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INTERSTITIAL ORDERING OF CARBON IN TANTALUM

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Robert Emerick Villagrana

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INTERSTITIAL ORDERING OF CARBON IN TANTALUM

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ABSTRACT

The effect of interstitial carbon in tantalum was investigated by transmission electron microscopy and selected area diffraction. Interstitial ordering was found, and the ordered structure was determined from computation and comparison with electron diffraction data. The superlattice structure is tetragonal, with a $\frac{c}{a}$ ratio of 1.128, and an ideal composition $Ta_{64}C$.

Since the superlattice was determined from thin foils, it was necessary to compare the thin foil results with bulk specimens, alloyed to correspond to $Ta_{64}C$. Microscopic examination of bulk specimens showed many domain boundaries, separating regions in which the tetragonality associated with ordering was oriented in different directions. An analysis of these domain boundaries indicates that there are three possible types: coherent, semicoherent, and antiphase.

I. INTRODUCTION

Although macroscopic studies have been made of the physical properties of solid solutions of interstitial solutes, such as H, C, N, O in the Group VB body-centered cubic metals, little is known about the microstructure of these alloys. As mechanical properties are strongly structure dependent, an understanding of the behavior of these alloys necessitates a knowledge of the structure under investigation. In the past two years, evidence has been obtained by transmission electron microscopy that the interstitials occupy preferred sites, resulting in interstitial ordering, in the crystal structure of the metal.

The use of x-ray diffraction to study this ordering is limited by the relatively low scattering power of these interstitial elements (H, C, N, O), and because relatively large volumes of crystal are irradiated. As electron diffraction intensities are about 10^4 times greater than those of x-rays, and because selected area diffraction can be done on relatively small volumes of crystal ($\sim 1\ \mu^3$), detection of interstitial ordering is more likely by electron diffraction than by x-ray diffraction. Therefore, transmission electron microscopy studies coupled with selected area diffraction techniques present an excellent means for structure analysis which would be difficult, if at all practical, with conventional x-ray diffraction techniques.

In an investigation of the effect of interstitial N in Ta, Seraphim et al.[1] were the first to attempt to correlate transmission electron microscopy observations with interstitial ordering in the

Group VB metals. Seraphim et al. proposed a ordered structure $Ta_{27}N$ on the basis of x-ray Weissenberg camera investigations. Van Torne and Thomas,[2] and more recently Van Landuyt,[3] have made detailed electron microscopy studies on the phase transformation induced by interstitial O in Nb. Oxygen exists in random interstitial positions in BCC niobium. When local composition fluctuations take place, ordering followed by a definite phase transformation to FCC NbO, is observed. With the aid of hot stage microscopy and ciné techniques, Van Torne and Thomas were able to determine the temperature at which the transformation occurs. Ordering of interstitial hydrogen in tantalum[4] has also been observed, but so far no results describing the ordered structure have been reported.

In this investigation the effect of interstitial carbon in tantalum is studied, the maximum carbon content being 2.94 at. %. Interstitial ordering of carbon in tantalum is found, and the composition ($Ta_{64}C$) and structure of the superlattice is determined. As the superlattice structure is determined on the basis of ordering induced during microscopy observations, it is necessary to investigate the ordering in bulk specimens and to compare the results with the thin foil observations. The domain boundaries associated with the ordered structure are determined from bulk specimens. From electron diffraction evidence the $Ta_{64}C$ superlattice is determined to be tetragonal. Finally, a method for calculating the $\frac{c}{a}$ ratio is developed utilizing paired Kikuchi lines.

II. EXPERIMENTAL PROCEDURE

A. Specimen Preparation

From commercial tantalum rod stock high purity single crystals,

0.6 cm diameter by 10 cm in length, were grown in an electron-beam zone refiner. Specific resistivities were measured (the ratio from liquid He to room temperature was 10^4), and from these data the ratio of interstitial impurities to tantalum atoms were calculated[5] to be 10^{-9}. The single crystals were carefully rolled into strips 6 - 10 mils in thickness, washed with methyl alcohol, and annealed at 1300°C for 5 hours in dynamic vacuum of approximately 10^{-6} mm Hg. At this point foils were examined in the electron microscope to determine if any ordering transformation had occurred due to possible impurity pickup, or if any transformation could be induced. In no case was any transformation detected, nor could any transformation be induced by beam heating in the microscope. This implies that the impurity pickup was negligible during the rolling and annealing operations.

After annealing, the tantalum strips were cleaned by dipping in hydrofluoric acid (48%), and then washed with methyl alcohol. At all stages extreme caution was exercised in the handling of the strips in order to avoid contamination. The strips were handled with tweezers, and at no time were they allowed to make contact with possible sources of impurities.

The clean tantalum strips were weighed on a Mettler type BC 1000 substitution balance to an accuracy of ±0.1 mg. They were then transferred to a vacuum evaporator, where a thin film of carbon was deposited on one surface of the metal. The specimens were then placed in the vacuum furnace, and the carbon allowed to diffuse into the tantalum at various times and temperatures. After treatment, the specimens were removed and reweighed, the difference in weight being equal to the

amount of carbon taken up by the tantalum. Table I summarizes the percent carbon, and the various treatments for each specimen.

TABLE I

At. % Carbon	Annealing Temp. °C	Annealing Time Hr.	Vacuum mm Hg
1.54	1000	24	$\simeq 10^{-6}$
1.82	1000	48	$\simeq 10^{-6}$
2.28	1300	24	$\simeq 10^{-6}$
2.94	1500	24	$\simeq 10^{-6}$

B. Preparation of Electron Transparent Foils

Thin foils suitable for transmission electron microscopy were prepared by chemical polishing in a solution of 50 vol. % hydrofluoric acid and 50 vol. % nitric acid. The specimens were held in the polishing solution for five minutes, washed with methyl alcohol to remove any surface film, then replaced.

While polishing, the specimen was periodically examined with an optical microscope. If etching was detected then the polishing solution was altered by the addition of more nitric acid.

C. Microscopic Investigation

Transmission electron microscopy and selected area diffraction investigations were performed in a Siemens Elmiskop 1B electron microscope. An electron accelerating voltage of 100kv and a projector pole piece 0.77 mm in diameter were employed.

The Ta-C specimens were first examined in the microscope under

conditions in which the transformation could occur during observation. The transformation was induced by regulating the electron beam to heat the foil. This procedure offered more control over the reaction rate than pulse heating (removal of the condenser aperture).

Observations on bulk specimens, which had been transformed outside the microscope, were made using the double tilt specimen stage. This was necessary to investigate the nature of the contrast and to facilitate interpretation of the diffraction patterns.

III. THIN FOIL RESULTS AND INTERPRETATION

A. Microscopic Observations

As reported by Van Torne and Thomas,[2] and Van Landuyt[3] for NbO, the thin foil ordering transformation observed in the present work occurs in two distinct steps. Under the effect of heating by the electron beam, thin regions of the foil were observed to transform with the simultaneous formation of discrete nuclei, whose habit planes were {110}. This nucleation process was observed to take place homogeneously, probably due to carbon composition fluctuations in the thin regions of the foil. These small domains then grew until they impinged, as shown in Fig. 1.

The final stage of the ordering transformation takes place with the formation of highly ordered regions separated by coherent and antiphase domain boundaries. The transition period from impingement to the highly ordered final stage is shown in Fig. 2a, b. The final stage of the transformation is shown in Fig. 3. In Fig. 3 the boundaries at A and B are coherent domain boundaries (the nature of these boundaries

will be discussed in the next section) on $(1\bar{1}0)$ and (110), respectively. At C the boundaries are primarily {210} antiphase domain boundaries.

The transformation just described is the idealized case, and subject to the morphology of the tantalum surface. This is shown in Fig. 4a, b, c, where the transformation appears quite different from the idealized case. The transformation in Fig. 4a has not quite gone to completion, as the diffraction pattern shows only the initial stages of superlattice relpoint formation.

B. Structure Determination of $Ta_{64}C$

From selected area diffraction patterns obtained in regions similar to that of Fig. 3 it became apparent that an ordering process had taken place. This was deduced because, besides the primary tantalum diffraction pattern, there was also the superposition of a second smaller diffraction pattern corresponding to a superlattice structure. The problem is to construct from the superlattice diffraction pattern the superlattice unit cell. Because of the inherent difficulties in correlating intensity calculations with selected area diffraction data, a variation of the algebraic methods described by Vainshtein[6] will be utilized. Using such algebraic methods it is only possible to derive geometric structures, and not precise atomic coordinates. A model will be constructed whose associated structure factor will account for all superlattice reflections either present or absent. The actual structure determination involved the analysis of many selected area diffraction patterns, and trial and error attempts to construct a model compatible with these diffraction data. The principal features are present in the diffraction pattern associated with Fig. 3. This diffraction

pattern is enlarged and shown in Fig. 5a; it contains enough data to illustrate how the structure was determined.

Figure 5a shows a [001] BCC tantalum pattern tilted slightly about [200], with a superlattice diffraction pattern superimposed. In this diffraction pattern first order superlattice relpoints are spaced parallel to $(1\bar{1}0)_{BCC}$ and $(110)_{BCC}$ relpoints at a distance of $1/4\ (\bar{g}_{110})_{BCC}$. This implies that in real space there are superlattice planes parallel to $(110)_{BCC}$ at a d spacing four times that of $(110)_{BCC}$. Similarly, there are first order superlattice planes parallel to $(200)_{BCC}$ each at a d spacing four times that of $(200)_{BCC}$. Considering these facts, it is concluded that the superlattice unit cell should be approximately equal to four a_o on edge, where a_o is the lattice parameter for BCC tantalum.

A model, in which four carbon atoms are placed in order to locate the corners of the superlattice unit cell, was then constructed. The carbon atoms were placed in octahedral sites, but tetrahedral sites might just as well be chosen (actually, octahedral sites were chosen for ease of illustration). Figure 6 shows the model. In Fig. 6 the carbon atoms are placed in $0\frac{1}{2}0$ octahedral positions defining the corners of a cube (neglect the body-centered atom for the present), approximately four a_o on an edge. The BCC tantalum unit cells are shown as squares in Fig. 6. It must now be determined if more carbon atoms are necessary to account for all the diffraction effects, and where they should be located in relation to the carbon atoms at the corners of the primitive cell (defined by carbon atoms only).

The basic structure factor equation for unit cells containing n atoms of the same kind is

$$F_{hk\ell} = \sum_{1}^{n} f_n \, e^{2\pi i \, (hx_n + ky_n + \ell z_n)} \qquad \text{Eq. 1}$$

where f_n is the atomic scattering factor, $(hk\ell)$ the Miller indices, and $(x_n \; y_n \; z_n)$ the atomic coordinates. The indicated sum is carried out over the unit cell under consideration. For the superlattice structure, $F_{hk\ell}$ will be a function of both tantalum atoms and carbon atoms, and so Eq. 1 is now written in the form

$$F_{hk\ell} = f_{Ta} \left[\sum_{1}^{n} e^{2\pi i \, (hx_n + ky_n + \ell z_n)}\right] + f_C \left[\sum_{1}^{j} e^{2\pi i \, (hx_j + ky_j + \ell z_j)}\right] \qquad \text{Eq. 2}$$

The tantalum terms have already been determined by the choice of superlattice cell size (those tantalum atoms enclosed by the superlattice unit cell in Fig. 6). Therefore, carbon atoms must be added in varying positions until a structure factor is obtained which is compatible with all the diffraction data. As the structure factor is quite large due to the many tantalum terms, it was necessary to utilize an IBM 7094 computer in order to solve the various structure factors. After numerous attempts, the structure factor which was consistent with all the diffraction data was determined to be

$$F_{hk\ell} = f_{Ta} \, [T] + f_C \, [C] \qquad \text{Eq. 3}$$

where $T = \sum_{x=o}^{3} \sum_{y=o}^{3} \sum_{z=o}^{3} e^{2\pi i \left(\frac{hx}{4} + \frac{ky}{4} + \frac{\ell z}{4}\right)} + \underbrace{\sum_{x=1}^{7} \sum_{y=1}^{7} \sum_{z=1}^{7}}_{\text{odd integers}} e^{2\pi i \left(\frac{hx}{8} + \frac{ky}{8} + \frac{\ell z}{8}\right)}$

and $C = e^{2\pi i \left(\frac{k}{8}\right)} + e^{2\pi i \left(\frac{h}{2} + \frac{5k}{8} + \frac{\ell}{2}\right)}$.

Equation 3 was written taking the tantalum atom at the origin of Fig. 6 as (000). The f_C terms correspond to a body-centered arrangement of carbon atoms as shown in Fig. 6. The selection rules predicted by Eq. 3 are the same as those for the body-centered space lattice, viz., $h + k + \ell$ even for reflections present, and $h + k + \ell$ odd for reflections absent.

The superlattice shown in Fig. 6 corresponds to an ideal composition of $Ta_{64}C$. Further a hard sphere model shows that by placing carbon atoms in $0\frac{1}{2}0$ type positions an expansion in the [010] direction, and a slight contraction in the [100] and [001] directions must occur. Therefore, the superlattice unit cell is tetragonal. The tetragonality was confirmed in other <100> patterns because a definite, but slight, contraction of one of the $(\bar{g}_{200})_{BCC}$ vectors, and a corresponding change in the angle between $(\bar{g}_{110})_{BCC}$ vectors was observed. These observations imply that the $\frac{c}{a}$ ratio cannot be unity.

C. Superlattice Pattern Indexing

The final test of the structure is the indexing of the superlattice pattern using the selection rules predicted by Eq. 3. Figure 5b shows the indexed superlattice diffraction pattern, only the strong first and second layer relpoints of Fig. 5a are indexed. To index this pattern the tantalum indices must be transposed to superlattice indices as predicted by the structure factor equation. The following expression, utilizing a similarity matrix, can be used to make this transformation.

$$\left\|\begin{matrix} h \\ k \\ \ell \end{matrix}\right\|_S = \left\|\begin{matrix} 4 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 4 \end{matrix}\right\| \left\|\begin{matrix} h \\ k \\ \ell \end{matrix}\right\|_{Ta} \qquad \text{Eq. 4}$$

Care must be taken in using Eq. 4, for in some cases the BCC tantalum relpoint might be tilted off the reflecting sphere, and the corresponding second layer superlattice relpoint tilted onto the reflecting sphere. In these cases, and certainly with all other superlattice relpoints, it is best to index patterns by using angular measurements and $|\bar{g}|$ ratios. As the structure is tetragonal, it is necessary to know the $\frac{c}{a}$ ratio in order that reasonable angles and d spacings can be calculated. The $\frac{c}{a}$ ratio was determined from Kikuchi lines (section IV D) to be 1.128.

IV. BULK SPECIMEN RESULTS AND INTERPRETATION

A. Microscopic Observations

As the superlattice structure in Fig. 6 was determined on the basis of thin foil observations, it was necessary to compare the thin foil behavior with that of bulk specimens. The composition of the ordered structure is $Ta_{64}C$, the bulk specimen alloyed to correspond to this composition contained 1.54 at. % C(see Table I) or a composition $Ta_{66}C$. Microscopic examination of this specimen, Fig. 7, showed a multitude of domain boundaries similar to those reported for impure Nb[7] and Ta[8].

The domain boundaries were seen to be highly mobile under the heating effect of the electron beam. This made microscopic examination difficult, as low beam currents could induce sufficient heat to cause the domain boundaries to migrate, and subsequently disappear. These domain boundaries move presumably because of the easy diffusion of interstitial carbon atoms. Upon lowering the beam current, the boundaries

returned to approximately their initial positions, but the contrast from the boundaries was not as sharp, nor could tilting bring the boundaries into better contrast.

It was also observed that some domain boundaries were more resistant to beam heating than others. In virtually all cases these boundaries were found to be on or near {110}.

B. Contrast from Domain Boundaries

A detailed dynamical theory explaining the contrast from domains, and the basic crystallographic conditions necessary for contrast, have been developed by Gevers et al.[9,10] Consider a thin foil, as in Fig. 8, which is separated into two regions by a domain boundary. Furthermore, let the two crystals be tetragonal with c axes oriented normal to each other as shown in Fig. 8, resulting in [001] being the orientation of crystal I and [010] the orientation of crystal II. In effect, the domain boundary divides the crystal into two wedged segments, with the crystal structure differing slightly in dimension in each segment. This slight difference in crystal structure appears in selected area diffraction patterns taken across domain boundaries. In Fig. 8, crystal I gives a four fold cubic pattern, and crystal II gives a two fold tetragonal pattern. The superposition of these two diffraction patterns show a pairing of the Kikuchi lines and higher order relpoints. The contrast associated with a boundary arises from three sources (i) differences in extinction distances in each segment (ii) a change in the phase angle at the boundary (iii) the diffraction conditions in crystal I differ from those in crystal II resulting in an excitation error.

The fringe patterns associated with domain boundaries are different

from those of stacking faults, or twin boundaries. In bright field the first and last fringes from domain boundaries are non-complementary, and in dark field they are complementary with respect to the fringe at the surface of the foil in bright field. This is shown in Fig. 9a, b.

As the angle ø in Fig. 8 approached 0 degrees the boundary disappears, but as ø approached 90 degrees the boundary appears as a line separating regions of opposite contrast. The latter case is visible in regions A and B of Fig. 3, and in Fig. 7 for the $(1\bar{1}0)$ boundaries. The contrast differences in Fig. 7 are not as evident as Fig. 3.

In Fig. 7 and Fig. 9 the domain boundaries are overlapping. The nature of the contrast effects in the central portions of these overlapping fringes are similar to the three cases of overlapping stacking faults in rutile.[11] The three possible configurations for overlapping domain boundaries are shown in Fig. 10.

C. Crystallography of Domain Boundaries

From the diffraction geometry associated with domain boundaries,[10] and trace analysis,[12] it is possible to determine the plane of the boundary. This was done for Fig. 7. If the conditions for observing domain boundary contrast are met and the plane of the boundary is known, it is possible to construct a boundary model based on the superlattice structure. When this was done, it was found that the resulting domain boundaries could be classified into three general types: coherent, semicoherent, or antiphase.

The coherent domain boundary is defined by a {110} plane, and is energetically the most stable. This type of boundary is shown in Fig. 11 as a (110) plane in edge view (in all the diagrams, squares

represent tantalum unit cells, and circles carbon atoms). On one side of this boundary the atoms are pictured as open circles in $\frac{1}{2}00$ octahedral positions, and on the other side as colored circles in $0\frac{1}{2}0$ octahedral positions. The resulting tetragonality is as indicated in the small diagram in Fig. 11. The formation of the boundary in Fig. 11 can be described by the following shift involving the carbon atoms on one side on the (110) plane only

$$\frac{a_s}{2}\langle 100\rangle + \frac{c_s}{2}\langle 100\rangle + \frac{a_o}{2}\langle 110\rangle$$

where a_s and c_s are the lattice parameters of the tetragonal superlattice, and a_o is the lattice parameter of the BCC tantalum. Positions 2 and 4 in Fig. 11 define coherent domain boundaries. The reaction for these positions would be

$$\text{Position 2} = \frac{a_s}{2}[010] + \frac{c_s}{2}[\bar{1}00] + \frac{a_o}{2}[110]$$

or

$$\text{Position 4} = \frac{a_s}{2}[010] + \frac{c_s}{2}[\bar{1}00] + \frac{a_o}{2}[\bar{1}\bar{1}0]$$

In the coherent domain boundary the tetragonal c axes are coupled (intersect at the same point on the boundary), and the carbon atoms are in twin relationship about the (110) plane (the carbon atoms are mirrored about the domain boundary). For position 4 the boundary is as indicated in Fig. 11, but for position 2 the boundary should be shifted up.

Positions 1 and 3 in Fig. 11 describe the semicoherent domain boundary. The same general reaction that was used in describing the coherent domain boundary can be used in describing the semicoherent

domain boundary in Fig. 11. The two positions can be described by the following shifts

$$\text{Position 1} = \frac{a_s}{2}[010] + \frac{c_s}{2}[\bar{1}00] + \frac{a_o}{2}[\bar{1}10]$$

or

$$\text{Position 3} = \frac{a_s}{2}[010] + \frac{c_s}{2}[\bar{1}00] + \frac{a_o}{2}[1\bar{1}0]$$

In this type of boundary the tetragonal c axes are coupled, but the carbon atoms are not mirrored about the (110) boundary plane. Once again, the boundary is drawn correctly for position 1, but should be shifted up for position 3.

The antiphase domain boundary is energetically the most unstable, and is not confined to any particular crystallographic plane. A (111) antiphase domain boundary is shown in Fig. 12. This domain boundary can be produced by a simple $\frac{1}{2}$ a_o <110> translation of carbon atoms on one-half of the boundary to opposite octahedral sites, without changing the carbon atom positions on the other side of the boundary. Figure 12 illustrates four possible positions. In this type of boundary there is no head to tail coupling of the tetragonal c axes, and the carbon atoms are not mirrored about the (111) plane.

It should be noted that some domain boundaries show mixed character, since they are not rigidly confined to a particular crystallographic plane. This can be seen in Fig. 7.

D. Determination of the $\frac{c}{a}$ Ratio for $Ta_{64}C$

As was mentioned previously, the diffraction patterns associated with domain boundaries showed a pairing of the relpoints, and the associated Kikuchi lines. It is possible to estimate the $\frac{c}{a}$ ratio for

the superstructure from these paired relpoints, but for a more accurate ratio, Kikuchi lines should be utilized. The advantage of using Kikuchi lines to make angle and distance measurements, instead of relpoints, has been described by Thomas.[13]

Figure 13 is a diagram of reciprocal space in [001] orientation. Consider an arbitrary relpoint, say the (210) cubic (this reflection is not an allowed BCC reflection, but is shown for convenience), and introduce some tetragonality along the [100] axis. The $(210)_C$ cubic relpoint now becomes the $(210)_T$ tetragonal relpoint. In the case of domain boundaries, both the paired cubic and tetragonal relpoints are visible for higher order reflections. In Fig. 13, the angle between the [100] axis and the $(210)_C$ relpoint is θ, and the angle between (210) relpoint and the $(210)_T$ relpoint is $\Delta\theta$. Therefore, the angle between the $(210)_T$ relpoint and the [100] axis is ϕ, where $\phi = \theta + \Delta\theta$. By substituting ϕ into the equation for the angle between two planes in the tetragonal system,

$$\cos\phi = \frac{\dfrac{h_1 h_2 + k_1 k_2}{a^2} + \dfrac{\ell_1 \ell_2}{c^2}}{\left[\left(\dfrac{h_1^2 + k_1^2}{a^2} + \dfrac{\ell_1^2}{c^2}\right)\left(\dfrac{h_2^2 + k_2^2}{a^2} + \dfrac{\ell_2^2}{c^2}\right)\right]^{\frac{1}{2}}} \qquad \text{Eq. 5}$$

it is then possible to solve for the $\frac{c}{a}$ ratio directly.

The problem is to calculate $\Delta\theta$ as accurately as possible, this is done using paired Kikuchi lines. The Kikuchi line associated with a given relpoint is normal to an imaginary line extending from the transmitted beam to the relpoint. Thus, by simple geometry, and as shown in Fig. 13, the paired Kikuchi lines associated with the $(210)_C$

and $(210)_T$ relpoints intersect at an angle $\Delta\theta$. In the general case for paired Kikuchi lines it is necessary to utilize a stereographic projection in determining the angular relationships.

Figure 14a shows the diffraction pattern associated with Fig. 7, and Fig. 14b shows the analysis of this pattern. In determining the $\frac{c}{a}$ ratio the $3\bar{3}2$ paired Kikuchi lines shown in Fig. 14b were used, and the $\frac{c}{a}$ ratio was calculated to be 1.128. The $\frac{c}{a}$ ratio calculated from a hard sphere model similar to Fig. 6 was found to be 1.08, but this ratio is low because the contraction along the a_s axes was neglected.

V. DISCUSSION

A. Thin Foil Observations

The ordering transformation is attributed to the alloyed interstitial carbon, since a pure tantalum foil was subjected to the same treatments as the Ta-C specimens and no transformation could be induced. Also, during microscopic examination, there is bound to be the deposition of minute traces of carbon or other impurities from the vacuum system, but this would only accelerate the ordering transformation. Except when beam heating was purposely done, the beam current and condenser illumination were adjusted so that the specimen temperature was kept to a minimum (<100°C), to ensure minimising effects from impurities deposited on the specimen during examination.

The ordering reaction has been attributed to composition fluctuations in the thin regions of the foil. The fact that the transformation started in thin regions was verified by many observations; the real question arises as to why it was initially restricted to these areas.

Two possible explanations are immediately evident. First, under the influence of the beam heat, carbon is caused to diffuse randomly throughout the specimen until the ideal ratio of carbon to tantalum (1:64) is achieved for the transformation to proceed. Statistically, the ideal carbon to tantalum ratio will be obtained first in the thin regions of the foil. The second possibility is that the minute traces of carbon deposited during microscopic examination diffuse into the specimen. This added influx of carbon would have the effect of speeding up the ordering reaction in the thin regions as the amount of interstitial carbon necessary for the transformation is lowered. When the microscope is operated under normal conditions, the impurity pickup from the vacuum is insufficient to cause the transformation in pure tantalum foils.

In all cases, microscopy studies were performed on tantalum specimens alloyed with, previously predicted, solid solution quantities of carbon. As the $Ta_{64}C$ superlattice transformation could be induced in all the specimens, the Ta-C phase diagram should be corrected to include this compound. In all the specimens examined the $Ta_{64}C$ structure was the only second phase material which could be detected.

B. Determination of $Ta_{64}C$

In deducing the structure from electron diffraction data it is necessary to avoid obtaining second layer relpoints. To ensure this, it is necessary that selected area diffraction patterns be taken in exact orientation.[13] Only under this condition can meaningful angular and distance relationships be measured. By exact orientation, it is meant that the plane of the reciprocal lattice is parallel to the

plane of the foil.* This orientation is most readily achieved with the use of a double tilt specimen stage. In a like fashion, for obtaining maximum information from the image, it is best to "gun tilt" into dark field.[13] This ensures maximum contrast as the specimen is now in exact Bragg diffraction conditions with a two beam case operating.

The $Ta_{64}C$ superstructure determined is a geometric model only, as the actual sites of the carbon atoms (octahedral or tetrahedral) were not established. Results from the $\frac{c}{a}$ ratio measurements indicate that the positions might be octahedral, but insufficient data are available at this time to warrant such a claim. It is possible with future refinements of selected area diffraction analysis techniques, or by utilizing field ion microscopy, that this question might be answered.

C. Bulk Specimen Observations

The observed migration, and subsequent disappearance of a domain boundary during beam heating, can be explained on the basis of a simple order-disorder reaction. The motion of the boundary during beam heating is caused by the diffusion of interstitial carbon. As the temperature of the specimen is raised, the diffusion becomes more rapid and the order in the regions adjacent to the domain boundary may be destroyed. With this destruction of order is coupled the simultaneous disappearance of the domain boundary.

*Under these conditions the diffraction pattern is perfectly symmetrical. If the foil is thick, the centers of symmetry of Kikuchi and relpoint patterns coincide.

The disappearance of these boundaries by localized heating, sets up an energetically unfavorable situation which, upon lowering the beam intensity, is remedied by the boundary returning to its initial configuration. The reason for the semi-reversibility of this reaction is thought to be associated with internal stress fields set up by neighboring domains that have been unaffected by the heat of the beam.

It was also observed that under the influence of beam heating, some boundaries were more resistant to motion than others. This implies that some boundaries are energetically more stable than others, and therefore, require more energy to dissociate. Although quantitative measurements are difficult to make, the {110} boundary was the last to dissociate in virtually all cases. This is in agreement with the domain boundary models as the {110} domain boundary can be coherent. The coherent domain boundary is energetically the most stable.

The diffraction phenomena associated with domain boundaries are also of interest. In regions with many overlapping domains, similar to Fig. 7, the absence of a coherent superlattice diffraction pattern is noticed; but, in regions where the domains are more widely spaced, superlattice diffraction patterns were found. This can be explained when one considers the high degree of order necessary to produce a superlattice diffraction pattern. In regions such as shown in Fig. 7, the superlattice diffraction pattern is not reinforced, due to the different diffracting conditions from domain to domain.

VI. CONCLUSIONS

1. Tantalum alloyed with less than 3 at. % interstitial carbon, underwent a two-stage interstitial ordering transformation during microscopy examination. The transformation was induced in the thin foil specimen by heating with the electron beam. The first stage is the nucleation of small ordered domains, on {110}, in thin regions of the foil. These small domains then grow, impinge, until the final stage of highly ordered regions is left.

2. The ordered structure was determined from electron diffraction analysis, and corresponded to a composition $Ta_{64}C$. The superlattice unit cell is tetragonal and is shown in Fig. 6.

3. The $\frac{c}{a}$ ratio for the ordered structure was determined from paired Kikuchi lines to be 1.128.

4. Bulk specimens, alloyed to correspond to the composition of the ordered structure, showed a multitude of ordered regions separated by domain boundaries.

5. Three types of domain boundaries are possible based on the ordered structure: coherent, semicoherent, and antiphase.

6. The Ta-C phase diagram should be modified to include the $Ta_{64}C$ ordered phase.

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FIGURE CAPTIONS

Fig. 1 Ta - 2.94 at. % C, showing the initial stages of the ordering transformation observed in the microscope. Ordering has taken place on {110} planes which are impinging. The foil orientation is $[\bar{1}03]$.

Fig. 2 (a) Ta - 1.82 at. % C, showing an intermediate stage of the ordering transformation observed in the microscope. The foil orientation is $[\bar{1}10]$.

(b) Dark field image of the 002 reflection. Note the improved contrast compared to 2(a) as a result of gun tilting into dark field.

Fig. 3 Ta - 1.82 at. % C, showing the highly ordered final stage of the transformation. The boundaries at A and B are coherent domain boundaries on $(1\bar{1}0)$ and (110), respectively. At C the boundaries are primarily {210} antiphase domain boundaries.

Fig. 4 (a) Ta - 2.28 at. % C. This specimen shows a different morphology from the idealized transformation, probably a result of the initial surface condition of the foil. From the diffraction pattern it appears to be at approximately the same stage of ordering as Fig. 2. The foil orientation is [001].

(b) Dark field image (gun tilt) of the $(110)_{BCC}$ reflection.

(c) Dark field image of the $(420)_S$ reflection.

Fig. 5 (a) Enlarged selected area diffraction pattern of Fig. 3, showing superlattice relpoints.

(b) Analysis of the more prominent relpoints in (a).

Fig. 6 Structure of the superlattice $Ta_{64}C$. The subscript s refers to the superlattice unit cell, where $a_s = 4a_o \neq c_s$. The lattice parameter of BCC tantalum is a_o. The tantalum unit cells are shown as squares. The spheres represent carbon atoms in $0\frac{1}{2}0$ octahedral positions, defining a BCT cell.

Fig. 7 Domain boundaries in Ta - 1.54 at. % C after annealing bulk material 24 hours at 1000°C. The domain boundaries at A and B are overlapping, and the boundary at C is normal to the surface of the foil. The foil orientation is approximately $[\bar{2}4\bar{3}]$.

Fig. 8 Schematic diagram showing ideal crystal geometry on either side of a domain boundary for maximum contrast.

Fig. 9 (a) Overlapping domain boundaries in Ta - 1.54 at. % C after annealing 24 hours at 1000°C. The foil orientation is approximately [111].

(b) Dark field image of the $\bar{1}\bar{2}3$ reflection. Note that the extreme fringes of the domain boundary at A are black-white in bright field (a), and are both white in dark field. This proves that the top of the domain corresponds to the first white fringe.

Fig. 10 Schematic diagram of possible contrast effects from overlapping domain boundaries. In case I the boundaries are not truly overlapping, and there is an obvious contrast difference on either side of the domain boundary. In Fig. 7, the $(1\bar{1}1)$ domain boundaries show contrast similar to case I, and the $(\bar{1}0\bar{2})$ domain boundaries show contrast similar to cases II and

III. The assumed operating $\bar{g}$ for all the cases is to the right.

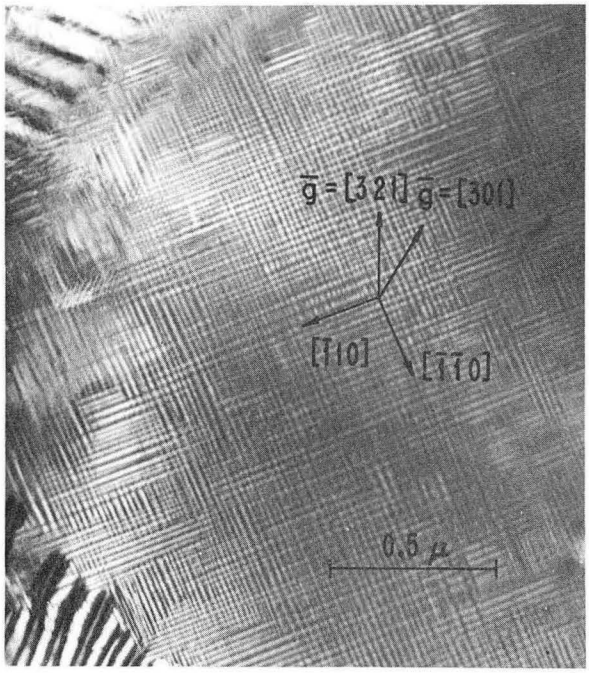
Fig. 11 Diagram of coherent and semicoherent domain boundaries. The carbon atoms are shown as circles in octahedral sites, and the tantalum unit cells are squares. Positions 2 and 4 define coherent domain boundaries, and positions 1 and 3 define semicoherent domain boundaries. The tetragonality associated with these boundaries is shown.

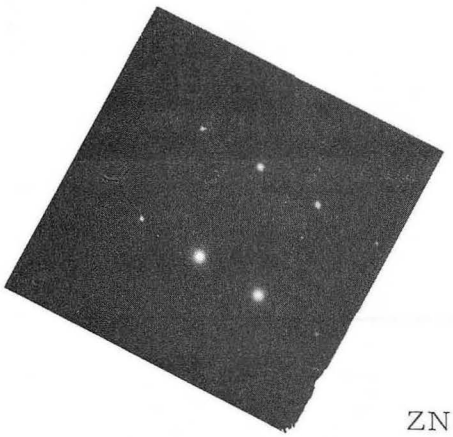
Fig. 12 Diagram of a (111) antiphase domain boundary. The upper half of the diagram shows a (111) antiphase domain boundary as seen down the [001] axis. The lower half of the diagram shows the (111) antiphase domain boundary when folded into edge view. The carbon atoms are shown as circles in octahedral positions, and the tantalum unit cells as squares. Four possible positions of the carbon atoms, which would yield a (111) antiphase domain boundary, are indicated. The tetragonality associated with this boundary is shown.

Fig. 13 Diagram of reciprocal space in [001] orientation showing the relationship between paired (210) relpoints and paired (210) Kikuchi lines.

Fig. 14 (a) Enlarged selected area diffraction pattern of Fig. 7 showing paired relpoints and Kikuchi lines.

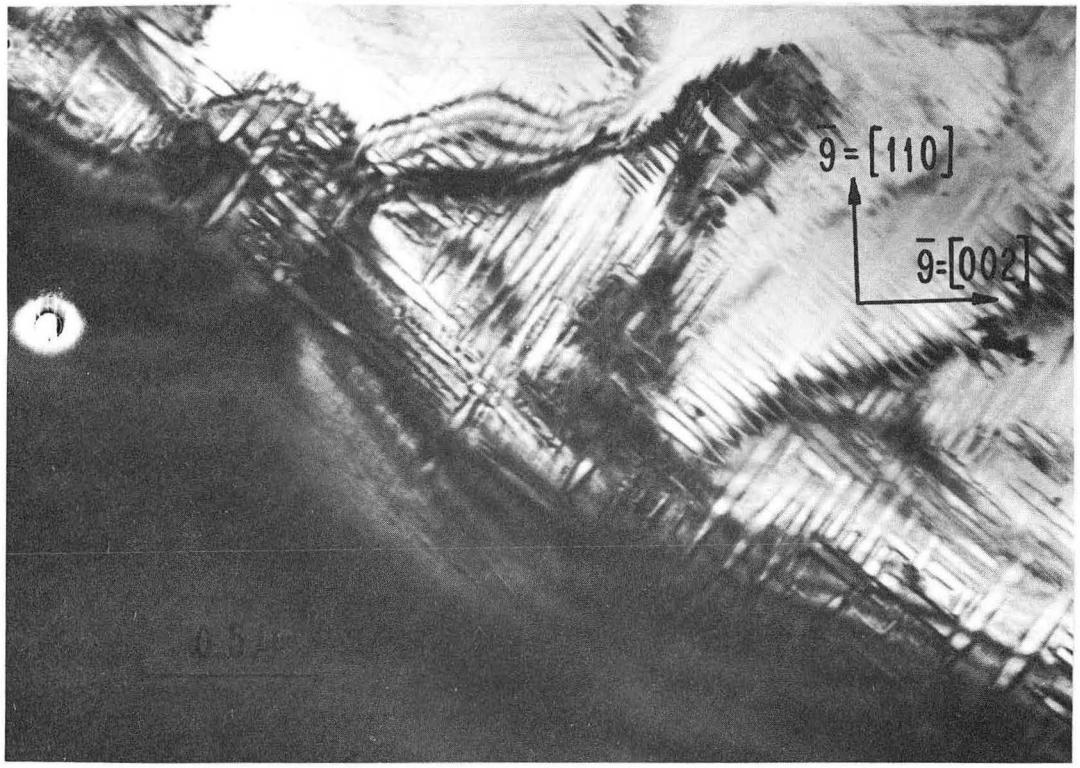
(b) Analysis of (a).





ZN-4667

Fig. 1



ZN-4652

Fig. 2a

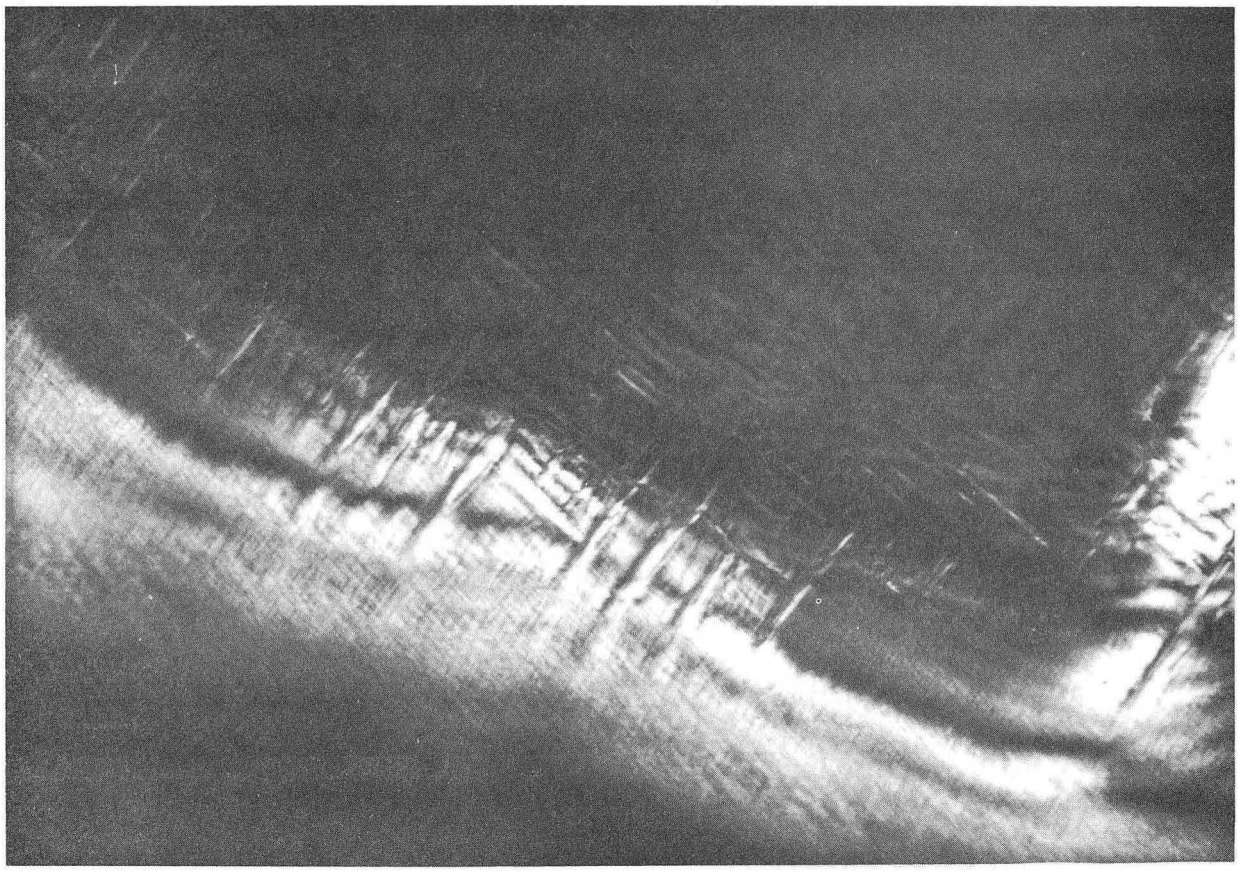


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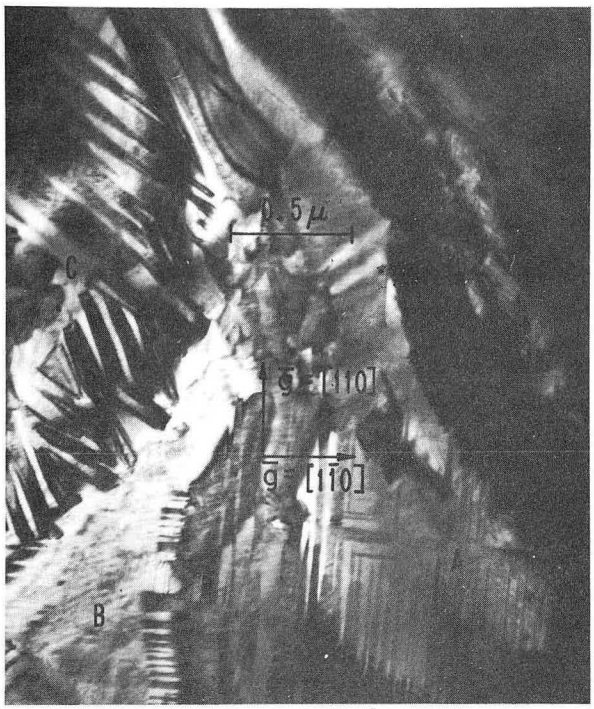
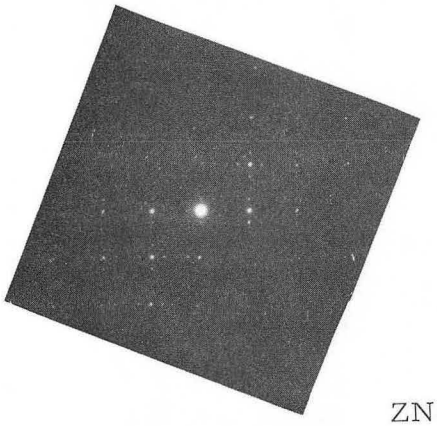
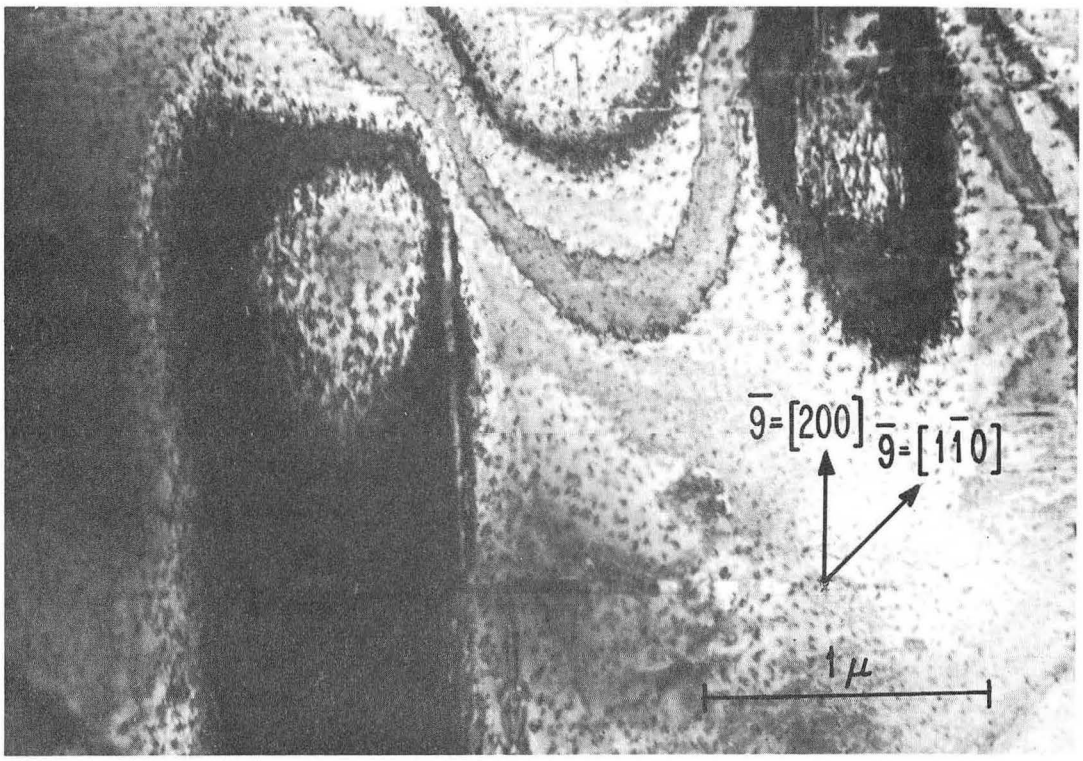
Fig. 2b

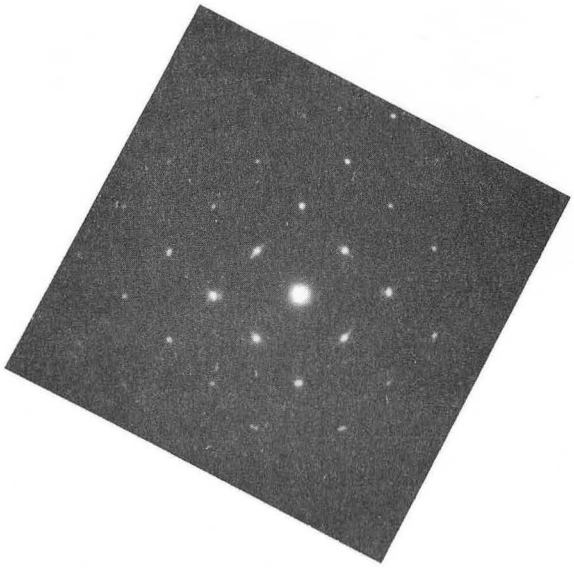




ZN-4668

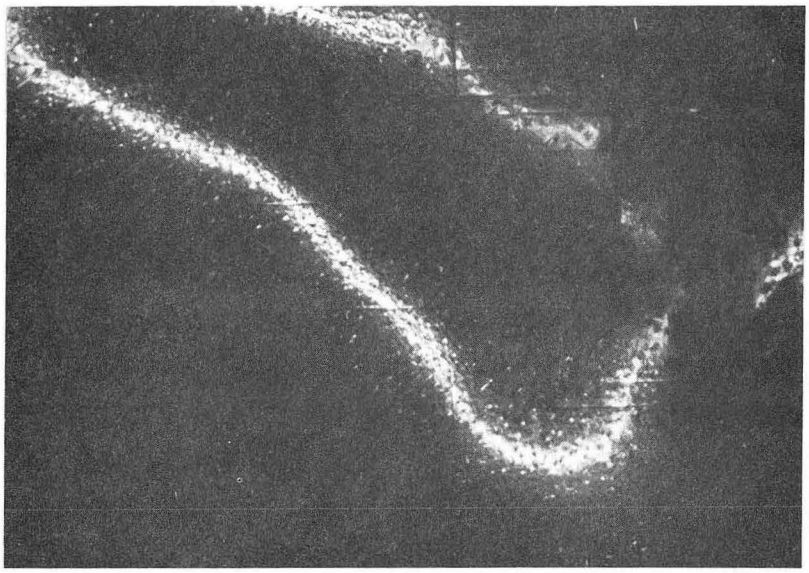
Fig. 3

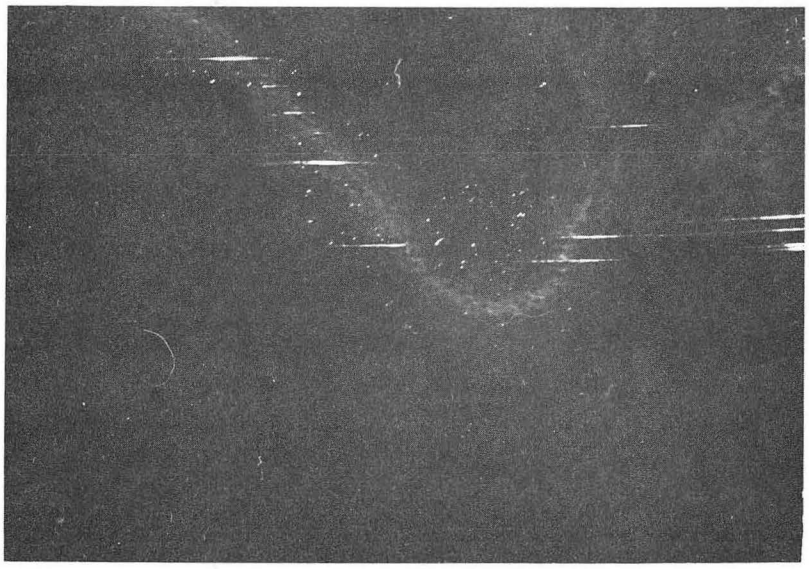




ZN-4651

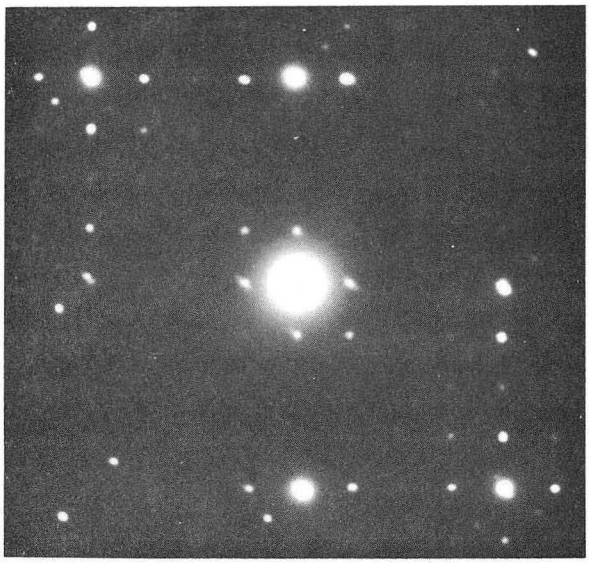
Fig. 4a

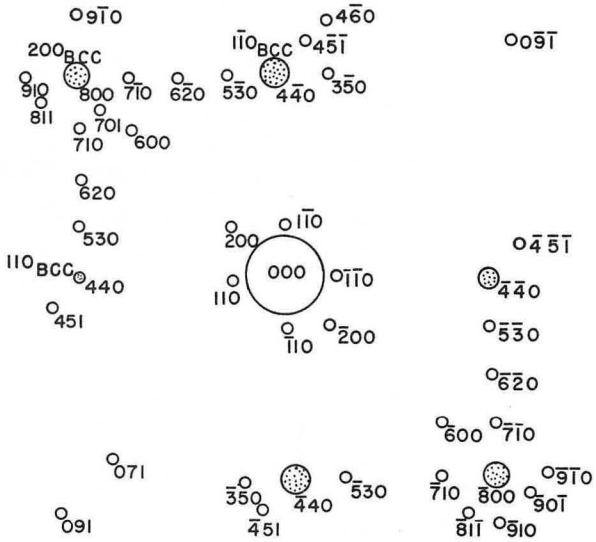




ZN-4647

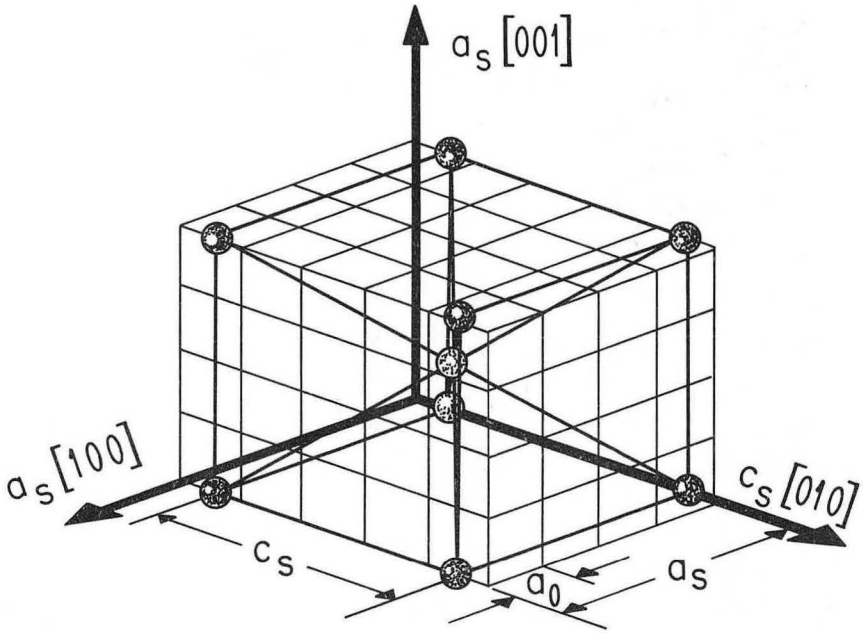
Fig. 4bc





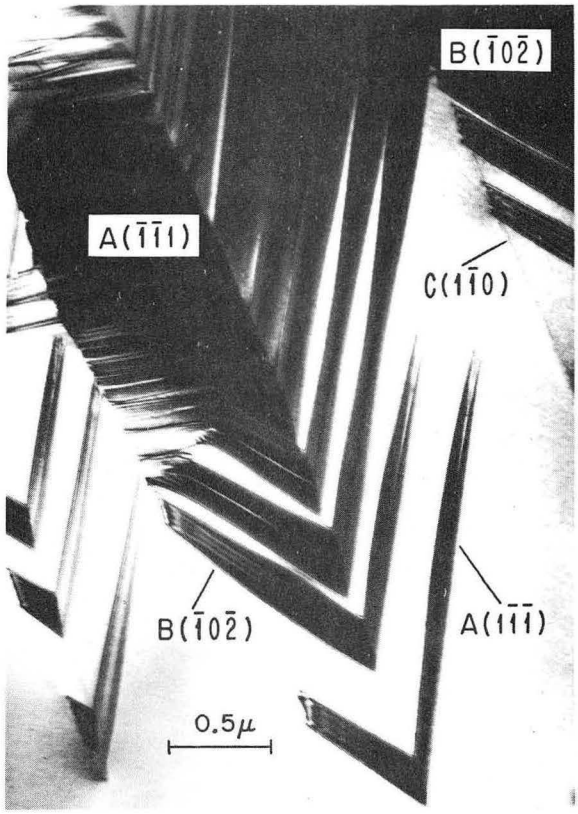
ZN-4653

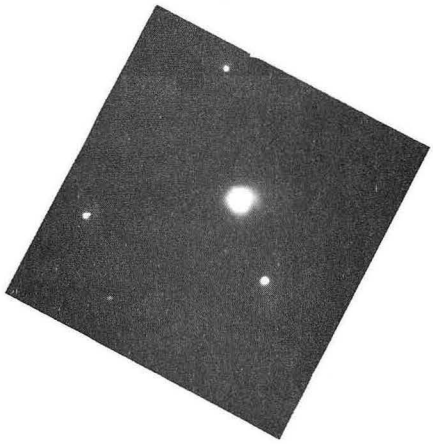
Fig. 5a b



MU-35009

Fig. 6


B($\bar{1}0\bar{2}$)
A($\bar{1}\bar{1}1$)
C($1\bar{1}0$)
B($\bar{1}0\bar{2}$)
A($1\bar{1}\bar{1}$)
0.5μ



ZN-4649

Fig. 7

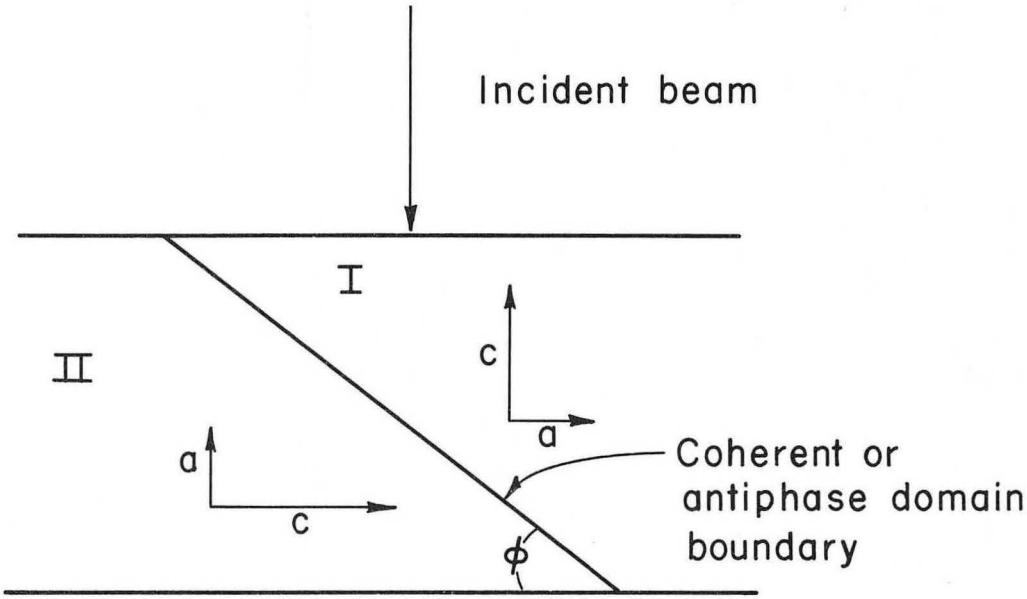


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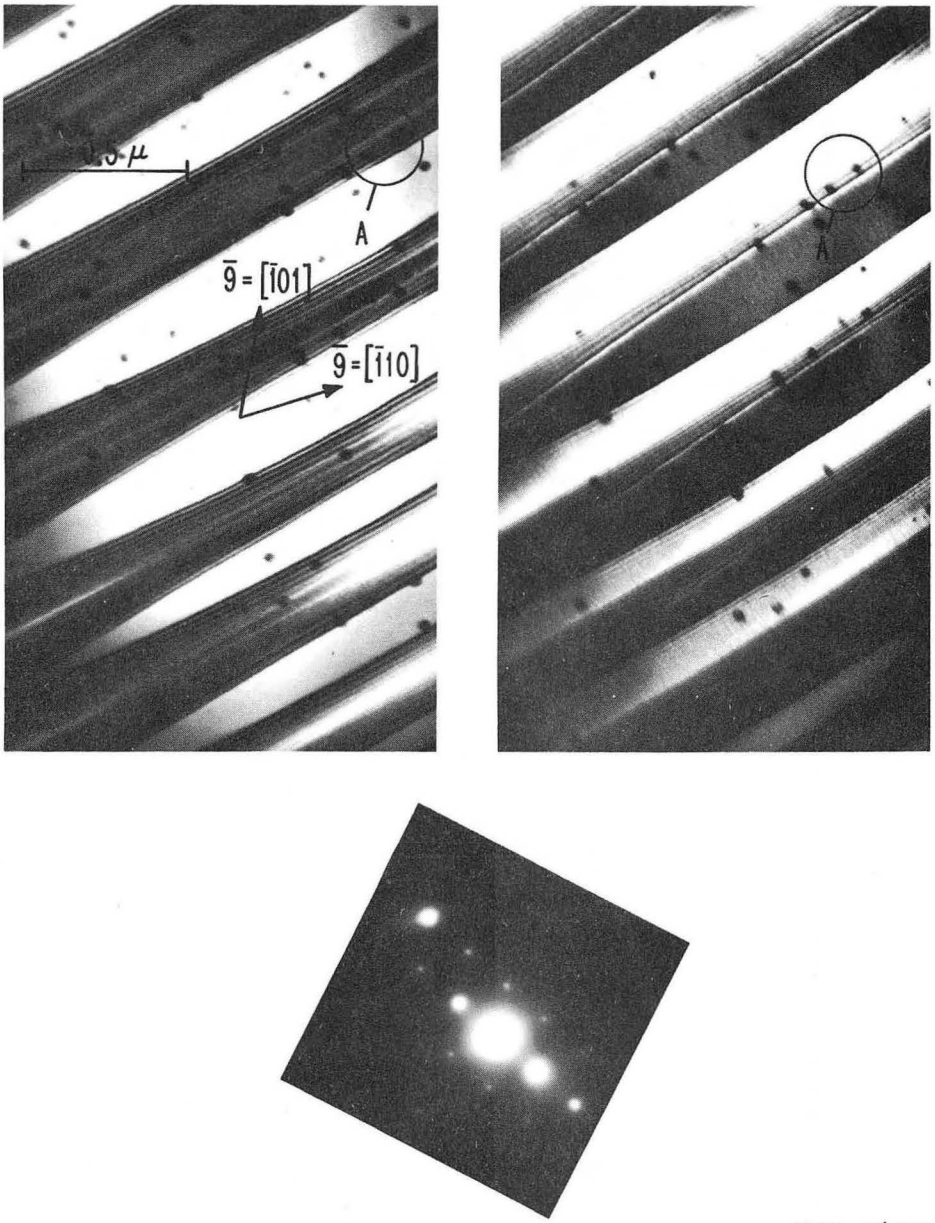
Fig. 8



ZN-4650

Fig. 9a b

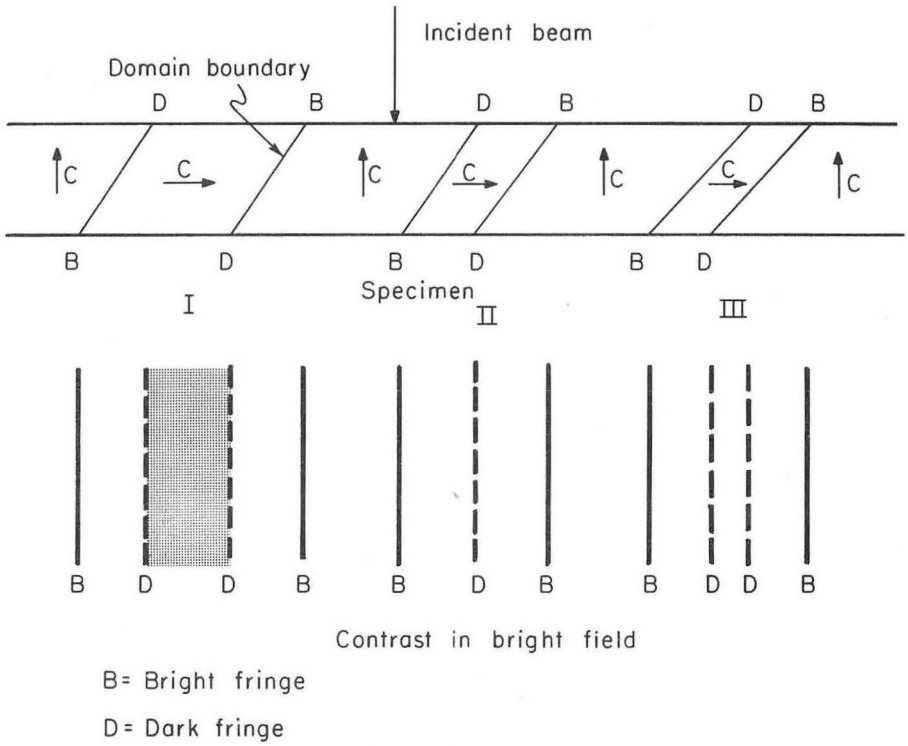
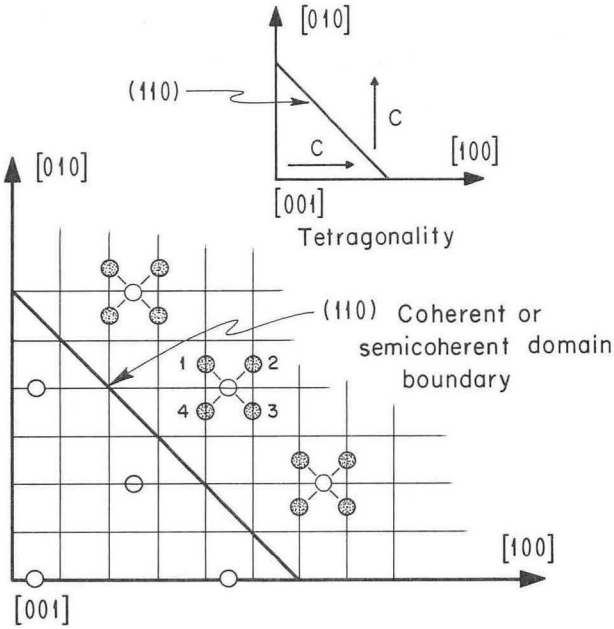

Incident beam
Domain boundary
D
B
D
B
D
B
C
C
C
C
C
C
B
D
B
D
B
D
Specimen
I
II
III
B
D
D
B
B
D
B
B
D
D
B
Contrast in bright field
B= Bright fringe
D= Dark fringe
MU-35089

Fig. 10



MU-35088

Fig. 11

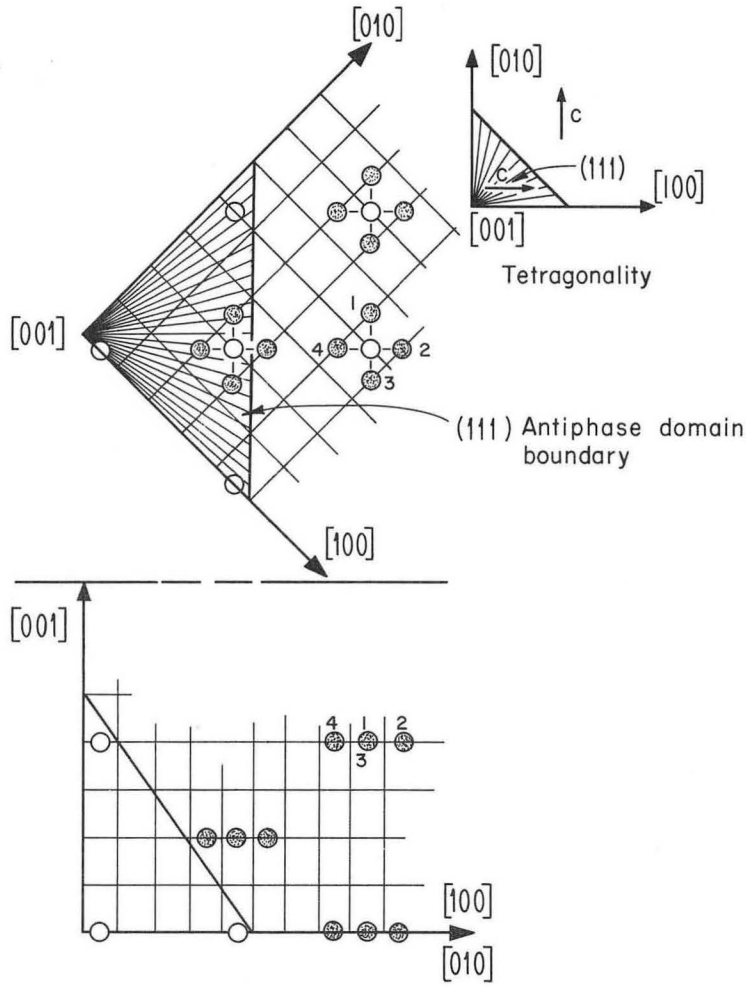


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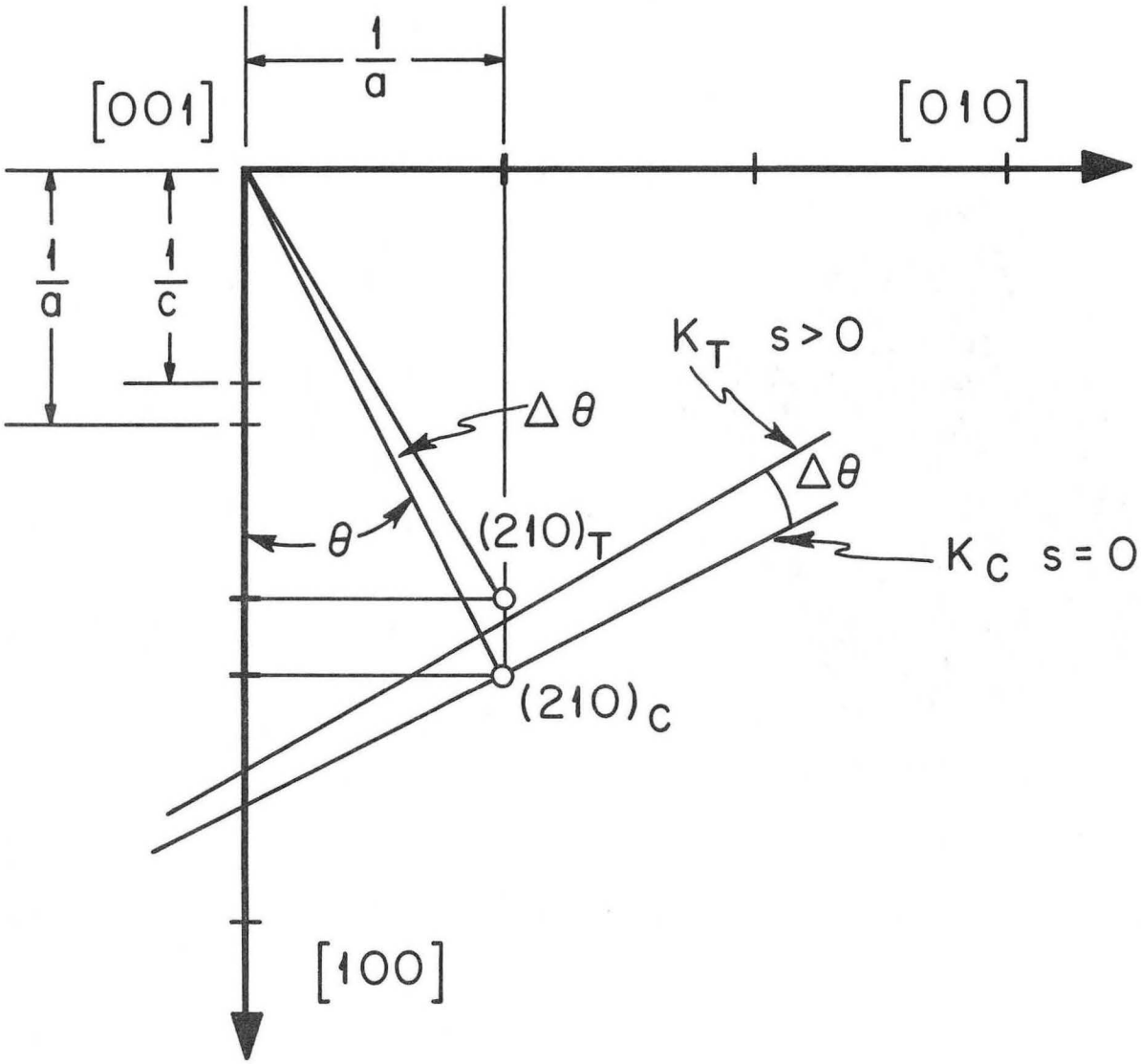
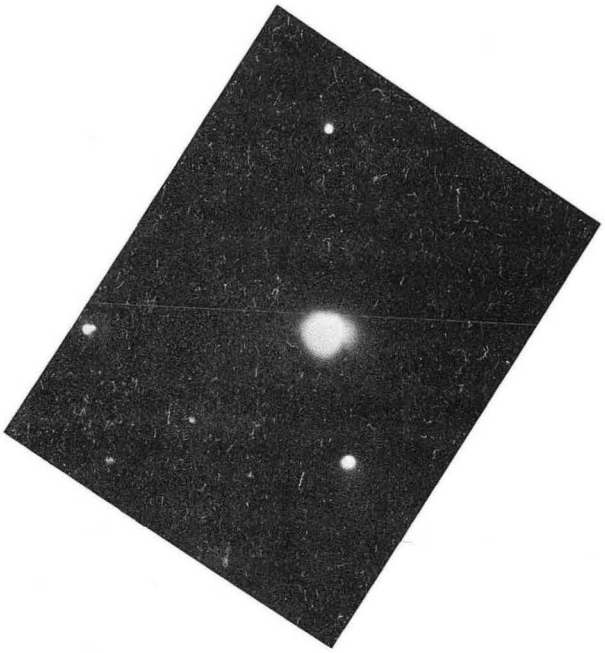
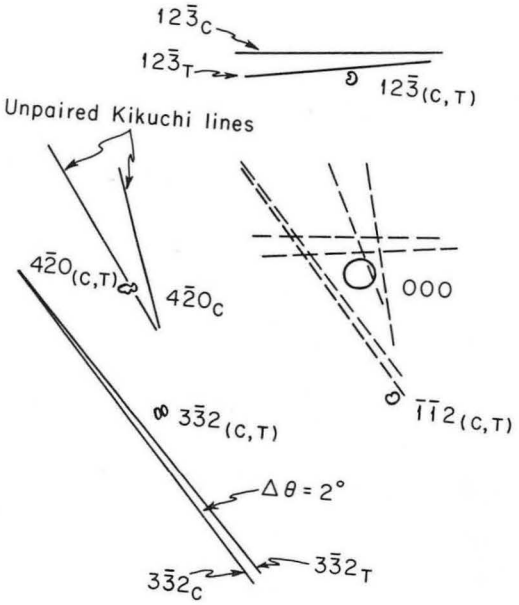
Fig. 12



MUB-4582

Fig. 13





ZN-4595

Fig. 14 a b

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