Lawrence Berkeley National Laboratory

Recent Work

Title

Comments on Interpretation of HREM Images of Mullite by S. Hamid Rahman and H.-T. Weichert

Permalink

https://escholarship.org/uc/item/80k4j5n9

Authors

Epicier, T.
Thomas, G.
O'Keefe, M.A.

Publication Date

1990-09-01

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

LBL-29597
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

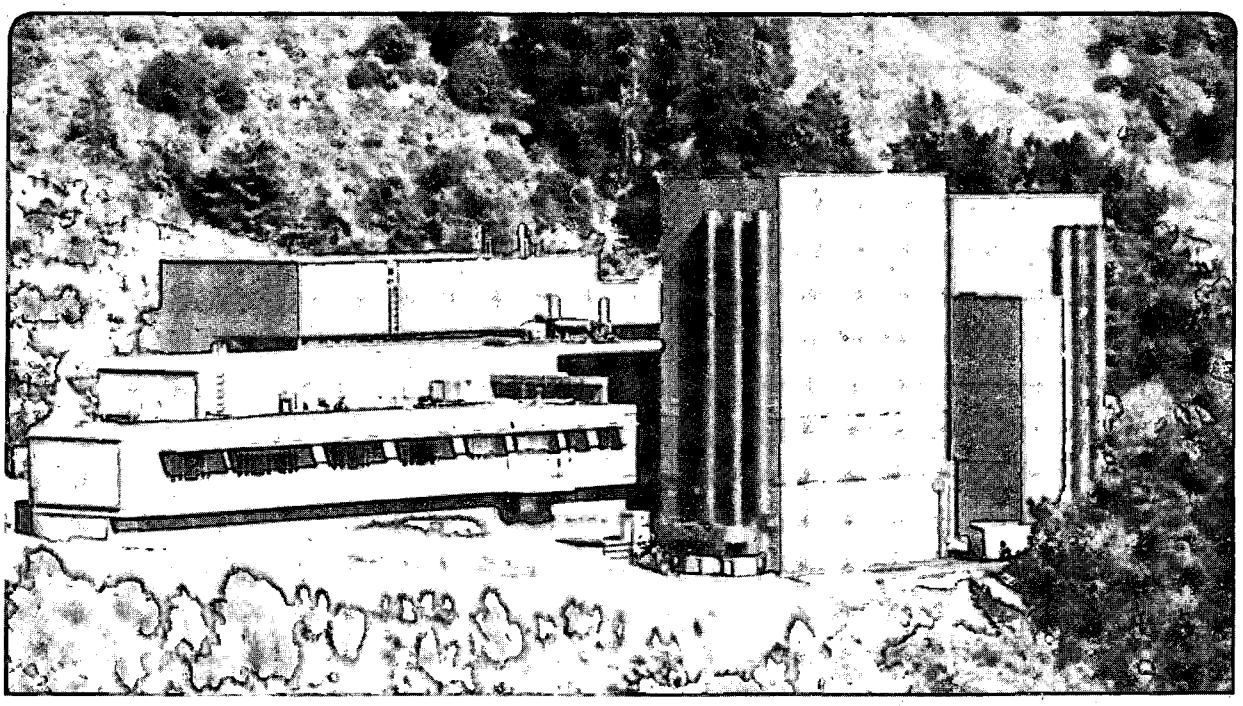
National Center for Electron Microscopy

Submitted to Acta Crystallographica

Comments on "Interpretation of HREM Images of Mullite" by S. Hamid Rahman and H.-T. Weichert

T. Epicier, G. Thomas, and M.A. O'Keefe

September 1990



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

LOAN COPY
Circulates
for 2 weeks
Bldg. 50 Library.
Copy 2
LBL-29597

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.

LBL-29597

COMMENTS ON "INTERPRETATION OF HREM IMAGES OF MULLITE" BY S. HAMID RAHMAN AND H.-T. WEICHERT

T. Epicier*, G. Thomas, and M.A. O'Keefe

Materials and Chemical Sciences Division
National Center for Electron Microscopy
Lawrence Berkeley Laboratory
University of California
Berkeley, CA. 94720

*INSA, GEMPPM,
Bat. 502, u.a. CNRS 341
69621 Villeurbanne
Cedex, France

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

Comments on "Interpretation of HREM images of Mullite" by S. Hamid Rahman and H.-T. Weichert

T. Epicier*, G. Thomas and M.A. O'Keefe

National Center for Electron Microscopy, Materials and Chemical Science Division, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, California 94720 USA

Abstract

A major part of the paper by Hamid Rahman and Weichert (1990) is devoted to the analysis of oxygen vacancy distribution in 3:2 mullite by high-resolution electron microscopy (HREM) in [001] orientation. Various statements appear to be inaccurate, and it is the purpose of this note to provide a correction.

1. Errors in simulation.

The usual "periodic continuation" method of computing an image of a non-periodic structure is to construct a "supercell" consisting of a number of perfect unit cells surrounding the cell(s) containing the defect (e.g. Iijima & O'Keefe, 1978). The image simulation is then carried out using the supercell as the new unit cell for the defect structure. Note that the model defect structure is now periodic with the periodicity of the chosen supercell, and thus the number, n, of original unit cells making up the supercell must be chosen to be large, not only to sample any reciprocal-space diffuse scattering sufficiently finely, but also to keep the images of adjacent defects from interfering. Such interferences can arise if electrons scattered from non-perfect

*permanent address : INSA, GEMPPM, Bât. 502, u. a. CNRS 341, 69621 Villeurbanne Cedex, France.

regions near to the defect in one supercell contribute to the image of the defect in an adjacent supercell.

Given that computation of an image of a supercell consisting of n perfect unit cells will require between n and n^2 times as much computing time as one unit cell, Hamid Rahman and Weichert (1990) attempt to shorten the process by constructing a type of "supercell" of the same size as the original cell. This "potential exchange" construction (Hamid Rahman, 1988) is described in figure 2 of Hamid Rahman and Weichert (1990) re-drawn here as figure 1. In this construction, the new cell is formed by computing the crystal potentials for two different cells, one perfect (fig.1a) and the other with periodic vacancies (fig.1b); a "cut and paste" technique is then used to produce a cell with a "vacancy" at one edge and an "atom" in the corresponding site at the opposite edge. Hamid Rahman and Weichert (1990) draw the resultant cell with a full vacancy at one edge, and a full atom at the other (fig.1c). However, because an atom potential has a finite extent, the actual result of the "potential exchange" approach is to produce a cell with a "half vacancy" at one edge and a "half atom" at the other. The resulting crystal potential may be reasonable for one cell when it is considered in isolation, but not when it is forced to repeat periodically by the discrete Fourier transforms used in computing the image. Regarded periodically, the new cell has an "atom/vacancy" site, consisting of a "half atom" mated to a "half vacancy", at each edge (fig.1d). O'Keefe & Kilaas (1990) point out that, in fact, the "atom/vacancy" site produced by "potential exchange" contributes an unphysical component to the total crystal potential. "Unphysical" because the oxygen potential is cut in half to produce a step function that attains the full height of the potential on one side of the unit cell boundary with zero contribution on the other, and an abrupt plunge to zero at the boundary.

Since the contribution of one oxygen atom to the total crystal potential of mullite is small, it might be expected that the presence or absence of an oxygen vacancy (or half of one) would make very little difference to the image character; this is especially so at 0.24nm resolution, since a resolution of better than 0.19nm is required to detect the presence of oxygen atoms in mullite (Epicier, O'Keefe & Thomas, 1990). However, the unphysical nature of the crystal potential

produced by the "potential exchange" method appears to have an exaggerated effect sufficient to provide a visible difference between vacancy sites in images simulated using normal periodic-continuation methods, and "atom/vacancy" sites in images produced by the "potential exchange" method. This difference, described as "negligible" by Hamid Rahman and Weichert (1990), can easily be seen by comparing the images in their figures 5 and 6, especially the images near Scherzer (-50nm) defocus.

An additional problem with the mullite images computed by Hamid Rahman and Weichert (1990) is that they appear to be reversed in contrast. Images near Scherzer defocus in their figures 5 and 6 show black contrast at tunnel positions and white at atom sites. On the other hand, their Scherzer-defocus experimental image (their fig.9) has "normal" (Scherzer-like) contrast, and can only be matched by their image computed at 50nm *over*focus. Such contrast reversals can occur if the sign of the wave aberration function does not match the sign chosen for the time-dependent Schrödinger equation in deriving the expressions used in the simulation programs (Saxton, O'Keefe, Cockayne & Wilkens, 1983). Images simulated with both of the well-tested simulation programs, SHRLI (O'Keefe, Buseck & Iijima, 1978) and NCEMSS (Kilaas, 1987) were found to match those computed by Hamid Rahman and Weichert (1990) only when the spherical aberration was set to a non-physical *negative* value, suggesting that such a sign mismatch has occurred in the simulation programs used by Hamid Rahman and Weichert (1990).

2. Effect of the presence of oxygen atoms on [001] HREM images.

In the text by Hamid Rahman and Weichert (1990), it is noted that "a striking feature (of images in [001] projection) is the appearance of channels beside the O_C atoms (that is, oxygen positions where vacancies can occur)". The authors also state that "under appropriate illumination conditions, these channels can be resolved", and "The existence of oxygen vacancies of the O_C site results in a large cavity between two unit cells. It is therefore expected that the local variation of the scattering potential owing to the existence of a vacancy causes a variation of the contrast

pattern, or, at least, its intensity". These latter affirmations are confusing, and can be shown to be inexact.

While it is true that, under certain conditions, HREM images of mullite in [001] projection can show the large channels adjacent to the O_C sites (Epicier and Thomas, 1989), it is absolutely clear that this "channel contrast" arises primarily from the presence of cations, not that of the oxygen atoms. Moreover, it has been shown by Epicier, O'Keefe and Thomas (1990), that a resolution of better than 0.2nm is required to get an actual direct transfer of information on oxygen atoms in the [001] projection of mullite. Then, at the 0.24nm Scherzer resolution of the electron microscope used by Hamid Rahman and Weichert (1990), very little effect is expected from the presence of oxygen atoms. Figure 2 compares images of mullite computed in [001] projection under the conditions specified by Hamid Rahman and Weichert (1990), both with (a) and without (b) oxygen atoms; there is very little change in the appearance of the channels. Similar calculations in [110] orientation also showed no difference in image character when the oxygens were removed. Related to the above point, it is clear that oxygen vacancies cannot be directly detected through intensity variations associated with a lower atomic density at the emplacement of O_C-defective columns. In recent investigations using the JEOL ARM-1000 electron microscope with a point-to-point resolution of below 0.17nm, it has been shown (Epicier et al, 1990) that oxygen vacancies in mullite are detected mainly through cation displacements (~0.12nm away from the vacant site); obviously, no better evidence can be obtained at a resolution of 0.24nm.

3. Simulations of oxygen-vacancy models

The discrepancy between the correct "supercell" method and the incorrect "potential exchange" method visible in figures 5 and 6 of Hamid Rahman and Weichert (1990) has already been discussed. Since the images of figure 5 of Hamid Rahman and Weichert (1990) were computed using the usual "supercell" method, they are "correct" (except for the fact that they are contrast-reversed as noted above), and can be compared with those presented here.

In figure 7 of Hamid Rahman and Weichert (1990), the authors endeavor to compare simulated HREM images from different stacking sequences, mixing unit cells of "perfect" mullite (e in fig.4 of Hamid Rahman and Weichert, 1990) and "defect" mullite (x, where x is one of a,b,c,d in fig.4 of Hamid Rahman and Weichert, 1990). Apart from the inconsistency of thickness values (sequences indicated in fig.7 of Hamid Rahman and Weichert (1990) contain four slices of unit thickness 0.288nm; the total thickness should then be 1.2nm, instead of the 2.4nm indicated in the figure caption), one may be surprised that the authors use these calculations to discern different vacancy arrangements as they do in analyzing their figure 10.

Although calculated images for fully vacant oxygen rows (fig.7a-d of Hamid Rahman and Weichert, 1990) do exhibit different contrast, it must be emphasized (as the authors mention) that the "existence of vacancy channels parallel to [001] is rather non-realistic". Elementary calculations show that the probability of having such a situation is close to zero for specimen thicknesses near or greater than 2 to 3 nm in 3:2 mullite (Epicier et al., 1990), where the average vacancy content is 0.3 per unit cell. More realistic (although still with a relatively low probability of occurrence), are the authors' sequences such as "exex", which lead to almost indiscernible differences in calculated images (e.g. the four images in fig.7f-i of Hamid Rahman and Weichert, 1990). It is then highly improbable that any difference could be detected in experimental images, contrary to the assumptions of Hamid Rahman and Weichert (1990). Indeed, Epicier et al. (1990) have demonstrated that a vacancy content close to 0.5 is required to allow defective columns to be detected even at the 0.17nm resolution attained by the JEOL ARM-1000; even at such resolutions, the contrast of such vacancy-containing O_C columns can be analyzed only through careful matching of through-focus series of experimental and simulated images. Even then, because of the low probability of getting [001] oxygen columns with sufficient vacancy content to be visible in thicker crystals, such an analysis is restricted to areas of specimens of very low thickness (nominally a few unit cells); thus, we believe that it is doubtful that any relevant result can be obtained on specimens thicker than 4nm, such as the experimental image shown in figures 9 and 10 of Hamid Rahman and Weichert (1990). For comparison with figure 5 of Hamid Rahman and Weichert

(1990), we present in figure 3 a set of images of mullite with the same microscope and specimen parameters, computed from a model with 100%-vacancy channels (formed by placing a vacancy at every level); as in figure 5 of Hamid Rahman and Weichert (1990), the vacancy positions are easily seen for this unrealistic model, especially on comparison with images of the average mullite (fig.4). A more realistic model contains 50% vacancies in selected columns (fig.5), but now the positions of the vacancies are much less striking, (even though the selected columns are regularly spaced in the example shown, and are thus very easy for the eye to perceive), and could be expected to disappear in the noise present in an experimental micrograph. Figure 5 shows that the visibility of the 50%-vacancy columns increases with increase in crystal thickness; the vacancy positions are much more visible at 5.8nm than at 2.3nm. However, the probability of a real specimen containing a column with 50% vacancies decreases sharply as the specimen thickness increases, from an already small value of 7% (one in 15 columns) at a thickness of 2.3nm, to 1.3% (one in 75 columns) at 3.5nm, and 0.01% (one in 10,000 columns) at 5.8nm thickness (Epicier et al., 1990).

It is surprising to note that Hamid Rahman and Weichert (1990) assign structural features related to light atoms on the basis of one "isolated" HREM image. It is generally acknowledged that analysis of defect contrast associated with the presence (or absence) of light atoms is best carried out by careful comparison of extensive through-focus series of simulated and experimentally-recorded images at more than one specimen thickness (see a general discussion of such approaches by Epicier, 1990). Hamid Rahman and Weichert (1990) attempt such an analysis on the basis of a "match" at one defocus value and specimen thickness, taking an image simulated for a crystal thickness of only 1.7nm, and "matching" it with an experimental image (shown as figures 9 and 10 of Hamid Rahman and Weichert, 1990) obviously taken from a far thicker area. In addition, in analyzing the variations of contrast in fig 10, Hamid Rahman and Weichert (1990) take no account of the roles played by artefacts such as strain contrast, local crystal tilt, or "noise" arising either from surface contamination of the specimen, or from any electron-beam-induced damage. The effect of local crystal tilt on image contrast has been discussed by Schryvers et al.

(1988). An even more spectacular example of image changes (qualitatively comparable to that observed by Eberhard, Hamid Rahman and Weichert (1986) and assigned by them to ordered domains in 3:2 mullite), can be seen in figure 6; here the "ordered domains" are actually caused by strain effects near a microcrack; identification of such artefacts is a further benefit of matching images over a range of specimen thickness and microscope defocus.

Acknowledgement

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

EBERHARD, E., HAMID RAHMAN, S. and WEICHERT, H.T. (1986) *Z. Kristallogr.* **174**, 44-46.

EPICIER, T., and THOMAS, G. (1989) *Proc. 47th Ann. Meeting of EMSA*, San Antonio, G.W Bailey (ed), 418-420.

EPICIER T., (1990) *Mat. Res. Soc. Symp. Proc.* **183**, 255-266.

EPICIER, T., O'KEEFE, M.A. and THOMAS, G. (1990) *Acta Cryst.* accepted.

HAMID RAHMAN, S. (1988) *Z. Kristallogr.* **186**, 113-116.

HAMID RAHMAN, S. and WEICHERT, H.T. (1990) *Acta Cryst.* B**46**, 139-149.

IIJIMA S. and O'KEEFE, M.A. (1978) *9th Internat. Cong. on Electron Microscopy,* Toronto **1**, 282-283.

KILAAS, R. (1987) *Proc. 45th Ann. Meeting of EMSA*, Baltimore, G.W. Bailey (ed), 66-69.

O'KEEFE, M.A., BUSECK P.R., and IIJIMA S. (1978) *Nature* **274**, 322-324.

O'KEEFE, M.A. and KILAAS, R. (1990) *Z. Kristallogr.* accepted.

SAXTON, W.O., O'KEEFE, M.A., COCKAYNE, D.J.H. and WILKINS, M. (1983) *Ultramicros.* **12**, 75-78, and *Ultramicros.* **13**, 349-350.

SCHRYVERS, D., SRIKRISHNA, K., O'KEEFE, M.A. and. THOMAS, G. (1988), *J. Material Res.* **3** (1988) 1355-1361.

Figure 1. The "potential exchange" method of Hamid Rahman and Weichert (1990). (a) unit cell with oxygen atom at O_C site (0,1/2,0). (b) unit cell with vacancy at O_C site. (c) how Hamid Rahman and Weichert (1990) represent the "unit cell" after exchange of potential -- an atom at (0,1/2,0) and a vacancy at (1,1/2,0). (d) what the "potential exchange" method actually produces -- half an atom and half a vacancy at each of the (0,1/2,0) and (1,1/2,0) positions.

Figure 2. Scherzer-defocus (-50nm) images of mullite simulated for a specimen thickness of 1.7nm under the imaging conditions of Hamid Rahman and Weichert (1990). (a) with oxygen atoms. (b) without oxygen atoms. Atom positions are marked with white crosses.

Figure 3. Set of mullite images simulated with 100%-vacancy channels for the conditions of figure 5 of Hamid Rahman and Weichert (1990); defocus and thickness values are marked in nm.

Figure 4. Set of mullite images with average structure simulated for the conditions of figure 5 of Hamid Rahman and Weichert (1990) with defocus and thickness values marked in nm.

Figure 5. Set of mullite images with 50%-vacancy channels simulated for the conditions of figure 5 of Hamid Rahman and Weichert (1990) with defocus and thickness values marked in nm.

Figure 6. Variation of HREM contrast in [001] mullite image due to strain. (a) detail, showing "domains" of different aspects (i.e. variation of intensities and shapes of white dots), suggesting the presence of oxygen vacancies. The superimposed simulated image reproduces the aspect of the arrowed region (computed from the "average" structure model for a crystal thickness of 8.1nm and a microscope defocus of -90nm). (b) low magnification view, showing that the region shown above (rectangular frame) is located at the tip of a microcrack (arrows); the contrast variations are clearly due to the elastic strain field around the fracture.

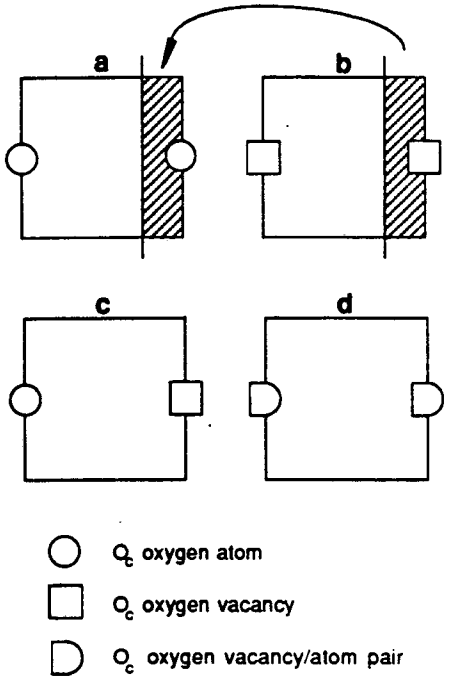


Figure 1.

XBL 909-2961

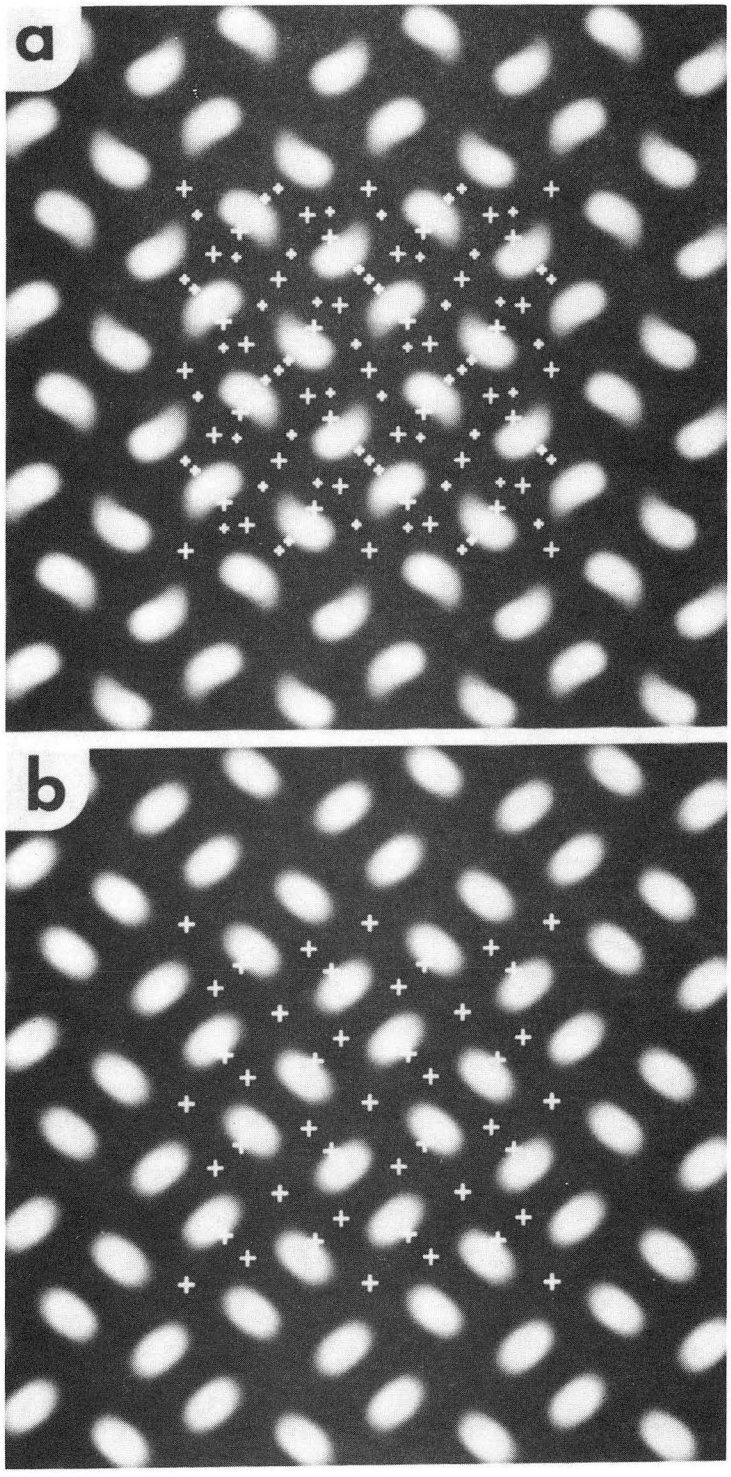


Figure 2.

XBB 908-7116

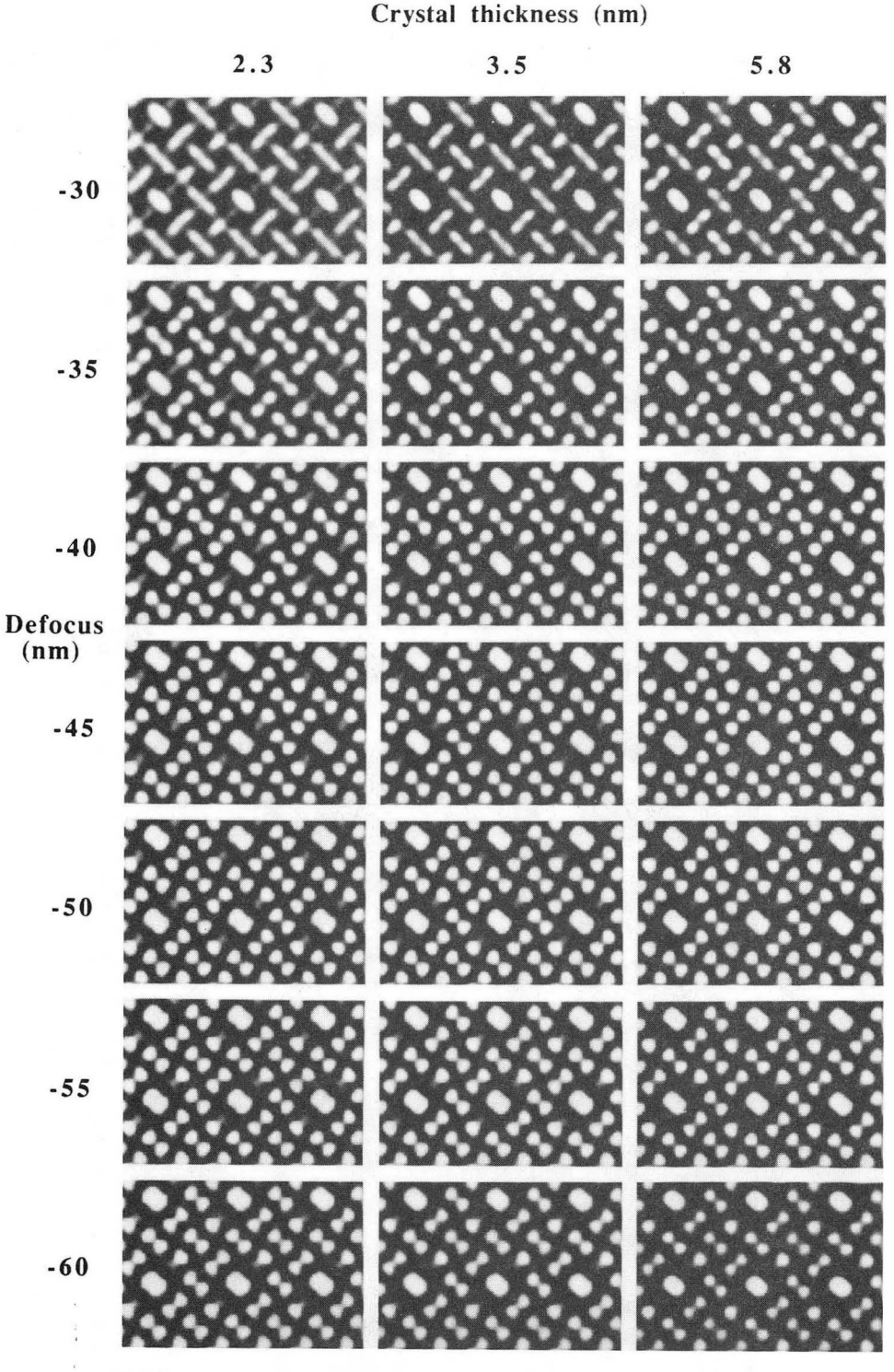


Figure 3.

XBB 908-7119

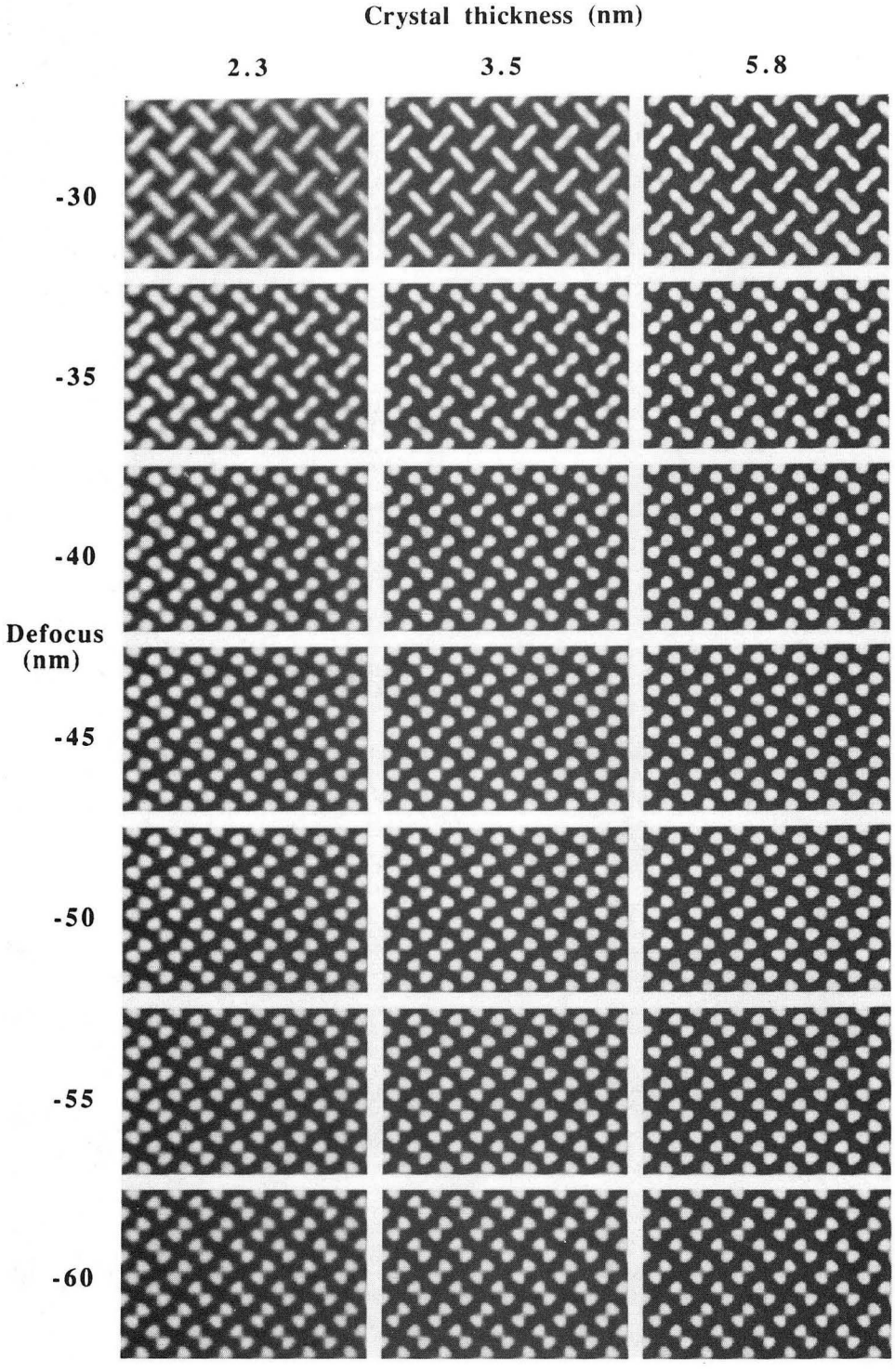


Figure 4.

XBB 908-7117

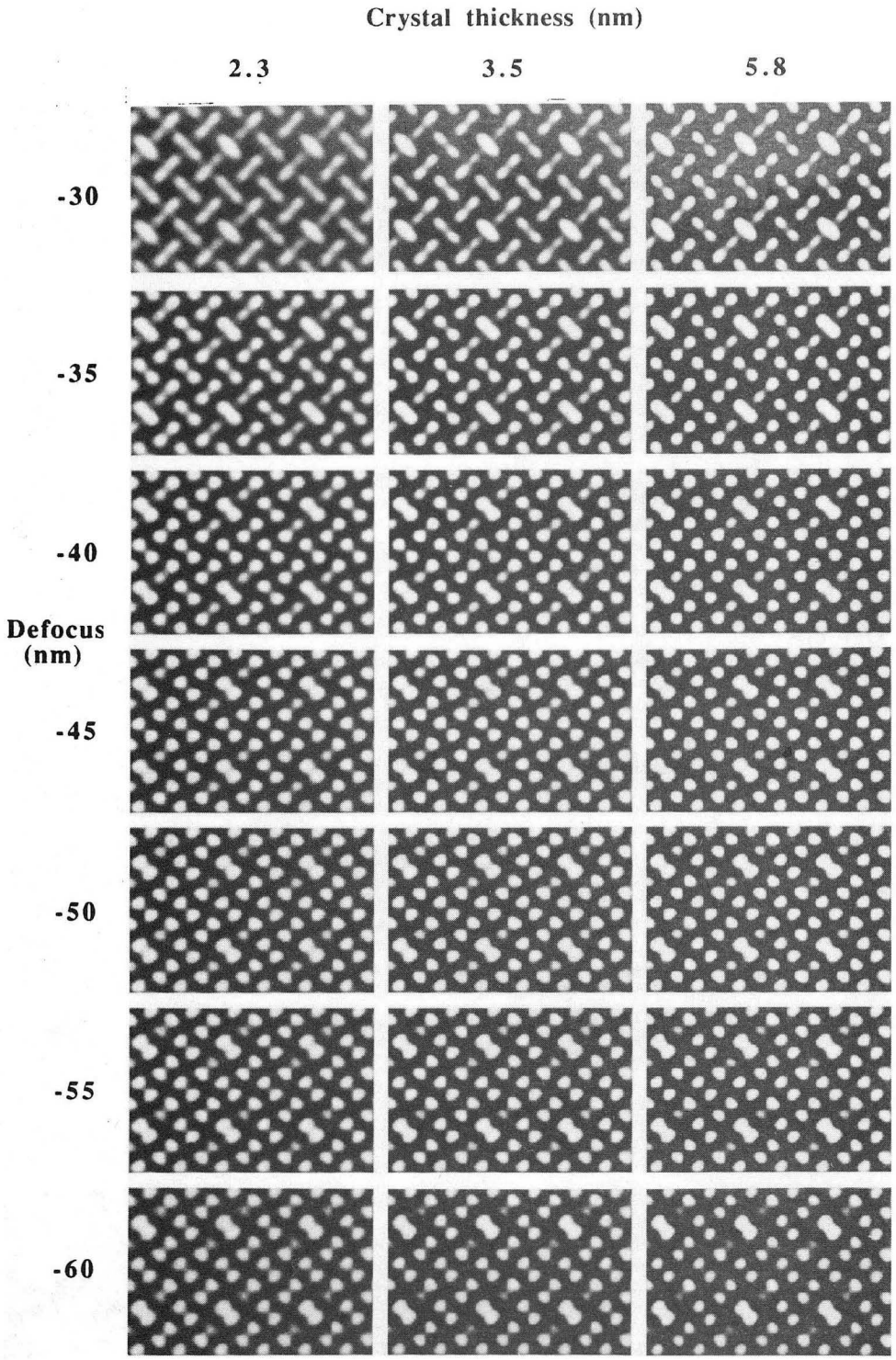
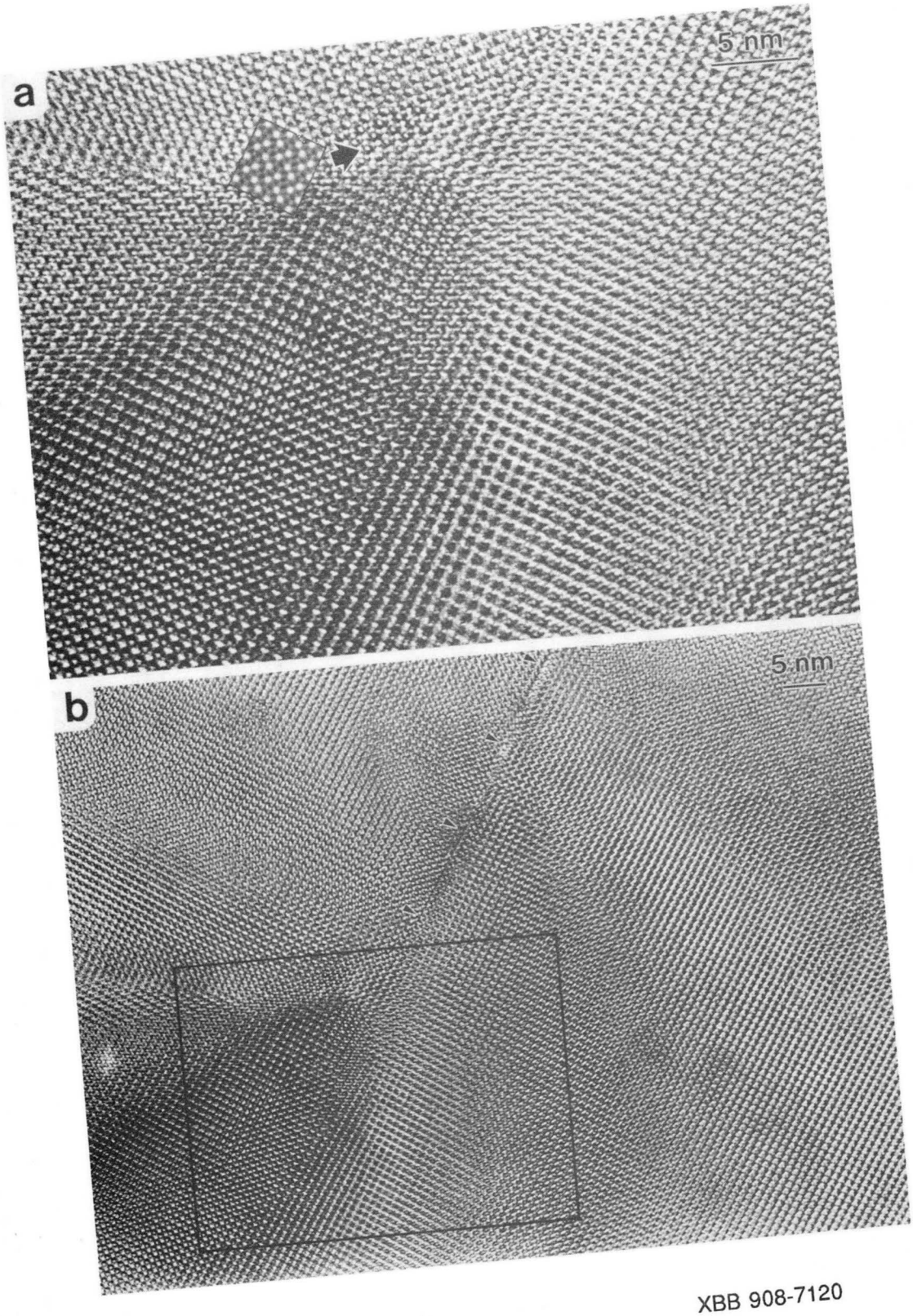


Figure 5.

XBB 908-7118



XBB 908-7120

Figure 6.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720