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Non-characteristic Defects in Thin Films of Cobalt Ferrites

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ABSTRACT

High voltage transmission electron microscopy has been used to study the structure of thin films of cobalt ferrites of various compositions. Small defects have been identified to result from a combination of chemical polishing used to prepare foils and subsequent radiation damage in the electron microscope. Such defects must be distinguished from the characteristic defects, such as small precipitates, since they are representative only of the preparation and examination techniques.

INTRODUCTION

The increased penetrating power and the low ionization radiation damage of the electron beam produced in high voltage electron microscopes[1] constitute the main reasons why extensive structural investigations are now possible of non-metallic materials from which very thin foils are not easily prepared, and are sometimes not desirable. During a high voltage transmission electron microscope study of phase transformations in cobalt ferrite spinels (to be reported later), small defects were observed which were not representative of the bulk samples. This paper discusses the identification and the origin of these non-characteristic defects.

EXPERIMENTAL

Specimens were obtained from the Airtron-Litton Industries in the form of small single crystals with a diameter from 2 to 3 mm. They were annealed in air at temperatures of about 900°C for about 50 hours. Then they were cooled slowly. The crystals were mechanically ground down to platelets with a thickness of about 75 microns, and subsequently polished. A chemical polishing technique was used similar to the one reported by Lewis[2] for magnesium aluminate spinels. The platelets were immersed in hot phosphoric acid kept at a temperature of about 400°C. When the platelets were dissolved to about 1/3 of their original size electron transparent areas could usually be found at the edges. Chemical polishing took 5 to 10 minutes. Immediately after polishing, the specimens were first washed in hot water, and then in alcohol. The foils were examined in a Hitachi 650 kV transmission electron microscope.

The composition of the microscope atmosphere was analyzed at

the specimen stage level with a Varian partial pressure gage. The total pressure was about 5×10^{-6} Torr. Fig. 1 shows the gage readout, from which the partial pressures can be calculated. Water vapor was the main gas phase, and this probably evolves from the photographic plates in the microscope camera chamber. The partial pressures of the three main gas phases (H_2O, N_2 and O_2) in the specimen neighborhood have been listed in fig. 1.

RESULTS

Numerous small defects were found in all the ferrites that were examined ($Co_{1.05}Fe_{1.95}O_4$ to $Co_{1.29}Fe_{1.79}O_4$). Fig. 2 shows the distribution of the defects around a nearly perfect conical etch pit. The observations were made at an accelerating voltage of 650 kV, and this allows the foils to be electron transparent with good resolution up to about 1 micron for $\bar{g} = 440$. When the number of defects per unit area is counted in this foil it is found that the projected defect density is invariant over the entire range of thicknesses. The defect images are black-white lobes, with a line of no contrast dividing the lobes. These kinds of images typically result from the matrix strain field around defects that are too small to be resolved directly. The contrast of such defects was first discussed by Ashby and Brown,[3] and subsequently examined in more detail particularly with regard to depth dependence by several authors, e.g. Ruhle et al.[4] The direction of the white-to-black contrast may be characterized by a vector $\bar{q}$ (see Bell and Thomas[5]). Consideration of the direction of the line of no contrast LC, $\bar{q}$ and $\bar{g}$, can for certain foil orientations allow the immediate identification of the displacement vector associated with

the defect. LC and $\bar{q}$ have been defined in the insert in fig. 2. In this bright field image $\bar{q}$ is the same for every defect, suggesting that they are all located near the top or near the bottom surface of the foil. In the many foils that were examined these defects were found with the same projected defect density right up to the foil edges. At 650 kV the extinction distance for 440 reflections is about 800Å for cobalt ferrites, so that it may be assumed that the defects are located within half an extinction distance from either surface. Further information must come from a comparison of bright and dark field images.[5] Image contrast calculations according to the procedures set up by Bell and Thomas[6] for a systematic 12 beam dynamical case at 650 kV showed that, as far as strain contrast from small defects is concerned, the same rules apply as were worked out by Ashby and Brown for a two beam case at 100 kV, when the defects are within half an extinction distance from the surface. Bright and dark field images are compared in figs. 3a and 3b. Note that $\bar{q}$ is in the same direction in both bright and dark field. From these observations it can be concluded that the defects are all near the surface of the foil that is facing the electron gun, and that they are of the vacancy type. For most of the defects LC is perpendicular to the operating diffraction vector $\bar{g}$, while the direction of $\bar{q}$ is anti-parallel to $\bar{g}$. Some defects marked L, for which LC is not perpendicular to $\bar{g}$, have been marked. For these defects LC is along the $[1\bar{1}0]$ direction while $\bar{q}$ is still antiparallel to $g = \bar{4}04$. This strongly suggests that the marked defects are vacancy loops on the $(11\bar{1})$ plane. The magnitude of the Burgers vectors has not been determined, but since

dislocations appear not to be dissociated in cobalt ferrite spinels,[7] the loops are probably perfect prismatic loops with b = a/2 110. Figs. 4a and 4b show two dark field images with different 440 operating vectors. A loop found in this area is marked L. For the other defect images LC is at all times perpendicular to $\bar{g}$ while at the same time $\bar{q}$ is antiparallel to $\bar{g}$. It must be concluded that the large majority of the defects are spherical vacancy clusters, while only occasionally a prismatic loop is formed.

The increase in projected defect density with constant irradiation in the microscope was followed. Figs. 5a to 5d show how the defect density changes with time. The diffracting vectors are different 440 reflections. This again allows one to distinguish between loops and spherical clusters. A loop that was found in this area has been marked L. Note that the defects retain their character within the observations interval: there is no switch from spherical cluster to loop, or conversely. The projected defect density versus time is plotted in fig. 6. These observations show that the projected defect density saturates at about 2×10^9 per cm^2 after about 20 minutes of observation. This kind of behavior is quite similar to that observed by Makin on copper.[8] In the present case the clusters do not continue to grow, however, beyond a radius of about 100Å, at least within the period of observation. In appearance, the defects are similar to those that result from the ion bombardment of some FCC metals.[9] The defects observed in the present work are likely to be oxygen vacancy clusters. Indeed, during polishing in hot phosphoric acid, hydrogen is produced on the surface of the dissolving crystal. The hydrogen reduces the

crystal over a very small depth and this reaction catalyzes the dissolution. The precipitation of the vacancies that are introduced in this way in the surfaces of the foils, would then be stimulated by the radiation damage produced during observation in the microscope. The radiation damage results from the impact of accelerated ions; it is unlikely that it would originate in primary electron knock-on events since then the defects should appear simultaneously in the top and the bottom surface of the foil. Also, the defects form with equal density in parts of the foil that are not electron irradiated. The accelerated ions are probably formed from the gases that are present in the microscope atmosphere, which, as was described in the experimental section, are most probably oxygen ions from dissociating water vapor, and nitrogen ions.

Upon heating in the hot stage the defects slowly disappear at about 400°C. Above these temperatures phase transformations occur in the foil and the behavior of the clusters can no longer be followed. An example of a partially transformed foil is shown in fig. 7.

Defect clusters were also observed to form during observation at liquid nitrogen temperatures. These defects are shown in fig. 8. Since there are presently no tilting facilities available for the cold stage, the number of diffraction experiments that can be carried out are rather limited. Still, it seems that the strain fields of the defects are not quite spherical. Instead, the strain contrast indicates that at this temperature small stacking fault tetrahedra form (strain contrast from small tetrahedra has been discussed by Chik.[10]) This change of defect character with temperature is not

clearly understood, unless one would assume that the stacking fault energy decreases with decreasing temperature.

CONCLUSIONS

a. Oxygen is lost from the surface layers of the cobalt ferrite spinels during chemical polishing in hot phosphoric acid.

b. Damage produced by the impingement of accelerated ions stimulates the precipitation of the oxygen vacancies in the top surface of the specimen. The ions that produce the damage are most likely to be nitrogen ions and oxygen ions from the dissociation of the water vapor that is present in the microscope atmosphere. Near room temperature the defects are nearly all spherical vacancy clusters, while occasionally a perfect prismatic vacancy loop is formed. At low temperatures, the indications are that small stacking fault tetrahedra are more frequent. The defects can be electrically neutral by an appropriate electron transfer among the neighboring cations.

c. As with certain metals, care must be exercised in electron microscope analyses of lattice defects in ceramic materials. In the present case, the preparation induced defects must be distinguished from characteristic defects and small precipitates. The maximum projected density of the non-characteristic defects is about 2×10^9 per cm^2, which clearly allows the study of other defects of interest in the foils without interference.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

1. Partial pressure gage read-out. From this, the partial pressures of the gases present in the microscope atmosphere can be determined. The main components are water vapor and nitrogen.

2. Distribution of defects around a nearly perfect conical etch pit. The insert defines the line of no contrast LC and the direction $\bar{q}$ of the white-to-black image contrast. Note that $\bar{q}$ is the same for all the defects.

3. Bright and dark field images of the defects. Prismatic vacancy loops are marked L.

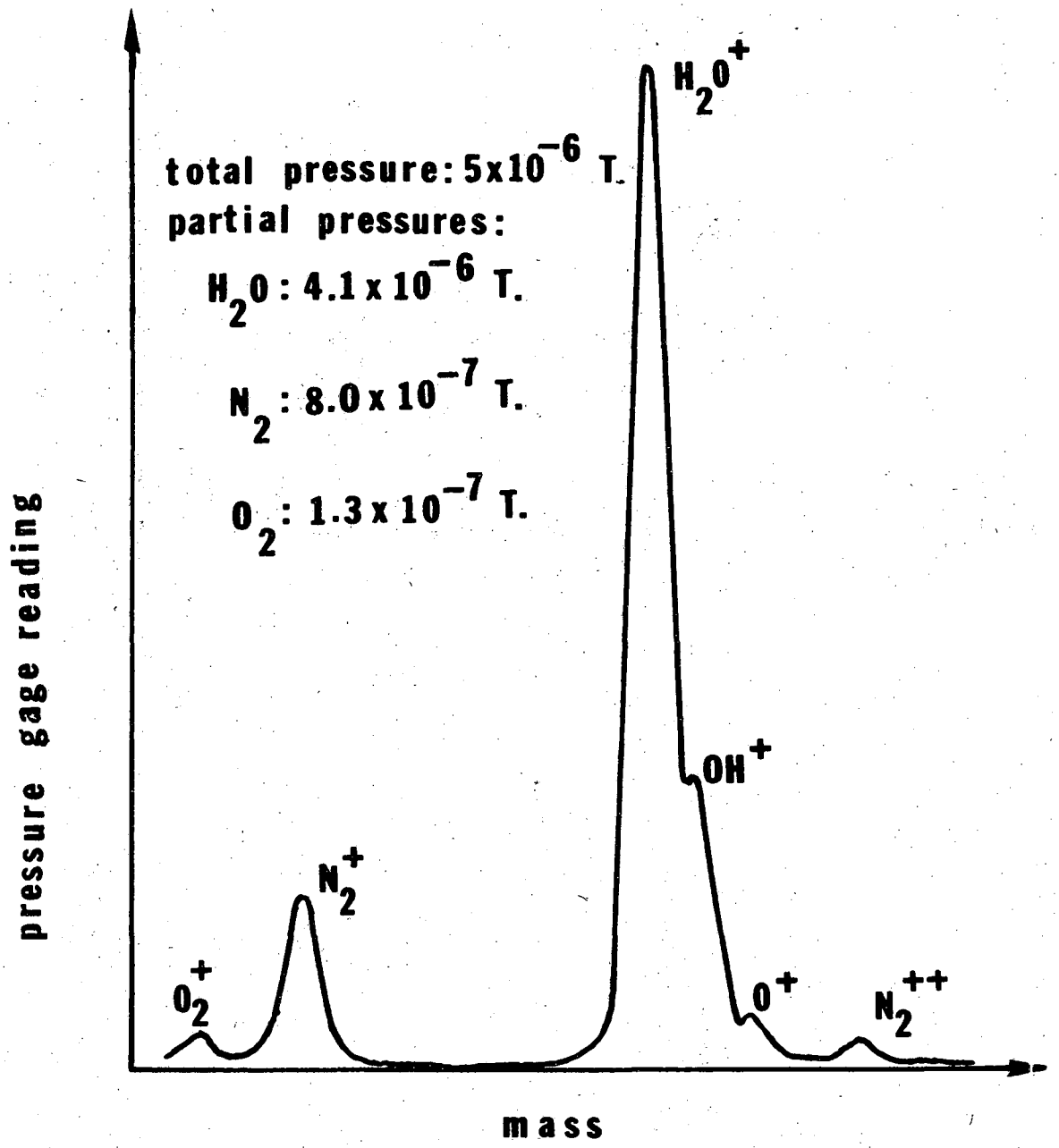
4. Dark field images of the defects with different 440 diffracting vectors operating. A loop has been marked as L. The majority of the defects are spherical vacancy clusters. Only occasionally are loops in evidence.

5. Change of the defect density with time. The different diffracting vectors allow at the same time distinction between spherical clusters and loops L. The elapsed time is indicated.

6. Increase of projected defect density versus time with continuous observation at 650 kV.

7. Cobalt ferrite spinel partially transformed in the hot stage above 400°C. Note the interface fringe contrast from the numerous larger defects and the strain contrast from the smaller ones.

8. Defects formed at liquid nitrogen temperatures. The contrast in a and b seems to indicate that most of the defects are tetrahedra rather than spherical clusters or prismatic loops.



XBL 706-1216

Fig. 1

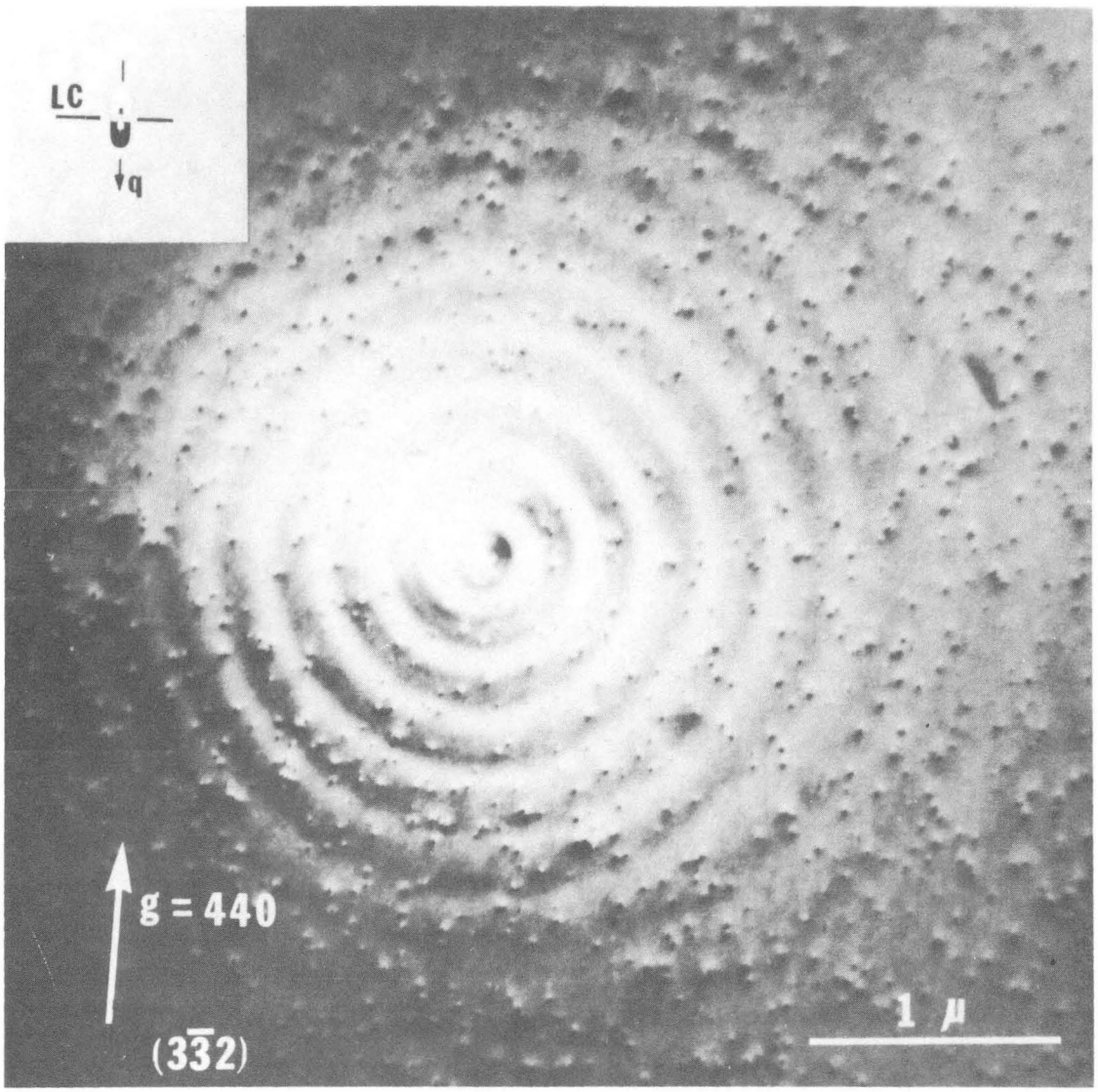


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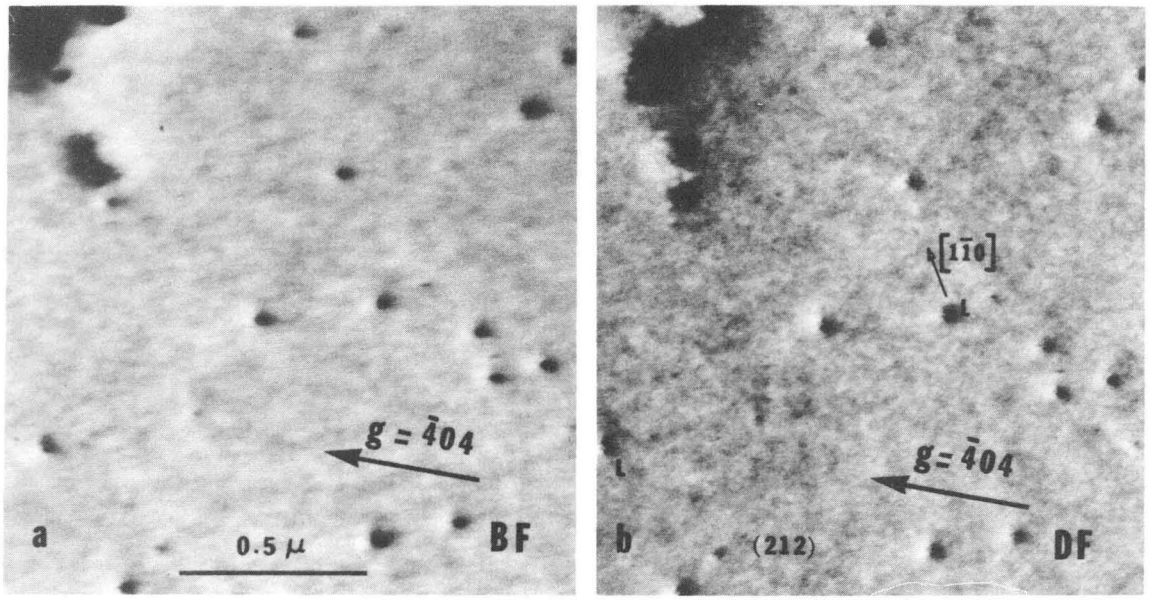
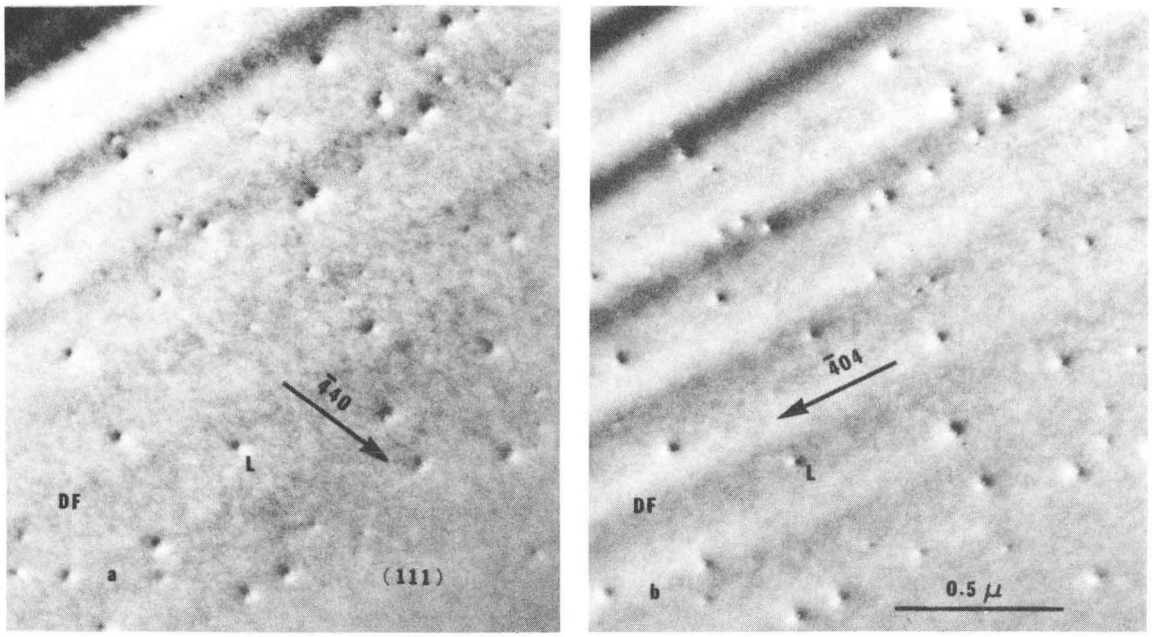
Fig. 2



XBB 706-2770

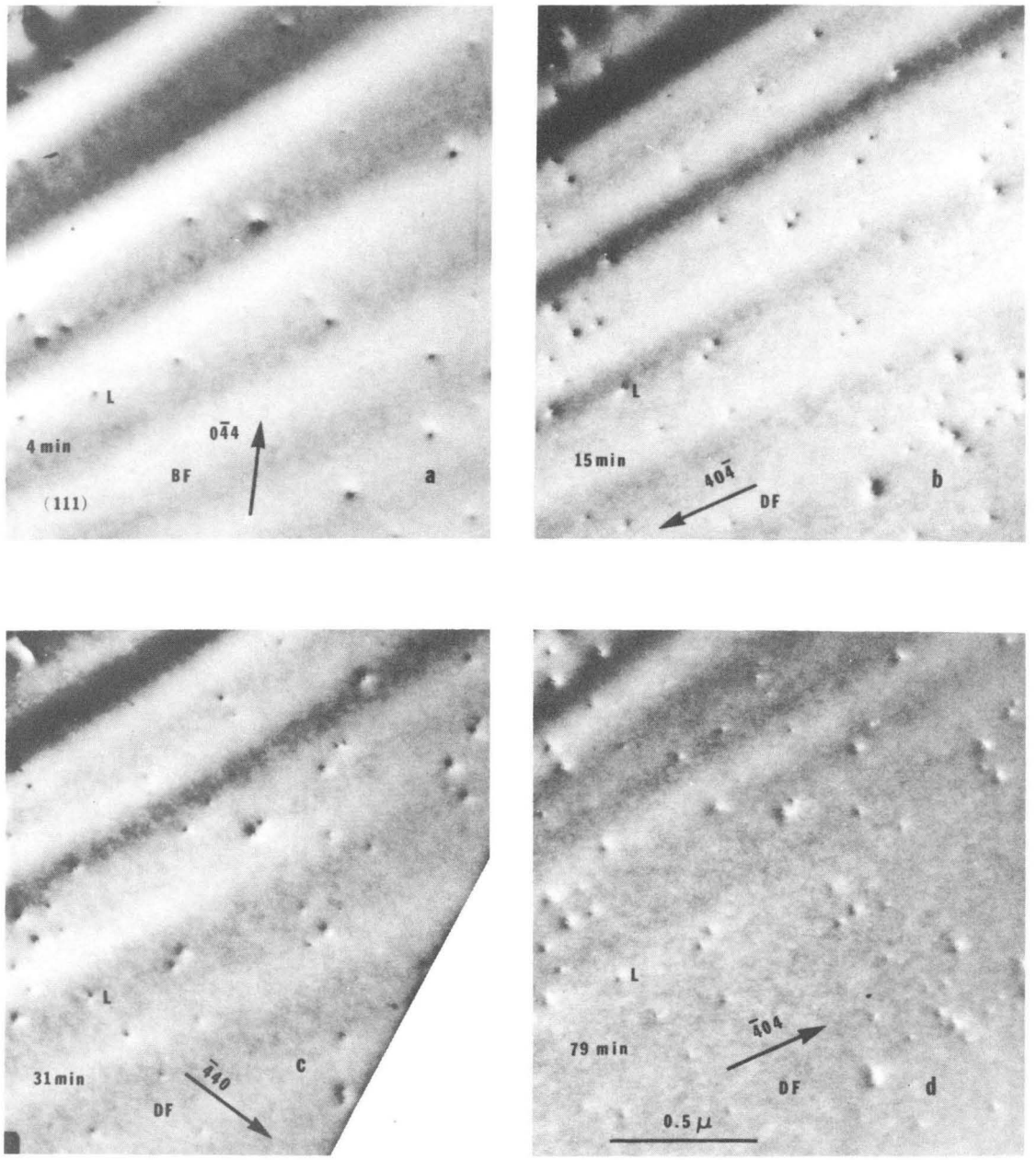
Fig. 3



(a) (b)

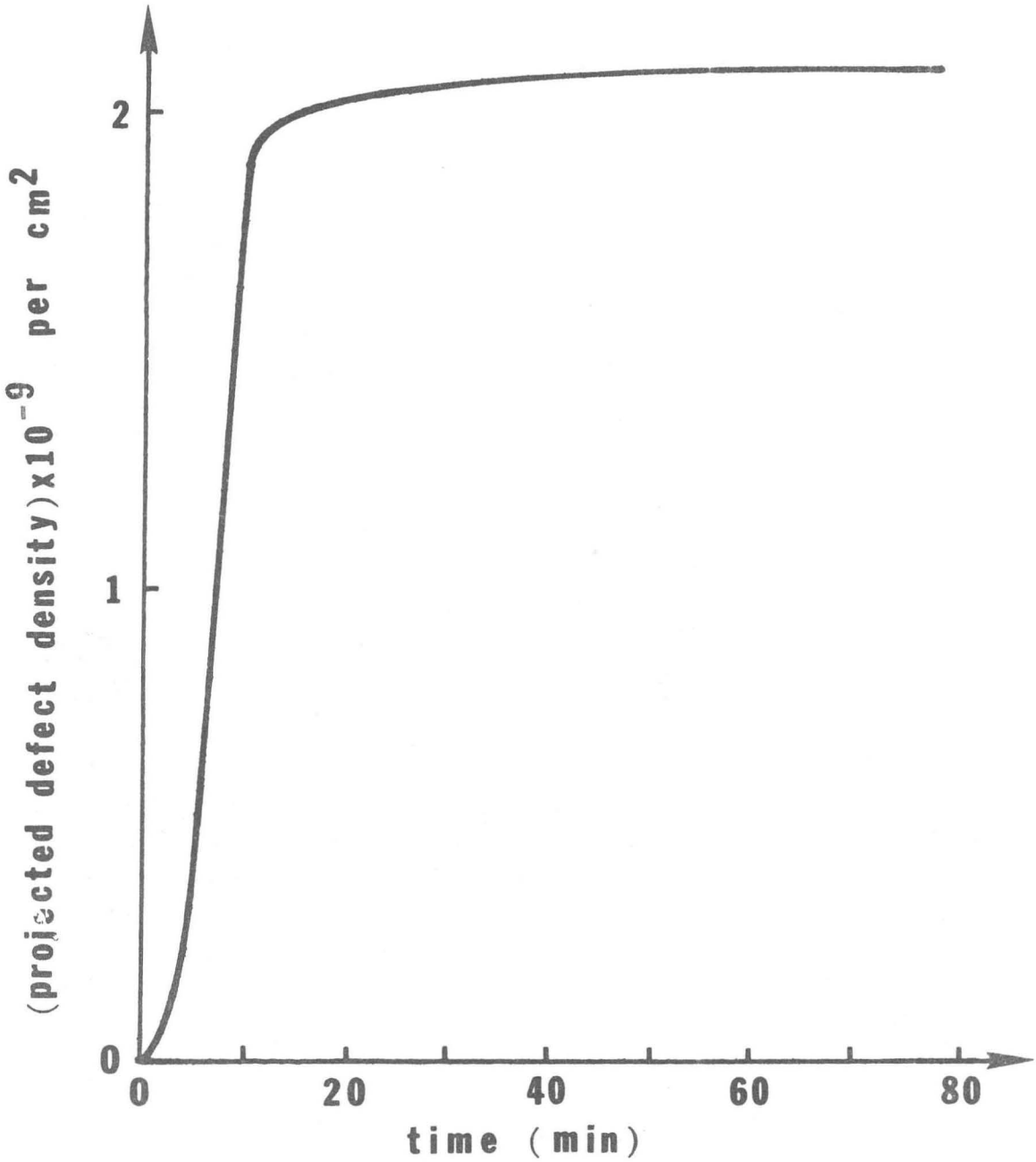
XBB 706-2769

Fig. 4



XBB 706-2774

Fig. 5



XBL 706-1217

Fig. 6

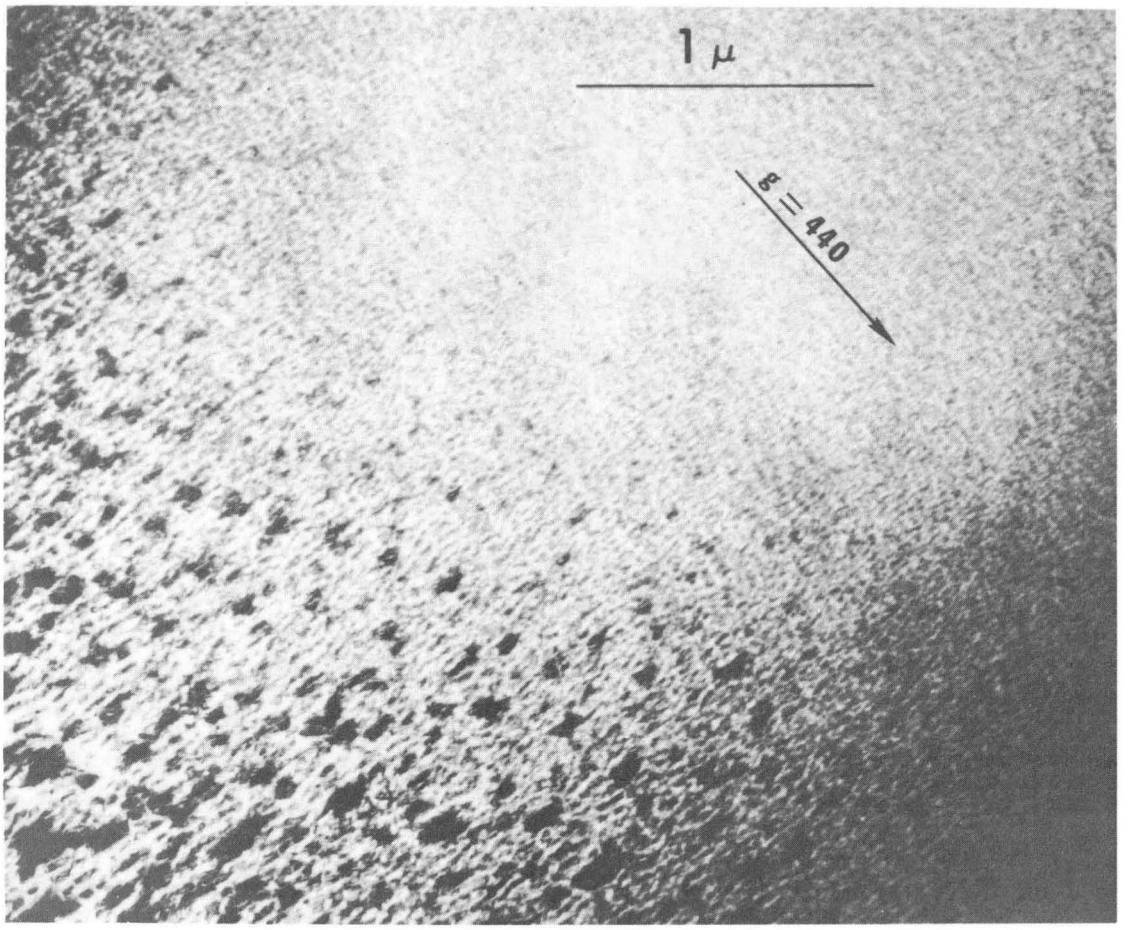


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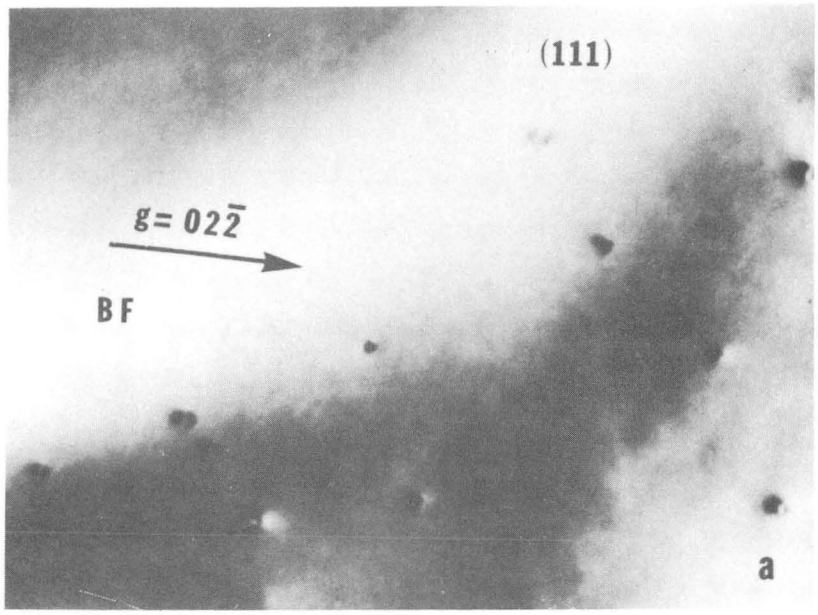
Fig. 7



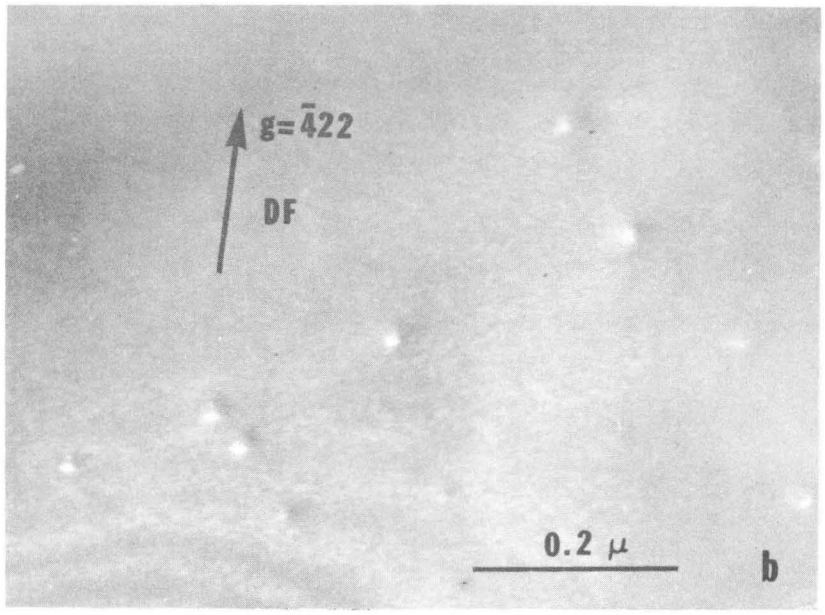


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Fig. 8

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