Lawrence Berkeley National Laboratory
Recent Work

## Title

EFFECT OF SPECIMEN THICKNESS ON SYMMETRY DETERMINATIONS BY CONVERGENT-BEAM ELECTRON DIFFRACTION

## Permalink

https://escholarship.org/uc/item/6c33v5ws

## Authors

Howe, J.M.
Gronsky, R.

## Publication Date

1985

eScholarship.org Powered by the California Digital Library
University of California

LBL-18894
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY
MAR 15 1985
LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular
Research Division

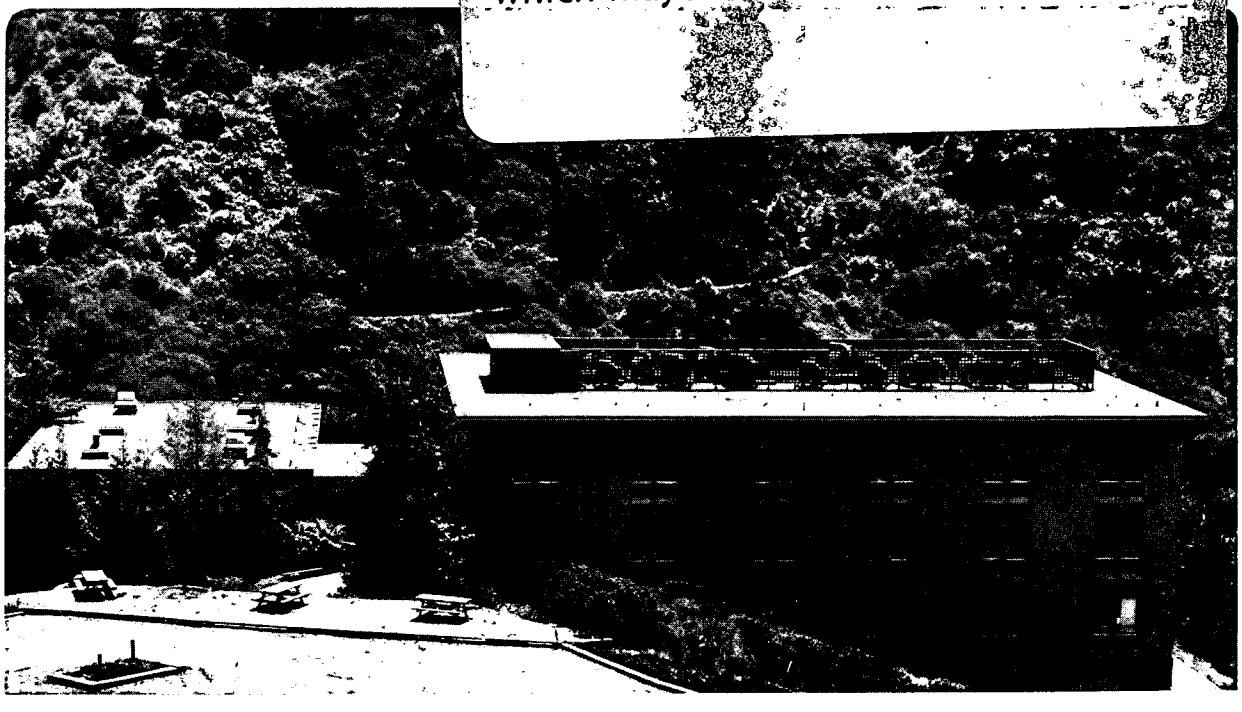
To be submitted to the Journal of Ultra Microscopy

# EFFECT OF SPECIMEN THICKNESS ON SYMMETRY DETERMINATIONS BY CONVERGENT-BEAM ELECTRON DIFFRACTION

J.M. Howe, and R. Gronsky

January 1985

TWO-WEEK LOAN COPY
This is a Library Circulating Copy
which may be borrowed for two weeks.



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-18894

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

# Effect of Specimen Thickness on Symmetry Determinations by Convergent-Beam Electron Diffraction

J.M. Howe and R. Gronsky
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Department of Materials Science and Mineral Engineering
University of California
Berkeley, CA 94720

## ABSTRACT

The application of covergent-beam electron diffraction to the study of local symmetry is becoming increasingly popular in the materials science community. One of the most important tests for determining the point and/or space group of a material is the $\pm$g experiment which is used to test for a center of symmetry. This study shows that thin specimens may appear to lack centrosymmetry due only to their limited thickness along the beam direction, rather than to the actual space group of the material. Also, zone axis convergent-beam patterns from thin specimens may display a symmetry which is higher than the actual symmetry of the material, due to a loss of higher-order Laue zone lines in the patterns under weak dynamical scattering conditions. Extreme care must therefore be taken to ensure that point and/or space group determinations are performed on specimens which most closely satisfy the conditions of an infinitely thick, parallel-sided crystal.

## INTRODUCTION

The determination of the point group of a material by convergent-beam electron diffraction (CBED) was originally introduced by Buxton et al.[1], who used group theory and graphical construction to determine the pattern symmetries of the 31 diffraction groups and relate these to the 32 crystal point groups. Further refinements of the technique by Steeds and Vincent[2] and Tanaka et al.[3,4] now make point and space group determinations by CBED relatively straightforward

procedures, and numerous examples of these applications have appeared in the literature[5,6]. The most commonly used procedure for determining the point group of a material requires a detailed examination of the intensity distributions and higher-order Laue zone (HOLZ) lines within the convergent-beam discs, and comparison with Tables 2 and 3 in Buxton et al.[1]. One of the most important tests for determining the point group of a material by this method is the $\pm g$ experiment, where the intensity distributions within opposite hkl discs are compared after having been set at their respective Bragg conditions. Such a test indicates whether the material possesses a center of symmetry. Columns 6 and 7 in Table 2 of Buxton et al.[1] list the symmetries observed between $\pm g$ pairs of reflections for the 31 diffraction groups. One of the main advantages that CBED has over x-ray diffraction for determining the point group of a material is the ability to readily distinguish between centrosymmetric and noncentrosymmetric crystals simply by comparing the intensity distributions between pairs of hkl discs, due to the breakdown of Friedel's law[7] for a noncentrosymmetric crystal in electron diffraction[8,9]. For electron diffraction, this law can be expressed as:

$$(I_{hkl})^{uvw} = (I_{\bar{h}\bar{k}\bar{l}})^{\bar{u}\bar{v}\bar{w}} \qquad (1)$$

where $I_{hkl}$ represent the dynamic intensities corresponding to the incident beam direction (uvw). Formal testing of this law requires that the intensity distributions be compared between the diffraction patterns of a crystal which has been rotated 180 degrees. However, since HOLZ lines may introduce asymmetry into a CBED pattern, the condition of centrosymmetry for a convergent-beam pattern

or group of patterns may be defined by:

$$(I_{hk0})^{uvw} = (I_{\bar{h}\bar{k}0})^{\bar{u}\bar{v}w} \qquad (2)$$

for all possible reflections for a structure which is at least centered in a [001] projection[9]. Consequently, violation of this law indicates a lack of center of symmetry in the projection and thus, in the crystal as a whole.

Our interest in the validity of center of symmetry determinations by CBED resulted from the application of this technique to the study of $\gamma'$ plate-shaped precipitates in an Al-Ag alloy (Fig. 1). These plates require both chemical and structural changes for growth, and it was hoped that CBED could be used to follow any symmetry or lattice parameter changes which might occur during the early stages of the growth process. Pure $\alpha$-titanium was chosen as a standard for lattice parameter measurements because it has similar lattice parameters, a similar average atomic scattering factor and the same space group anticipated for the $\gamma'$ precipitates. However, space group analyses of the thin $\gamma'$ plates yielded confusing results; that is, the combination of symmetry elements and Gjonnes-Moodie lines of dynamical extinction[10] that were observed in the patterns indicated that the precipitates should contain a center of symmetry, although $\pm g$ experiments in several orientations failed to verify this symmetry element. Subsequently, this same group analysis was performed on the $\alpha$-titanium standard for comparison with the precipitates. In addition, $\pm g$ experiments were performed over a range of sample thickness for the $\alpha$-titanium in a $[1\bar{1}02]$ orientation, because it was suspected that the limited thickness of the $\gamma'$ precipitates might be responsible for their apparent loss of symmetry. This paper reports the results of these $\pm g$ experiments.

## EXPERIMENTAL PROCEDURES

Hot-rolled 0.8 mm thick, 99.99% Ti sheet was ground to 125 μm thickness on water-cooled SiC papers down to 600 grit. Discs 3.0 mm in diameter were punched from the sheet, vacuum encapsulated, and annealed for 1 hour at 600°C to produce a completely recrystallized α-phase microstructure. Thin foils were polished in a twin-jet Fischione apparatus using a 25% $HNO_3$ / 75% $CH_3OH$ electrolyte at about -35°C, 16 V and 25 mA. All CBED experiments were performed on a Philips EM400, modified such that the objective and 2nd condenser lens currents could be independently varied to achieve a wide range of incident beam convergence angles on the specimen. Convergence angles of about 15 mrad were obtained in the TEM mode by using a 300 μm 2nd condenser aperature, an 0.2 1st condenser spot size (probe diameter $\sim$400 Å), and then increasing the objective lens current so that the diffraction discs in the zero-order Laue zone (ZOLZ) just touched without overlapping, while focussing the probe independently on the sample with the 2nd condenser lens control. Tilting experiments were performed by translating the 2nd condenser aperture (equivalent to a gun tilt), after having obtained a zone axis pattern. A 450 mm camera length was used to photograph the intensity distributions within the ZOLZ discs, and a double-tilt, liquid nitrogen cooled specimen holder (Temp. = -188° C) was employed to eliminate contamination and reduce diffuse scattering in the specimen.

## RESULTS AND DISCUSSION

In its α-phase form, Ti has a hexagonal close-packed structure with a = 2.950 Å and c = 4.683 Å. Alternatively stated, it has a two atom unit cell basis and is centrosymmetric, with the space group $P6_3/mmc$. Goodman[11] and Goodman and Whitfield[12] have shown that the $\pm g$ test for centrosymmetry is most effective

if performed at a low-symmetry zone axis, where the electron intensity is concentrated in the pair of hkl discs of interest and these discs lack mirror symmetry perpendicular to the horizontal rotation diad, thus enabling the perfect translation operation between hkl and $\bar{h}\bar{k}\bar{l}$ discs in a centrosymmetric material to be easily identified. In this investigation the $[1\bar{1}02]$ zone axis was chosen for the center of symmetry versus thickness tests, because the zone-axis pattern and $\bar{1}101/1\bar{1}0\bar{1}$ discs satisfy these conditions. The $[1\bar{1}02]$ zone axis lies at an angle of about 11 degrees from the high-symmetry [0001] principal zone and can usually be reached by rotating the specimen about a $[11\bar{2}0]$ axis from this zone. However, the Ti thin foil used here contained a grain at the edge of the hole which has already near a $[1\bar{1}02]$ zone axis and hence, a rotation of only a few degrees was required to achieve an exact zone axis orientation. The letters (a) through (d) In Fig. 2(a) indicate where the probe was positioned relative to the edge of the foil (lower right corner) for the thickness versus center of symmetry determinations, and correspond directly to the four series of $\pm g$ CBED patterns labelled (a) through (d) in Fig. 3. The probe was located at these positions by observing the ghost image with the 2nd condenser lens in an underfocussed condition, as illustrated in Fig. 2(b), where the probe is located at position (d) in the thinnest region of the foil. The results of the center of symmetry tests are shown in Fig. 3, where the sample thickness decreases from (a) to (d), and $\bar{1}101$ and $1\bar{1}0\bar{1}$ discs are shown on either side of the $[1\bar{1}02]$ zone axis pattern for each thickness.

Examination of the intensity fringes and HOLZ lines within the ZOLZ discs in the zone axis pattern in Fig. 3(a) shows that both the bright field disc and whole pattern have 1m symmetry, as indicated in the figure. In addition, the $\bar{1}101$ and $1\bar{1}0\bar{1}$ discs both have the same 1m symmetry when located at the Bragg

position, and the detail within these discs is related by a perfect translation operation rather than by a 180 degree rotation. Thus, reference to Table 2 in Buxton et al.[1] indicates that the diffraction group of this specimen is $2_R mmm_R$, where the perfect translation operation ($2_R$) between the hkl and $\bar{h}\bar{k}\bar{l}$ reflections consists of a rotation of either hkl disc by 180 degrees about the center of the pattern, followed by an additional rotation of 180 degrees about its own center. Further knowing that the zone axis is $[\bar{1}\bar{1}02]$, allows determination of the point group from Table 3 as 6/mmm, which is correct for the space group $P6_3/mmc$.

Fig. 3(b) shows a similar series of patterns taken in a thinner area of the specimen, where HOLZ lines are just visible in the bright field disc in the zone axis pattern. Analysis of these patterns yields the same results as above, and the point group is again identified as 6/mmm. However, when the same $\pm g$ experiment is performed in a slightly thinner area, where HOLZ lines are no longer visible in the pattern and only weak 3-dimensional dynamical diffraction is occurring, a different point group is obtained. First, notice that the intensity fringes in the zone axis ZOLZ discs in Fig. 3(c) have 2mm symmetry. This is not different from the previous patterns, but the absence of HOLZ lines now allows this pattern to be interpreted as having a higher symmetry than before. In addition, although the $\bar{1}101$ and $1\bar{1}0\bar{1}$ discs still have 1m symmetry, they are no longer related by a perfect translation operation but rather, by a 180 degree rotation. Hence, reference to Table 2 in Buxton et al.[1] now indicates that the diffraction group of this specimen is 2mm, rather than $2_R mmm_R$, and similar reference to Table 3 yields a lower-symmetry point group of $\bar{6}m2$, which is incorrect for the space group $P6_3/mmc$. The same experiment was again repeated in the thinnest areas of the foil, where intensity distributions were just visible within the

ZOLZ discs. As shown by Fig. 3(d), the same incorrect diffraction and point groups are obtained.

These results demonstrate conclusively that pattern symmetries which are not representative of the actual projected symmetry of a material may be obtained by CBED from thin specimens. In this investigation, two separate but related effects were observed. First, Friedel's law (Eqn. (1)) is a valid test for centrosymmetry only under dynamical scattering conditions, where the intensities in the CBED patterns are sensitive to the phases of the structure factors and hence, to all of the symmetry elements of the space group. Thus, under conditions where dynamical scattering is very weak and approaching kinematical scattering, Eqns. (1) and (2) may not apply. The result of approaching kinematical scattering conditions in the CBED patterns in Fig. 3 is evidenced by an increase in the overall symmetry of the zone axis patterns, as large angle scattering is reduced to the extent that HOLZ lines, which lower the symmetry of the zone axis patterns, are no longer present. Second, Goodman and Moodie[13] have shown by n-beam dynamical theory, that the presence of an incomplete unit cell at the surface of a crystal can significantly alter the diffracted amplitudes from that crystal. Goodman[14] has also illustrated the effect of having such an incomplete unit cell on the element of centrosymmetry in CBED. Hence, if relaxations or rearrangements of atoms occur on the surfaces of specimens or through part of the bulk due to a loss of elastic constraint in the thin dimension, the alterations of phases introduced by these changes may be severe enough in thin specimens to mask the element of centrosymmetry actually present in the material. This effect is thought to have resulted in the failure of the specific $\pm\underline{g}$ test to identify the element of centrosymmetry in thinner areas of the specimen in Figs. 3(c) and (d), where only weak dynamical diffraction is occurring. A similar effect might also be

observed for thin specimens which are slightly bent. Thus, both of these effects lead to the result that the symmetry which is observed in the CBED pattern may be related to the conditions of the specimen, rather than to the actual space group of the material. Obviously the ideal case of an infinitely-thick, parallel-sided specimen is never achieved; however, for correct interpretation of CBED patterns during point and space group determinations, these conditions should be satisfied as nearly as possible.

It is also significant that the failure of the $\pm g$ test for centrosymmetry occurs at about the same specimen thickness as the loss of HOLZ lines and concurrent increase in the overall symmetry of the zone axis patterns. Thus, as long as HOLZ lines are visible within the convergent-beam discs, the $\pm g$ test for centrosymmetry appears to be valid. The presence of these HOLZ lines in CBED patterns can then be used to experimentally verify that symmetry determinations are being performed in an area of the specimen which satisfies the required conditions of strong dynamical scattering.

## CONCLUSIONS

The results of specific $\pm g$ CBED tests for centrosymmetry performed over a range of specimen thicknesses in $\alpha$-titanium demonstrate experimentally that thin specimens may display a lack of centrosymmetry and/or a high zone axis pattern symmetry due to the limited specimen thickness, rather than to the space group of the material. It is therefore important that point and/or space group determinations be performed on specimens which are thick enough for strong dynamical diffraction to occur, as evidenced by the presence of HOLZ lines within the CBED discs. Particular care must be taken when performing symmetry determinations on the small particles ($<1000$ Å) which are of greatest to materials scientsts because of their strong influence on the properties of engineering materials.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

## REFERENCES

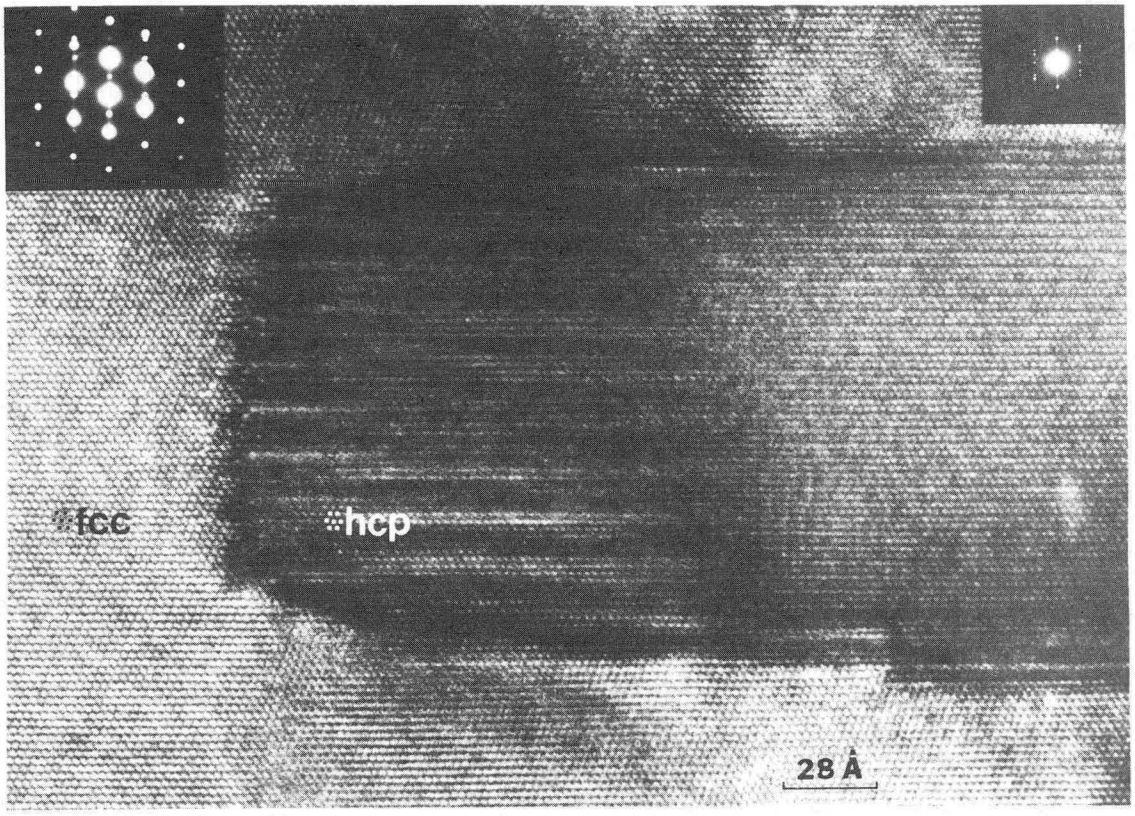

1. B.F. Buxton, J.A. Eades, J.W. Steeds and G.M. Rackham, Phil. Trans. Roy. Soc. London A281 (1976) 171.
2. J.W. Steeds and R. Vincent, J. Appl. Cryst. 16 (1983) 317.
3. M. Tanaka, R. Saito and H. Sekii, Acta Cryst. A39 (1983) 357.
4. M. Tanaka, H. Sekii and T. Nagasawa, Acta Cryst. A39 (1983) 825.
5. R. Vincent and T.A. Bielicki, Inst. Phys. Conf. Ser. No. 61 (1981) 491.
6. C.Y. Yang, Y.Q. Zhou and K.K. Fung, Acta Cryst. A39 (1983) 531.
7. M.G. Friedel, C.R. Acad. Sci. Paris 157 (1913) 1533.
8. A.P. Pogany and P.S. Turner, Acta Cryst. A24 (1968) 103.
9. P. Goodman and G. Lehmpfuhl, Acta Cryst. A24 (1968) 339.
10. J. Gjonnes and A.F. Moodies, Acta Cryst. 19 (1965) 65.
11. P. Goodman, Acta Cryst. A31 (1975) 804.
12. P. Goodman and H.J. Whitfield, Acta Cryst. A36 (1980) 219.
13. P. Goodman and A.F. Moodie, Acta Cryst. A30 (1974) 280.
14. P. Goodman, Nature 251 (1974) 698.

## FIGURE CAPTIONS

1. High-resolution electron micrograph showing the interfacial structure at the edge of a $\gamma'$ plate-shaped precipitate. The foil orientation is such that the electron beam is parallel to the face of the precipitate, and the matrix and precipitate are viewed along $\langle 110\rangle_{fcc}//\langle 11\bar{2}0\rangle_{hcp}$ directions, respectively. These precipitates grow by the passage of Shockley partial dislocations along alternate $\{111\}$ matrix planes, which changes the fcc matrix stacking to the hcp precipitate structure. A chemical change must accompany this structural transformation, in order to produce $\gamma'$ precipitates with the composition $Ag_2Al$ from the Al-rich solid solution matrix.

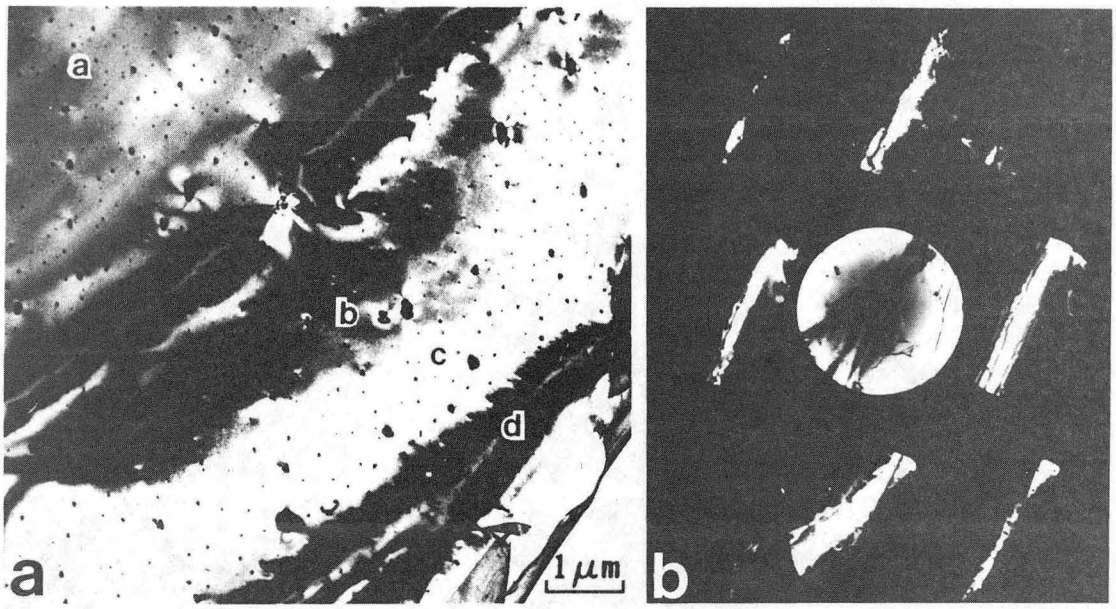
2. (a) Bright field electron micrograph showing where the electron beam was located relative to the edge of the foil (a through d), for the four series of $\pm g$ CBED experiments in Figs. 3(a) through (d). (b) Ghost image of foil with probe positioned at location (d), near the edge of the hole. The probe diameter is about 400 Å.

3. (a) through (d) Four series of $\pm g$ experiments performed over a range of specimen thicknesses for $\alpha$-titanium in a $[\bar{1}\bar{1}02]$ orientation. For each thickness, the zone axis pattern is shown in the center, with the $\bar{1}101$ and $1\bar{1}0\bar{1}$ discs at their Bragg positions located to the left and right, respectively. Notice that the decrease in specimen thickness from (b) to (c) produces an increase in the overall symmetry of the zone axis pattern and a loss of translational symmetry between the intensity fringes in the $\bar{1}101$ and $1\bar{1}0\bar{1}$ CBED discs.



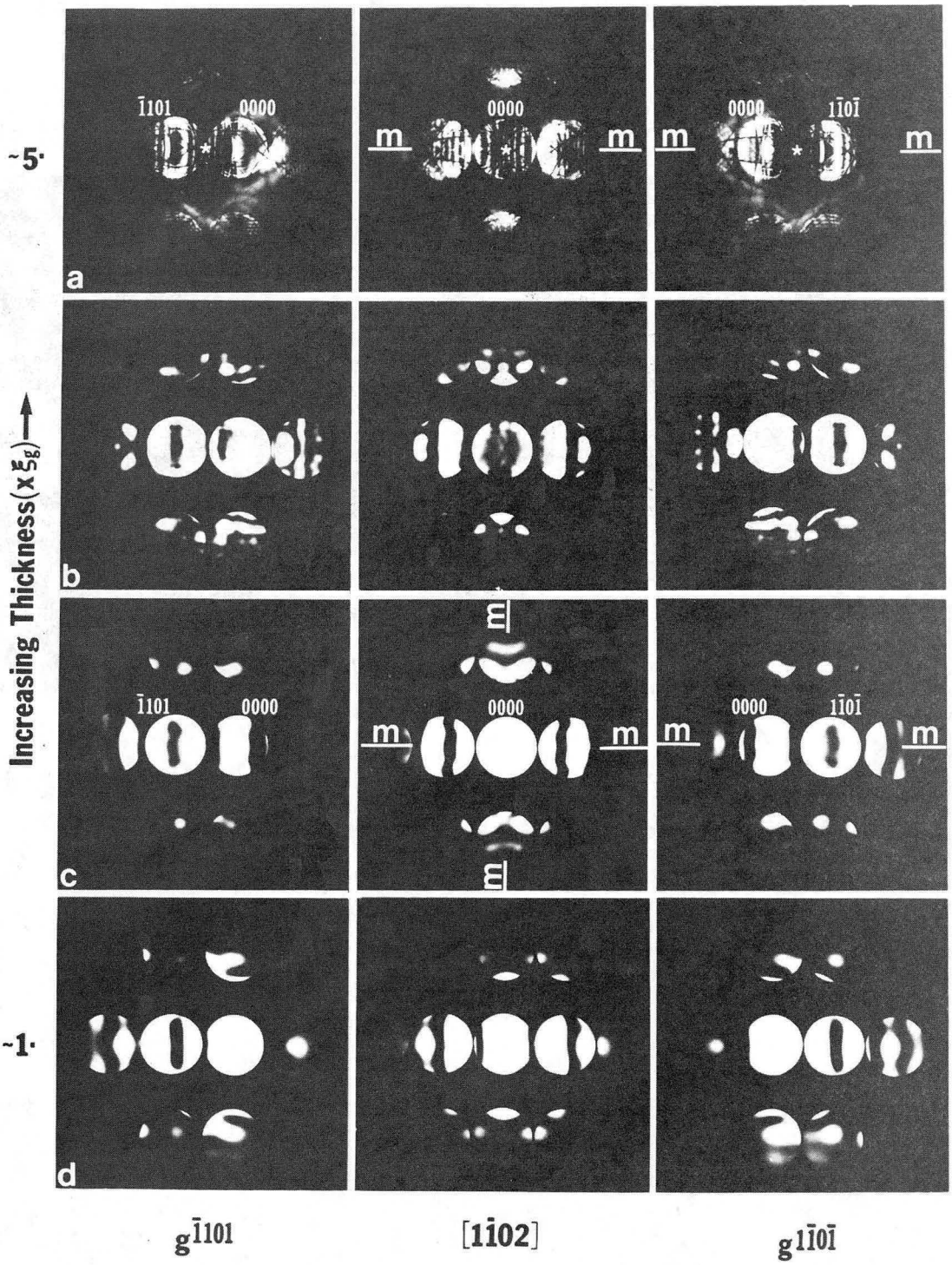

XBB 842-1212

Fig. 1




XBB 840-7654

Fig. 2




XBB 840-7664

Fig. 3

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

*TECHNICAL INFORMATION DEPARTMENT*
*LAWRENCE BERKELEY LABORATORY*
*UNIVERSITY OF CALIFORNIA*
*BERKELEY, CALIFORNIA 94720*