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PLASTIC DEFORMATION OF CUPROUS OXIDE

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ABSTRACT

Slip line and transmission electron microscopy observations on the plastic deformation of cuprous oxide were made on large grained polycrystalline specimens. The specimens were prepared by the complete oxidation of OFHC copper strips in air followed by a high temperature anneal. Plastic deformation in this material was found to take place by motion of a<100> dislocations on {100} glide planes. Some dislocation segments of a<110> Burgers vector were present but were probably formed by recombination reactions between a<100> dislocations. The unusual structure of Cu_2O, which can be described as two interpenetrating and identical frameworks of copper and oxygen which are not cross-connected by any primary copper-oxygen bonds, did not result in any unusual behavior of dislocations. The effect of temperature on plasticity was explained in the same way as for other materials of less complex structure such as MgO.

I. INTRODUCTION

Cuprous oxide Cu_2O has an unusual crystal structure.[1] It is reproduced in Fig. 1. The oxygen ions are ordered on a body centered cubic lattice while the copper ions are ordered on a face centered cubic lattice. This structure consists of two completely interpenetrating and identical frameworks (1 and 2) which are not cross-connected by any primary Cu-O bonds.

Previous experimental work[2] has shown that this material is highly ductile at high temperature. The present work was undertaken to identify the slip systems that operate and to study the behavior of dislocations in this unusual structure.

II. EXPERIMENTAL PROCEDURES

A. Specimen Preparation

Test specimens of cuprous oxide containing big crystals were prepared according to a method similar to the one indicated by Toth et. al[3]: copper plates were completely oxidized in air and then annealed at a higher temperature.

Plates of OFHC copper, having dimensions of approximately 0.2 x 2 x 2.5 cm were supported on platinum hooks which were inserted through a small hole drilled at one end. They were suspended in a vertical furnace in air at a temperature between 1020 and 1030°C for about 160 hours. The temperature was measured by a thermocouple located very close to the specimen surface. After the oxidation was complete, the temperature of the furnace was raised to 1110°C and the specimens were annealed at this temperature for 150 hours. The specimens were cooled by quick withdrawal from the furnace. During this operation a thin layer of cupric oxide was formed at the surface of the plates, but it was easily removed by mechanical polishing. The grains were revealed by etching in 50% nitric acid. Most specimens contained crystals of surface area varying between 10^{-2} to about 10^{-1} cm^2 (Fig. 2a). A few contained much larger crystals (Fig. 2b). The thickness of all the crystals were approximately the same as the original thickness of the copper. In the center of the specimens there were many small holes which were created during the diffusion of the last remaining copper.

Specimens of about 0.2 x 1 x 1.5 cm were cut from the plates with a diamond saw. From the plates containing the largest grains, a few single crystals were obtained, they were prisms with rectangular sections

and of average dimensions 0.2 x 0.4 x 0.5 cm.

Before mechanical tests, the specimens were chemically polished at 20-25°C in a mixture of 70% orthophosphoric acid, 30% nitric acid. This produced a smooth surface on which to observe slip lines.

B. Deformation Tests

Compression tests were performed with an Instron machine at temperatures between room temperature and 600°C at a cross-head speed of 5×10^{-3} in. per minute. The compressed faces of the specimens were those having the largest and smallest dimensions. During the deformation the specimens were heated by a small resistance furnace which fitted around the testing frame. A jet of argon gas was directed into the tube of the furnace during heating, deformation and cooling to avoid oxidation to cupric oxide.

C. Thin Foil Preparation

Compressed specimens having dimensions 0.2 x 1 x 1.5 cm were cut with a diamond saw into thin plates of about 0.08 cm thickness parallel to the face of the largest dimensions. (The slices which include the central part, which contained many holes, were discarded.) These plates were further thinned to 0.025 cm by mechanical polishing prior to chemical thinning for transmission electron microscopy.

A mixture of 90% orthophosphoric acid and 10% nitric acid was used for the chemical thinning. For the final chemical thinning, the specimen was translated above a small jet of acid producing a circular thinned area of 0.2 cm diameter[4] (Fig. 3). The progress of the thinning was followed by observing the color of the specimen. Thick cuprous oxide is red in transmitted light, but becomes yellow as its thickness

decreases. When the thinned area had become pale yellow, the specimen was removed from above the jet and was dipped in a mxiture of 80% orthophosphoric acid, 10% nitric acid at 0°C until a small hole appeared. The specimen was then washed in water and alcohol. Usually several areas around the hole were thin enough for electron transmission. The most suitable areas could be located by observation of the optical interference fringes due to reflection from top and bottom surfaces (Fig. 4).

Uniformly thin parts were broken off with a needle, the small pieces being allowed to fall into an electron microscope holder. Observations were made using a Siemens Elmiskop I electron microscope operating at 100 kv. Surface damage caused by the mechanical polishing was removed during the chemical polishing since no defects were observed in an undeformed specimen.

III. RESULTS

A. Mechanical Tests and Optical Microsocpe Observations

Figure 5 shows typical stress-strain curves of single crystals and polycrystalline specimens of cuprous oxide [the parts of the curves corresponding to the elastic deformation have not been included because the supports of the specimens were slightly deformed during the compression, causing the initial part of the stress-strain curve to be very inaccurate]. Figure 6 shows the effect of temperature on the yield stress.

No plastic deformation was detected at room temperature; all specimens broke without yielding and no slip lines were observed on the recovered small pieces. Between 200 and 350°C, there was a small plasticity; single crystals and polycrystalline specimens could be deformed by about 1% but cracks were created. Slip markings and cracks are shown in Figs. 7, 8 and 9. At 200°C the slip lines were straight and occurred mainly as wide bands (Fig. 7); at 300°C some lines began to be wavy and strain was distributed more homogeneously (Fig. 8 and 9).

At 400 and 500°C the ductility of cuprous oxide increases significantly; single crystals and polycrystalline specimens can be deformed up to 4% without formation of cracks. The slip lines are wavy and uniformly distributed in all the grains (Fig. 10).

At 600°C cuprous oxide is highly ductile. Polycrystalline specimens were deformed by 12% without breaking. Slip traces could not be observed at this temperature because of the formation of a thin layer of cupric oxide on the surface.

B. Determination of Glide Planes

The operative glide plane was {100}. Slip traces were observed on

two perpendicular surfaces of single crystals deformed at 350 and 400°C.

Figure 11 shows the slip lines that appeared on one of these specimens. The plane of the stereographic projection (Fig. 12) has been taken parallel to the face A. On this projection plane, B and the points T_A and T_B, which represent the directions of the traces of one glide plane on the two surfaces, have been plotted; the pole of the meridian passing through the points T_A and T_B which is the projection of the glide plane is (010). The other glide planes giving the traces T'_A, T'_B, T''_A and T''_B are also plotted; their poles are (001) and $(\bar{1}00)$.

Because the {100} planes intersect the most general plane along three lines, it is expected that on surfaces of deformed crystals, slip lines should appear in at most three different directions. In no case were more than three observed.

C. Transmission Electron Microscope Observations

It was impossible to prepare thin foils from specimens deformed under 400°C; there were numerous cracks and the specimens always broke into small and useless parts.

1. Specimens deformed at 400 and 500°C:

After deformation these specimens contained dislocations as is shown in Fig. 13 and 14. Diffraction contrast experiments showed that most of the dislocations had Burgers vectors of the type <100> but a few with <110> Burgers vectors were present.

This result is illustrated by Fig. 15 which shows an area in a foil with {110} orientation under four different diffraction conditions; many dislocations like B, C, D, E, G, H having Burgers vectors <100> are out of contrast under [002] or $[2\bar{2}0]$ reflections, while a few like A, F

are out of contrast for $[1\bar{1}1]$ or $[\bar{1}11]$ reflections and have <110> Burgers vectors. At nodes between dislocations ABC and DEF, these reactions appeared to have occurred:

$$[010] + [00\bar{1}] \rightarrow [01\bar{1}] \quad (B + C \rightarrow A)$$

and

$$[100] + [00\bar{1}] \rightarrow [10\bar{1}] \quad (E + D \rightarrow F)$$

Loops (L) can be observed on Figs. 14 and 15; they probably are formed as in MgO by the break up of dipoles[4,5,6]. The general arrangement of dislocations was similar to that observed in MgO after deformations above 1500°C.

2. Specimens deformed at 600°C:

In specimens deformed slightly at 600°C, dislocations were present only as two dimensional arrays forming the boundaries of large subgrains. The subgrain size decreased with increasing deformation and the density of dislocations in the sharp two dimensional arrays increased (Fig. 16). Formation of subgrains in specimens deformed at 600°C had been detected previously by x-ray diffraction[2].

The subgrain boundary networks consisted of <100> and <110> dislocation segments as can be seen in Fig. 17. Here segments of [011] or $[1\bar{1}0]$ Burgers vector are out of contrast.

IV. DISCUSSION

A. Cleavage Planes

The cleavage planes in cuprous oxide are {111}[2] even though the {110} planes are the most densely packed with atoms and, therefore, the most widely spaced. However, an examination of the structure suggests an explanation. None of the low index planes consist of layers of atoms for which electrical neutrality exists within the layer. Therefore, to produce uncharged surfaces during cleavage, the atoms of one of the copper layers or one of the oxygen layers must be divided between the two surfaces being created. Figure 18 shows that the arrangement of oxygen atoms between adjacent copper layers for the {111} planes is such that half the oxygens are very close to one of the copper layers, while the other half are very close to the other copper layer. This arrangement provides a natural separation of the double oxygen layer, one half to each cleavage surface. The spacing of adjacent copper layers is also greatest for {111}.

B. Glide Elements

1. Slip Direction

The electron diffraction contrast experiments showed that most dislocations in deformed cuprous oxide had <100> type Burgers vectors while a few were <110> type. An examination of the crystallographic structure (Fig. 1) shows that the shortest distance for structural identity is a <100>.

As Nabarro first pointed out[7], an a[110] dislocation can dissociate according to the reaction:

$$a[110] \rightarrow a[100] \rightarrow a[010]$$

involving no change of elastic energy so that a stress acting more strongly on one component would move this component independently of the other. This appears to happen in Cu_2O. However, the existence of many <110> segments in the dislocation networks suggests that energy is released by the recombination of two <100> dislocations. It seems likely that dislocation core energy may be relatively important in this structure.

2. Slip planes.

The active slip planes were {100} although {110} might be expected a priori, since they are the most densely packed with atoms and contain the slip direction <100>. However, referring to Fig. 1, it can be seen that a translation <001> {110} in this structure involves the close approach of a copper ion with two others while a translation <001> {100} involves only the juxtaposition of two copper ions.

Consequently, gliding according to <100> {100} is not surprising. An [010] (001) edge dislocation is illustrated in Fig. 19; when such a dislocation glides, the copper ions of the layer nearest the dislocation must be divided between the two adjoining oxygen layers in order to maintain neutrality.

It might also have been expected that {111} planes would be the glide planes, since, as pointed out previously, the bonding between {111} layers is weakest. However, the main glide direction, <100>, does not lie in these planes and, if <110> glide did occur in (111), it can be seen by considering the intermediate position that close approach of two nearest neighbor oxygen ions is required.

Effects attributed to stacking faults were not observed in the

electron micrographs. It is probable that no low energy stacking faults exist for Cu_2O.

C. Effect of Temperature upon the Plastic Deformation of Cuprous Oxide

It has been shown that polycrystalline cuprous oxide has no ductility up to 300-350°C; between 400 and 500°C it is slightly ductile and at 600°C its plasticity becomes important.

In order for a grain in a polycrystalline specimen to be able to deform to an arbitrary shape, Taylor has pointed out[8] that it must have five independant slip systems. Groves and Kelly[9] have shown that the elements <010> {100} give only three independant systems. For example, a change in length along <100> is impossible. Consequently, an explanation is needed for the extensive ductility of polycrystalline specimens at high temperature.

At temperatures below 400°C, the slip lines are straight and at 200°C are confined to sharply defined bands, only the glide elements <010> {100} appear to operate. Crystals cannot undergo significant plastic deformation because local stress concentrations develop where slip lines intersect and where they meet grain boundaries. Thus, high local stresses result in crack formation.

Cross slip from one {100} plane to another {100} plane apparently is aided by thermal activation because at 400 and 500°C the slip lines become wavy. The slightly greater ductility in the 400 to 500°C temperature range may be due to the somewhat more uniform distribution of shear strain that is the result of more frequent cross slips and the concomitant reduction in the severity of stress concentrations. Another possibility is that other slip systems start to operate. The most likely systems

are of the type $\langle\bar{1}01\rangle$ {111}; the cleavage along {111} suggests that bonding between {111} layers is relatively weak; also dislocations with <110> Burgers vector were present. $\langle\bar{1}01\rangle$ {111} glide at low temperature is probably associated with an extremely high Peirls Nabarro stress, but like $\langle 1\bar{1}0\rangle$ {001} slip in magnesium oxide, the critical shear stress for dislocation motion may fall rapidly with temperature. Thus, above 400°C, the stress for {110} dislocation glide on {111} planes may become less than the critical stress to nucleate cleavage cracks; permitting local stress concentrations to be relaxed.

At 600°C, which represents 0.58Tm, where Tm is the absolute melting temperature of cuprous oxide, self diffusion certainly becomes important. Consequently, dislocation climb is almost surely involved in the plastic deformation. The dislocations we observed after deformation at this temperature were always in perfect two dimensional arrays, the formation of which requires extensive climb. Climb provides an additional mechanism for continuous relaxation of local stress concentrations and a mechanism other than $\langle\bar{1}01\rangle$ {111} slip for dimensional changes along <100>. Therefore, cracks do not nucleate and cuprous oxide becomes highly ductile.

V. CONCLUSION

In this study, the glide elements of cuprous oxide have been determined as ⟨100⟩ {001}. These glide elements and the {111} cleavage were explained on the basis of the crystal structure. No imperfect dislocations or stacking faults were observed.

In spite of the unusual structure of this oxide, the characteristic aspects of its deformation, i.e., brittleness at low temperature, plasticity above 0.5Tm and the most likely explanations for this behavior are very similar to those of ionic crystals like Na Cl[10] and MgO[11].

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1 Crystallographic structure of Cu_2O: light balls represent oxygen ions, black balls represent copper ions.

Fig. 2 Examples of Cu_2O plates from which compression test specimens were cut.

Fig. 3 Chemical polishing apparatus.

Fig. 4 Optical micrograph of a thin area suitable for transmission electron microscopy.

Fig. 5 Typical stress-strain curves of single crystals and polycrystalline specimens of Cu_2O.

Fig. 6 Effect of temperature on the yield stress of Cu_2O.

Fig. 7 Slip markings in a polycrystalline specimen of Cu_2O deformed 0.9% at 200°C.

Fig. 8 Slip in a polycrystalline specimen of Cu_2O deformed 1% at 300°C.

Fig. 9 Slip markings in a large crystal of polycrystalline specimen of Cu_2O deformed 1% at 300°C.

Fig. 10 Wavy slip in a polycrystalline specimen of Cu_2O deformed 1.2% at 400°C.

Fig. 11 Slip lines observed on two perpendicular faces, A and B, of a single crystal deformed 1.2% at 350°C.

Fig. 12 Stereographic projection of face A (Fig. 11) on which projections of face B, of traces of slip lines T_A, T_B and of the corresponding glide planes have been plotted.

Fig. 13 Dislocations in Cu_2O deformed 1% at 400°C.

Fig. 14 Dislocations in Cu_2O deformed 3.5% at 500°C (the foil has an {110} orientation).

Fig. 15 Dislocations in a {110} foil of Cu_2O under four different two beam diffraction contrast conditions. Arrows show operating reflection. Dislocations B, C, D, E, G, and H are of type <100>, while A and F are <110> (specimen was deformed at 500°C).

Fig. 16 Subgrain boundary in a {110} foil of a specimen deformed 12% at 600°C.

Fig. 17 Two dimensional network of dislocations in cuprous oxide deformed 12% at 600°C. [011] dislocation segments in the network are out of contrast (the foil has an {112} orientation).

Fig. 18 Stacking of ions in crystallographic structure of Cu_2O for three different directions.

Fig. 19 Core structure for a [100] edge dislocation in Cu_2O.

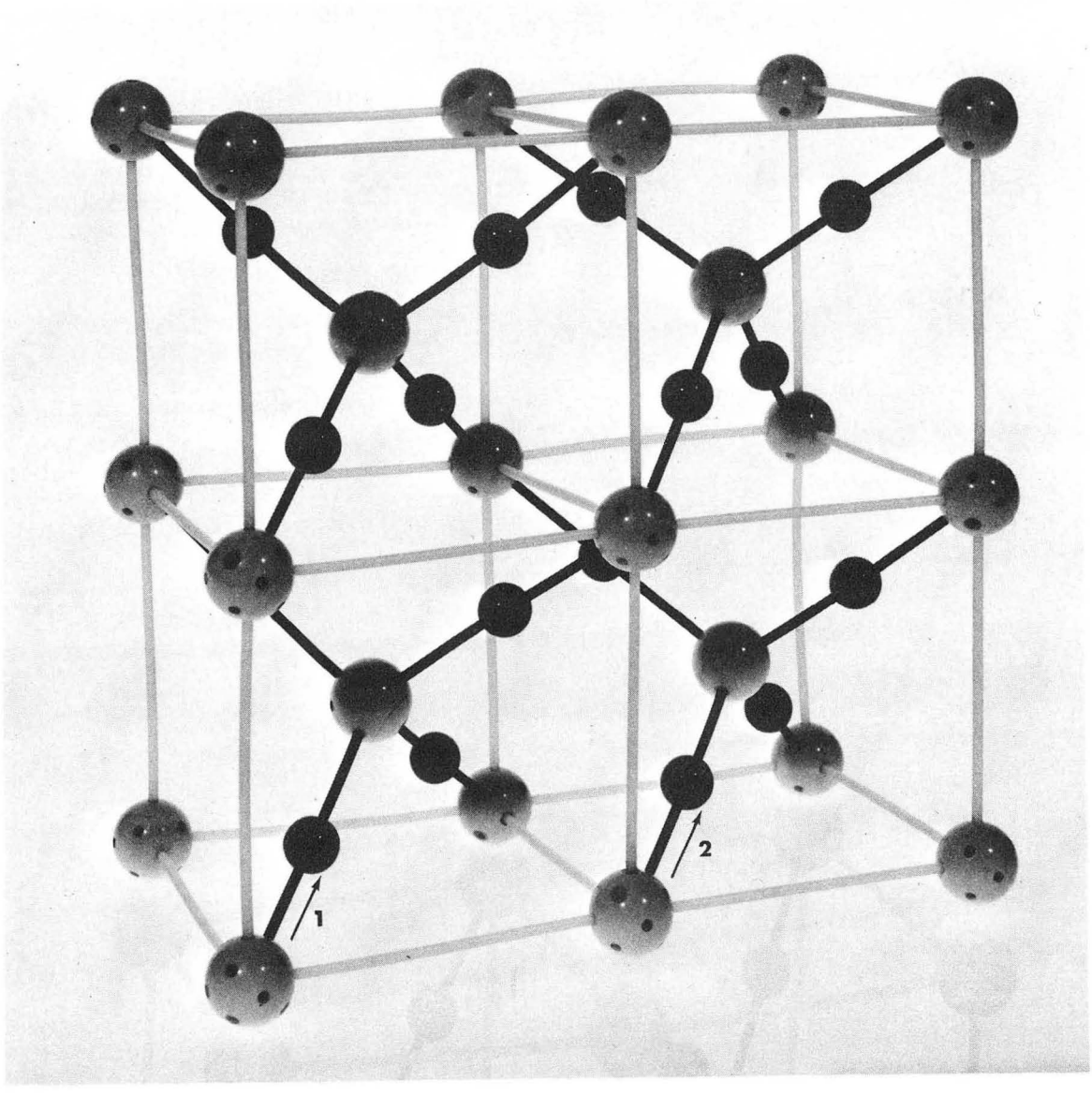

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Fig. 1

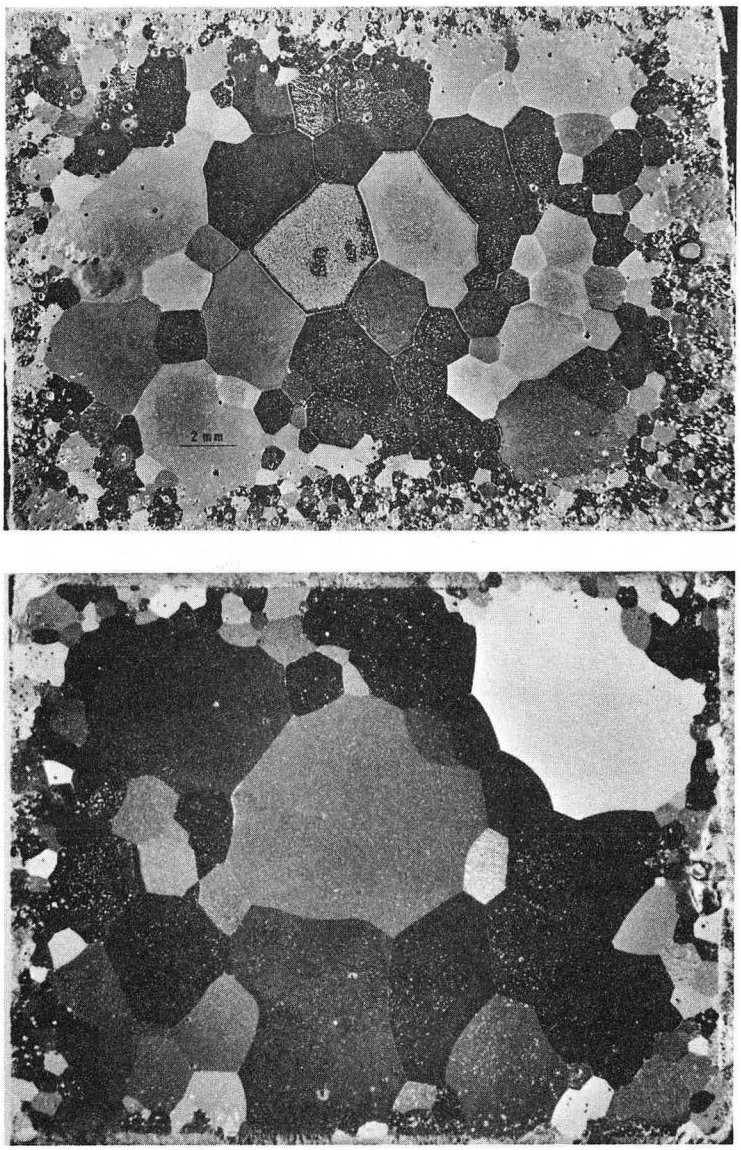

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Fig. 2

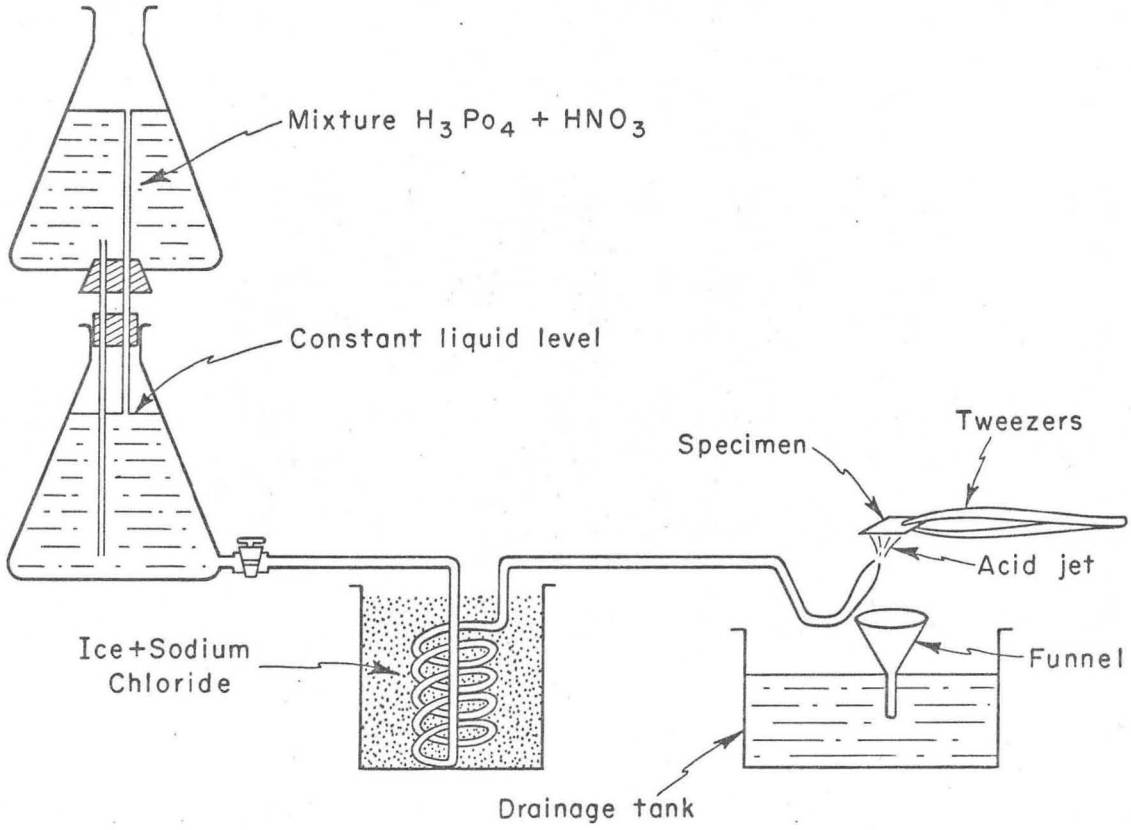

Fig. 3

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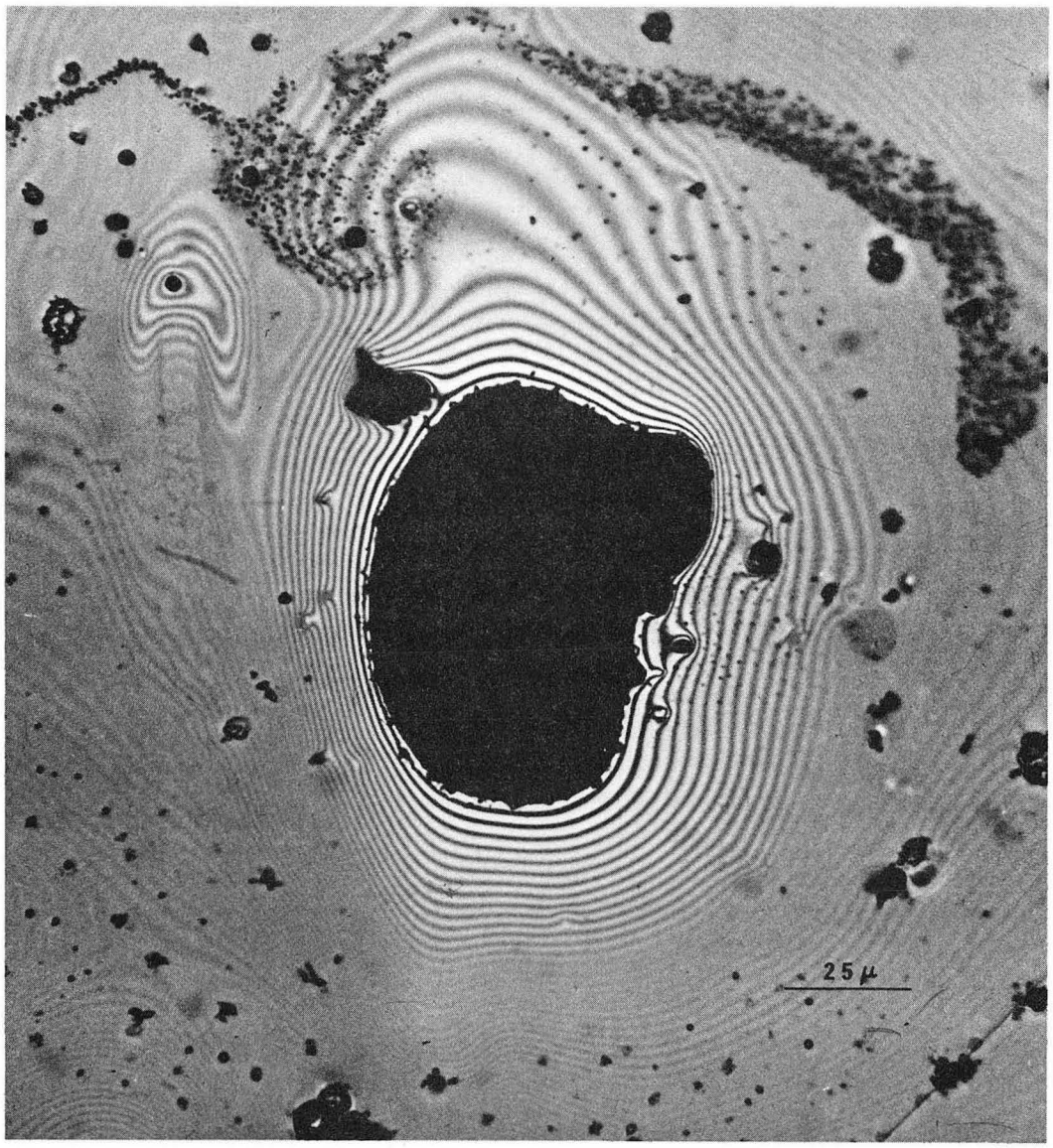

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Fig. 4

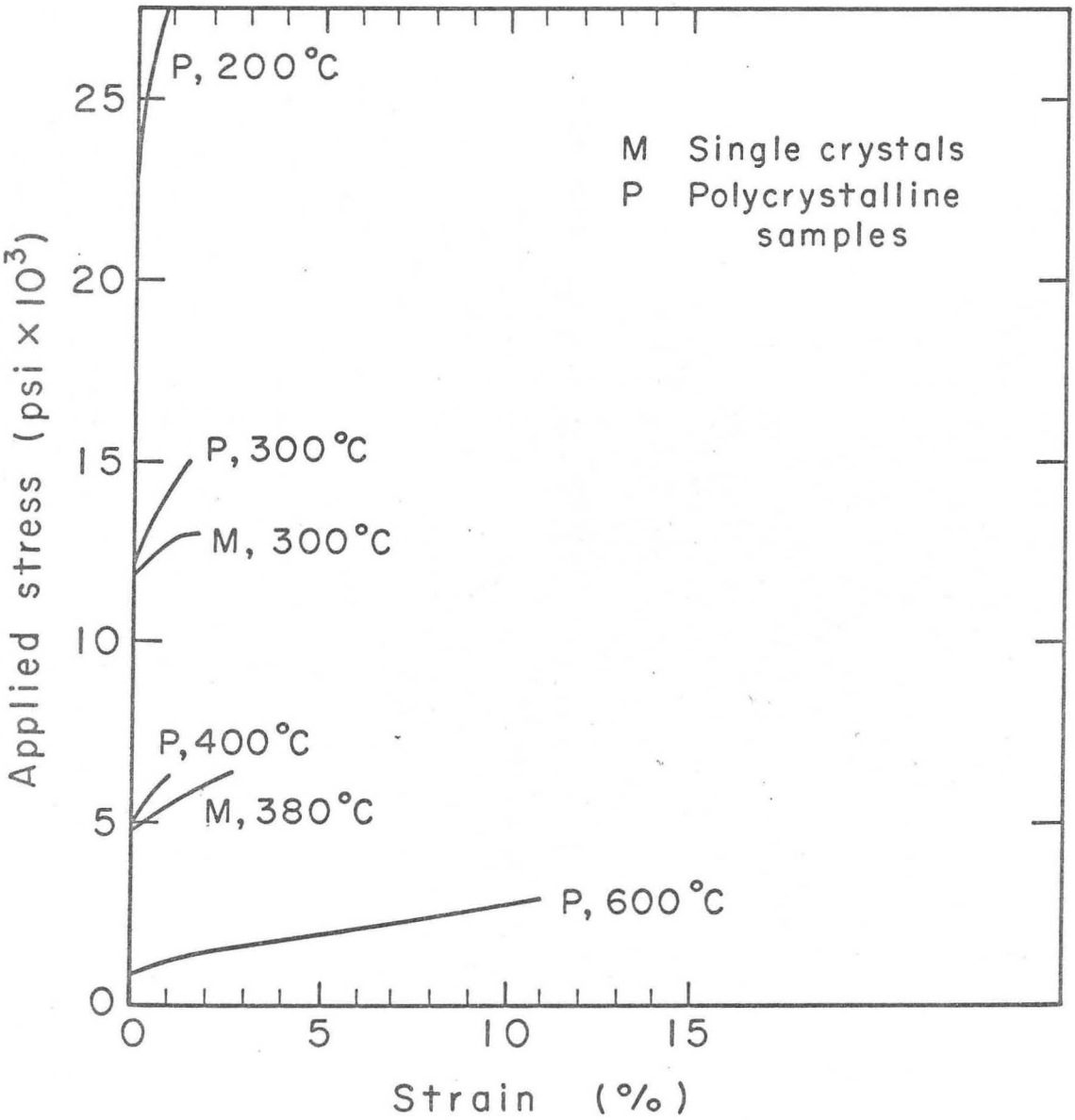

Fig. 5

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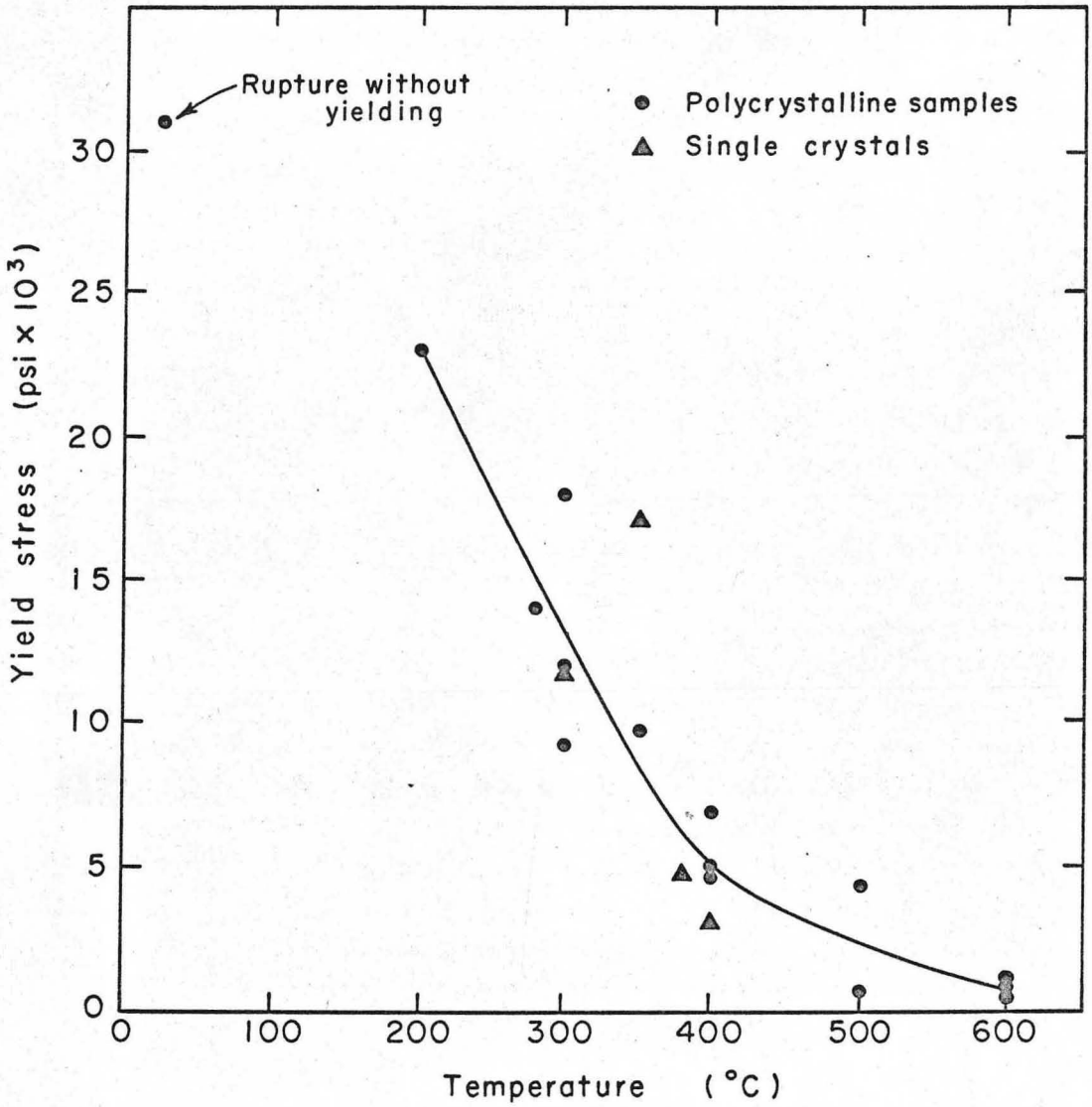

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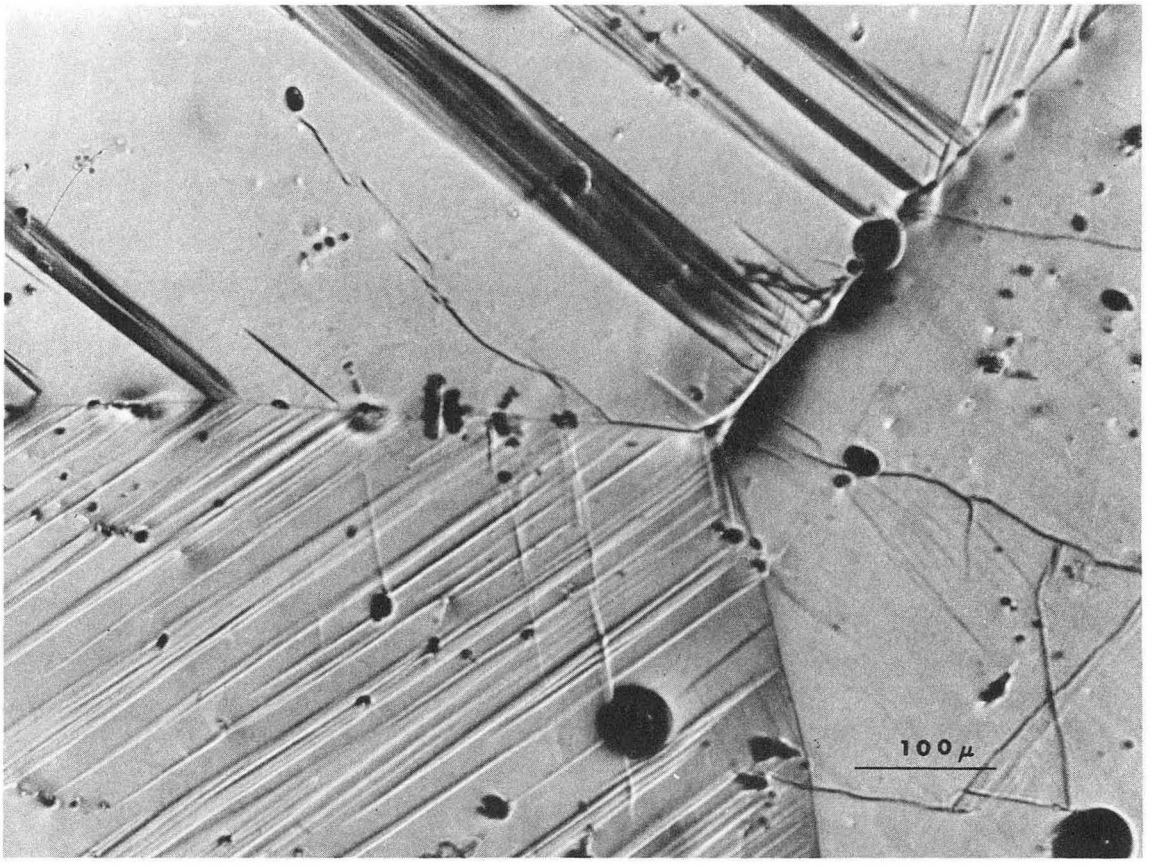

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Fig. 7

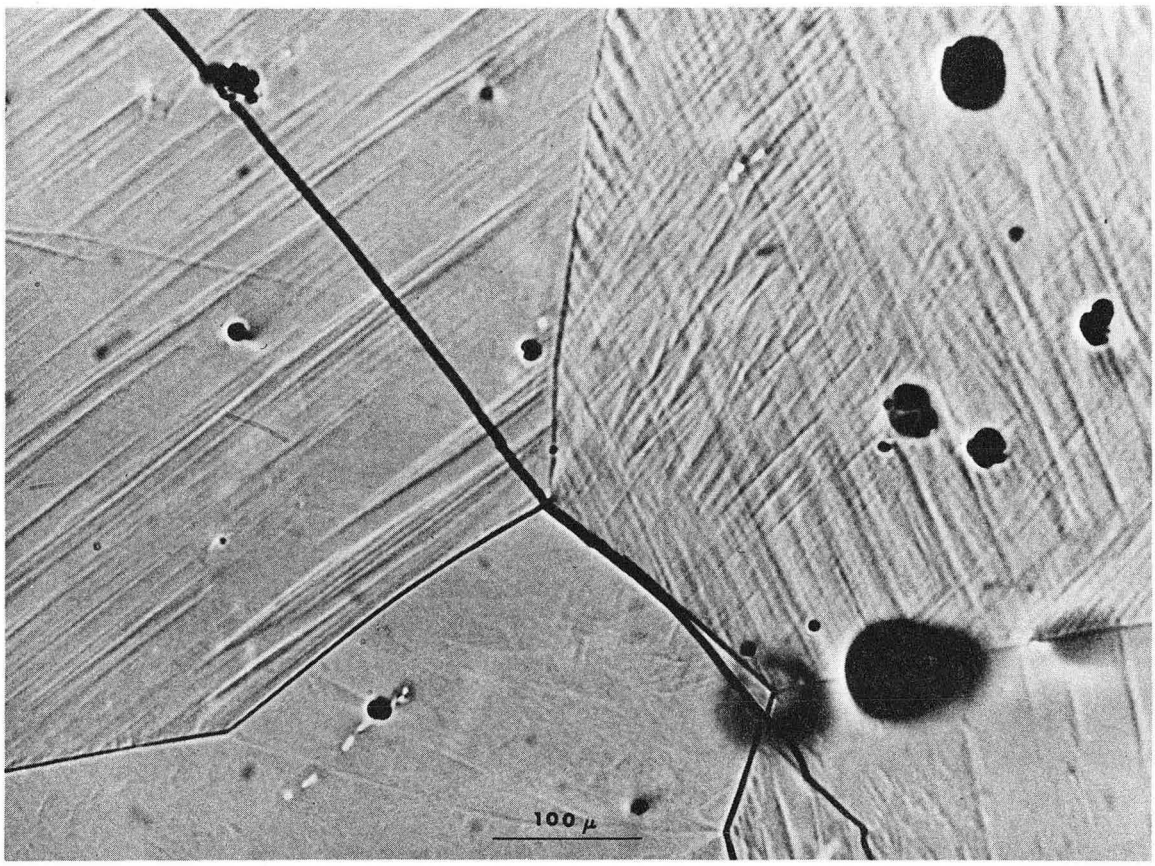

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Fig. 8

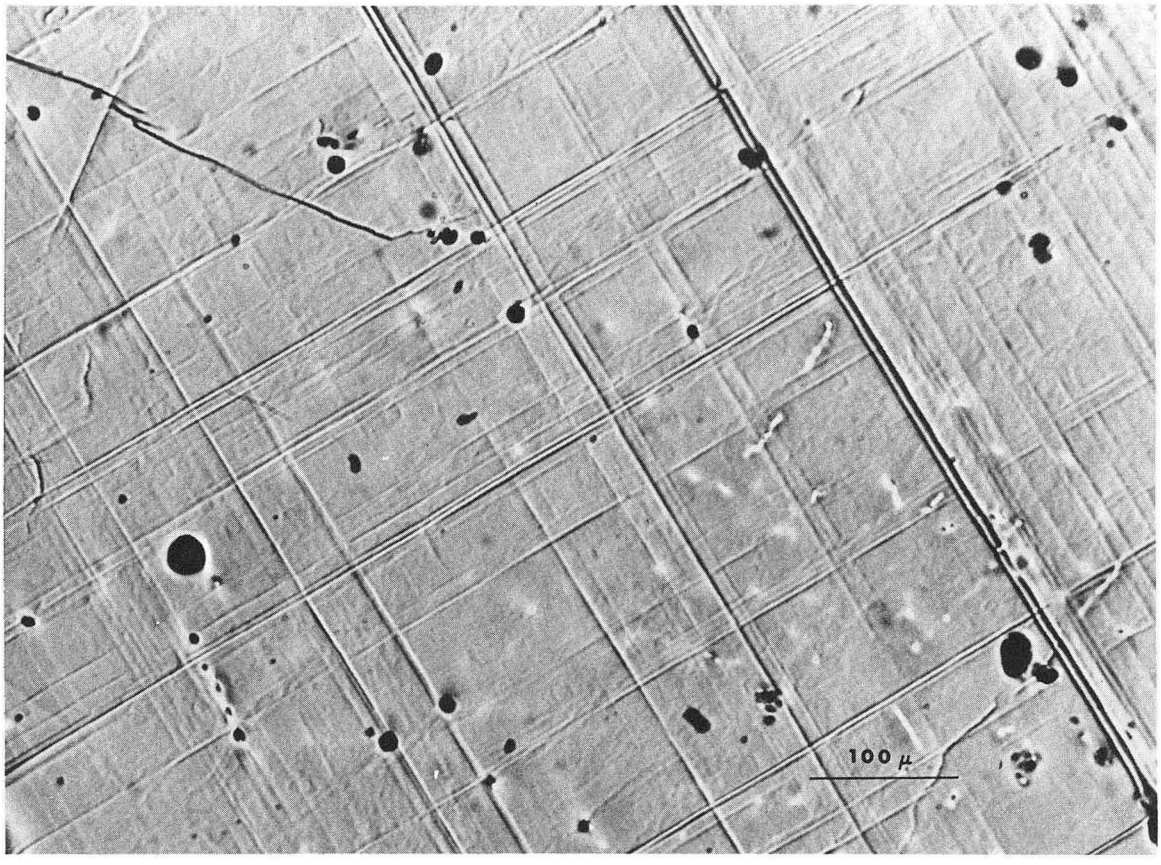

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Fig. 9

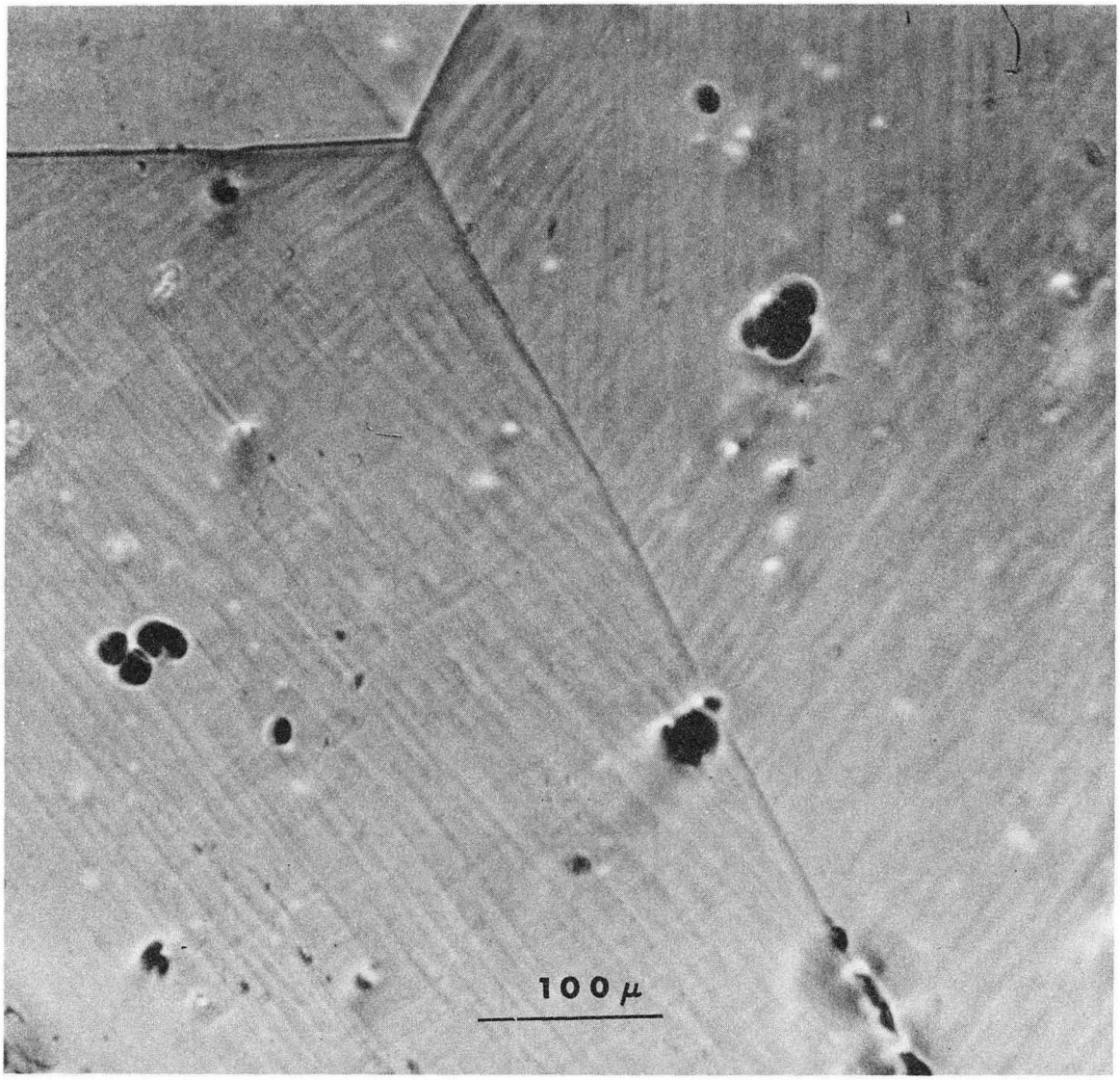

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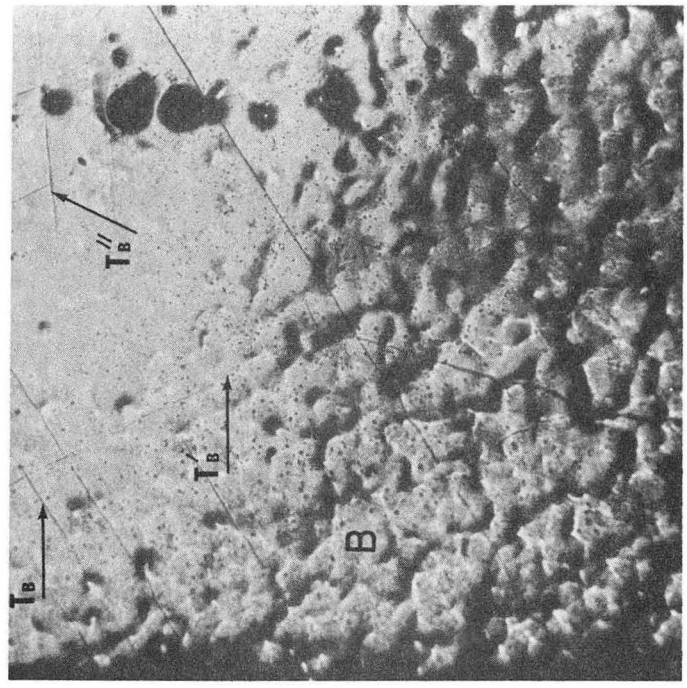
Fig. 10



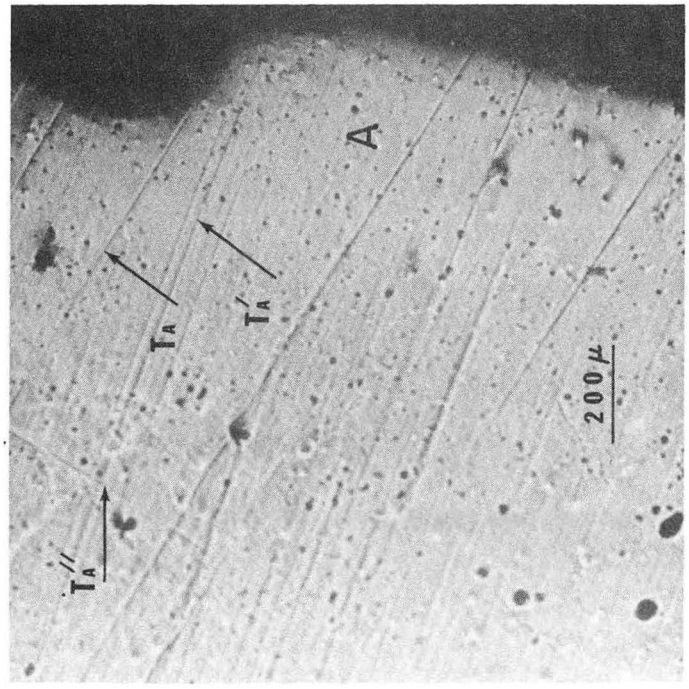


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Fig. 11

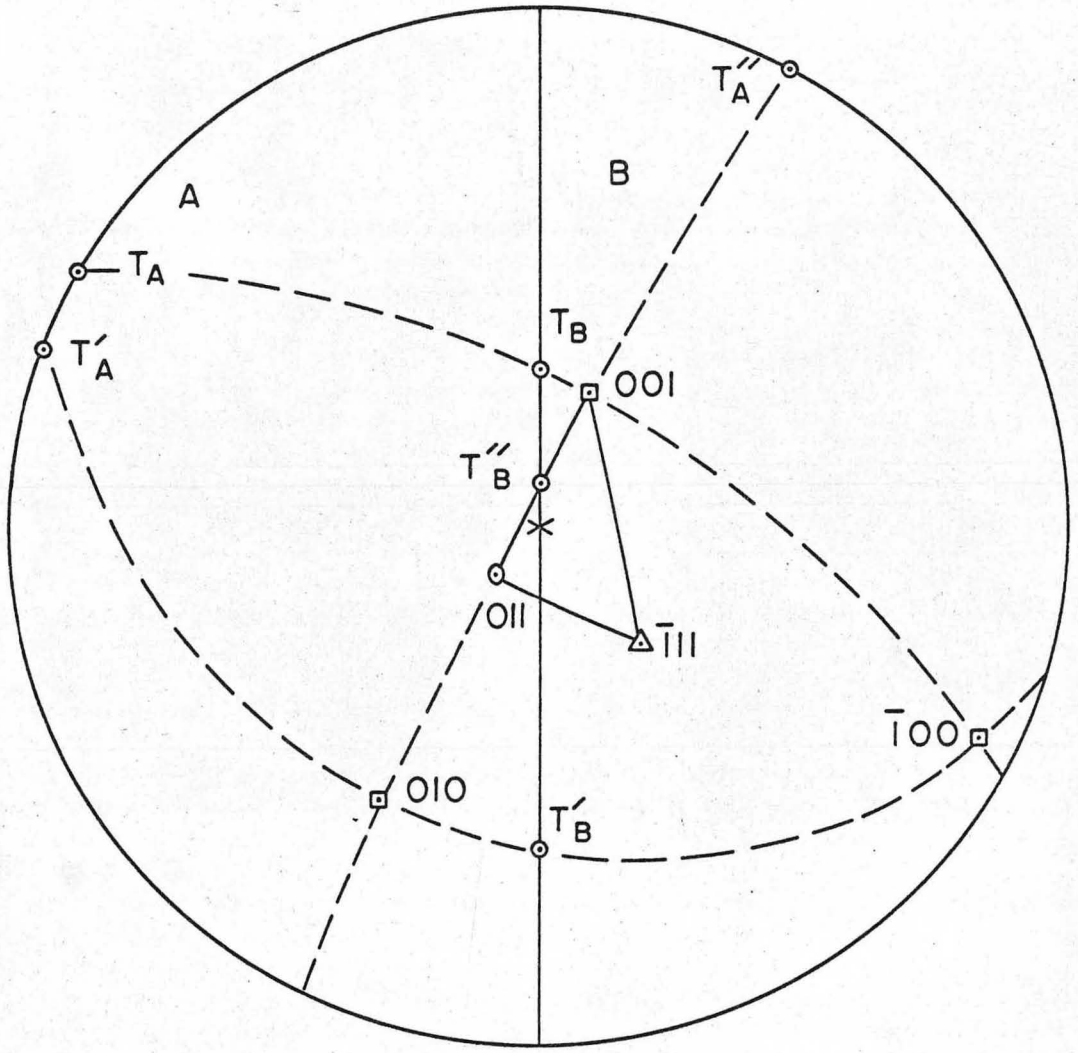

Fig. 12

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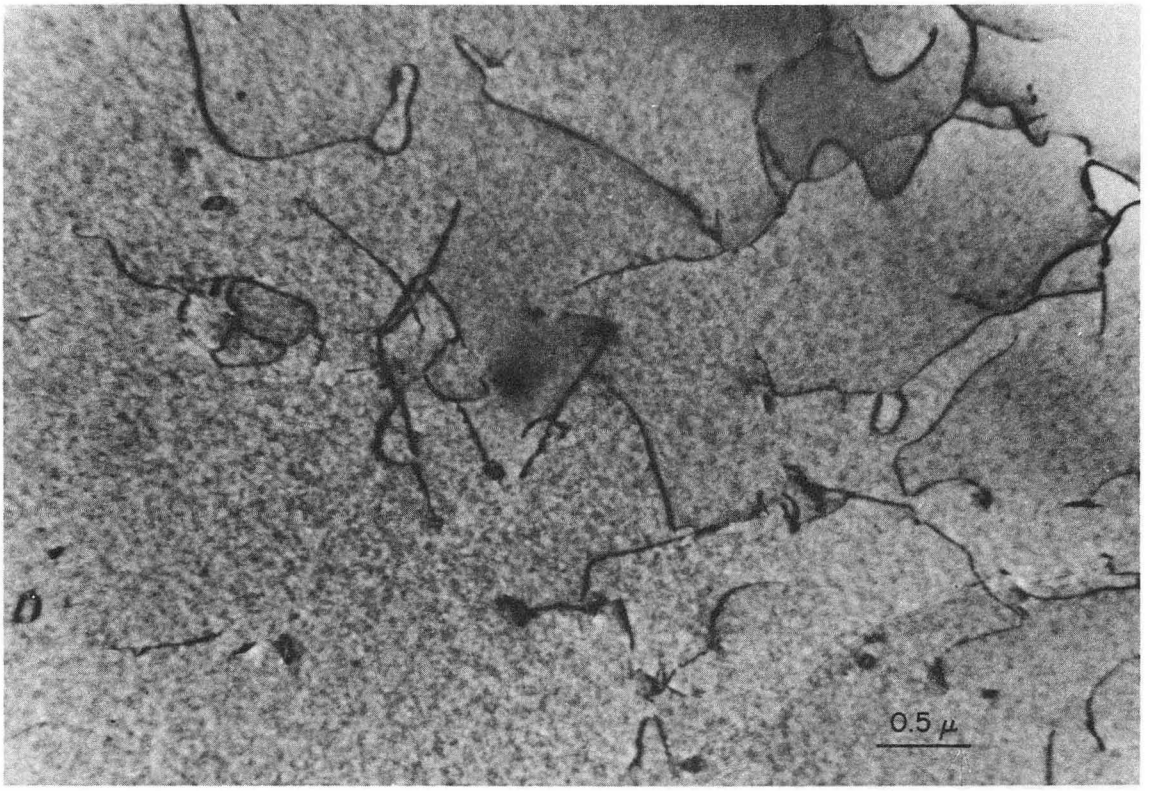

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Fig. 13

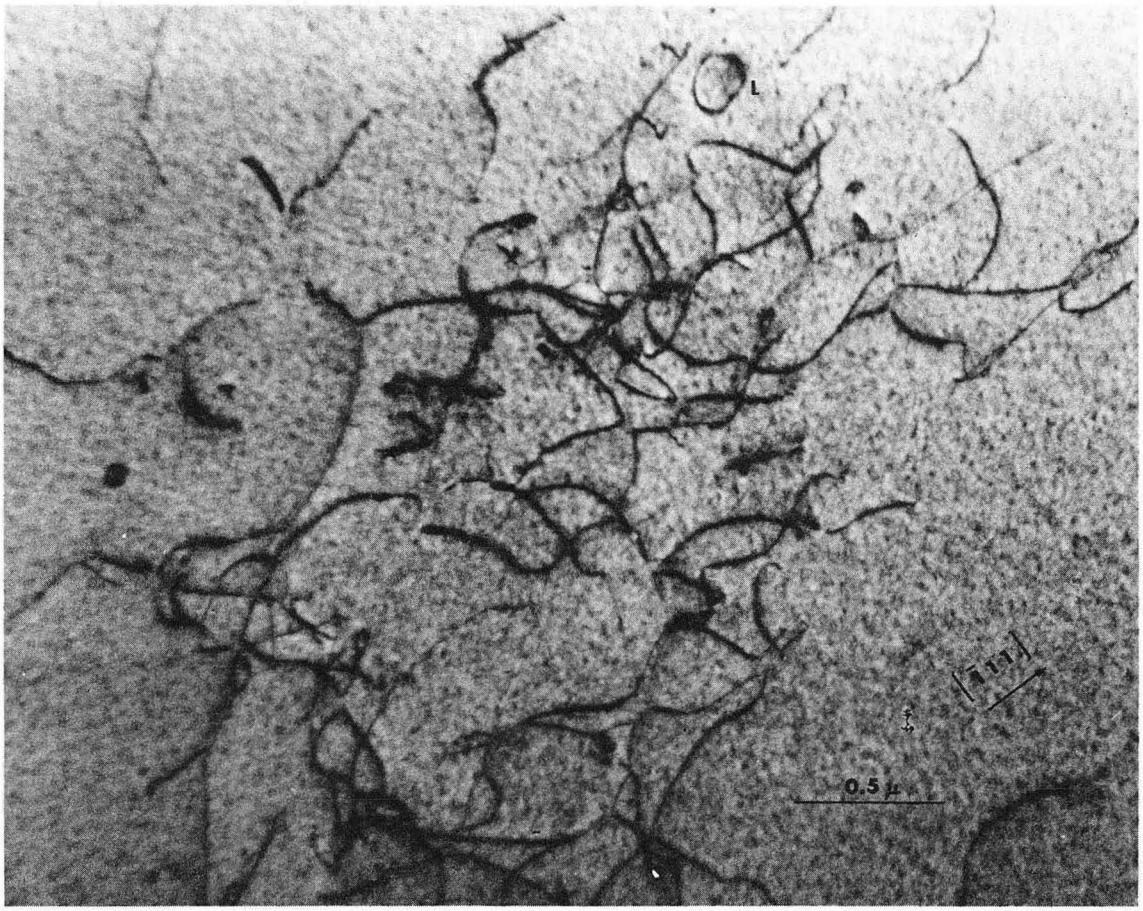

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Fig. 14

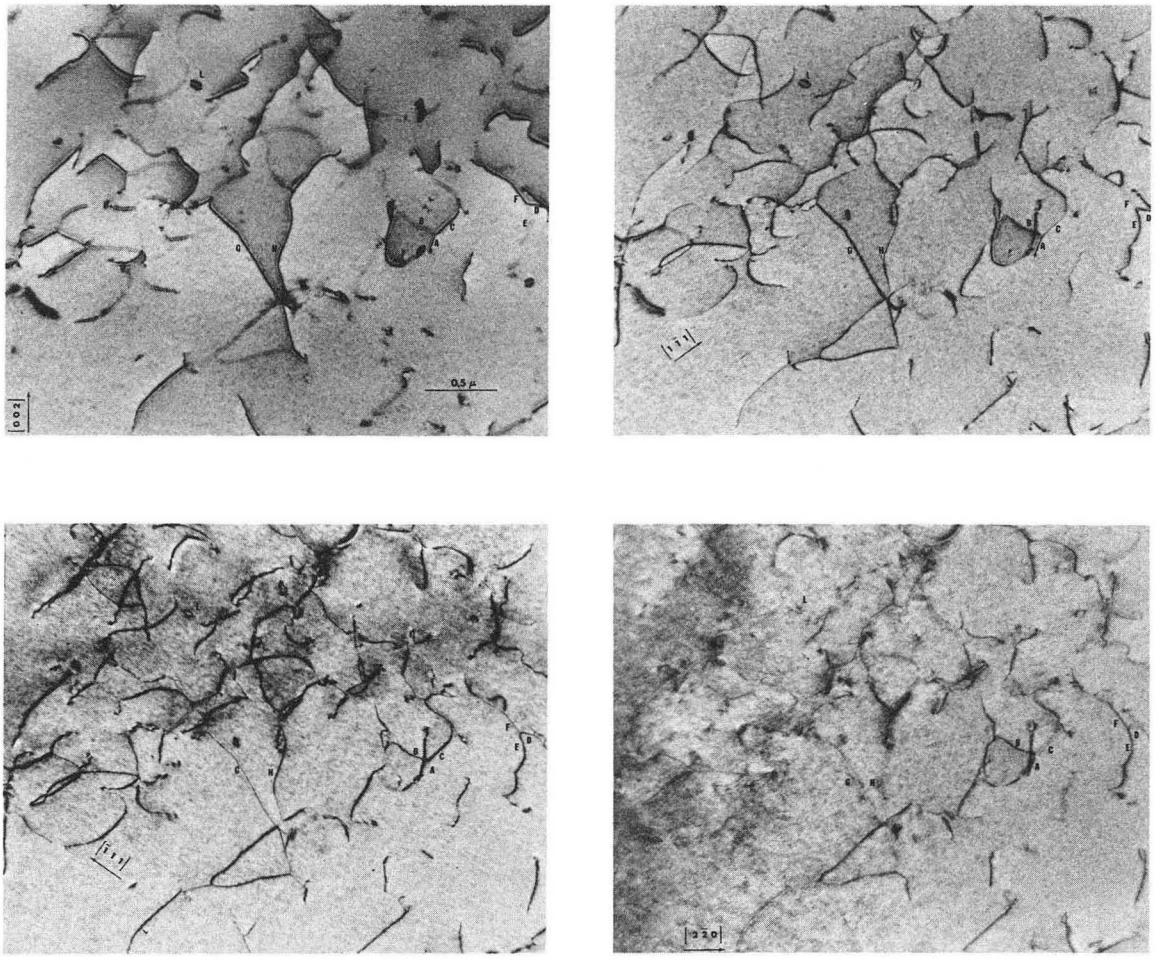

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Fig. 15

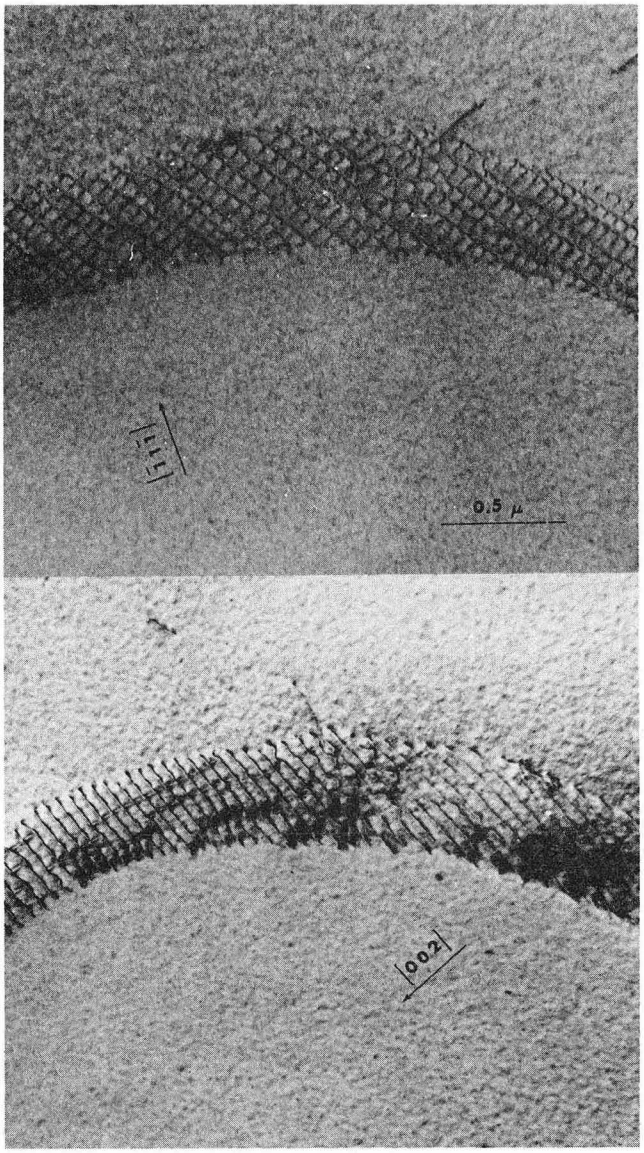

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Fig. 16

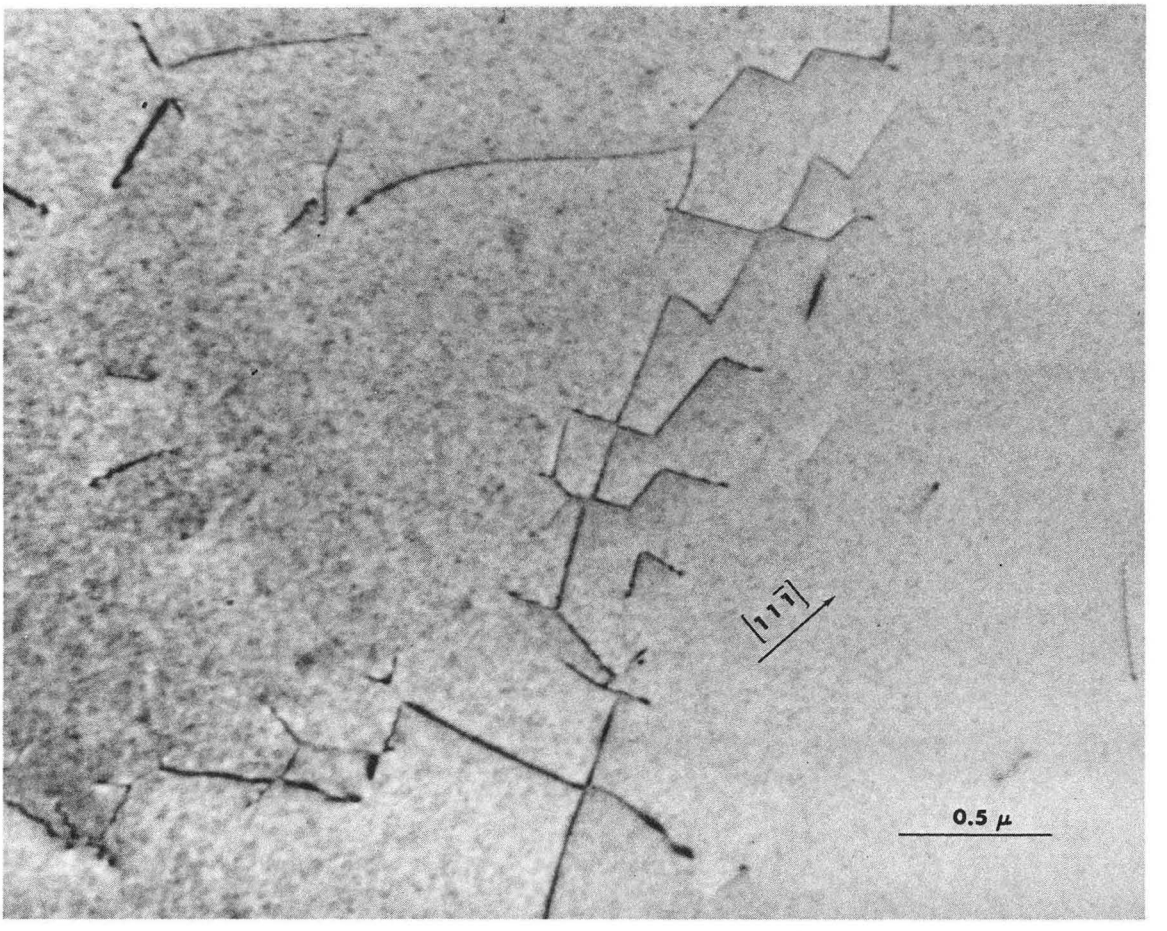

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Fig. 17

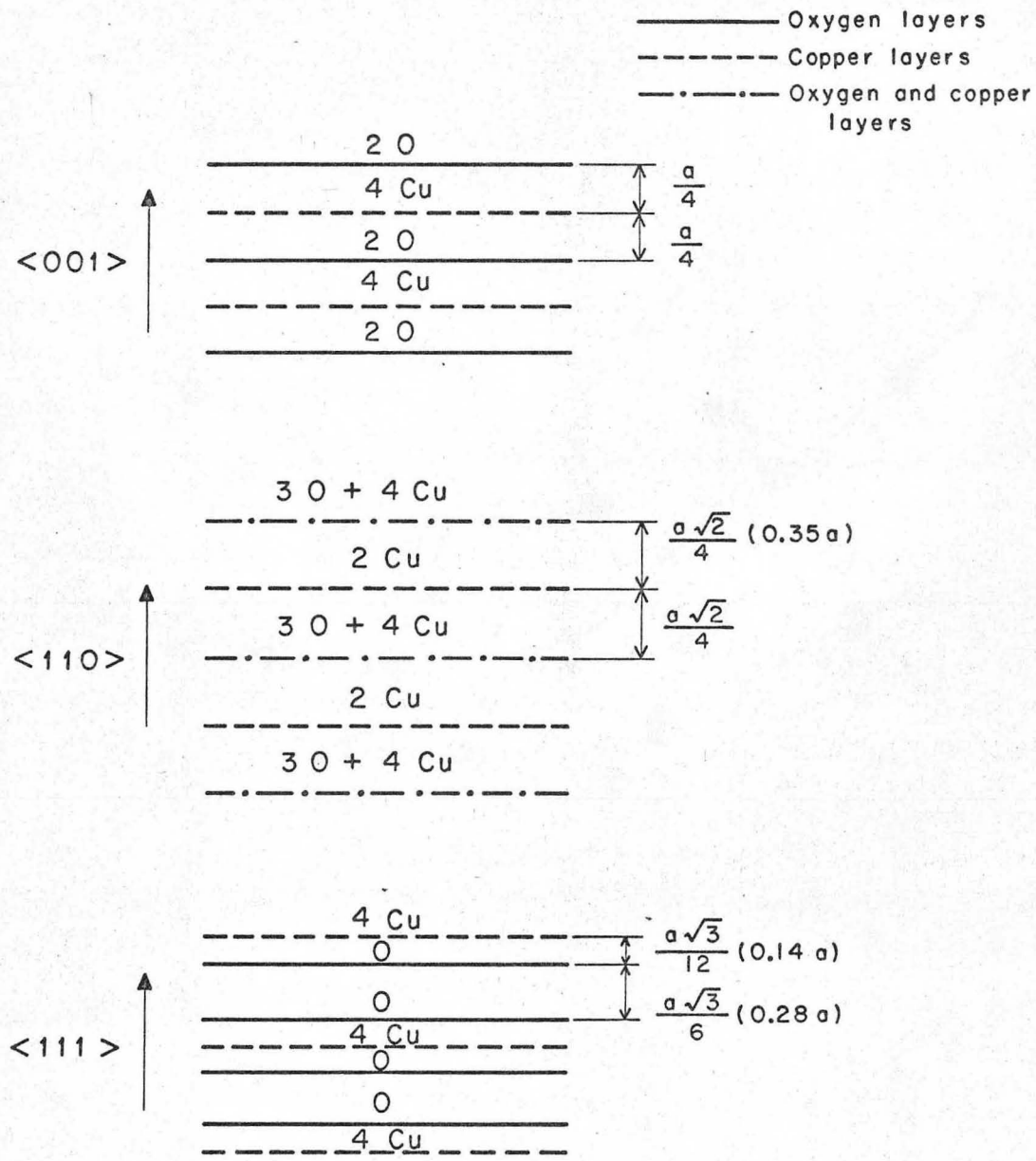

Fig. 18

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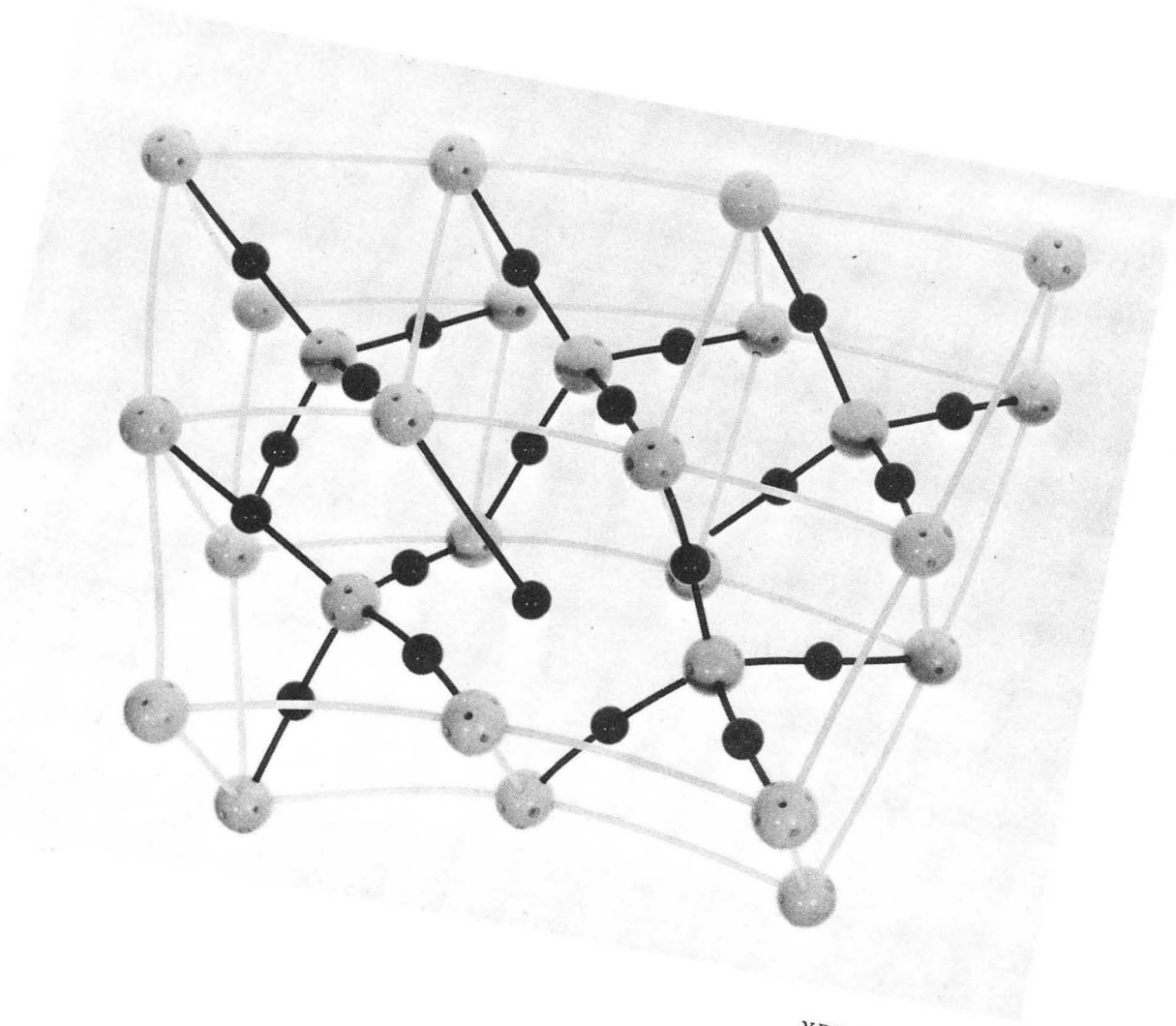

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Fig. 19

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