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FIELD ION MICROSCOPE INVESTIGATIONS OF SOLID SOLUTIONS

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Introduction

The objective of the Field Ion Microscope research, under Grant NsG-294-63, is to achieve an understanding of solid solution phenomena on the atomic scale. There are two types of solid solutions. In one, the solute atoms occupy interstitial lattice sites. In the other, the solute atoms occupy substitutional lattice sites. Both these solid solutions are of great interest. Hence, both will be investigated in this program.

The sequence and choice of experimental materials are to a large extent dictated by the constraints of the ion microscopes available. At the start of the 1964-65 fiscal year, only liquid-nitrogen-cooled microscopes were available. Hence, the experimental solvent was limited to a choice from the group: W, Ir, Ta. For practical reasons, therefore, W was chosen as the initial solid solvent. Also, at the start of the experimentation, it appeared from published statements of Mueller(1) that subsurface interstitial solutes could be imaged. Because of the further practical interest in interstitial solutes in W, the first class of solid solutions chosen for study was that of interstitial solutes C,O,N in W as a solvent.

As pointed out in the doctoral proposal of I. Gupta (Appendix B), the reported maximum solid solubilities of C in W vary by several orders of magnitude (i.e., less than 1 ppm (Stein at General Electric) to about 3000 ppm by Goldschmidt and Brand(2)). (Similar statements cannot be made about the other solutes, O and N.) Further, no reported solid solubility can distinguish between lattice solubility or defect solubility. That is, one possible explanation of the range of reported solubilities is a range of variation in defect content with the defect site being the major site for the interstitials in the specimens.

Now, the literature also contains contradictory statements concerning the ease of injecting interstitial solutes into W by diffusional processes. For example, Goldschmidt and Brand(2) and Allen et al(3) find no difficulty in diffusing interstitials into W whereas Atkinson et al(4) report special techniques are required to inject interstitial solutes into the W lattice. Thus, any conclusion that no interstitials are present in the W lattice must pass the test of demonstration of the availability of the interstitial elements in the vicinity of the lattice that is observed in the field ion microscope patterns.

The initial portion of the experimentation has therefore been devoted to the development of techniques of injecting interstitials into the W lattice. In the development of these techniques, care was exercised to achieve an equilibrium distribution of the solute. As will be described in detail later, this problem has been solved for C and N in W but not yet for O in W.

It became apparent in the course of the experimentation that the initial assumption about visibility of subsurface interstitials in tungsten was false. Hence, a program was devised with the objective of developing a procedure which would positively differentiate interstitial solute atoms form substitutional solute atoms. This program, which is described in detail in Appendix A, has been the thesis problem of D. Jeannotte. Its results will be described later, also.

From results already at hand, it appeared likely that the techniques developed by Jeannotte could be used to measure the total interstitial content in a specimen at least for oxygen in tungsten. Hence, a program was undertaken by I. Gupta to measure the lattice solid solubilities of carbon, nitrogen and oxygen. This program is in Appendix B.

The final program undertaken had as its objective a determination of the effect of Re as a lattice trap for interstitial solute elements in W. This program comprises the thesis problem of D. Novick which is described in Appendix C.

During the previous year, 1964-65, W. DuBroff succeeded in constructing a low temperature microscope which makes use of a cryotip to achieve liquid hydrogen temperature in the finger in thermal contact with the specimen. This microscope greatly extends the range of observable materials. Because nothing is known about either the behavior of solute atoms in the field evaporation process, which must be used to form a surface for observation in the microscope, orthe image contrast due to substitutional solute atoms, it was decided that a necessary first step in the study of substitutional solid solutions required investigations of these phenomena. Accordingly, the thesis problem of W. DuBroff, as described in Appendix D, had as its objective a study of the field evaporation characteristics of dilute alloys with a secondary objective of image contrast behavior of substitutional solutes wherever such behavior was exhibited by the alloys being observed. The solvent was chosen to be Pt because it was desired to observe the field evaporation event, and the imaging and evaporation potentials of Pt are close. The results obtained to date are significant and will be described later in detail.

From the results of DuBroff on W in Pt and Co in Pt, it appears that no difficulty is experienced in defining the lattice positions of solute atoms in these alloys. However, motion picture recordings could provide a recording of the continuous evaporation of (102) planes, in which the individual atoms can be imaged, and hence a record of the lattice positions in three dimensions of the solute atoms. Thus, a study of short range order in these alloys is feasible. The thesis problem of E. Gold, therefore, comprises a study of short-range order in selected Pt base alloys, making use of image intensification and motion picture recording. This problem is described in Appendix E.

Methods of Producing Interstitial Solid Solutions in Tungsten

Goldschmidt and Brand(2) describes a method in which a compound of tungsten with the particular interstitial solute is "painted onto" a tungsten wire and brought into equilibrium contact with the tungsten at some elevated temperature following a recommended temperature-time cycle. This technique suffers from the problem that contact must be assured by solid state sintering. With the attendant uncertainty that contact existed at the particular position of the tip surface along the wire length, it was decided to choose a technique with a greater certainty of producing the interstitial compound on the wire surface.

The method arrived at for C and N was to fill a static system with sufficient pure gas of the interstitial solute to convert one-third of the wire diameter to the particular compound in equilibrium with the solid solution of the interstitial solute in tungsten. From estimates of dislocation density in drawn and annealed tungsten wire from data by Meieran and Thomas(5) and estimates of the maximum activation energy for diffusion of interstitials along dislocations, as well as from estimates of the maximum lattice activation energy for interstitial diffusion, a minimum time was estimated to produce a homogeneous solid solution by diffusion at the estimated temperature of the maximum solid solubility (i.e., about 2400°C and 30 minutes for all the interstitial solutes). This minimum time actually exceeded the corresponding minimum time used by Goldschmidt and Brand(2) and by Allen et al(3) to produce their solid solutions.

For oxygen, an entirely different technique has to be developed because of the inability to prevent wire burn up on heating even in a controlled atmosphere containing a known partial pressure of oxygen. One technique under study is to pack W wire with WO_2 inside a sealed tungsten foil. This assembly is then heated to 2400°C for one-half hour. Although a similar technique worked for Allen et al(3) no results have been obtained which can be used to evaluate it for this report.

Imaging of Interstitial Solutes

The contention of Mueller that extra bright spots are formed by subsurface interstitials has been subjected to test as follows: A tungstentip was field evaporated to produce a clean end form as shown in Figure 1a. The voltage on the tip was then removed. The gas in the tube was then allowed to adsorb on the tip surface for a few seconds. The tip potential was then reversed to about 1500 volts negative to about a current of 10^{-8} amperes. This process bombarded the specimen with helium ions which acted to knock the surface gas atoms into the specimen as Mueller has suggested already. The potential was then reversed to its normal positive value and raised slowly to the imaging potential at which Figure 1b was taken. The voltage was then pulsed to remove the central plane and Figure 1c photographed. If now the spot density in either Figure 1b or 1c is superimposed over the central (110) plane in Figure 1c, it is apparent that if the spot density were due to subsurface interstitials many such spots should still be observed within the central (110) plane. Such spots are not observed. Hence, most if not all of these spots cannot arise from subsurface interstitial origin. These spots do arise however from a surface origin, which is removed whenever a 110 ledge traverses the position of the spot or even, as will be shown later, without traversal of this region.

Thus, one may conclude that if interstitial solutes are present in tungsten, there exists no evidence that they can be imaged as subsurface interstitials per the mechanism of Mueller (reference 1, p. 158). This program was therefore faced with the problem of imaging interstitials as surface species.

Mueller(6) has reported that chemisorbed oxygen "is removed from the 011 vicinity at 480 MV/cm and only at 500 MV/cm is the desorption almost completed." Ehrlich and Hudda(7) have reported that adsorbed nitrogen is removed from the central 110 plane but not the ledge positions at 450 MV/cm. The best imaging potential of helium is 450 MV/cm. Partial evaporation of tungsten from (110) has been reported by Mueller(8) to occur at 520 MV/cm. At the ledge positions there exists a field enhancement by a factor of at least 1.8(9). The latter fact and the liklihood that the field enhancement markedly decreases in the region between the ledges are probably responsible for the observation of surface atoms of low evaporation potential at (110) interledge positions as shown in Figure 1 even though slight evaporation of the tungsten atoms at the 110 ledges has taken place. This observation -- an example of the process of serendipity which is to be credited to D. Jeannotte -- has suggested to us a method of visualizing interstitial solutes in tungsten. It is probably applicable to oxygen and nitrogen. Its applicability to carbon depends on the field evaporation potential of carbon from (110) regions on tungsten surfaces, which number is not known.

The method referred to in the previous paragraph is that of sequential partial evaporation. Before discussing results obtained with its use, it is necessary to refer to an additional statement by Mueller(10); namely, that tungsten atoms in metastable 3 atom bonded sites are the source of extra bright spots observed along the [100] zone and along the 111 zone near the (112) plane in the region between these two zone lines. Hence, it is necessary at this time to exclude observations of extra bright spots in these sectors from the analysis of those due to interstitial solute atoms.

The technique can be evaluated using Figures 2 and 3. The specimen for the patterns of Figure 2 was degassed in a vacuum of better than 10^{-5} mm Hg for 35 hours at 1000°C. The specimen for the patterns of Figure 3 was heated in impure nitrogen at one atmosphere and was at 2400°C for about thirty seconds prior to developing a hot spot and burning out. The tip was produced from near the burned section. A voltage pulse, of as yet indeterminate character, produced by a switch in the power supply to the FIM, was used to field evaporate fractions of a central (110) plane from the surface. Several observations can be made.

First, in the degassed specimen no extra bright spots were counted in the removal of a totoal of 4 central 110 planes. That is, the volume concentration of interstitial solute (on the assumption the bright spot is an interstitial solute) is less than 50 ppm. Second, in the specimen heated in impure nitrogen, one finds some spots which appear for a lifetime of about 1/5 of the removal of a central (110) plane and others which have a longer lifetime. The total number of such spots varies from five to ten per central (110) plane or between 500 to 1000 ppm. Third, one can also see in the sequence of removal of the central (110) plane that some spots have weak intensity when close to a shielding ledge, but that the intensity increases as the shielding ledge moves away from the spot. For example, see the spot marked "A" in the sequence in Figure 3. The second observation confirms the previous conclusion that some of these spots are due to surface species. The fact that the total substitutional impurity level is less than 200 ppm suggests that most of the observed spots cannot be due to substitutional impurities. The fact that such spots cannot be induced in degassed material eliminates the possibility that they are due to metastable tungsten atoms. (Incidentally, spots can be seen in the degassed material in the <111> to <100> sector where metastable tungsten atoms are expected per Mueller.) Hence, by elimination we are left with the conclusion that the extra spots in the specimen heated in impure nitrogen arise from interstitial solutes on the surface. Because all the previous measurements reported in the literature are unanimous that the maximum nitrogen solubility at 2400°C is less than 10 ppm it seems reasonable to conclude that the interstitial solute atoms observed in Figure 3 are oxygen atoms.

This program, which is the thesis problem of D. Jeannotte, will be continued as outlined in Appendix A.

Lattice Solid Solubility of Interstitial Solutes

The work of Jeannotte already discussed has shown the liklihood of imaging oxygen and nitrogen in tungsten by the pulse evaporation technique. The possibility of imaging carbon by this technique is not known at this time. Further, the work of Jeannotte has already shown that the normal field evaporation process used in preparing a surface for observation in the field ion microscope will at best reveal only a small fraction of the interstitial solute. That is, for oxygen in tungsten Jeannotte found that the ledge life distance was no more than one-fifth the interledge spacing. Hence, no more than 20 percent of the oxygen in tungsten would be revealed in the normal field evaporation process. The ledge life distance for carbon in W is unknown, but from patterns at 78°K already obtained in the normal manner from W treated to contain its maximum solid solubility of carbon on the assumption of the presence of carbon in the specimen (almost certainly there), the lack of extra bright spots suggests a much smaller interledge life distance for C in W as compared to O in W. This result is in qualitative agreement with the order of the field evaporation strengths expected. Some extra bright spots can be seen in patterns from such carburized specimens which were field evaporated and imaged at 21°K. Compare Figures 4 and 5. It is possible that the binding energy of carbon to the (110) surface might be sufficiently small that the decrease in temperature yields an effective increase in the work required to remove C from the (110) plane of W in analogy with the results of Ehrlich and Hudda(7) on nitrogen on W. This result suggests a test pulse field evaporation at 21°K for C in W if C is not imaged on pulse evaporation at 78°K. Because of the above results, the initial stages of this program will concentrate on an evaluation of the solid solubility of oxygen in tungsten.

The problem of interpreting the streaks observed in FIM patterns of carburized tungsten (see Appendix B and previously reported) has now been solved. First, streakless material can be produced by careful etching procedures. In particular, if during etching a point is produced by tip fracture then the final position of the tip must be etched sufficiently away from the fracture position. It is believed that the streaks are microtwins produced by stresses introduced during tip fracture which are propagated into the tip by the field stresses in the FIM. It is further believed that the reason that streaks are not observed in pure tungsten is that plastic flow does not allow the stress to reach the level required to nucleate twins. Thus, for the purposes of the present study, the streaks are artifacts. They may be of interest in themselves to those interested in the microtwinning phenomenon. Thus, the work reported in the First Technical Report under this Grant must now be considered to be invalid.

Evidence for the presence of carbon in carburized tip specimens is available from observations of enhanced brightness along 111 and 123 zone lines as compared to control specimens. This observation checks on the reported results of Mueller as presented at the Eighth Field Emission Symposium.

Interstitial Solutes in Tungsten-Rhenium Alloys

Preliminary studies have been carried out on oxidized 5% Re-W alloys. The results may be described as follows:

1. The [100] zone line is extraordinarily broadened in oxidized 5% Re-W.
2. Many extra bright spots in the [111] zones bounded sector are apparent even on normal field evaporated surfaces (See Figure 6).
3. The lattice mobility of oxygen is consistent with that reported by Allen et al.

Studies have also been made on pulse evaporated tungsten in which over 100 planes of the [111] type have been removed while the atoms in the plane were observed. It has been found that

1. No extra bright spots appear in the center region of these planes. (See Figure 7 for example)
2. Only one vacancy was counted in the center of the [111] plane in over 100 such planes imaged. Based on the substitutional impurity level of 200 ppm there is a 33 percent chance of seeing one vacancy due to a substitutional impurity in 100 planes each containing 20 atoms. (See Figure 7 for a typical plane.)

Also, studies have been made of pulse evaporated 5% Re-W alloys with the following results:

1. No vacancies have been detected.
2. No extra bright spots have been detected on the [111] plane although a few have been observed elsewheres in over twenty such planes observed. (See Figure 8)

The following conclusions have been drawn from the above work:

1. Re does not selectively evaporate from tungsten.
2. Re atoms do not yield image contrast.
3. Oxygen in the lattice can be imaged and from a rough count in the 5% Re-W alloy one can expect the partial solid solubility in the presence of a 5% Re-W solid solution to be at least 1000 ppm at 2500°C.
4. It is concluded that the program outlined in Appendix C is justified and should be acted upon. This program is the thesis problem of D. Novick.

Incidentally, the above studies were carried out using primarily the commercial microscope produced by CENCO. However, the power supply was specially built to our design.

Field Evaporation Characteristics of Dilute Substitutional Solid Solutions with Platinum as a Solvent

As mentioned in the Introduction and Appendix D, platinum is the ideal solvent for this study because its field evaporation potential is just above the imaging potential at 20°K. This program required a low temperature microscope and one of the results of this program is the successful design, construction, and operation of this microscope in the 1964-65 fiscal year. This microscope makes use of a cryo-tip (Air Products, Inc.) to produce small amounts of liquid hydrogen at the cold finger in a closed system. This system is considered safe by New York City Fire Regulations.

Already the program as outlined in Appendix D has been completed for the 2% W in Pt alloy. The results are extremely exciting, as follows:

1. Individual bright spots are imaged in the center of the (102) plane and elsewheres and quantitatively correspond to the 2% concentration of W in Pt. (See Figure 9a and 9b)
2. Vacancies are imaged in the center of the (102) plane and elsewheres. Single, di- and tri-vacancy groups have been observed on the (102) plane. The appearance of these vacancies is <u>not</u> preceded by the appearance of bright spots <u>in the same plane</u>, i.e., one can suddenly see a vacancy at a

site previously occupied by a normal intensity atom. The total average concentration of vacancies is about twice the number of bright spots, i.e., ~ 4 atom percent. (See Figures 10a and b for vacancies on (102) planes.)

3. Sequential evaporation of successive (102) planes shows that a bright spot is in one of the three (102) planes underneath a surface plane that reveals vacancies. For example, see Figures 11a and b.
4. Bright spots on (111) interledge spaces are mobile at the field evaporation potential moving parallel to the ledge and sometimes outward from the inner ledge to the outer ledge.
5. Bright spots can be found proud on any of a number of planes.

These are the first quantitative results on the evaporation and imaging of substitutional solute atoms obtained anywheres in the world! They yield these inescapable conclusions:

1. W does not selectively evaporate from Pt.
2. W atoms image bright relative to adjacent Pt atoms.
3. Subsurface W atoms cause nearest neighbor Pt atoms on the surface to selectively field evaporate with respect to the other nearby Pt atoms.

There are certain consequences of these conclusions with respect to the electron theory of solid solutions which we are currently investigating. Already they have disproved Brandon's choice of ionization potentials for tungsten.

A preliminary study of the 2% Co in Pt alloy reveals a pattern of evaporation different from that described above. That is, bright spots are seen to appear and disappear on a (102) plane during its lifetime. These bright spots appear to correspond to the 2% Co concentration although it is too early to be certain about this result. Further study is underway following in detail the program in Appendix D.

Short Range Order Measurements in Solid Solutions

This program has not been started as yet but is planned for the present 1965-66 fiscal year. The observations of DuBroff have shown after calculation the certainty of obtaining motion picture records of continuous slow evaporation through the (102) planar region, providing that the RCA three-stage cascade-type image intensifier is used. This image intensifier has already been purchased. It is planned to assemble the image intensifier, associated optical equipment and focussing table by the beginning of 1966. E. Gold will then proceed to study short range order in dilute solid solutions in platinum using the procedure outlined above and in Appendix E.

References

1. Mueller, E.W.: Adv. in Electronics and Electron Physics, Vol XIII, 1960, p. 83-179
2. Goldschmidt, H.J., and Brand, J.A.: Jl. Less Common Metals, 5, 1963, p. 181
3. Allen, B.C., Maykuth, D.J. and Jaffee, R.I.: Jl. Inst. Metals, 90, 1961, p. 120
4. Atkinson, R.H. Wadd Tech. Report 60-37, Part I
5. Meieran, E.S., and Thomas, D.A.: Trans AIME, V. 233, 1965, p. 937
6. Mueller, E.W.: Phys. Rev., 102, 1956, p. 618
7. Ehrlich, G. and Hudda, F.G.: Jl. Chem. Phys., 36, 1962, p. 3233
8. Mueller, E.W.: Z. Elektrochem., 61, 1957, p. 43
9. Mueller, E.W., and Young, R.D.: Jl. App. Phys., 32, 1961, p. 2425
10. Mueller, E.W.: Surface Science, 2, 1964, p. 484

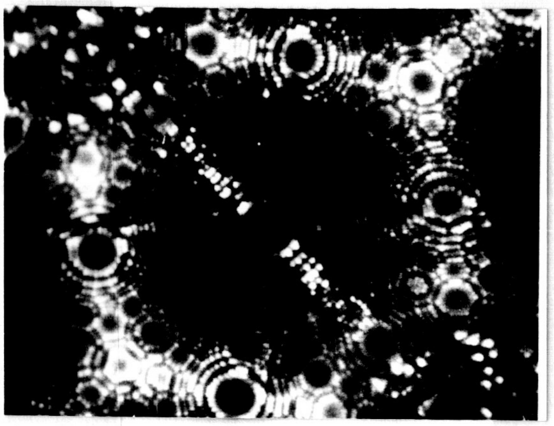


Fig. 1a W field-evaporated end form immediately before field reversal and bombardment with low energy helium ions. Image voltage 15KV

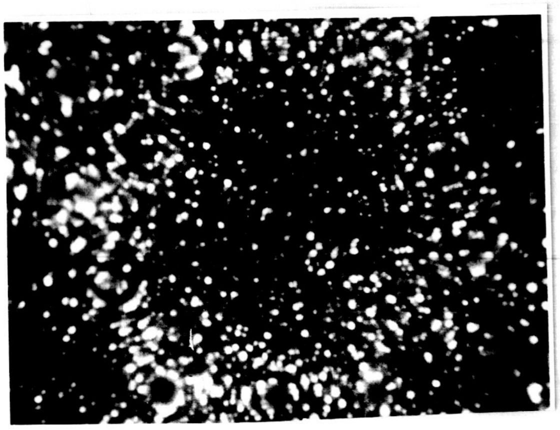


Fig. 1b Same after bombardment at approx. 1500 volts in He at approx. 1 micron pressure. Image voltage 15KV

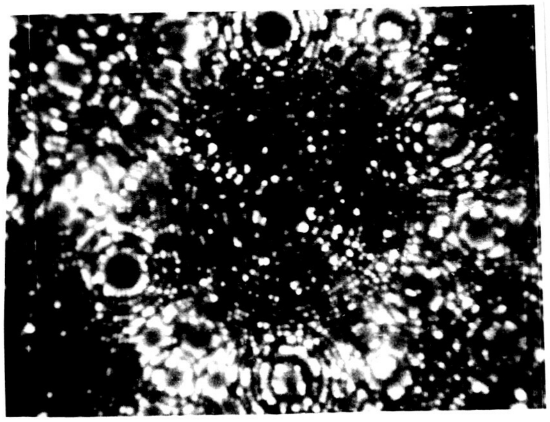
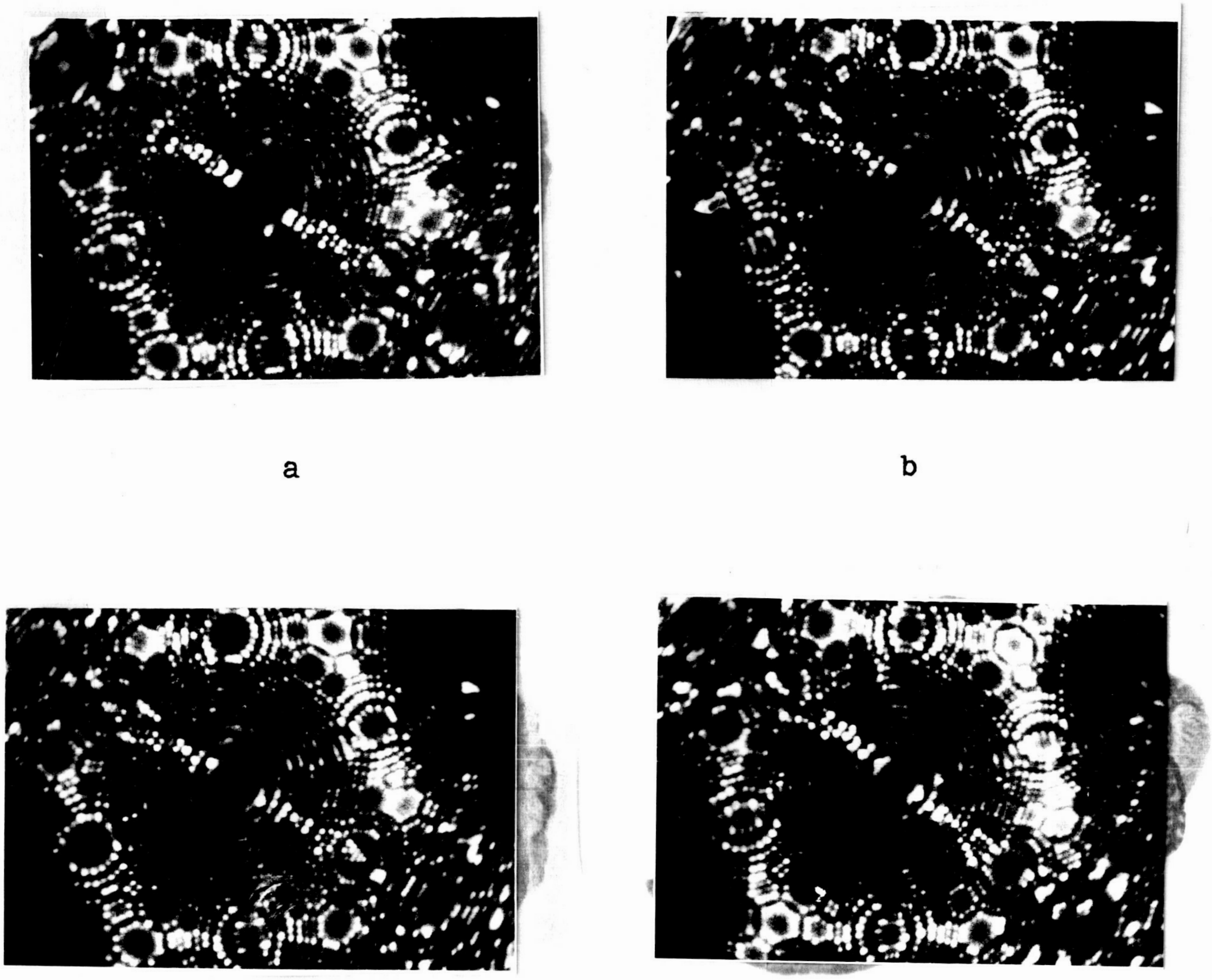


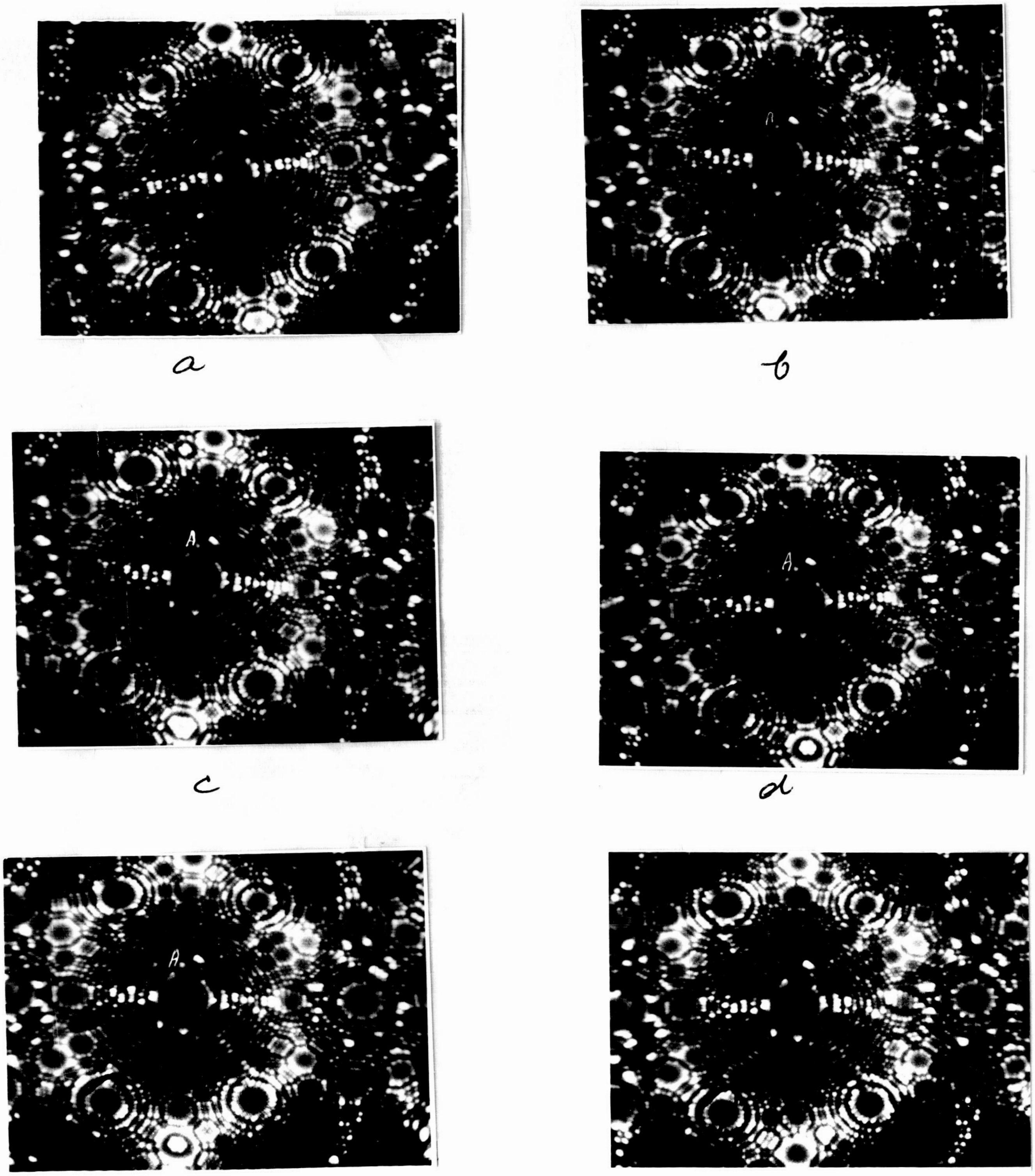
Figure 1c Same after field evaporation of 1 central 110 plane.



a b

c d

Figure 2 Sequential field evaporation degassed tungsten illustrating absence of bright spots between [111] zone lines.



a

b

c

d

e

f

Fig. 3 W containing interstitials field evaporated by successive small steps image voltage 15 1/4 KV.

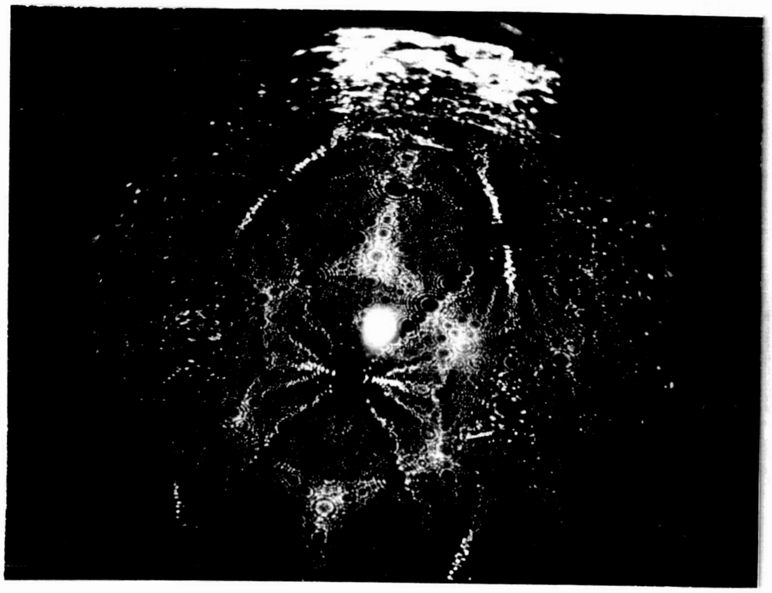


Fig. 4 Carburized tungsten, 21°K

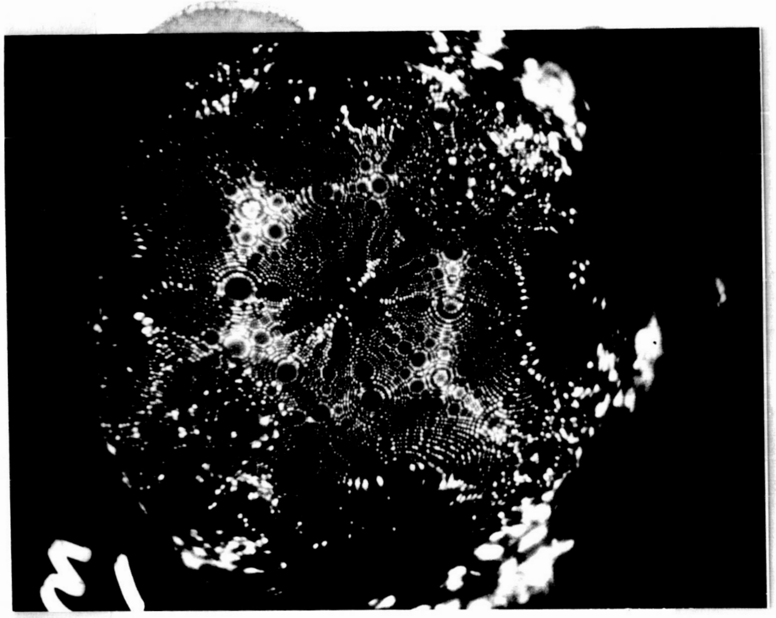


Fig. 5 Tungsten free of carbon, 21°K

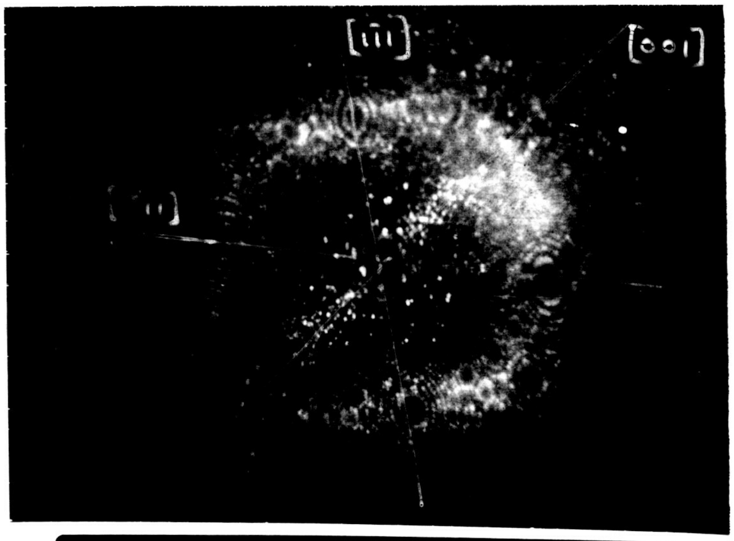


Figure 6 Normal field evaporated surface of W-5% Re showing [111] zones bounded sector with extra bright spots.

Figure 7 Normal pulse evaporated surface of tungsten showing completely resolved (111) plane with 10 atoms.

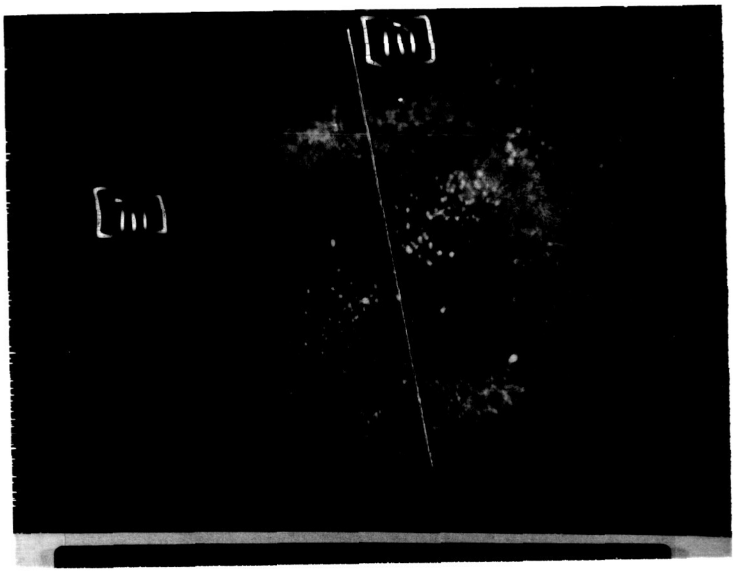


Figure 8 W-5% Re material of Figure 6 following pulse evaporation removal of 1 (110) type plane. Note continued appearance of extra bright spots in [111] zones bounded sector.

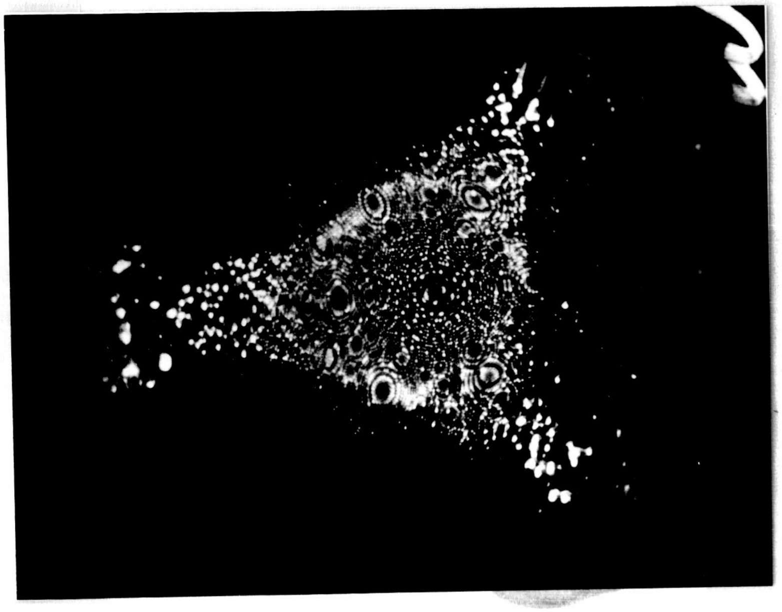


Fig. 9A Platinum 2^{a}/o Tungsten, 21°K

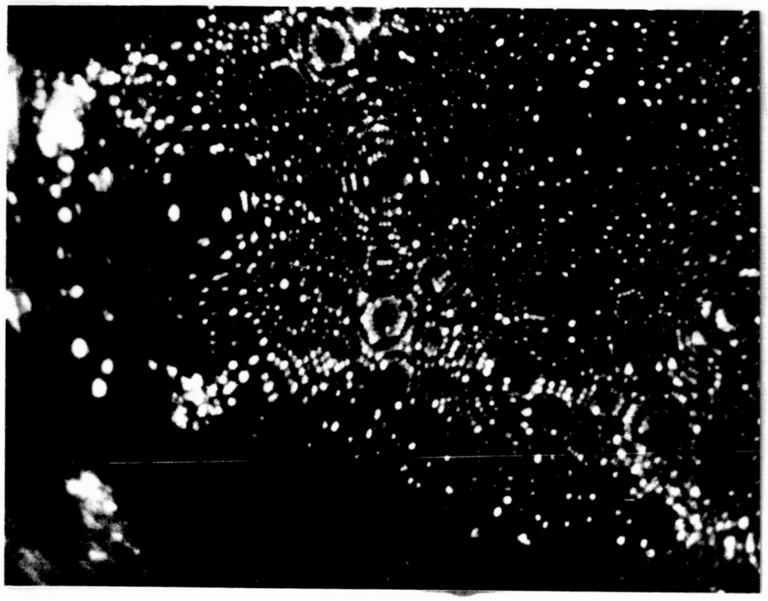


Fig. 9B Platinum 2^a/o tungsten (102) plane containing bright spot, 21°K

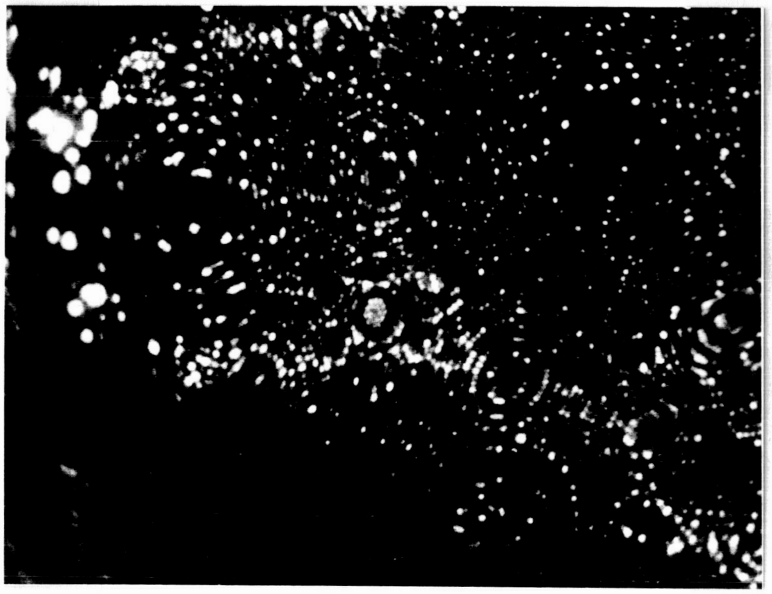


Fig. 10A Platinum 2^a/o tungsten (102) plane containing vacancy, 21°K

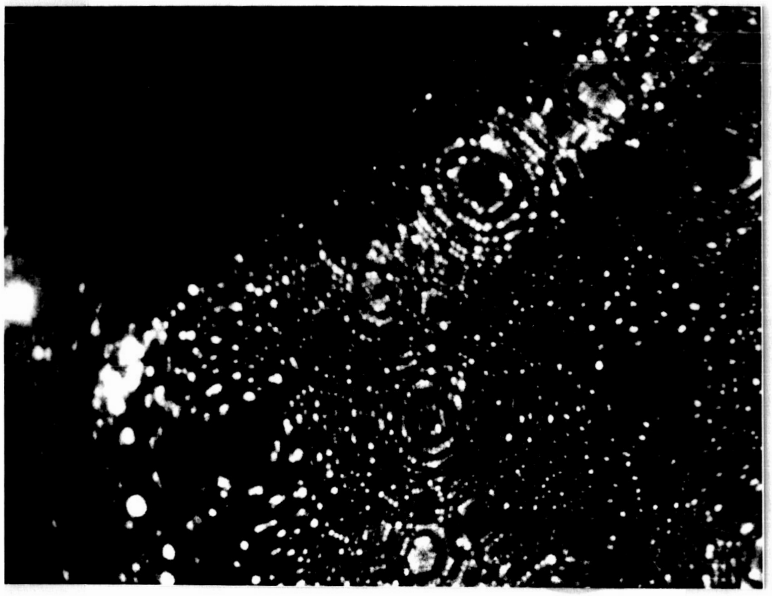


Fig. 10B Platinum 2^a/o tungsten (102) plane containing vacancy cluster, 21°K

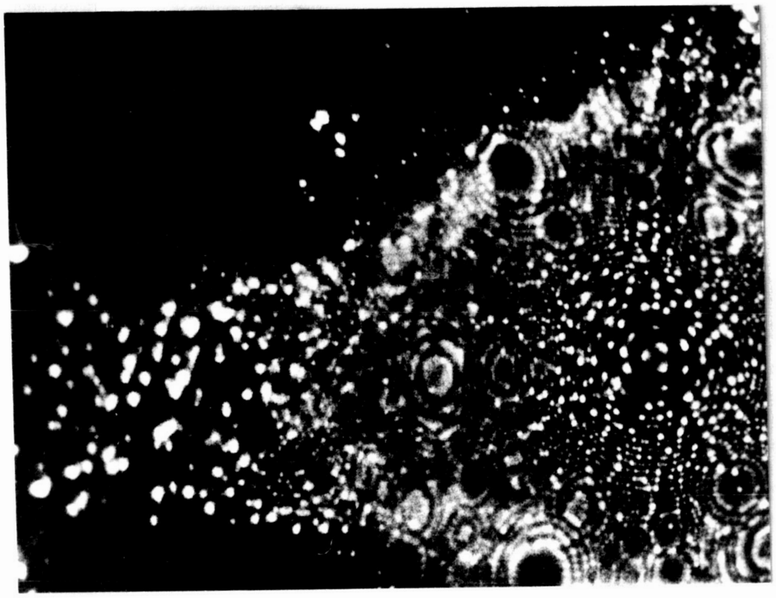


Fig. 11A Platinum 2^a/o tungsten (102) plane containing vacancy, 21°K

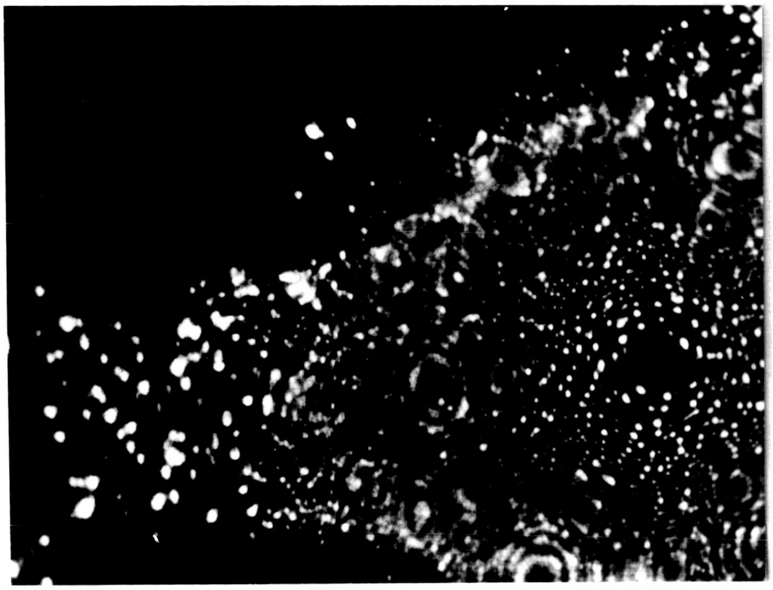


Fig. 11B Platinum 2^{a}/o tungsten (102) plane immediately below the (102) plane in Fig. 11A containing bright spots, 21°K