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Topics in Precipitation and Ordering Reactions and Their Related Phenomena

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The application of High Voltage Electron Microscopy to the study of phase transformations is illustrated with a number of examples of precipitation reactions. The importance of lattice defects is emphasized and it is shown how strain accommodation is accomplished for various types of transformations.

I. INTRODUCTION

An important application of High Voltage Electron Microscopy is the study of the microstructural changes that occur during solid-solid phase transformations. The microstructures which develop in-situ mirror those observed in bulk treated samples provided the alloy system is chosen judiciously and thick regions of the TEM foil are used in the study. Several advantages accrue; often precipitation and dissolution processes are reversible allowing extensive data to be rapidly recorded from the same foil, new insights into transformation mechanisms can often be obtained from dynamic observations, the effects of electron irradiation on the transformation can be assessed directly.

Recent research at Berkeley has been concentrated on understanding the role of crystal lattice defects in the precipitation of a second phase. By studying different simple alloy systems characterized by different types of transformation strain the various defects required for the optimum elastic/plastic accommodation of the product phase have been identified.

In the present contribution the results of five categories of transformations are summarised. An invariant plane strain (IPS) transformation is typified by precipitation of carbide plates on {001} in platinum-carbon alloys. This system also exhibits an unusual ordering reaction stimulated by the high energy electron beam.

A mechanism for the loss of coherency of needle-shaped precipitates in an invariant line strain transformation (ILS) without volume change is illustrated with results of a study of an Fe-Cu alloy.

In some systems several precipitate morphologies arise concomitantly. Examples include Al-Si and Al-Ge, where the precipitates have a simple composition (that of the pure solute) but more complex crystal structure (DC). When an invariant line strain transformation occurs with a volume change, plate-shaped precipitates form on high index habit planes. Some results on an Fe-N alloy illustrating the characteristics of this type of transformation are presented last.

Each example was selected to illustrate the different ways in which optimum accommodation of the transformation strain is accomplished. It has been found that the mechanisms do not depend on the type of alloy system, i.e. they are common to fcc, bcc and cph crystal structures, and to interstitial, substitutional and mixed interstitial/substitutional alloys.

II. EXPERIMENTAL DETAILS

All specimen foils were prepared using conventional electropolishing techniques [1]. Most of the microscopy was performed on a Kratos 1500kV instrument equipped with a double-tilt heating stage. The accelerating voltage could be set at 100kV increments allowing maximum flexibility in inducing or avoiding radiation damage. A video camera and recording system was used to monitor dynamic events during in-situ heating or cooling.

III. RESULTS

III.1. Precipitation in platinum-carbon

The terminal interstitial solid solubility of carbon in platinum at 1760° C is only $\sim 10^{-3}$ at.fr. (about the same as the equilibrium vacancy concentration). Nevertheless, during aging following a quench the solid solution decomposes and precipitation of a metastable carbide phase occurs in two stages. The sequence closely resembles that found in substitutional Al-4w/o Cu alloys. Initially, an α phase consisting of semicoherent GP zones of carbon formed on {001} planes precipitates by the condensation of tightly bound carbon/atom vacancy complexes. These subsequently transform to α', Pt_2C, isomorphous with Al_2Cu, by a mechanism in which further vacancies are systematically incorporated in the precipitate structure. It has been shown [2] that in this alloy system, as well as others with IPS transformation, vacancies are condensed as prismatic dislocation loops in a way that changes the habit plane stacking sequence and spacing from that of the parent phase to one closely resembling that of the precipitating product phase. Vacancies are thus used in both a volume accommodation and structural role in IPS transformations.

It has been possible to capture the transition of the α-α' phases both in- and ex-situ, allowing the process to be followed in detail.

Figure 1 shows an example of a few large α plates growing and thickening at the expense of nearby shrinking plates. By conventional diffraction contrast analysis it was shown that the outer annuli of the large plates have 1/3<001> vacancy strain field characteristic of α phase, whereas the inner discs have ½<001> vacancy type displacement typical of α'. The ½<001> plate structure analysis was supplemented with microbeam electron diffraction evidence to show it corresponded to one unit cell of Pt_2C with the CaF_2 structure, 50% oversize relative to the Pt matrix.

III.2. Ordering in Pt-C alloys

Many different experiments on Pt-C alloys had provided indirect evidence that carbon atoms are strongly bound to vacancies at low temperatures and diffuse as a complex [3]. Direct confirmation that this occurs was found in equilibrium diffusion experiments conducted on platinum membranes at 700-900°C [4]. Large mounds and pits formed at the Pt foil surfaces as carbon diffused through the

membrane (see Fig. 2). From the magnitude of the mass transport, estimated from the mound/pit size density, a value of $\sim$ 0.6eV was found for the binding free energy of a carbon atom/vacancy pair.

The mass transport effects were particularly pronounced in the grain boundaries, as illustrated in Fig. 2, and an analysis by Auger Electron Spectroscopy showed that the regions adjacent to boundaries were greatly enriched with carbon. It was during examination of these specimens in the HVEM that the ordered phase was discovered. Heating experiments were being conducted in-situ to study decomposition in concentrated alloys. No precipitation of the type described earlier was observed, instead the nucleation and growth of domains of an ordered phase occurred in a certain range of temperatures and accelerating voltages.

A typical dark field micrograph of the ordered structure along with the corresponding diffraction pattern is given in Fig. 3. Both radiation-ordering and radiation-disordering was observed depending on the temperature/voltage conditions. However, only disordering occurred during in-situ heating at voltages below the ordering threshold; apparently the conditions for ordering were not fully satisfied in the absence of electron irradiation.

The Table below summarizes the various threshold voltages and temperature ranges over which the ordered phase was stable.

TABLE 1 - SUMMARY OF ORDERING/DISORDERING CONDITIONS

PHENOMENON	TEMP. (°C)	ACCEL. VOLT. (kV)
PHASE RADIATION-ORDERS	260<T<670	V>300
PHASE RAD.-DISORDERS	T<260	V>400
PHASE THERMALLY DISORDERS	T>700	V<300

Identification of the ordered phase was made from electron diffraction patterns taken with many different zone axes. In every case the superlattice spots were found to bisect the matrix Pt spot patterns. The simplest structure consistent with the observations is shown in Fig. 4. It is made by substituting 4 of the 32 Pt atoms comprising 8 unit cells of the fcc Pt with psuedo-substitutional carbon atom/vacancy complexes and locating them on the face-centered sites of the new fcc cell.

The new cell then has a lattice parameter twice that of the Pt from which it forms and a stoichiometric composition of Pt_7C. In contrast to earlier studies of radiation-induced order in substitutional alloys (see for example [5]) the ordered phase forms from initially interstitially dissolved solute atoms. Several aspects are of interest: (1) the phase will only form when suitable concentrations of both carbon and vacancies are present in the material; (2) the required amounts of carbon ($\sim$12.5 a/o) greatly exceed the "usual" interstitial solubility limits (0.1 a/o) suggesting that it is present in the material in an unusual form (pseudo-substitutionally); (3) Pt_7C is isomorphous with Pt_7Cu and the manner of its formation suggests that other phases of the type Pt_xC could be produced under suitable non-equilibrium conditions; (4) the phase apparently forms and disorders by electron-stimulated migration of carbon

atom/vacancy complexes. Further studies could provide direct evidence on defect/impurity diffusion mechanisms.

III. 3. Precipitate growth mechanisms in Fe-Cu

An invariant line strain transformation is characterized by the occurrence of directions in the crystal common to both parent and product in which the atom spacings remain unchanged during the transformation. When such a transformation occurs without significant volume change, needle-shaped precipitates with axes oriented along invariant line directions represent the most energetically favorable morphology. As solute precipitation continues, however, coherency strains normal to the needle axis develop inhibiting further growth. Recently it was shown [6] that loss of coherency and continued precipitation requires the nucleation and growth of shear dislocation loops.

The growth morphologies of two alloys of this type, Cu-Cr (fcc/bcc) [7] and Fe-Cu (bcc/fcc) have been studied using the HVEM. Some representative results for the Fe-Cu case are given here.

HVEM was particularly useful in this work since the ability to examine thick sections far from the edges of the foil obviated problems associated with the preferential etching out of the Cu precipitates, and greatly facilitated the compilation of statistically significant data. In this study advantage was also taken of the symmetry properties of the matrix to optimize the observation conditions for maximum accuracy in the measurement of needle directions. This was possible because the prediction of which precipitate needles would be favored for losing coherency was made from first principles.

As shown in detail elsewhere [6] coherent needles are free to lie in any directions provided their axes fall on the cones of unextended lines. On the otherhand the optimum relief of the developing coherency strains limits the favored needle growth directions to those corresponding to the intersection of the cones with matrix slip planes. For the case of the Fe-Cu alloy (fcc precipitates in a bcc matrix) this leads to the prediction of needle directions shown in the stereogram of Fig. 5. The needle directions are clustered around the <111> poles and it is clear that it would be difficult to distinguish between them in a <001> oriented foil. However, by selecting a <011> beam direction the angular separation of the needles is maximized and the predicted directions (Fig. 6a,b) can be compared directly with experiment (Fig. 6c). Thus by using the crystal symmetry properties a large number of measurements of needle directions can be rapidly made. The results of an extensive analysis carried out in this manner showed excellent agreement between theory and experiment. The predicted needle directions, <557> and <665>, were accurately confirmed; moreover, a greater incidence of the former type over the latter could be related to a greater relative efficiency of the available matrix slip system in providing transformation strain relief by shear loop propagation.

III. 4. Precipitation in Al-Si and Al-Ge alloys

Needle-shaped precipitate morphologies are also found in quenched-aged Al-Si [8] and Al-Ge [9] alloys. However, in these systems the transformation is accompanied by a large volume change and there is not a simple relationship between the crystal structures of the parent and product phases. As a consequence, vacancies are essential in the nucleation of these precipitates

[10] and a variety of different orientation relationships and corresponding morphologies develop concurrently, perhaps due to variations in the local vacancy concentration.

Fig. 7 illustrates the complex morphologies observed in an Al-Si alloy. Similar structures are found in Al-Ge alloys. In addition to needle precipitates with axes lying along <100>, <110> and <113> directions, lath and plate precipitates with various shapes are also found. Studies, performed ex- and in-situ with and without electron irradiation, are being conducted to elucidate the role of lattice defects and to determine the factors influencing the morphology and growth processes.

Preliminary results indicate that several of the transformation strain accommodation mechanisms isolated in the studies on simpler alloy systems, such as vacancy involvement in both structural and volume accommodation roles, slip, twinning and variant accommodation operate simultaneously.

The effects of electron irradiation on precipitation in Al-2.25 w/o Ge is shown in Fig. 8. The region shown in (a) was irradiated at 300 kV and 150° C for 20 minutes. The foil was then heated to 206° C where precipitation of the Ge occurred over the course of 40 minutes. Fig. 7(b) shows a nearby area not subjected to irradiation. Clear differences in the precipitate densities and morphologies are seen. In the absence of irradiations mostly needle precipitates form, whereas a high density of plate or spherical precipitates form in the irradiated region. This difference is related to the vacancy concentration present at the nucleation stage. Similar differences are found when changes in the quench/age schedule alter the concentration of quenched-in vacancies [9].

High resolution studies on precipitate and interface structures have been employed throughout this research to complement the information obtained by more traditional methods.

A striking example of the detailed structural information presently obtainable using carefully prepared specimens in an HREM is given in Fig. 9. The image, taken on Berkeley's ARM, shows the structure of an interface between a <110> Ge needle precipitate, viewed end-on, and the <100> Al matrix. Such pictures provide direct evidence on orientation-relationships, accommodation mechanisms and growth histories. As these are naturally occuring interfaces their crystallography, defect structure and local atomic relaxations are of particular interest in the study of metal-semiconductor interface boundaries.

III. 5. Precipitation of γ' Fe_4N from (α) Fe-N alloys

Iron-nitrogen alloys are particularly suited for in-situ studies of precipitation phenomena since it has been shown repeatedly [e.g. 11] that the microstructures are generally representative of those found in bulk-aged samples. The only limitation found in the present study is that stress relaxation at the foil surfaces favors the formation of some precipitate variants over others. This deficiency was overcome by supplementing the in-situ work with observations on bulk aged and extracted replica specimens.

The emphasis here is again on the value of HVEM for forming precipitates in-situ in thick foils which then allows rapid and accurate measurements of crystallographic features of the precipitate structures.

Two examples of large V-shaped γ' precipitates formed in-situ are shown in Fig. 10a and b. The V-shaped morphology arises as two variants with different habit planes grow from a common apex. The large angle tilting capability of the HVEM allowed determination of the matrix mirror plane relating the variants as {110} (Fig. 10b). In precisely oriented foils the angle subtended by the two variants was measured with precision for several examples one of which is shown in Fig. 10a and found to be 42°. The corresponding habit planes are of {049} type slightly different from the {012} reported from earlier metallographic determinations [12,13]. Fig. 10c is a composite diffraction pattern taken from a "V" precipitate and the surrounding matrix and also shows the twin relation between the two precipitate arms. It has been concluded from the observations that while each precipitate plate individually develops with a morphology which minimizes the tranformation strains locally, further relief of the residual strains is accomplished by nucleating and growing the plates in V-shaped groupings.

IV. SUMMARY AND CONCLUSIONS

The large tilting and heating capabilities of an HVEM, together with its ability to penetrate thick sections, can be used to advantage in studying solid state phase transformations.

Results of a systematic study of precipitation in various alloys are summarized. Strain accommodation processes associated with various types of transformation are discussed and experimental results are given which illustrate the critical role of lattice defects and crystal symmetry in the development of precipitate morphologies.

V. ACKNOWLEDGEMENTS

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We thank John Posthill and Chris Nelson for taking the micrographs shown in Figs. 2 and 8, respectively.

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Fig. 1. Analysis illustrating the different contrast behavior of α (1/3<001> displacements) and α' (½<001> displacements) precipitate. The three large α/α' plates are growing at the expense of the shrinking α plates surrounding them (courtesy of Acta Met.).

Fig. 2. Stereographic pair of SEM micrographs showing large Pt mounds formed on the surface of a Pt foil exposed to a carburizing atmosphere for 5 days at 900°C. Note enhancement of the effect at the grain boundaries.

Fig. 3. (a) Dark field image of radiation-induced ordered phase in Pt formed with a superlattice reflection. (b) the corresponding diffraction pattern showing extra reflections at half the matrix spot spacings.

Fig. 4. Unit cell of Pt_7C ordered phase. The face-centered sites of the cell are occupied by closely spaced pairs of carbon atoms and vacancies.

Fig. 5. Stereogram showing predicted precipitate directions for needles lying on both the cone of unextended lines and a matrix slip plane.

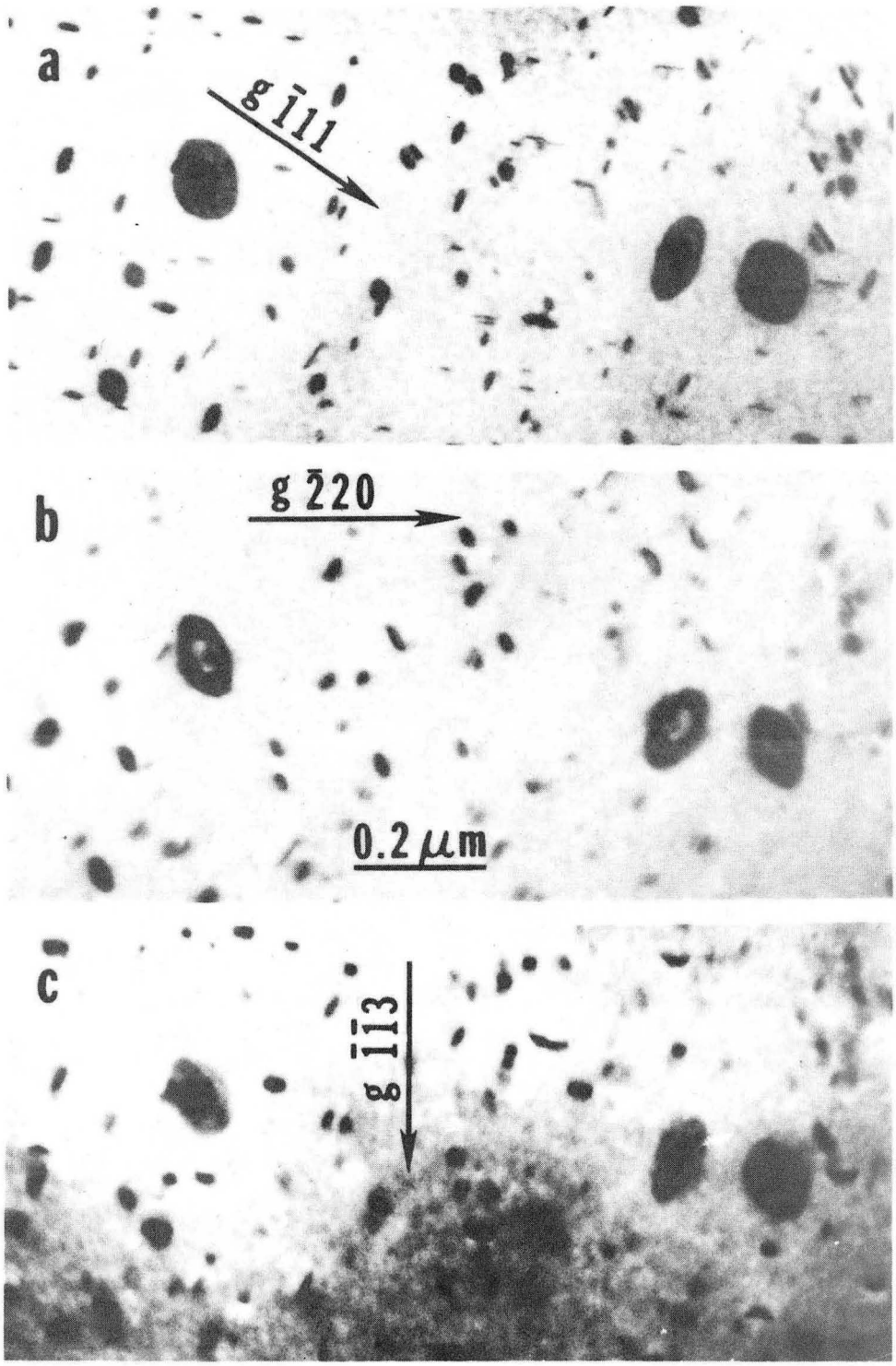
Fig. 6. Comparison of predicted and experimentally observed needle directions in Fe-Cu for a <110> zone axis.

Fig. 7. Micrograph illustrating the variety of precipitate morphologies found in a quench/aged Al- 1w/o Si alloy. The sample was aged in-situ at ∿200°C.

Fig. 8. The effects of electron irradiation on the precipitate morphology in Al-Ge are illustrated in dark field micrographs; (a) irradiated and (b) unirradiated.

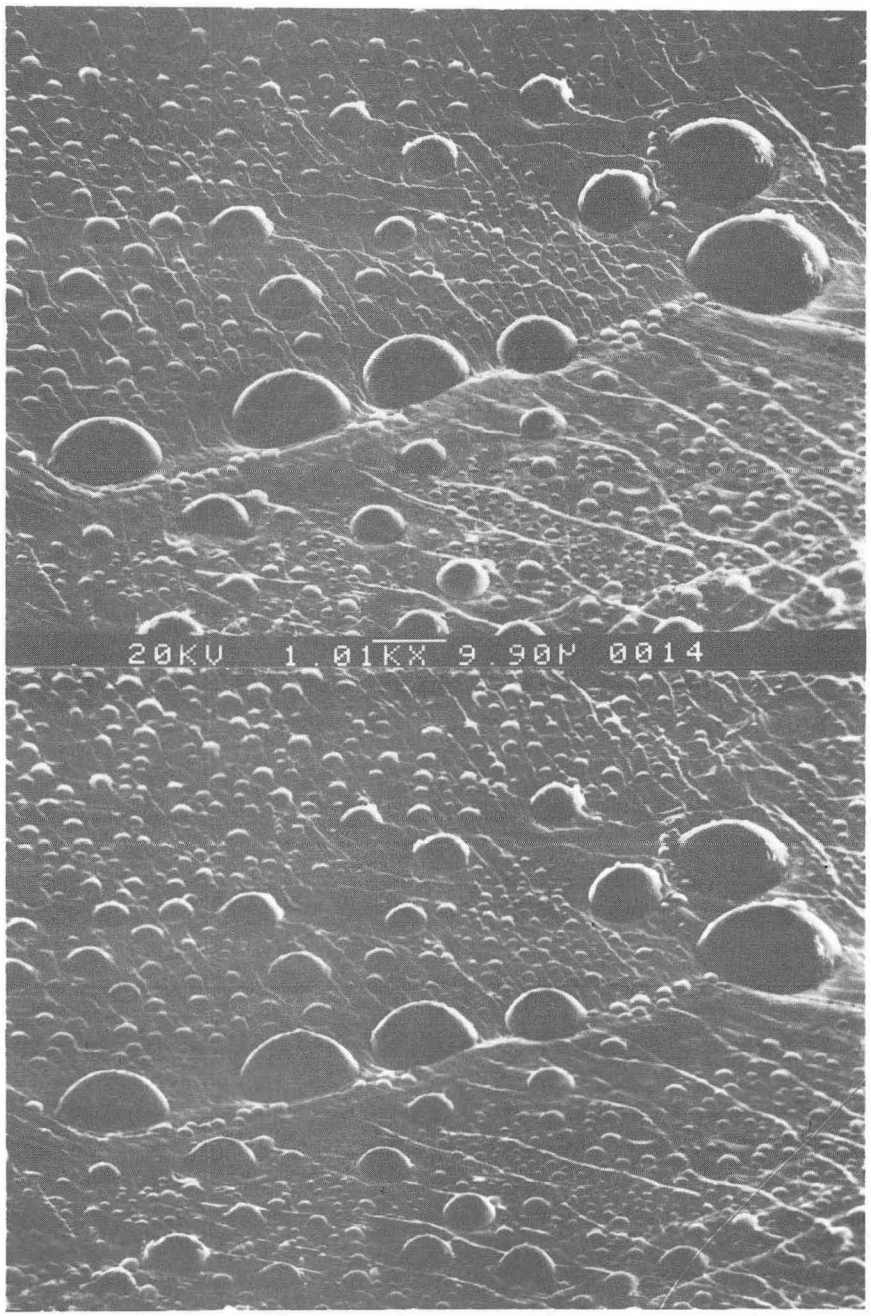
Fig. 9. Atomic resolution structure image of a <110> Ge precipitate needle in a <100> Al matrix. The image was formed at 1000 kV 9 beams of the Al matrix.

Fig. 10. Examples of V-shaped pairs of γ' precipitates formed in Fe-N alloys during in-situ aging at ∿300°C.



XBB 827-5932

Fig. 1



XBB 8512-10049

Fig. 2

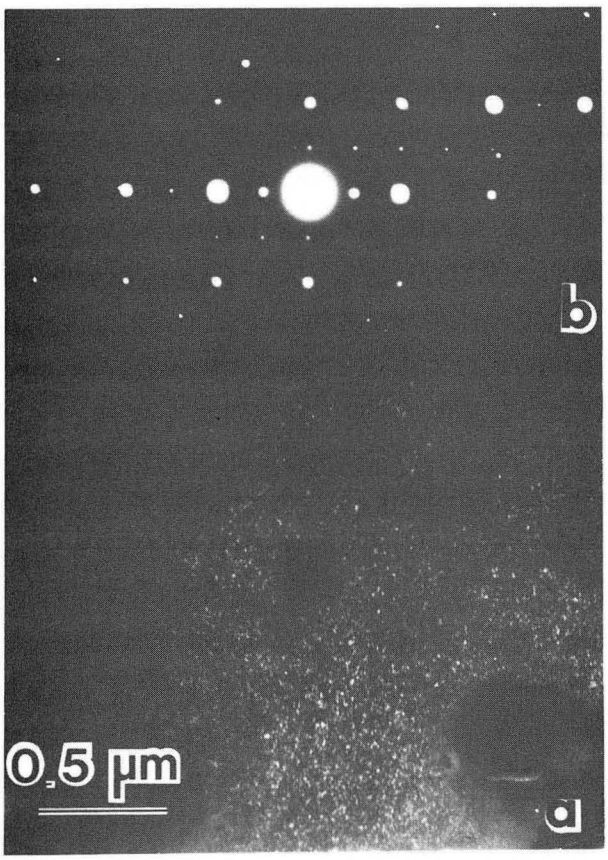


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Fig. 3

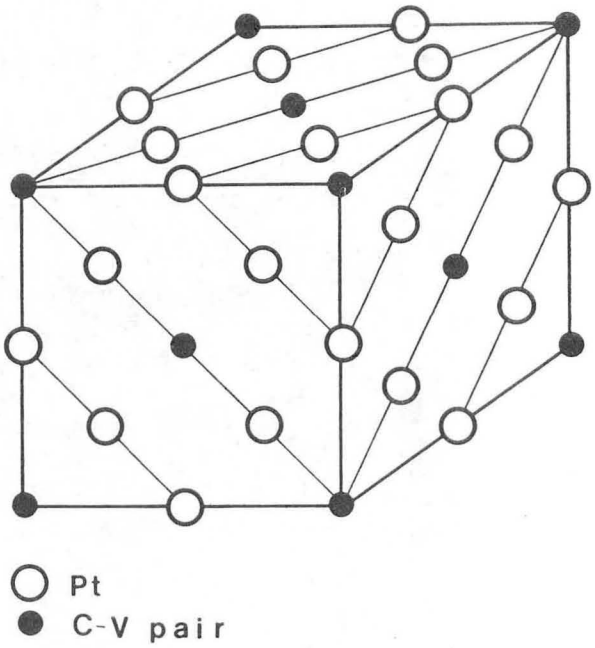

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Fig. 4

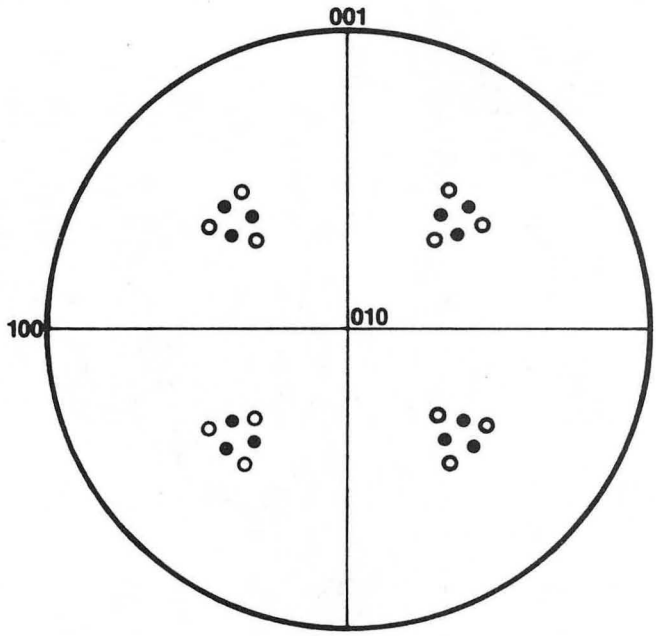

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Fig. 5

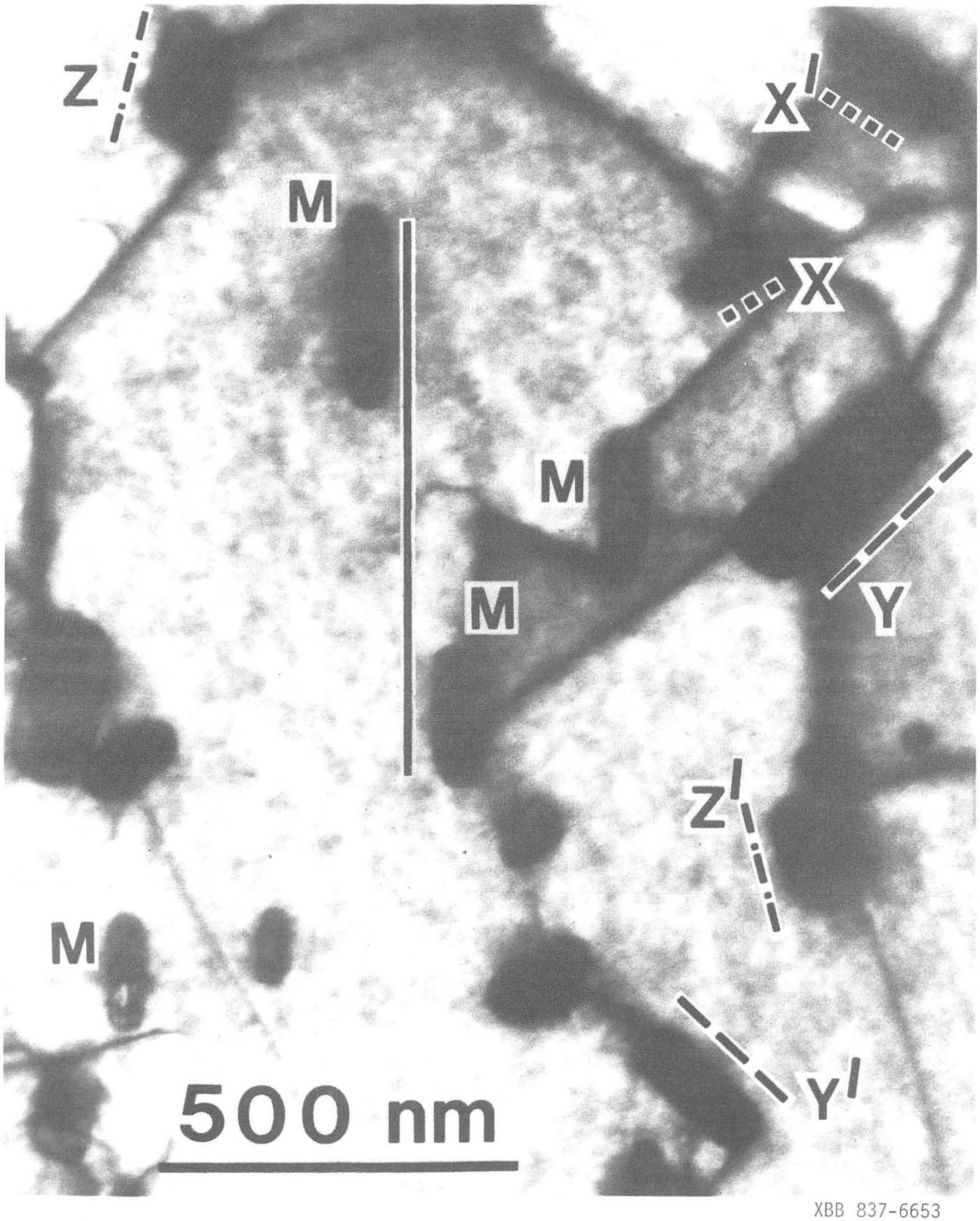

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Fig. 6

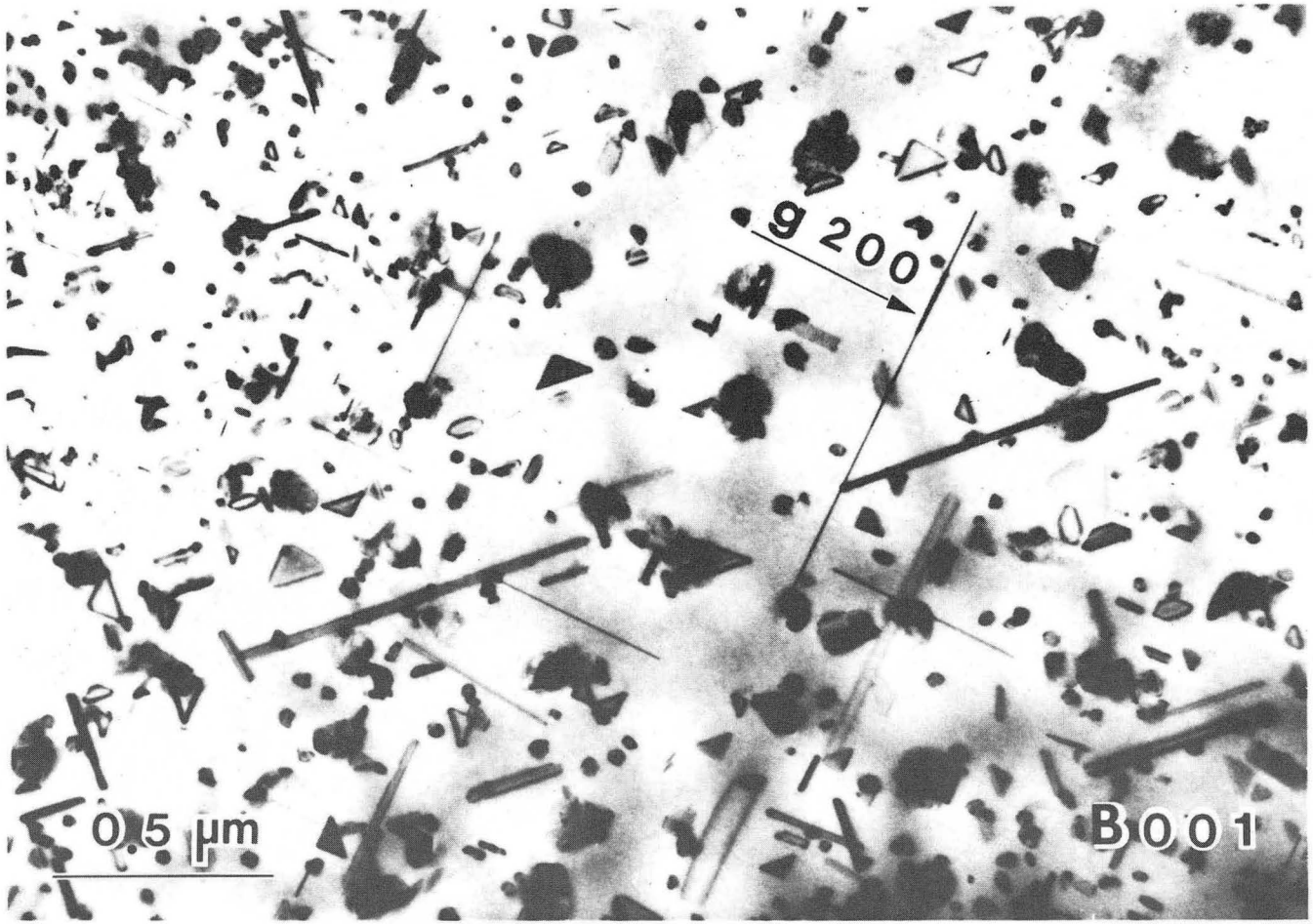

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Fig. 7

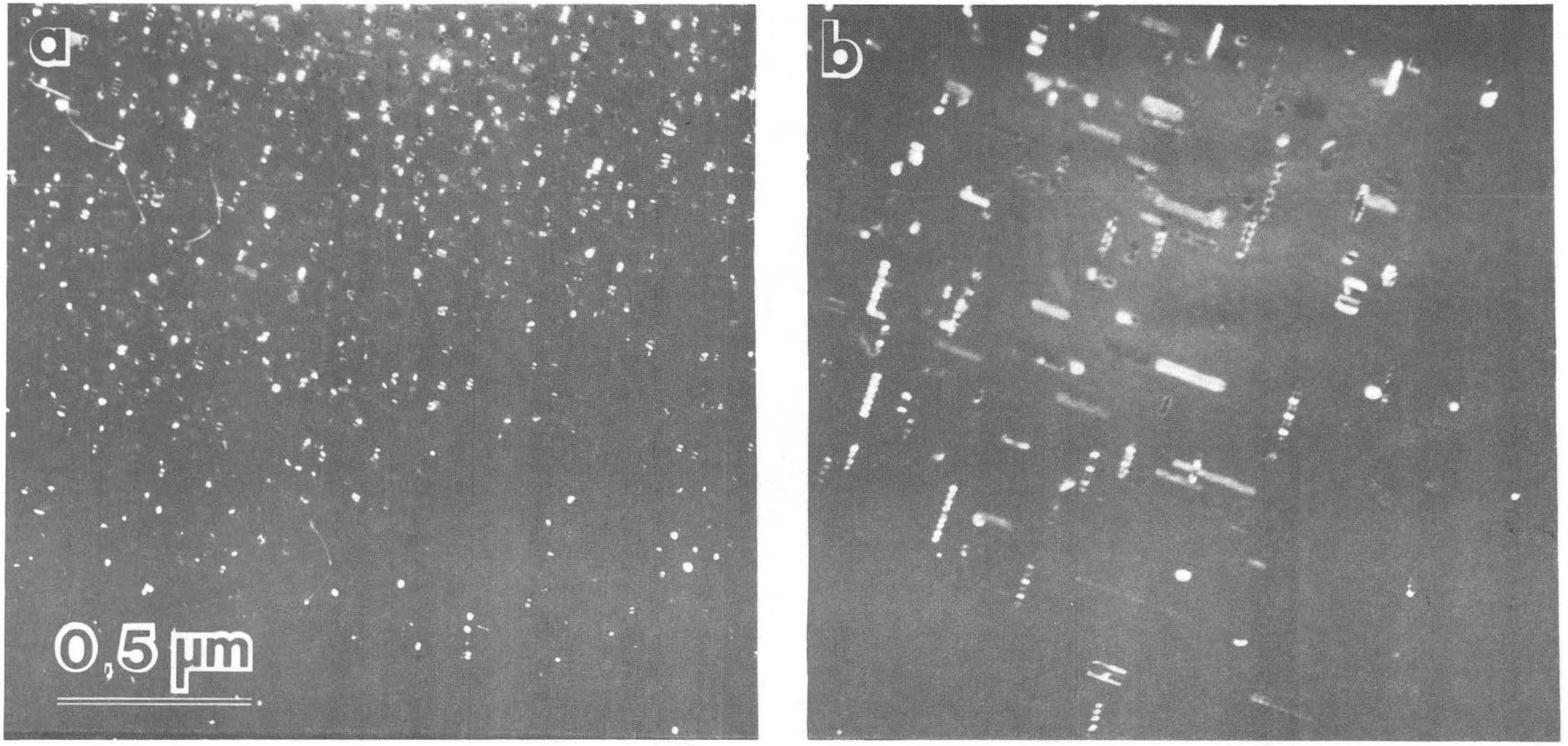

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Fig. 8

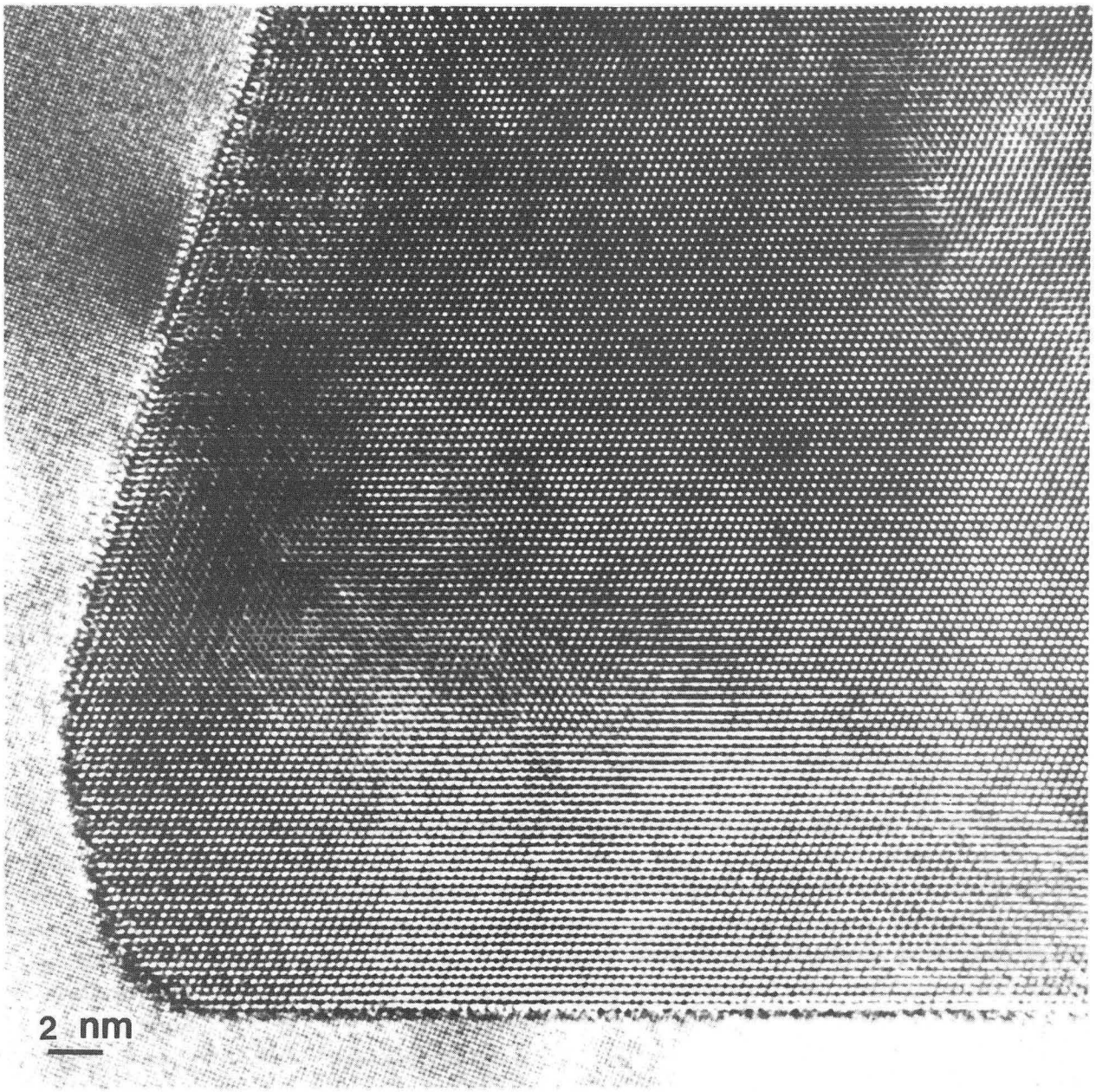

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Fig. 9

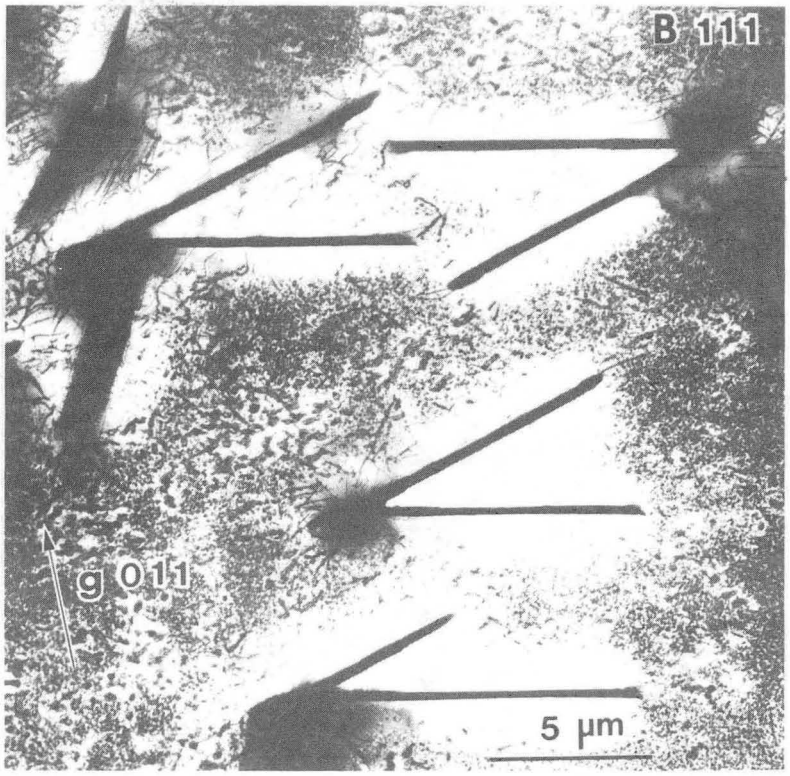

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Fig. 10

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