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ABSTRACT

Annealed iridium specimens of 99.99% purity were irradiated at 5°K with 10 Mev protons in a field ion microscope attached to a cyclotron. Contrast effects due to point defects and their clusters were analyzed. By a field evaporation technique the point defect distribution in the bulk was investigated. Interstitial migration to the surface was directly observed upon annealing in the temperature range 15°K to 42°K. The decrease in the bulk concentration of interstitials during annealing in the temperature range 5°K to 300°K indicated that stage I is caused by interstitial migration to close-by vacancies and traps and stage II was due to interstitial detrapping. Damage caused by irradiation at 5°K was compared to that introduced at 300°K. The damage which was large voids (400 to 500 vacancies) and dislocation loops suggested a different formation mechanism in the specimens irradiated at higher temperature.

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I. INTRODUCTION

Radiation-induced damage in crystals has been extensively studied by measuring changes in resistivity or internal friction and by electron microscopy. As a result of these studies, a fairly detailed picture of the nature of the damage and its recovery on heating has been built up for some materials. However, the clusters of elementary defects that are observed by electron microscopy are only indirectly related to the migration of individual point defects. Controversy has remained as to the nature of the point defect or defect complex that in a particular case has migrated to give the observed effects.

Field ion microscopy,[1] which permits the observation of the surface of a crystal with atomic scale resolution, is potentially capable of answering some of the remaining questions. FIM has been applied to a study of neutron-irradiated tungsten [2,3] and platinum. [4] Information has been obtained concerning the recovery processes that take place above 300°K.

The present paper describes a direct investigation of radiation damage and its recovery during stages I and II in iridium single crystals bombarded with 10 Mev protons at temperatures down to 10°K. Some effects of the irradiation temperature on the nature of the damage are also presented. The uncertainties concerning association of particular point defects with the details of the field ion images are discussed in detail.

II. EXPERIMENTAL PROCEDURE

A. General

Iridium specimens were prepared from 5/1000 of an inch diameter wires of 99.99% purity (from Englehart Company). The wires were annealed at 600°C

for 10 hours in a vacuum better than 10^{-8} torr in order to remove any defects introduced in cold-drawing. From these wires, specimens suitable for field ion microscopy were obtained by electropolishing in a saturated solution of chromic acid at room temperature.

A first series of 5 specimens were bombarded at 5°K with 10 Mev protons in place in a liquid helium cooled field ion microscope which was coupled to the 88" cyclotron at the Berkeley Lawrence Radiation Laboratory. The experimental set-up, which is shown schematically in Fig. 1, has been described in a previous publication. [5]

A second series of 4 annealed iridium wires were irradiated at room temperature. Four specimens were prepared from these irradiated wires by electropolishing at 0°C after irradiation.

B. Irradiation and Field Evaporation Procedures

The proton beam was focused and aligned on a quartz plate set 5 feet in front of the target. Immediately behind the quartz a dummy target enabled setting the beam current to the proper intensity. During the alignment procedure, the specimen was protected from energetic radiation by a 5" thick carbon dummy target. No changes in the surface structure of the iridium specimen were detected during these operations. Because of the optical design, the beam was slightly divergent. Nevertheless, the dose of incident radiation on the target could be evaluated with an accuracy of 20%. When the specimen had been irradiated to the desired integrated dose, investigation of the bulk damage was carried out without warming the specimen by using the field evaporation technique. [1]

The field evaporation process must be carried out in a carefully-controlled fashion in order to control the field-induced migration of defects

and to prevent extensive evaporation in the neighborhood of clustered defects. For this purpose, a pulsed technique was adopted. Short positive voltage pulses were superimposed on the best imaging voltage. By increasing the amplitude of these pulses, the evaporation field was reached. The amount of material removed from the surface during each pulse could be controlled by the duration of the pulse. Because of the short duration of the pulse (10^{-5} sec.), the blurring of the image, [1] which for iridium would appear otherwise at 5°K for values of the field lower than the field evaporation threshold, did not occur. Thus, the method permitted the observation of the removal of individual atoms in the most favorable conditions.

C. Annealing Procedures

The annealing experiments were performed in two steps for the low temperature irradiated specimens. By letting the liquid helium evaporate, the specimen was slowly warmed from 4°K to 77°K at a rate of about 10° per minute. During the heating, the imaging field was maintained at 1 Kv below the best imaging voltage in order to avoid any contamination of the surface. Furthermore, except when taking pictures, the annealing was done under vacuum (below 10^{-8} torr). In this way, bombardment of the specimen by energetic copper ions sputtered from the heat shield by helium ions was avoided. Continuous recording of the annealing temperature was achieved between 14°K and 77°K with a Cu constantan thermocouple with a cold junction at liquid nitrogen temperature.

By warming up the cryotip with heated helium gas, the specimen was heated from 77°K to 230°K in steps of 30 degrees. As in the previous annealing experiments, precautions were taken to avoid contamination or bombardment of the surface during the annealing steps.

III. RESULTS AND DISCUSSION

A. Contrast from Point Defects and Their Clusters in Field Ion Micrographs

1. Interstitial Contrast

Interstitial atoms were detected in two ways. During slow warming of the specimens after irradiation at 5°K, bright spots were observed to pop up to the surface in the temperature range 15°K-42°K, as shown in Fig. 2. These bright spots were the only detectable changes of the metal surface: the effect did not appear on heating non-irradiated specimens through the same temperature range.

The possibility that the bright spots could be cuased by trapped hydrogen atoms migrating to the surface was discounted because the probability of trapping the protons in a specimen of 5/1000" diameter upon irradiation with 10 Mev protons is extremely small and approaches zero in the observed area of the tip where the diameter is reduced to less than 2000 Å. The possibility of impurities migrating to the surface and giving rise to bright spots upon annealing was also discounted because of the extremely low temperature. Therefore, it is almost certain that these bright spots were caused by the popping up to the surface of interstitial atoms created during irradiation.

Low temperature migration of interstitials has also been observed by a similar method [6,7] in irradiated W. In the temperature range 21° K - 77° K, bright spots would pop up to the surface and disappear immediately. However, in the present experiments conditions were achieved which permitted retention of the extra atom on the metal surface. Moreover, they could easily be removed by a sharp temperature increase as shown in Fig. 2d, or

by a small increase of the applied field.

A second procedure for bringing interstitial atoms to the surface was discovered during controlled pulse field evaporation. A field evaporation pulse often caused bright spots to appear on the surface at planes which had lost no atoms or only very few atoms at their edges. Since this contrast effect was not observed in non-irradiated iridium, these bright spots were associated with interstitials. They appeared as single or as pairs of bright spots and were preferentially removed from the surface during a second pulse as seen in Figs. 3 and 4.

Interstitial atoms that lay within a few interatomic distances of the surface were probably induced to move by the increased electrostatic strain associated with the momentary increase in field. The change in stored energy ΔE corresponding to a variation of the field, F, is obtained from the elasticity theory if we assume an hemispherical tip and an elastic deformation of the specimen. Then ΔE is given by:

$$\Delta E = \frac{1}{2} \frac{\left(\sigma_1^2 - \sigma_2^2\right)}{k}$$

where $\sigma_1 = F_1^2/8\pi$ and $\sigma_2 = F_2^2/8\pi$ are the negative hydrostatic pressure applied on the tip for values of the field F_1 and F_o in volts/$\mathring{A}$ and k is the bulk modulus in dynes/cm^2. If v is the atomic volume in $\mathring{A}^3$, the change in stored energy per atom is:

$$\Delta E_m = 1.22v \frac{\left(F_1^4 - F_o^4\right)}{k} \text{ in ev/atom} \qquad (1)$$

If F_1 and F_o respectively are taken as the evaporation field and the best imaging field, the values of ΔE_m given in Table I are obtained for Ir, Pt and W at 5°K. As a comparison, the migration energies for interstitials,

E_{1I}^{M} for Ir is assumed to be the same as E_{1I}^{M} for Pt.

Table I

	Computed Changes in Elastic Stored Energy: ΔE_m in eV/atom	Interstitial Migration Energy E_{1I}^{M} in eV/atom
Pt	0.009	0.065[9]
Ir	0.016	(0.065)
W	0.065	0.25[8]

These results indicate that the changes in elastic stored energy due to a field evaporation pulse should not suffice to induce interstitial migration. However, our experiments and similar results obtained on irradiated W [6,7] and Pt [4] suggest that in some regions near the surface the field evaporation pulse causes local disturbances that are much greater than the average because of local variations of radius of curvature. Presumably it is in these regions that interstitial atoms near the surface are given enough extra-energy to jump to the surface at a temperature lower than that ordinarily required for migration.

Attardo and Galligan [4] have reported a second kind of interstitial contrast in irradiated Pt. Bright spot contrast was attributed to the presence of an interstitial one or two layers below the surface. Their removal occurred after field evaporation of the atomic planes on top of them. This type of contrast was not observed in iridium.

The double bright spot contrast observed at low temperature as seen in Fig. 4 was not definitely associated with the presence of di-interstitials,

since immediately after irradiation, 10% of the total number of interstitials gave rise to pairs of bright spots.

It is possible that when an interstitial atom arrives within one interatomic distance of the surface, there are metastable configurations that result in protrusion of two atoms. Something like the split <100> configuration which has been suggested by computer simulations [10] may exist near a surface. Depending on the orientation of the splitting direction with respect to the surface or depending on the lattice distortion near a split interstitial at the edge of an atomic plane, one or two atoms might be in a more protruding position.

In most cases, pairs of bright spots were aligned along the closest-packed rows of atoms. However, this was not always observed, as seen in Fig. 5.

2. Contrast from Vacancy and Vacancy Clusters

Vacancies are identified as dark spots in the middle of completely imaged planes. [1] However, in some cases impurities can also give a similar contrast. [11] Müller [12] has also reported a high vacancy concentration in loosely packed planes of well annealed Pt, Ir and W. These vacancies were formed by the field evaporation of atoms from the center of fully imaged planes during a field evaporation pulse. This phenomenon makes the vacancy concentration measurements by field ion microscopy very unreliable.

Di-vacancies appear as double dark spots and are easily identified on high index planes as shown in Fig. 6a.

Larger vacancy clusters were also observed in the low-temperature

as well as in the room-temperature irradiated specimens. These clusters were of two kinds: 1) diffuse clusters which consisted of groups of 20 to 30 vacancies dispersed in a small volume of the crystal (about 800 $\mathring{A}^3$), as shown in Fig. 6; 2) large voids corresponding to 400 to 500 vacancies exhibited irregular edges and containing no atoms inside as shown in Fig. 7. The void shape was generally close to an ellipsoid elongated along a <111> direction. The information on cluster size obtained through the field ion microscopy technique must be considered with caution, since field evaporation may occur in an unpredictable way at vacancy clusters and at void edges.

Dislocation loops of two types were also observed in the room-temperature irradiated specimens: 1/2 <110> perfect loops lying in a {110} plane as shown in Fig. 7. The second type of loop shown in Fig. 8 was the 1/3 <111> faulted loop lying in {111} planes. The stacking fault shows up as inter-spaced rings as predicted by computer simulations of intrinsic stacking faults. [13] Loops were characterized according to the method of Fortes and Ralph, [14] who reported similar loops in iridium after irradiation at room-temperature with neutrons. The loop size varied from 20 - 40 $\mathring{A}$ in diameter and their contrast was heavily distorted by the preferential field evaporation at the intersection of the dislocations with the surface as can be seen in Fig. 8.

B. Annealing of Proton Damage in Iridium

Although no resistivity annealing studies of irradiated or quenched iridium are presently available, its annealing behavior was assumed to be similar to that of irradiated platinum. Recent resistivity annealing

studies carried out on Pt irradiated at low temperature with 20 Mev deuterons [15] will be used as a model of the annealing behavior of Ir bombarded at low temperature with 10 Mev protons. The assumption of similar annealing behavior is not unreasonable, since these two metals have an fcc structure and have very similar electronic structures, atomic weight and displacement threshold energies. The relatively high impurity content of the 99.99% iridium used in the present experiment will probably shift some recovery substages or decrease the amount of recovery in some stages as observed in other fcc metals.

1. Stage I Recovery

Upon annealing in the temperature range 14°K - 40°K, interstitial migration to the specimen surface was observed. Therefore the recovery during stage I corresponds to interstitial migration. A 60% decrease in the interstitial concentration, as revealed by the field evaporation technique, took place within the temperature range 5°k to 77°K (see Fig. 9). Close pair recombination as well as interstitial migration to traps is taking place during stage I recovery. These results disprove Von Jan's conclusion [16] since he argued that in no fcc metals are interstitials mobile in stage I recovery.

The different types of interstitials that may have taken part in stage I recovery could not be identified.

2. Stage II Recovery

After a 10-hour annealing at 300°K, a marked increase in the concentration of pairs of bright spots coincided with a lower concentration of single bright spots than was observed after a 10-hour annealing at 77°K.

The relative variations in these concentrations are shown in Fig. 9. These results suggest that stage II involves the escape of interstitials from impurity interstitial clusters and the formation of di-interstitials. Small clusters of 4 to 5 interstitials were also observed in the annealed specimens.

C. Influence of the Irradiation Temperature on the Damage

The defects observed in the low-temperature irradiated specimens were also present in the three specimens irradiated at 300°K with a total dose of 10^{18} protons/cm^2. In addition these specimens contained larger voids with 400 to 500 vacancies and dislocation loops of 20 - 40 Å diameter. The loops were of both types 1/2 <110> and 1/3 <111>.

The greater size of the defects in the room-temperature irradiated specimens suggests a different formation mechanism. As shown by Nelson et al., [17] thermal lattice vibrations during irradiation are expected to scatter energy out of focused collision sequences and to curtail their maximum range. As a direct consequence the separation of interstitials and vacancies becomes smaller. This would result in a more localized defect concentration and a greater localization of the heating of the specimen in the region of the primary knock on. This might be responsible for the observed differences in the room-temperature damage and the low-temperature damage.

IV. CONCLUSIONS

1. The analysis of the contrast in field ion micrographs of proton-irradiated iridium has shown that interstitials are associated with extra

bright spots popping up to the surface upon an increase of the electrostatic field applied to the specimen or upon a rise in the specimen temperature. Pairs of bright spots also popping up to the surface may be associated with single interstitials as well as with di-interstitials.

2. A direct observation of the variations in the interstitial concentration as a function of the temperature of recovery showed that the migration of interstitials is responsible for stage I recovery. Stage II of recovery was also tentatively associated with motion of interstitials which were probably released from impurity-interstitial complexes to form small interstitial clusters.

3. The low-temperature damage was composed of single vacancies, interstitials and small "diffuse" vacancy clusters of 30 to 40 vacancies. Irradiations at room-temperature produce the same point defects as in low-temperature irradiation. In addition, large voids corresponding to 400 - 500 vacancies and dislocation loops were observed in the room-temperature irradiated specimen.

ACKNOWLEDGEMENTS

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REFERENCES

[1] E. W. Müller, in: Advances in Electronics and Electron Physics, Academic Press, New York, 1960, Vol. 13, p. 83.

[2] K. M. Bowkett, J. Hren and B. Ralph, in: Fifth European Conference on Electron Microscopy, Prague, 1964, Vol. A, p. 191.

[3] M. J. Attardo and J. M. Galligan, phys. stat. sol. 16, 449 (1966).

[4] M. J. Attardo and J. M. Galligan, phys. rev. 161, 558 (1967).

[5] P. Petroff and J. Washburn, rev. sci. inst. 39, 317 (1968).

[6] E. W. Müller, in: Proceedings of the Fourth International Conference on Reactivity of Solids, Elsevier Publishing Company, Incorporated, Amsterdam, 1960, p. 682.

[7] M. K. Sinha and E. W. Müller, j. appl. phys. 35, 1256 (1964).

[8] J. W. Corbett, R. B. Smith and R. M. Walker, phys. rev. 114, 1460 (1959).

[9] W. Bauer and G. W. F. Goepinger, phys. rev. 154, 588 (1967).

[10] R. A. Johnson, phys. rev. 145, 423 (1966).

[11] E. Gold and E. S. Machlin, phil. mag. 18, 453 (1968).

[12] E. W. Müller, in: Vacancies and Interstitials in Metals, J. Diehl, W. Shilling, D. Schumacher and A. Seeger, (Eds.), North Holland Publishing Co. (to be published).

[13] S. Ranganathan, private communication.

[14] M. A. Fortes and B. Ralph, phil. mag. 17, 145 (1968).

[15] J. J. Jackson and K. Herschback, phys. rev. 164, 951 (1967).

[16] R. Von Jan, phys. stat. sol. 17, 361 (1966).

[17] R. S. Nelson, M. W. Thompson and H. Montgomery, phil. mag. 7, 1385 (1962).

FIGURE CAPTIONS

Figure 1. Schematic of the experimental set-up.

Figure 2. Surface changes in iridium upon heating up after irradiation at 5°K: the only surface changes are dotted atoms indicating interstitials which have migrated to the surface.

Figure 3. Field evaporation sequence in iridium after irradiation at 5°K. Dotted spot in Picture b shows an interstitial popping up on top of a plane which did not field evaporate.

Figure 4. Field evaporation sequence in iridium after irradiation at 5°K and a subsequent annealing at 300°K. Dotted spots indicate contrast effects from interstitials popping up on top of planes which did not field evaporate. Interstitial shown in Frame A of Picture 2 field evaporates preferentially during the following pulse.

Figure 5. Field evaporation sequence showing the contrast effects (dotted spots) of an interstitial popping up to the surface of an iridium specimen irradiated at 5°K and annealed at 300°K.

Figure 6. Field evaporation sequence of a specimen irradiated at 300°K. dv is a divacancy; D identifies "diffuse" vacancy clusters. Between (a) and (d) a few central planes have been removed.

Figure 7. Field evaporation sequence of a specimen irradiated at 300°K. Dark arrows show a dislocation loop lying in a {110} plane. Black and white arrows identify a void.

Figure 8. Field evaporation sequence of a specimen irradiated at 300°K. White arrows locate a Frank loop. Between (a) and (b) a few atoms were removed from the central plane.

Figure 9. Relative variations of the concentration of bulk interstitials as a function of the annealing temperature. C and Co are respectively the interstitial concentration at 5°K and T°K as revealed by field evaporation. The surface changes indicate the frequency (in arbitrary units) of interstitial arrivals at the surface upon annealing.

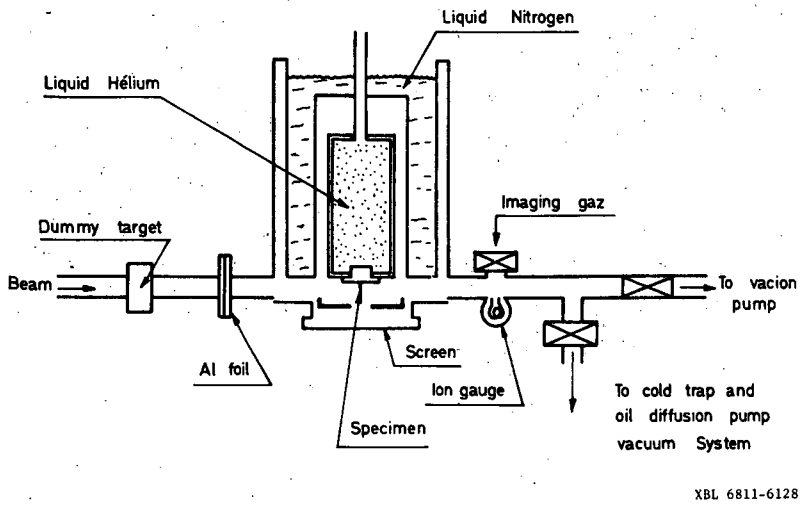
Liquid Nitrogen
Liquid Hélium
Imaging gaz
Dummy target
Beam
To vacion pump
Al foil
Screen
Ion gauge
Specimen
To cold trap and oil diffusion pump vacuum System
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Fig. 1

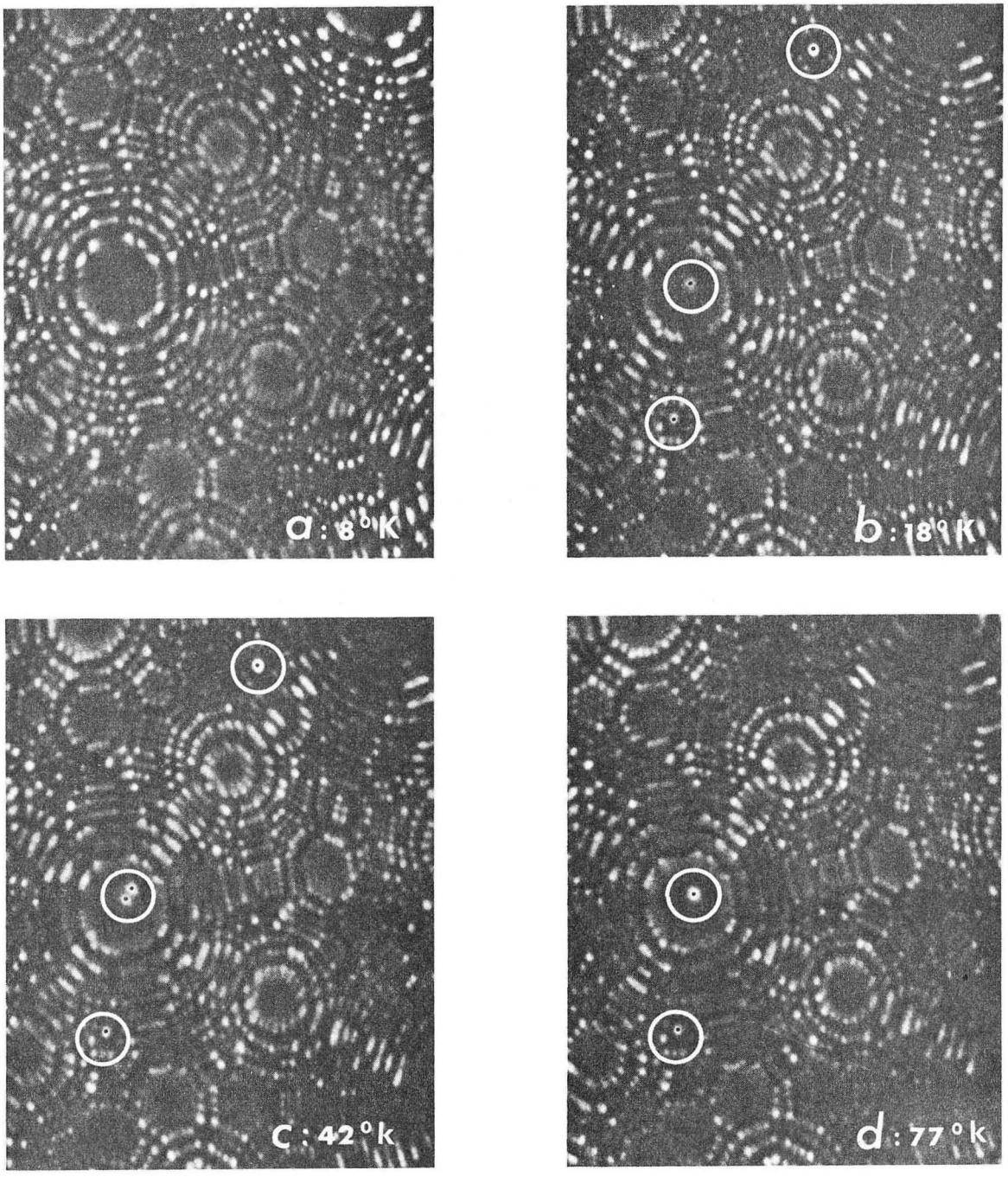

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Fig. 2

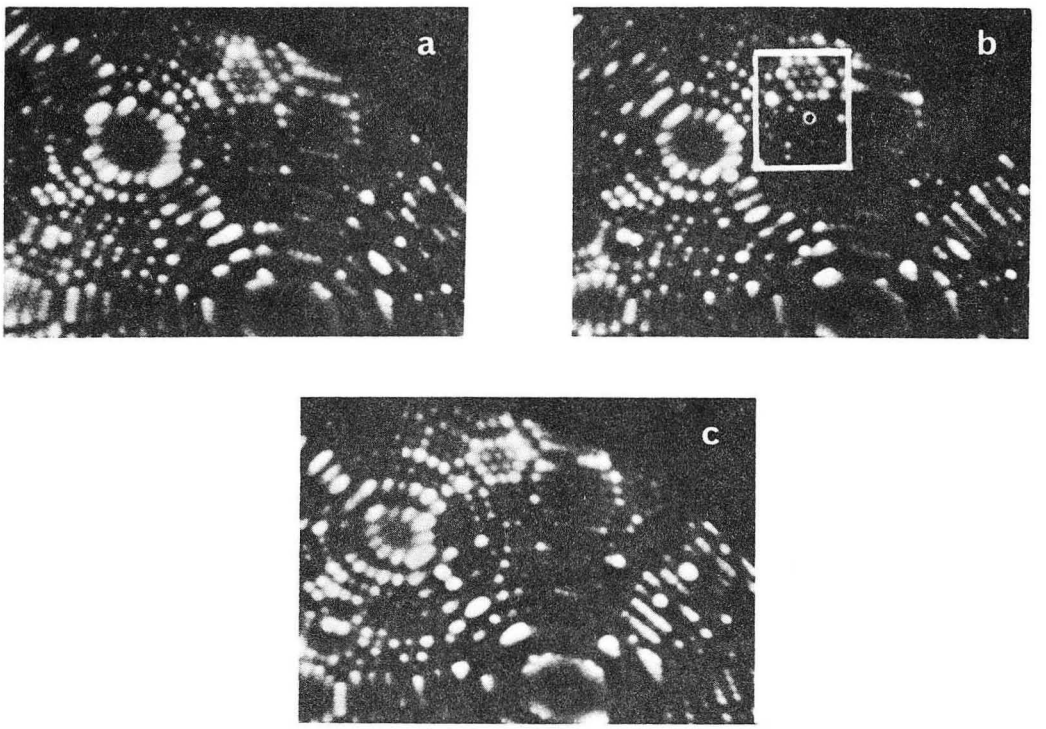

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Fig. 3

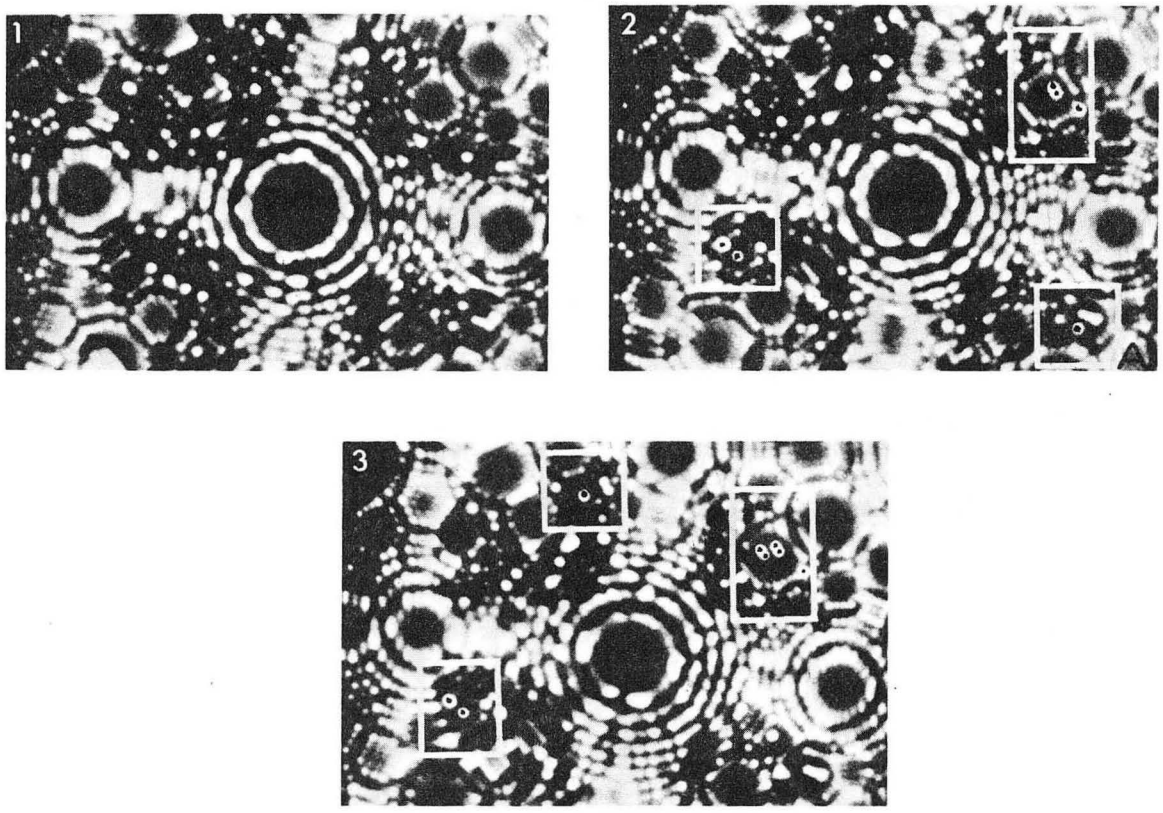

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Fig. 4

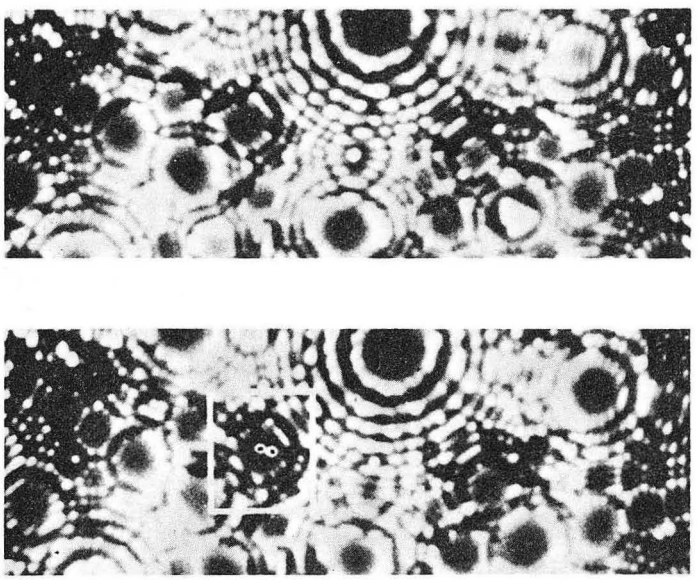

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Fig. 5

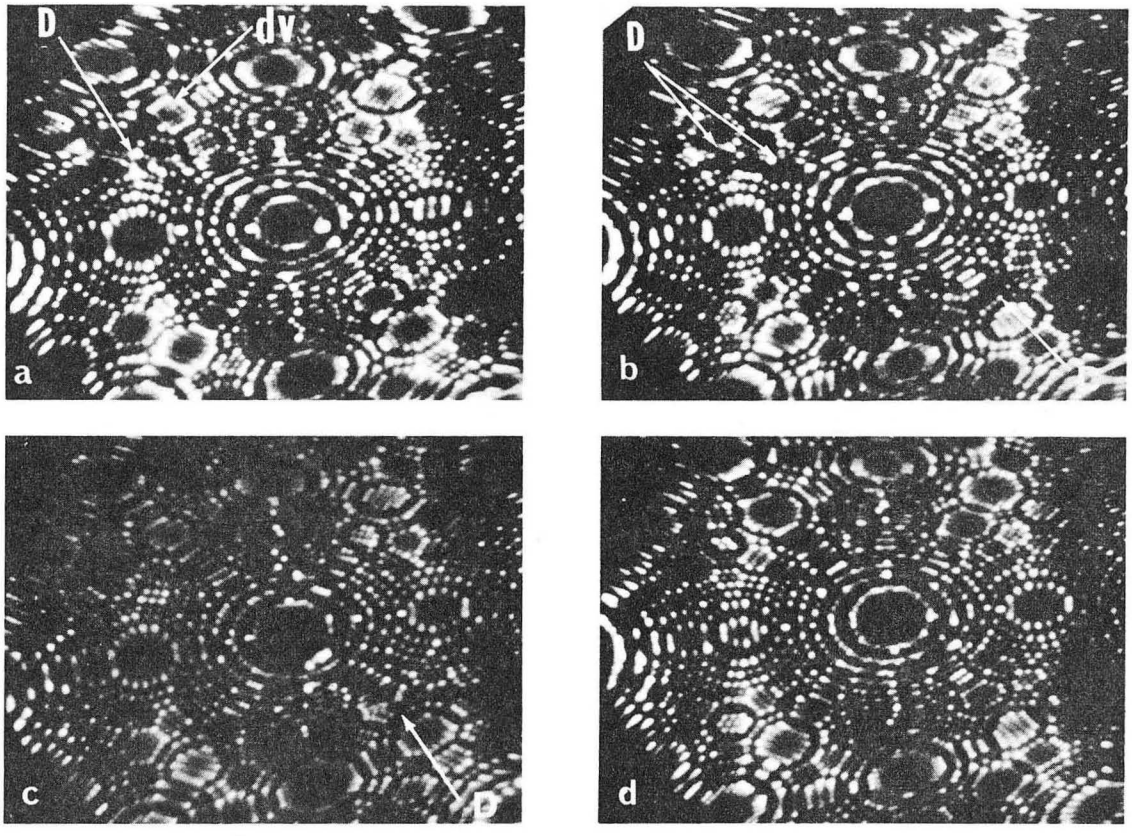

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Fig. 6

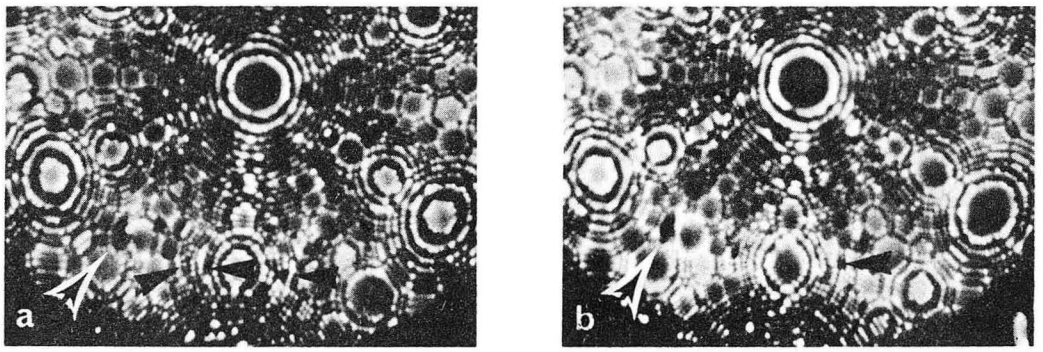

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Fig. 7

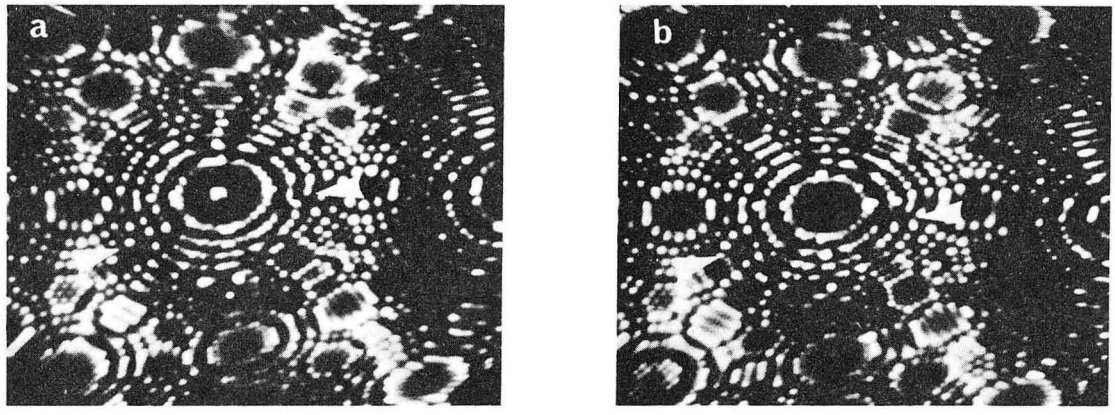

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Fig. 8

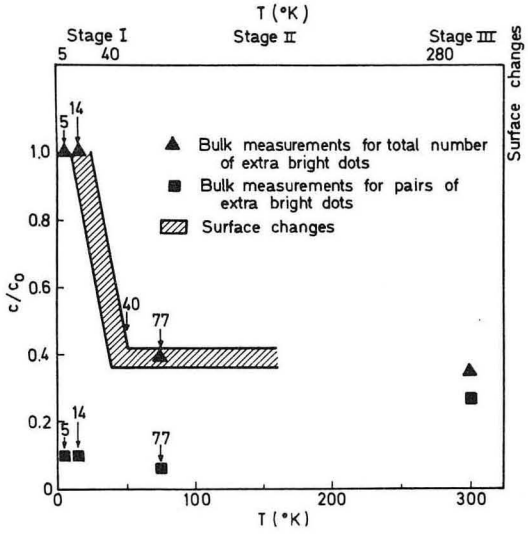

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Fig. 9

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