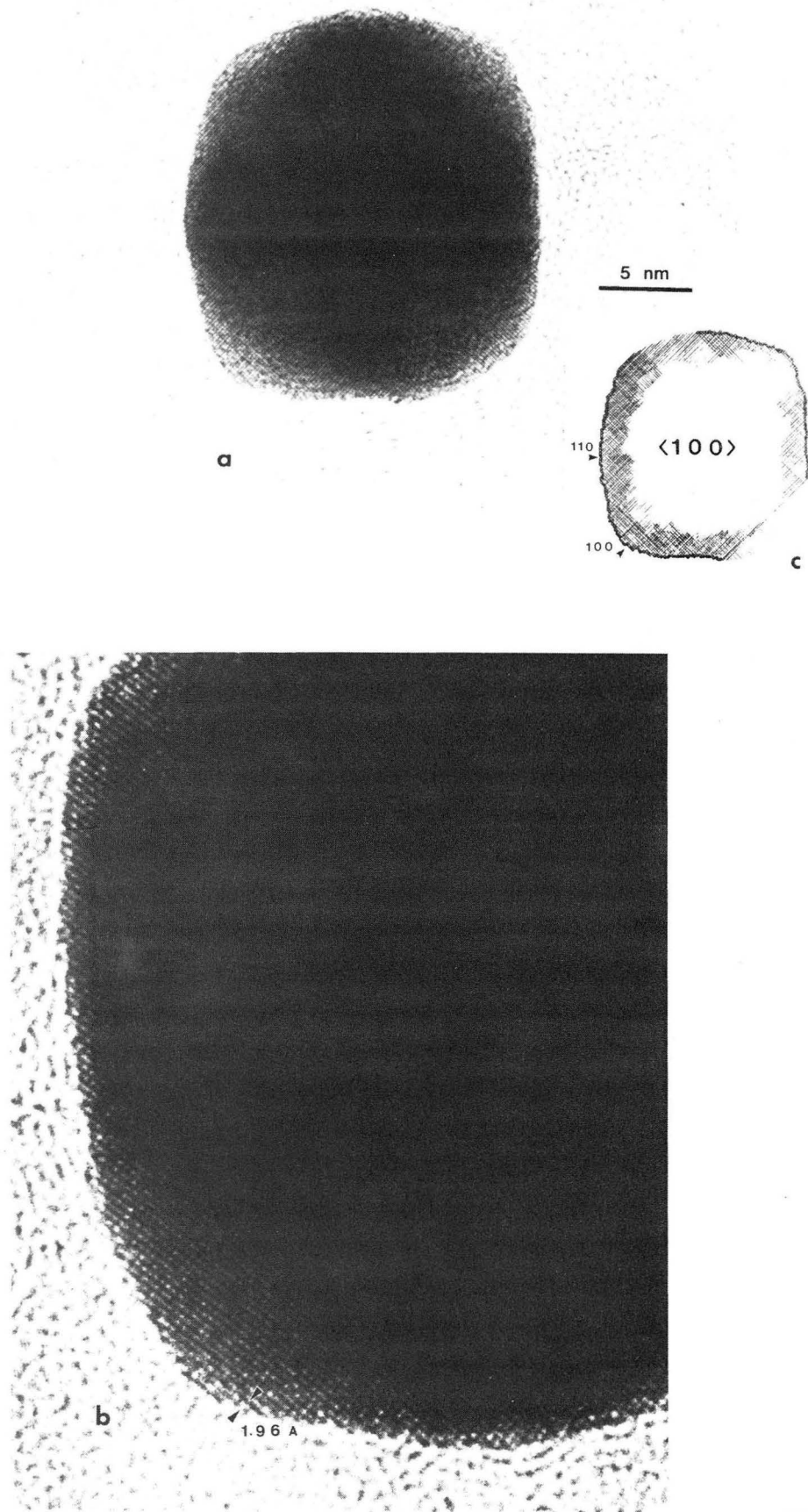


Fig. 4

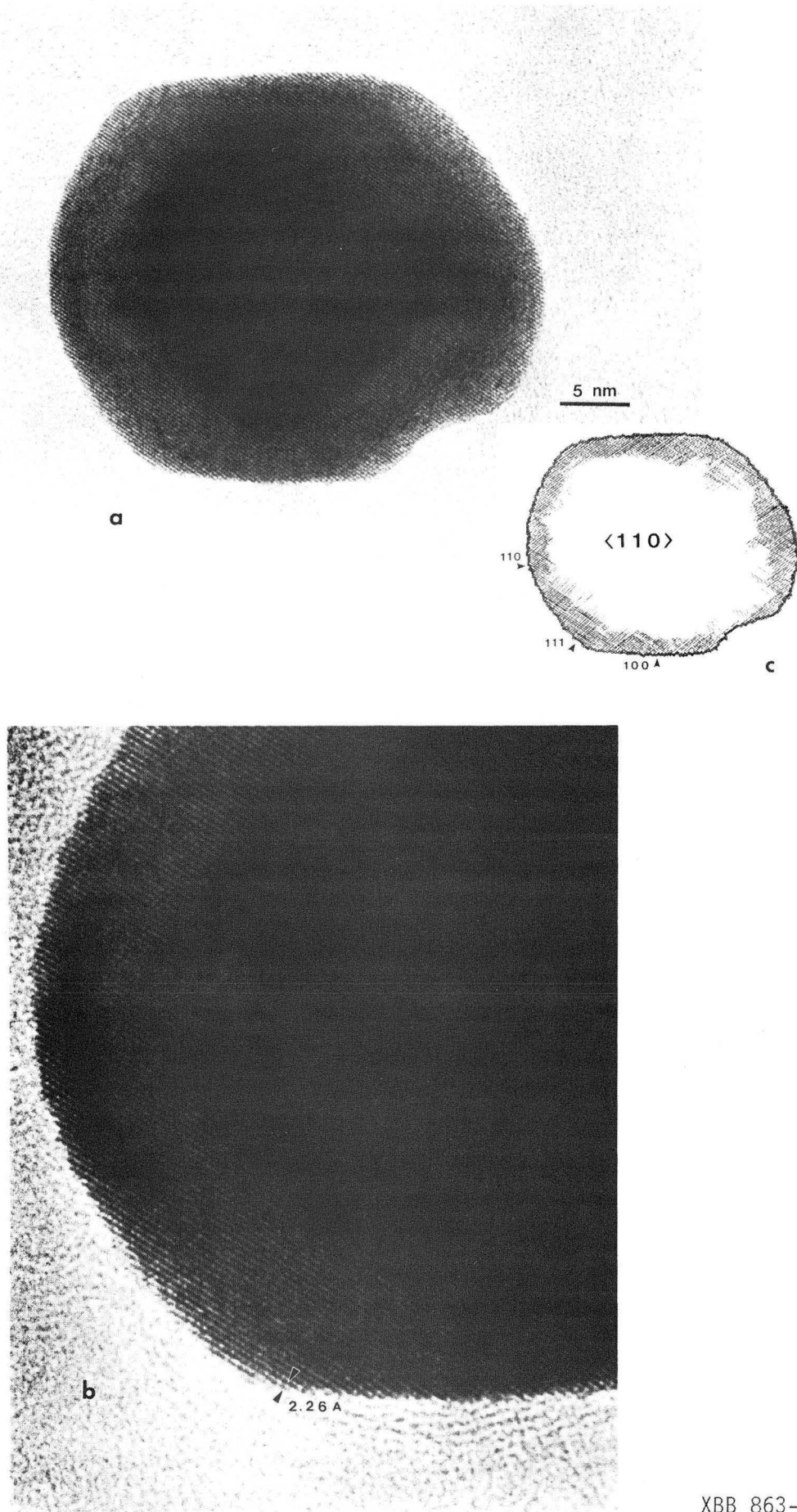
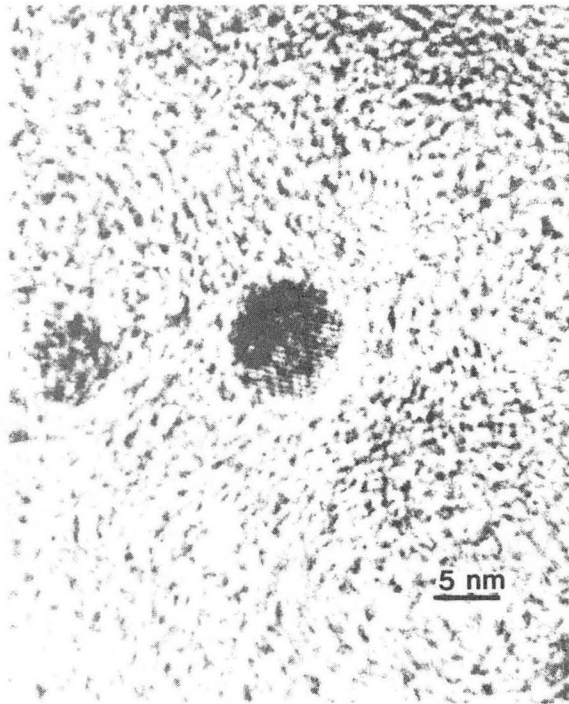


Fig. 5



XBB 863-1869

Fig. 6



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