

FROM 2D to 3D: II. TEM and AFM IMAGES

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PREFACE TO INSTRUCTOR

The problems in the accompanying exercises, "From 2D to 3D: I. Escher drawings" (Buseck, this volume), deal with abstractions that can be related to minerals through geometrical features they have in common. However, we are ultimately interested in real minerals, their symmetries and complexities. High-resolution transmission electron microscopy (HRTEM) provides 2-D projections of mineral structures at almost the atomic scale, and atomic force microscopy (AFM) provides 3-D information about the surfaces of minerals.

Although obtained by using completely different instruments that are based on totally different principles, the two approaches provide complementary information. Both can yield information about defects in minerals. They thus leap the broad gap between the idealized structure models that we commonly use to introduce minerals and the actuality of minerals, their faults and other complexities.

The mineral examples in this problem set include representative of several silicates structure types (cordierite, crocidolite, alkali feldspar), sulfides (bornite, digenite, pyrrhotite), a sulfosalt (frankeite), and a carbonate (dolomite/ankerite). Interpretation of the images is less clear-cut than of the idealized drawings. In some cases the results can be ambiguous, but they provide scope for fruitful discussions among class members. Parts of the section on alkali feldspars require a basic familiarity with and knowledge of the reciprocal lattice and interpreting simple diffraction patterns.

In a few cases, references are given to the published papers from which the images are taken (*American Mineralogist*, *Science*, *Physics and Chemistry of Minerals*). These can be used to draw students into the professional literature, although even then it will not always be possible to arrive at unambiguous answers. These problems should be thought provoking and yet manageable at several levels of complexity. Good luck!

HRTEM IMAGES, PLANE GROUPS, AND SYMMETRY

- Plane groups and symmetry: cordierite/"problemite"** Figure 1 (which also appears as Figure 3.19 in Klein and Hurlbut *21st ed.*, p.128) is a high-resolution photograph of a crystal of cordierite taken with the transmission electron microscope. Assume that the authors misidentified it and that this new mineral, we'll call it "problemite," should have $a = 16.8\text{\AA}$ (instead of 17.1\AA). It can now be assigned to a crystal system having a higher symmetry than the one of cordierite.
 - For the "problemite" locate rotation axes with "folds" greater than two that are oriented perpendicular to the page. Mark these on an overlay
 - Mark a unit cell for the "problemite." (Hint: is it rectangular?)
 - Does it have the same number of lattice nodes as the cordierite cell? If not, how do they differ?
 - What is the crystallographic system of problemite? Explain your answer.

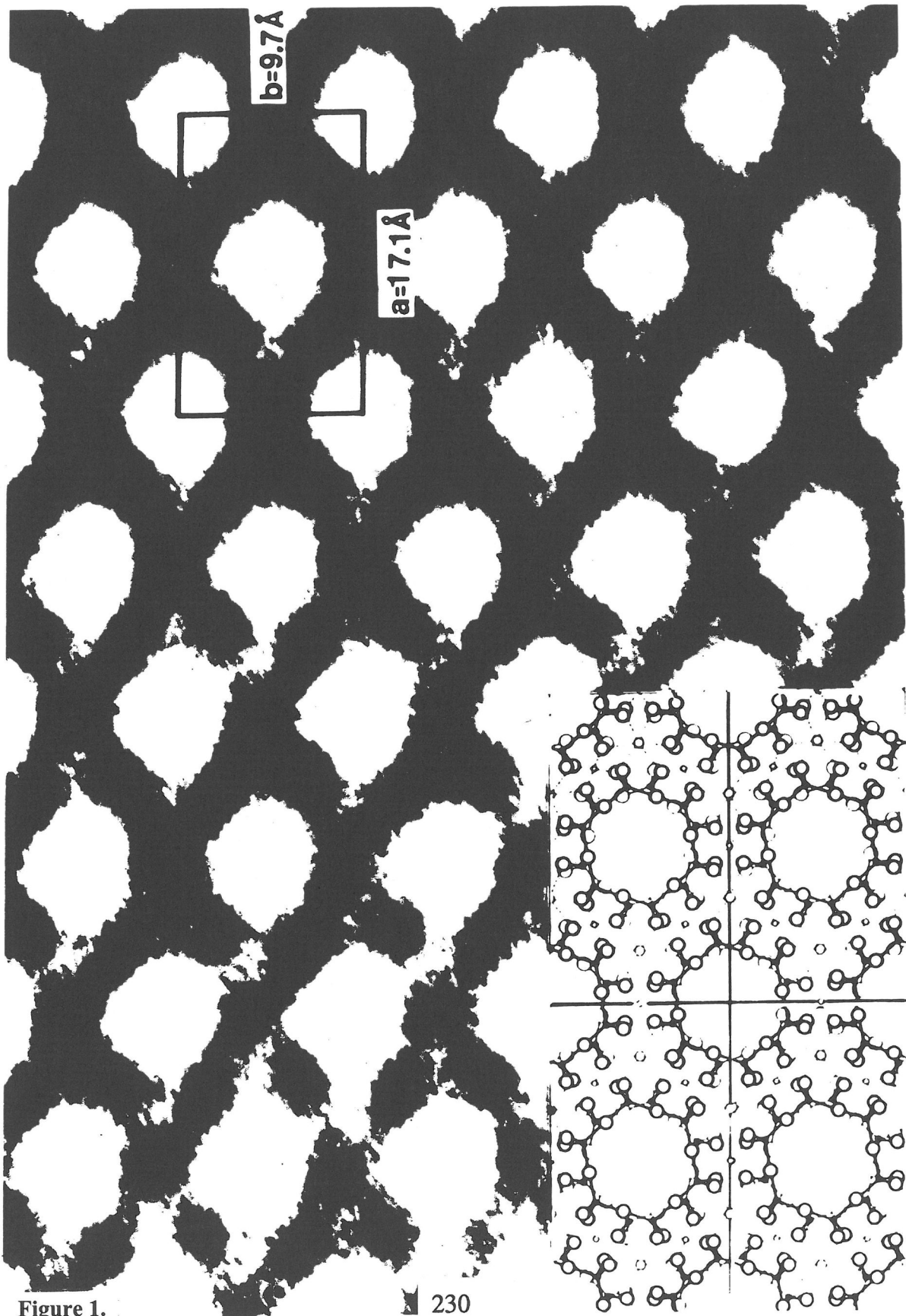


Figure 1.

2. HRTEM images and the Escher and Schaschl drawings

The following consist of HRTEM images of real minerals that display some of the features that were illustrated through the use of the Escher and Schaschl drawings. The challenge is to try and correlate the TEM images of real minerals with the idealizations represented by the art drawings. The answers are not always obvious, and the interpretations are open to question, which can provide scope for discussion.

- a) **Bornite and digenite.** Superstructures can form through the ordering of vacancies along the join connecting digenite ($\sim\text{Cu}_{7.2}\text{S}_4$) and bornite (Cu_5FeS_4), two minerals that are abundant in Cu ore deposits. The end-member species contain ordered vacancies, and these vacancies diffuse and cluster in minerals having intermediate compositions (Pierce and Buseck, *Am. Min.* **63**, 1–16, 1978). Figures 2a₁ and a₂ (taken by L. Pierce) show periodically arranged light and dark regions in bornite and digenite, respectively.
- [1] Mark a unit cell on each of the images (since they are projections of the crystal structures, assume they are of 2-dimensional crystals). If you encounter difficulties, explain why.
 - [2] Indicate the symmetry elements consistent with a plane (reflection lines and rotation axes perpendicular to the plane).
 - [3] To which Escher or Schaschl drawing(s) in the previous problem set, "From 2D to 3D: I. Escher drawings" (Buseck, this volume), do they best correspond? Explain your answer.
- b) **Franckeite.** The HRTEM image of franckeite ($\sim\text{FeSn}_3\text{Pb}_5\text{Sb}_2\text{S}_{14}$; Figure 2b), a mineral found in hydrothermal Ag-Sn ore deposits, shows a wavy structure (modulation) that results from the dimensional misfit between interleaved PbS and SnS₂ sheets. (Wang, Buseck, and Liu, 1995, *Am. Min.* **80**, 1174-78; photo by T. Sharp).
- [1] Mark a unit cell on the image. Indicate the symmetry elements consistent with a plane (rotation axes, reflection lines). If you encounter difficulties, explain why.
 - [2] Which is the PbS layer? Explain your answer.
 - [3] Which of the Escher or Schaschl drawings does it best match? Explain why.
- c) **Pyrrhotite.** The dark-field HRTEM image of Figure 2c is of Fe_{1-x}S , pyrrhotite (Pierce and Buseck, *Science* **186**, 1209–1212, 1974; a similar photo is reproduced on p. 236 of Klein and Hurlbut, 21st ed.). This is an example of a "defect structure," and it displays "omission" solid solution. The white spots represent columns of iron atoms viewed end on; their intensity presumably reflects their approximate concentration, i.e., occupancy in those positions. The "missing" irons give rise to the darker spots in the image (and to the "x" in the formula).
- [1] Mark a unit cell on the image. Indicate the symmetry elements consistent with a plane (rotation axes, reflection lines). If you encounter difficulties, explain why.
 - [2] What is the relation between an Fe-deficient cell and a subcell that does not indicate an Fe deficiency? Explain your answer.
 - [3] Which of the Escher or Schaschl drawings does it best match? Explain why.
- d) **Dolomite/ankerite.** The HRTEM image (Figure 2d) of ankerite (Ca, Fe, Mg carbonate) with a superimposed simulated image of dolomite (Ca, Mg carbonate; region D) and γ -dolomite (Ca-rich dolomite; region C). Assume that the white spots represent columns of cations viewed end-on. (Because of their relatively low electron density, i.e., light atoms, the CO₃ anions are not visible). γ -dolomite contains layers of Ca that alternate with layers of Ca + Mg. The excellent matches between experimental and simulated

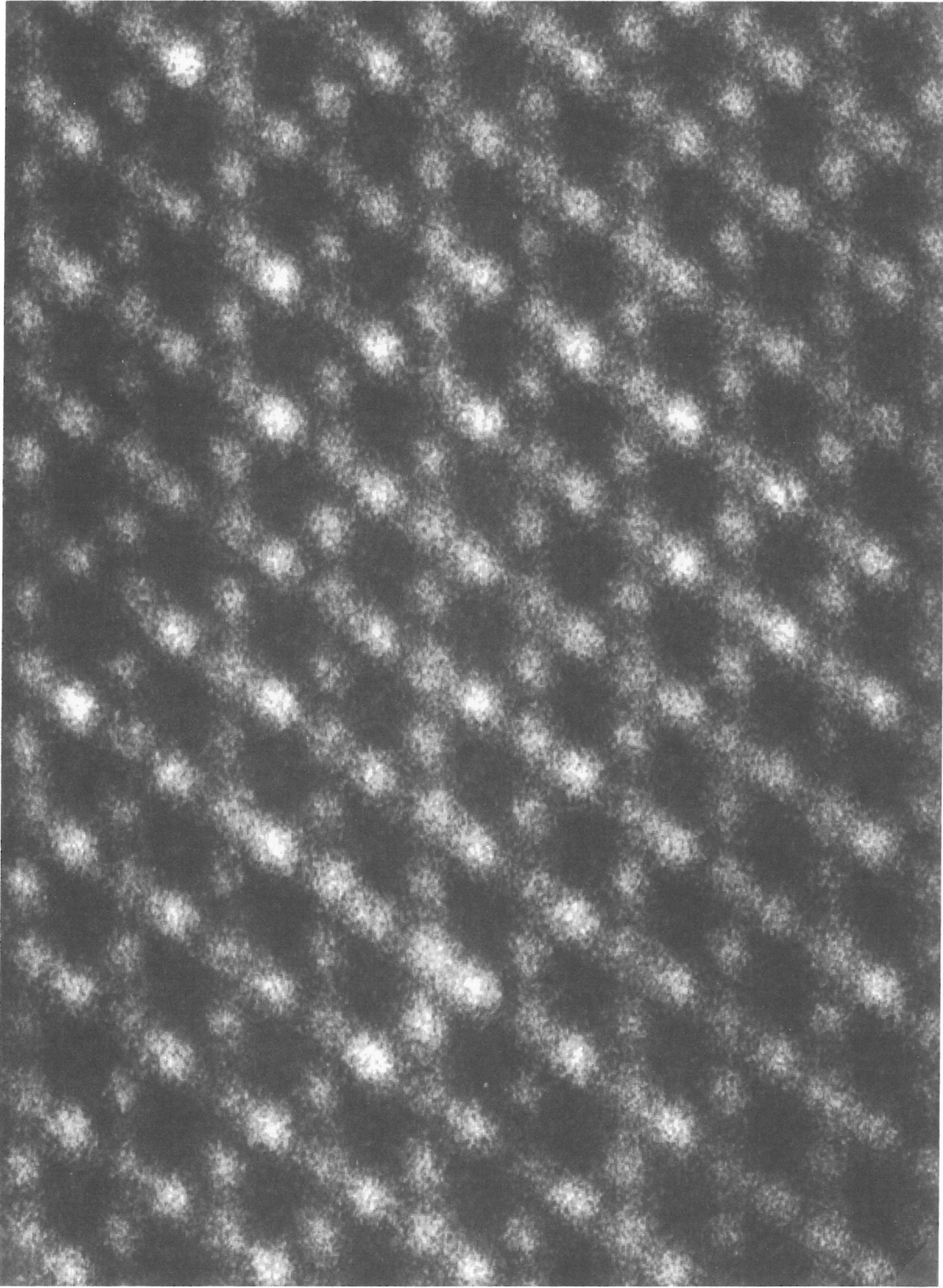


Figure 2a₁. HRTEM image of bornite.

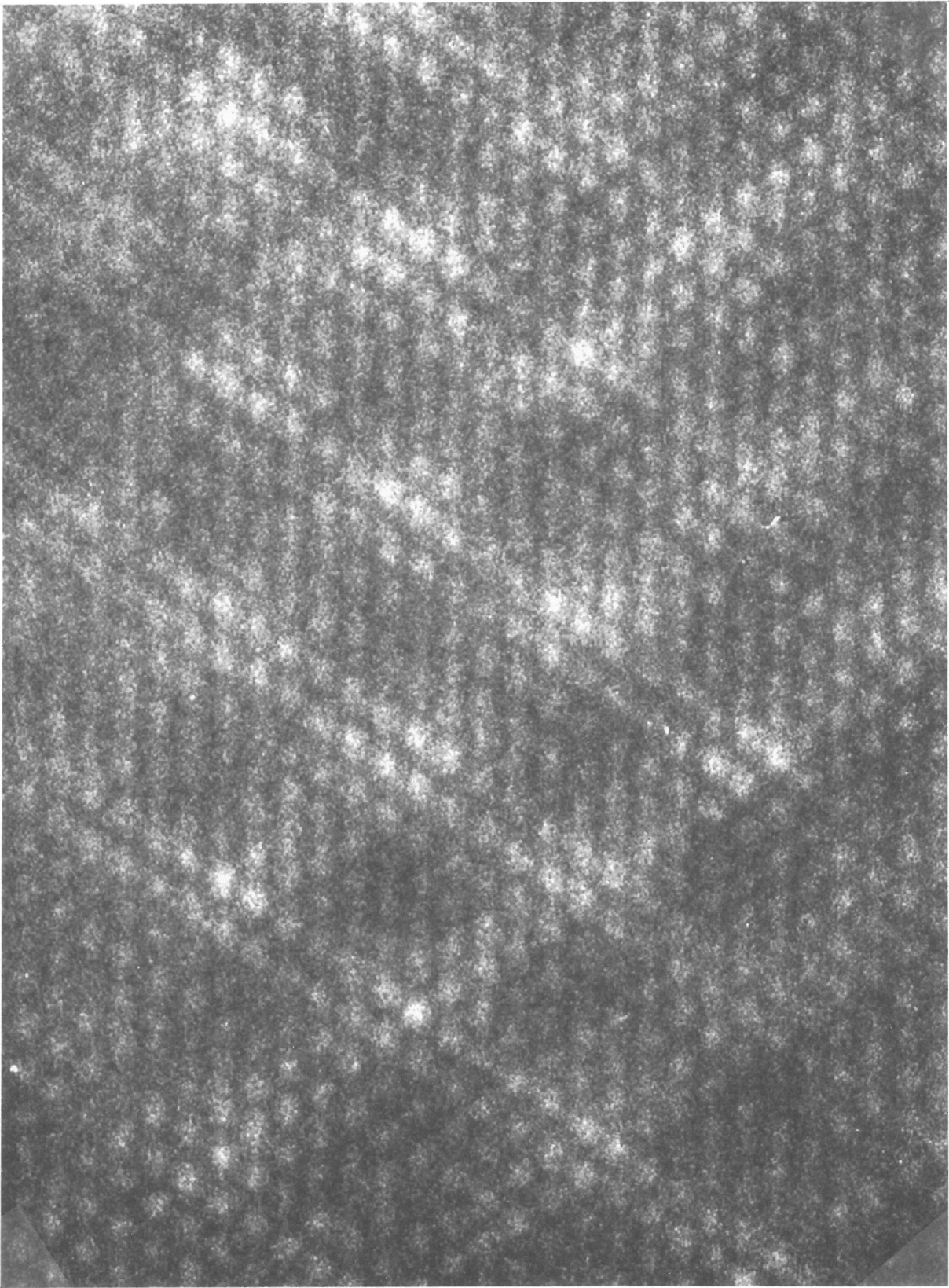


Figure 2a₂. HRTEM image of digenite.

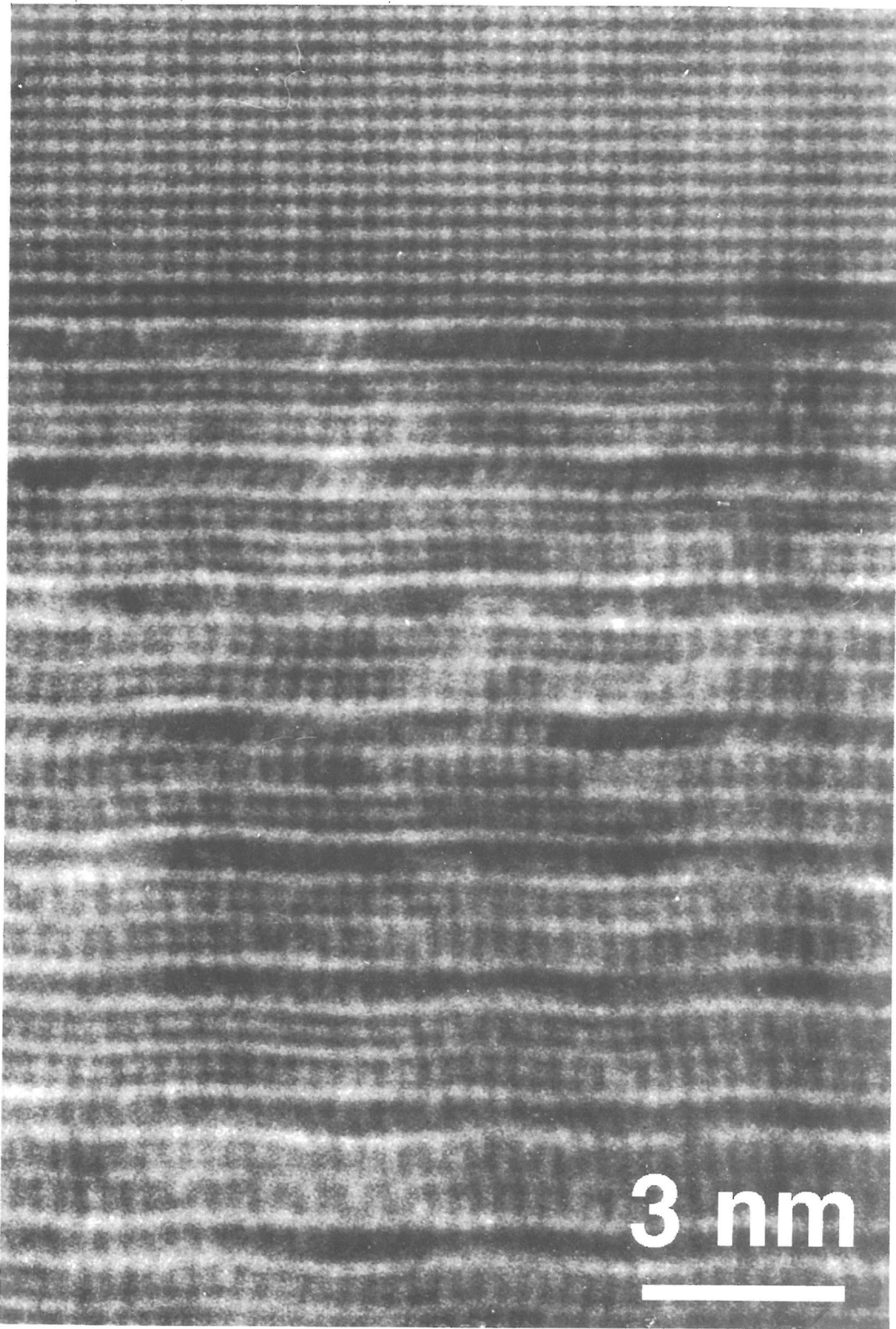


Figure 2b. HRTEM image of franckeite.

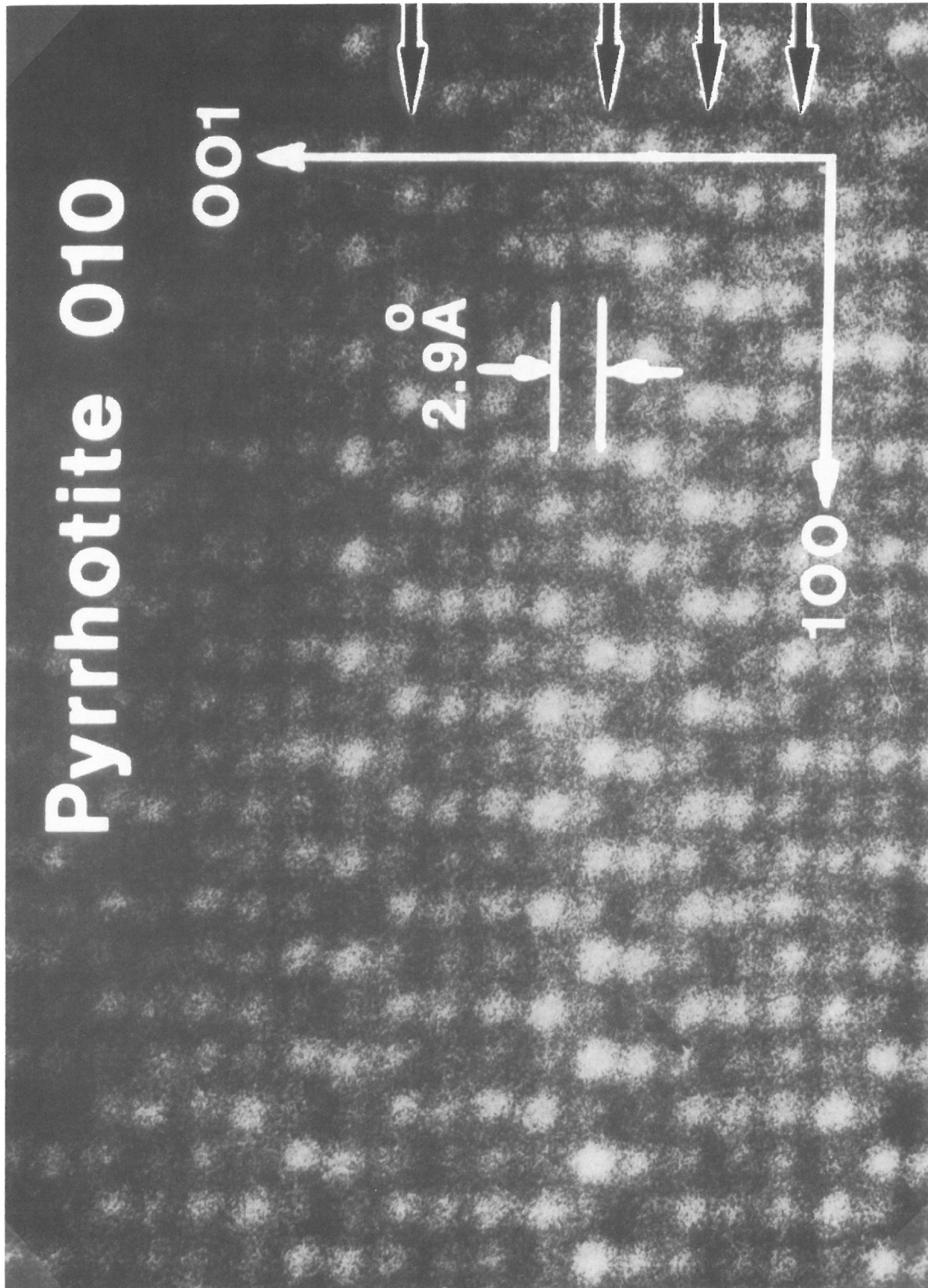


Figure 2c. HRTEM image of pyrrhotite.

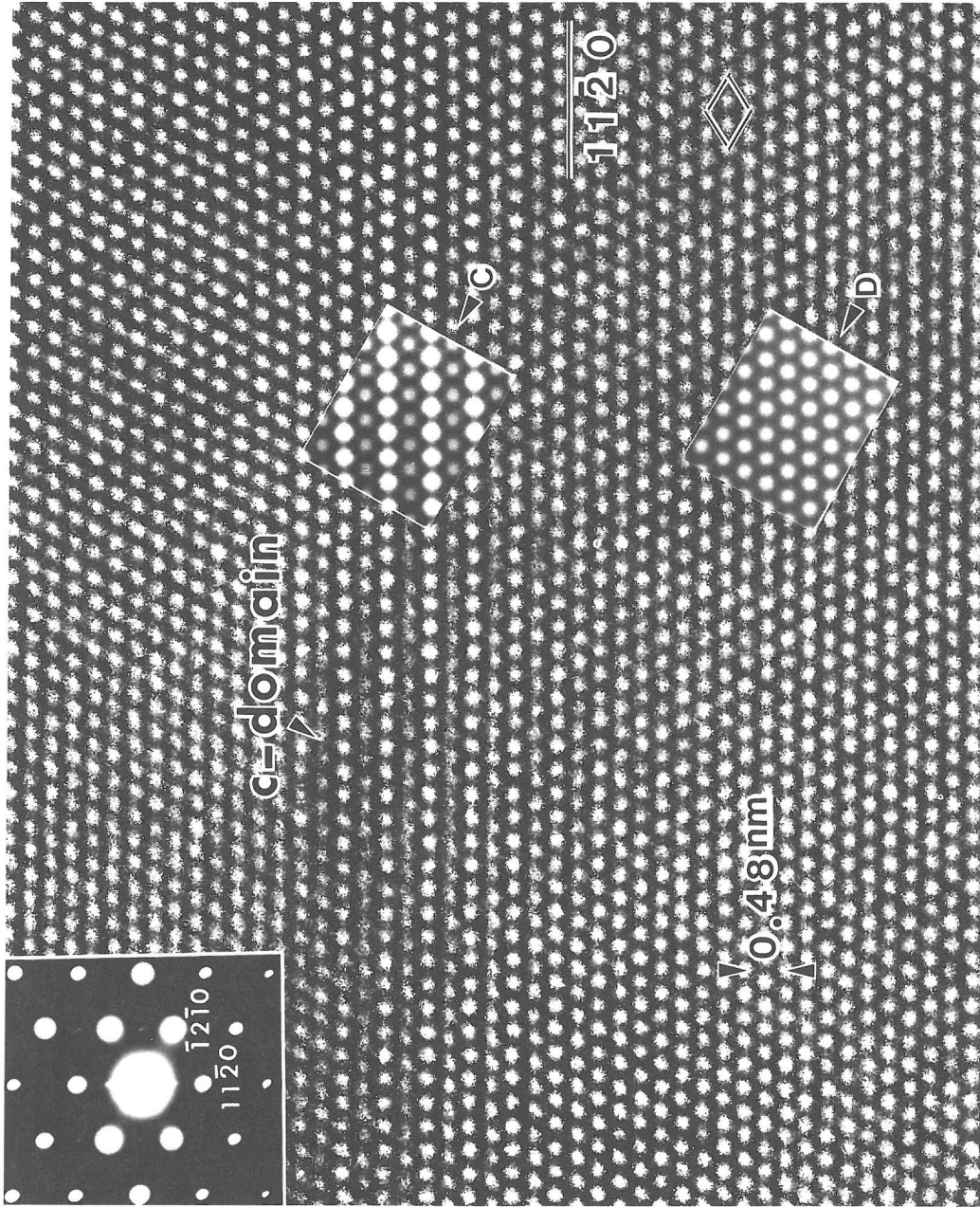


Figure 2d. HRTEM image of ankerite with a superimposed simulated image of dolomite.

images show the dolomite approximations are reasonable. (Photo from Wenk et al., *Phys. Chem. Min.* **17**, 527-529, 1991).

- [1] For region C, indicate on an overlay which layers represent mainly Ca atoms and which Ca + Mg atoms. Explain your answer.
- [2] Which of the Escher or Schaschl drawings does region C best match? Explain why.

3. HRTEM IMAGES AND FIBROUS CROCIDOLITE

- a) **Crocidolite: fibrous amphibole asbestos.** The HRTEM image in Figure 3a shows fibrous crocidolite end-on (from Fig. 3 in Ahn and Buseck, *Am. Mineral.* **76**, 1467–1478, 1991). Note the large crystal that occupies the greatest part of this image and the medium-sized grain in the lower-right area.
 - [1] What is the crystallographic and geometric relation between these two grains?
 - [2] What evidence is there that these two grains did or did not form independently of one another or that one formed from the other?
 - [3] What implications might this observation have regarding the origin of fibrosity in crocidolite asbestos?
- b) Figure 3b is another HRTEM image that shows crocidolite fibers end-on (from Fig. 13 in Ahn and Buseck, *Am. Mineral.* **76**, 1467–1478, 1991; also in Klein and Hurlbut, 21st ed., p. 165). The orientations of these grains can be determined from the defects – called “zippers” or “chain-width errors” – that are oriented perpendicular to [010]. They are chains that are wider than the double-chains of the idealized host crocidolite amphibole.
 - [1] Using the zippers, measure the angular mismatch between adjacent grains
 - [2] Note the material along the grain boundaries. From your knowledge of mineralogy and the structure of amphiboles, what might this material be?
 - [3] There are many additional questions that could be posed about the “defects.” For example, are they in fact defects? Do they change the composition and, if so, how? How might they influence fibrosity? Grain size? What effects might their relatively larger spaces have on trace-element contents? Are they growth or alteration products?

HIGH-RESOLUTION TEM IMAGES AND ATOMIC-FORCE MICROSCOPY

(the photos for this problem were taken by Huifang Xu)

4. Alkali feldspars: surface and bulk structures

Diffraction measurements are probably the most common approach to determining mineral structures, but direct visual methods have had increasing appeal as methods for imaging methods at the near-atomic scale have improved. Such direct imaging is especially useful when studying crystal defects, twinning, and other deviations from ideality.

Here we consider the effects of Al-Si ordering and twinning in alkali feldspars. We will use electron diffraction, high-resolution TEM imaging, and atomic-force microscopy.

Each spot on a diffraction pattern (DP) represents a set of parallel planes in a crystal. The DP spots can be represented by the Miller indices of the diffracting planes, except that no parentheses are used in diffraction (or “reciprocal”) space. Thus, the diffraction spot from the (*hkl*) planes has indices *hkl* in the DP. The separation between (*hkl*) planes can be determined from the reciprocals of the separation of (*hkl*) diffraction spots, corrected for the appropriate angles if $\alpha, \beta, \gamma = 90^\circ$.

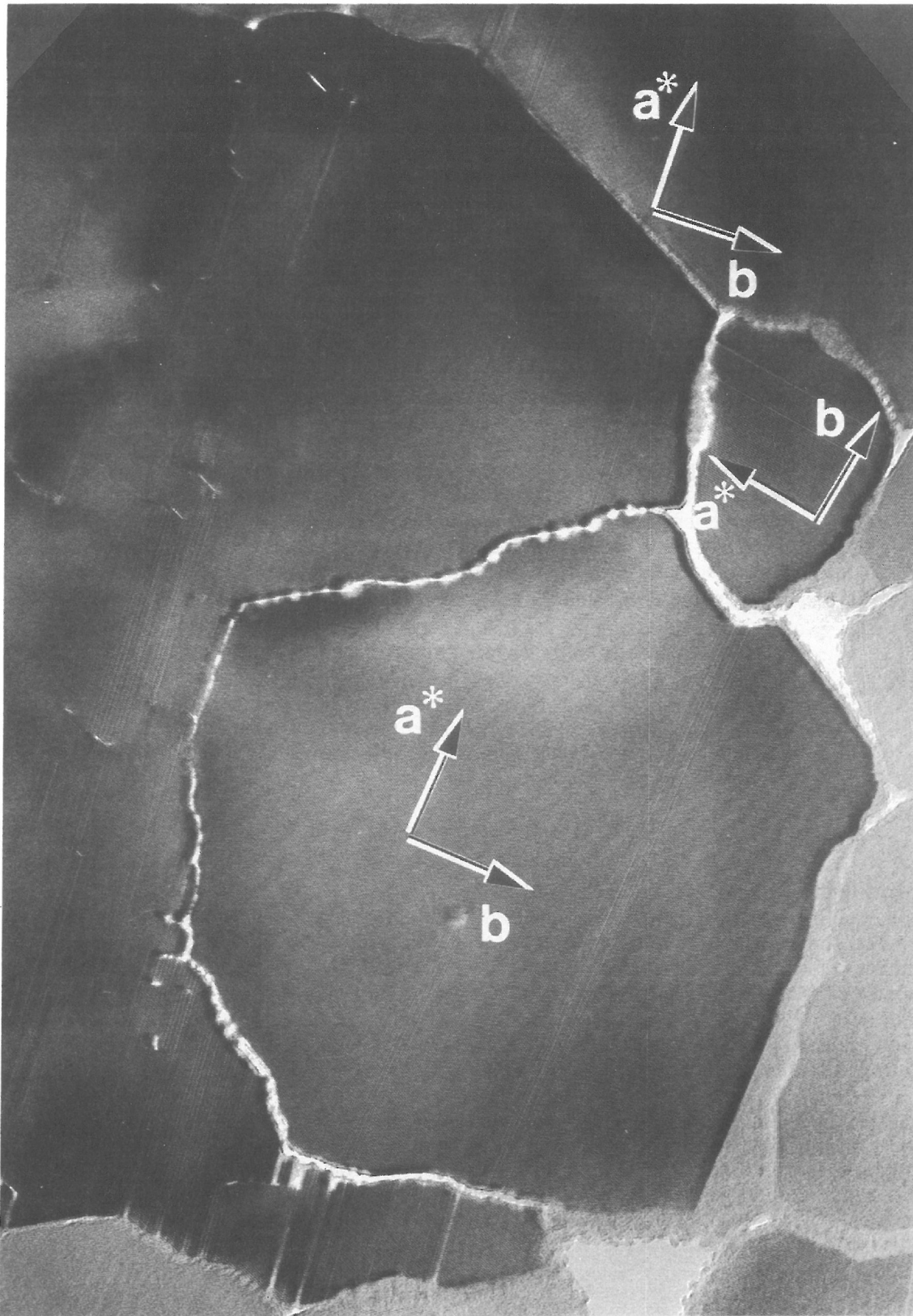


Figure 3a. HRTEM image of crocidolite.

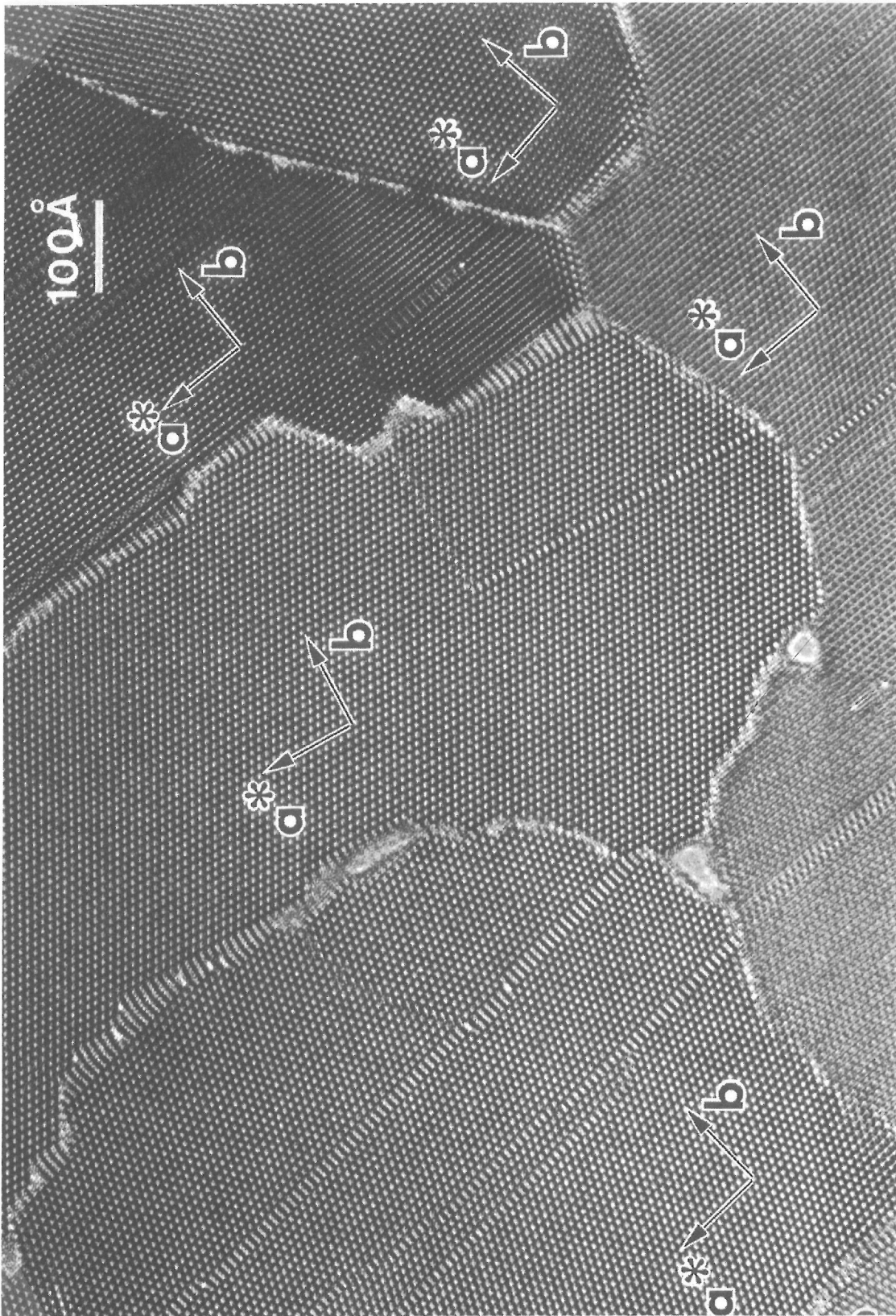


Figure 3b. HRTEM image of crocidolite.

An $a^* - b^*$ electron-diffraction pattern of feldspar is shown in Figure 4a. It provides information about the interplanar spacings of the $(h00)$ and $(0k0)$ sets of planes and the angles between them. Photographic processing has produced minor distortions, so measurements can have errors of a few percent.

- a) **Electron diffraction** Using a metric ruler, determine the separations in mm of the spots along the vertical and horizontal directions. These are directly proportional to the interplanar spacings in nanometers.

For the crystal that yielded this DP, these directions turn out to be parallel to crystallographic axes.

- [1] Using the ratio of the spacings along these directions (i.e., the distance from the 000 spot representing the center of the DP and the position of the radiation beam), and the values in the following table, determine which crystallographic axis is horizontal and which is vertical.

Values for a sodic K-spar of the appropriate composition:

$$a = 0.84 \text{ nm} \quad b = 1.30 \text{ nm} \quad c = 0.72 \text{ nm} \quad \alpha, \gamma = 90^\circ \quad \beta = 116^\circ$$

- [2] Give the Miller indices and spacings of the crystal planes perpendicular to the crystallographic directions determined above.
- [3] What is the zone axis for this diffraction pattern?
- b) **HRTEM imaging** Consider the high-resolution image (Figure 4b) of the crystal studied above.
- [1] Two sets of planes are dominant in the HRTEM image: those that slant NE-SW and those that slant NW-SE. From the information developed in a), what are the indices of these planes?
- [2] The image shows three lamellae; the ones at the top and bottom are of the same mineral (and are truncated along their lengths). The arrows indicate the positions of twin planes (slightly shaded). From what you know of feldspar and its twinning, which is orthoclase and which is albite (actually potassic albite)?
- [3] Confirm your estimates from measurements of the enlargement and your knowledge of the relative dimensions of Na and K.
- [4] What might cause the “scalloping” along the boundary (most prominent in the box) between the two minerals? How is it related to the twinning?

- c) **AFM (surface) microscopy** The atomic-force image (Figure 4c) shows the surface configuration of the sample studied above. Note that we now see a 3-D image of the projection illustrated in b), above. The images are not from the identical regions shown in the HRTEM image and so the K/Na ratios may differ slightly. As a result, the lamellae widths also differ slightly.

[1] Which are the more Na-rich (albitic) lamellae and which are of orthoclase?

[2] What are the widths (\sim wavelengths) of the lamella?

The sample displays a peristeritic optical effect (a greenish yellow iridescence) that results from the diffraction of light from the intergrowths. Are the twin or the exsolution lamellae the most likely sources of this optical effect? Explain your reasoning.

[3] Locate and mark the surface steps.

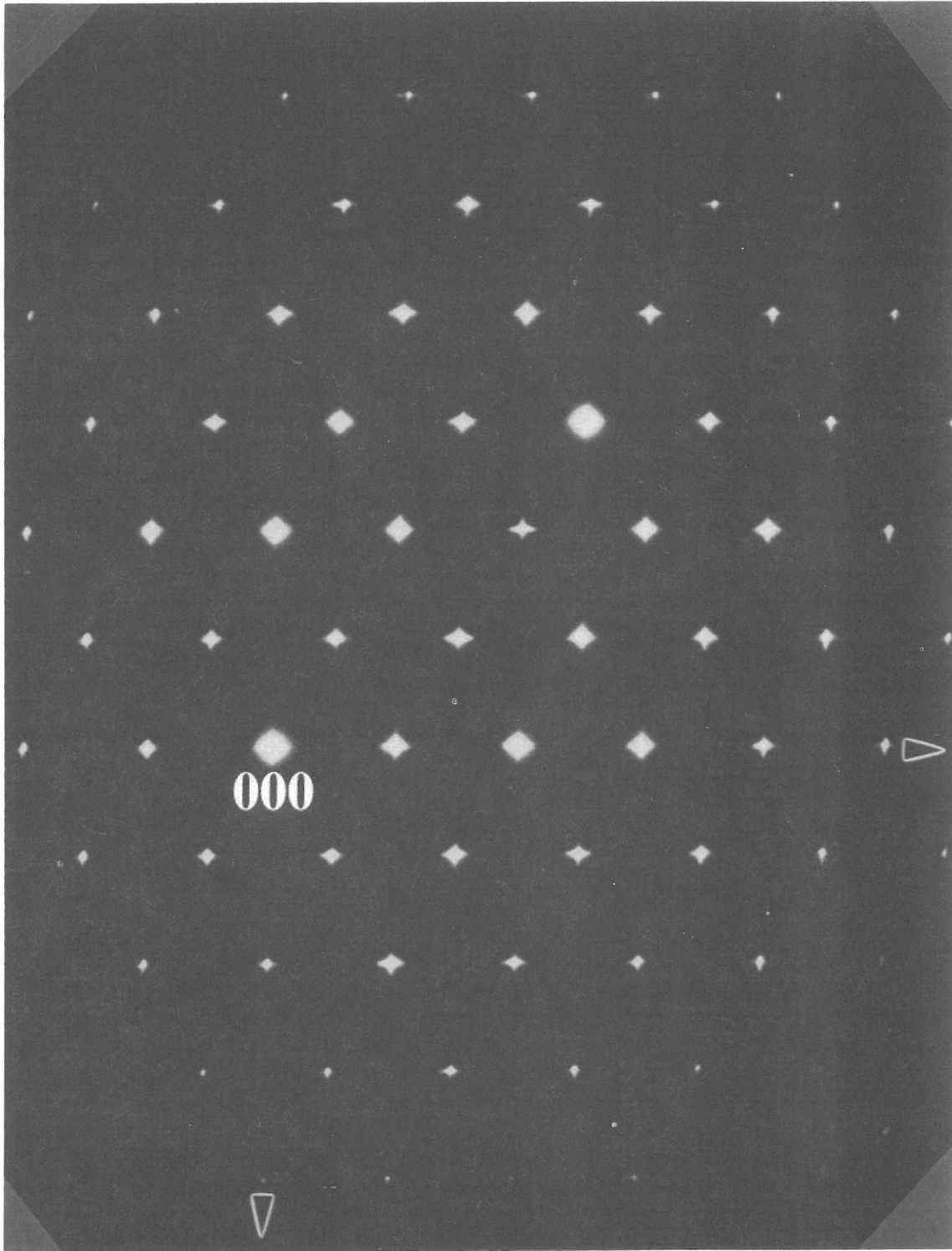


Figure 4a. $a^* - b^*$ electron diffraction pattern of feldspar.

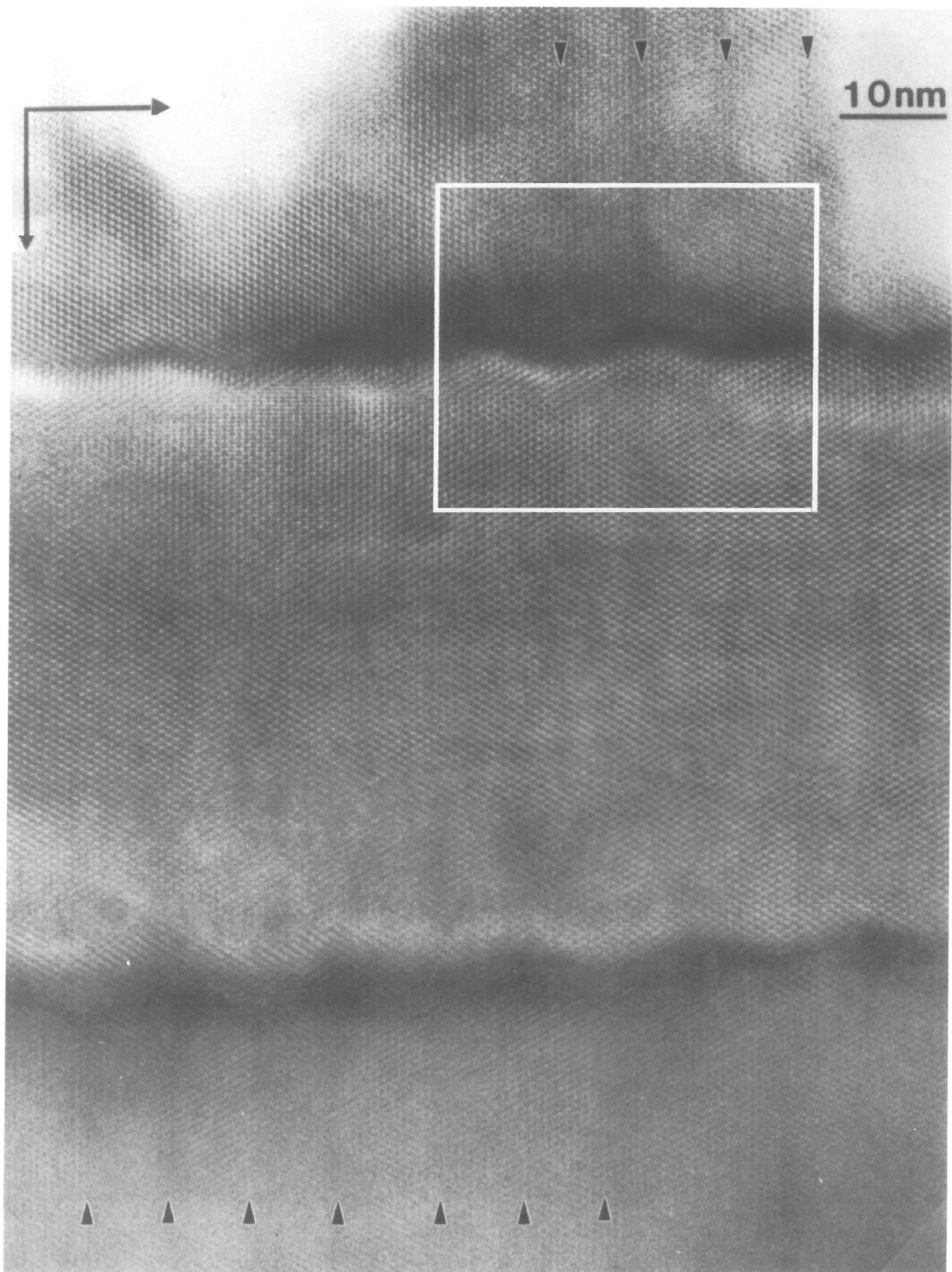


Figure 4b. HRTEM image of feldspar.

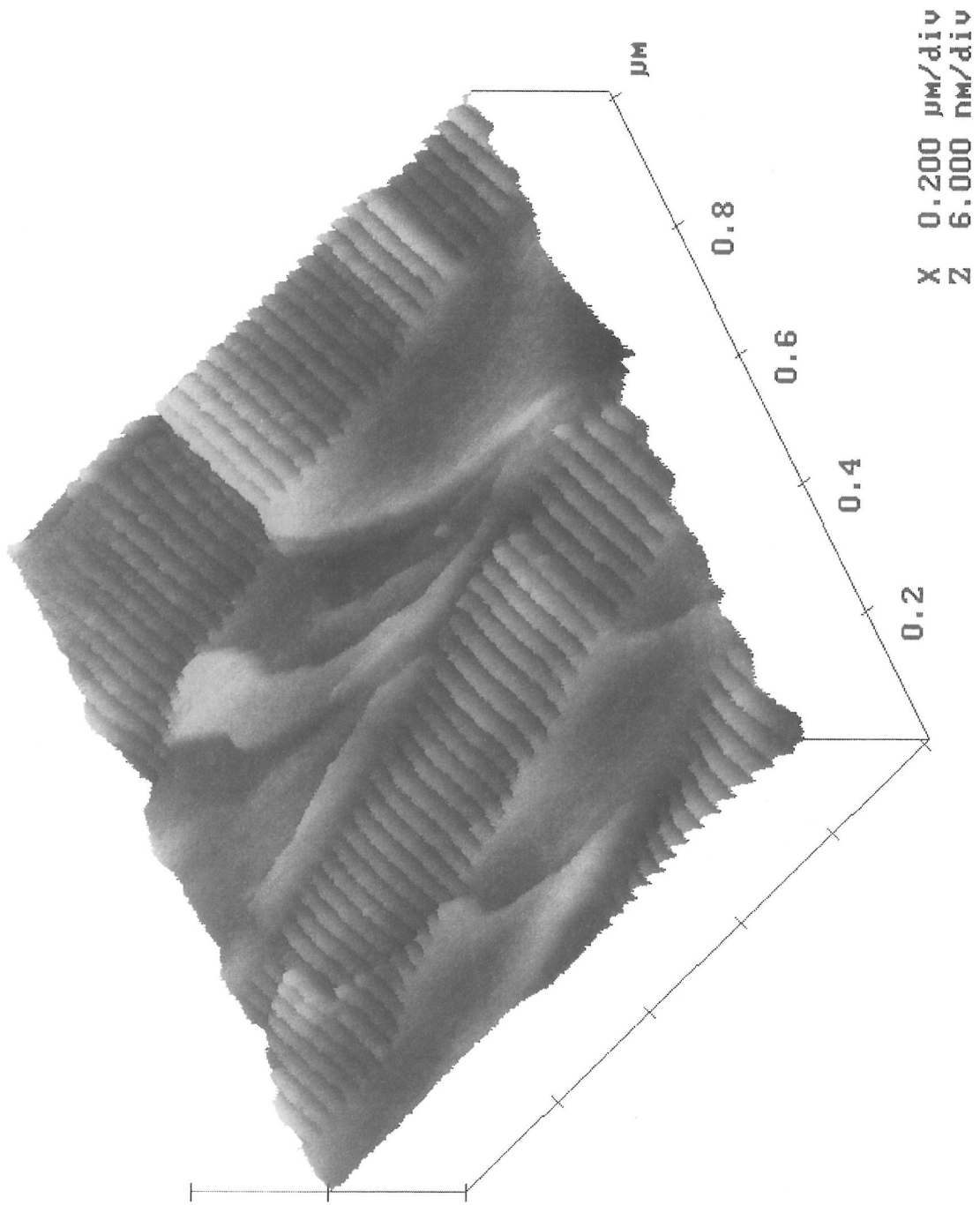


Figure 4c. AFM image of feldspar.

ANSWERS for "FROM 2D to 3D: II. HRTEM and AFM IMAGES"

1.
 - a) there are 6-fold rotation axes in the centers of the channels, 3-folds at along the long body diagonal at $1/3$, $2/3$ and $2/3$, $1/3$, and 2-folds in the center of the cell and in the centers of each cell edge;
 - b) the unit cell has a rhombic shape;
 - c) problemite contains one lattice node while cordierite is centered, i.e., it contains two nodes;
 - d) hexagonal.

2.
 - a) [1] if the differences in intensity are ignored, then a unit cell can be defined; such differences are harder to overlook for the digenite than for the bornite: [2] there are horizontal and vertical m's, and 2- and 4-folds in bornite but none in the digenite image; [3] bornite: #3 – "Unicorns" (Escher #78); #4 – "Iselberg"; digenite: "Birds in Space" provides a fairly good match. The clustered vacancies give rise to superstructures.
 - b) [1] The modulations make it difficult to define a unit cell; it would need to be large enough to include a full wave and would then be considered a supercell. [2] The small squares define the PbS layer. [3] The modulations of #6 – "Birds in Space" by Escher probably provides the best match.
 - c) [1] The variations in site occupancies make it difficult to define a unit cell; [2] Cells containing a site with less than a full complement of Fe atoms, i.e., those with a black (unoccupied) site in its center, are superstructure cells that are larger than the subcells; [3] The best analogy to the presumed point defects are probably provided by "Shells and clams" (Escher #42), although where they are ordered into superstructures problems #3 – "Unicorns" (Escher #78) and #4 – "Iselberg" may be applicable. Clearly, there is scope for discussion.
 - d) [1] The combination of Mg and Ca have a lower mass and therefore lower electron density than does Ca alone, and therefore the columns that contain Mg plus Ca will have lower contrast. [2] The Ca/Mg ordering produces an enlarged unit cell (a small superstructure) and so roughly resembles that in #3 – "Unicorns" (Escher #78) and #4 – "Iselberg."

3.
 - a) [1] Their "zippers" are in view and are almost exactly parallel, and so we assume the two grains have almost identical orientations. [2] Their orientational relations and "lock and key" type of intergrowth suggests that the smaller grain is being "calved" from the larger one. [3] Fibers seem to form from larger grains.
 - b) [1] The angular mismatch varies but is only a few degrees for most fibers. [2] Wide chain pyribole on its way to forming a layer silicate such as a mica.

4.
 - a) [1] The two axes in this pattern are \mathbf{a}^* and \mathbf{b}^* . \mathbf{b}^* is horizontal and \mathbf{a}^* is vertical. [2] And along \mathbf{a}^* : 200 (0.42 nm), 400 (0.21 nm), ... and along \mathbf{b}^* : 020 (0.65 nm), 040 (0.325 nm), ... Extinct reflections are of type $h00$ and $0k0$, where h and k are odd. The zone axis is $[001]$.
 - b) [1] The NE-SW set of planes correspond to (110), while those that slant NW-SE correspond to $(1\bar{1}0)$. [2] The lamellae at top and bottom contain fine albitic twins and serve to identify this mineral as albite, while the central lamella is the "orthoclase." [3] The spacings of the planes in the potassic material are slightly larger, reflecting the greater diameter of K than Na. [4] The scalloping is produced by the interfaces of the albitic twins with the potassic feldspar (not a very adequate explanation!).
 - c) [1] The average widths are ~12 nm and ~2 nm. [2] The twin lamellae define the albite and the broader lamella are the "orthoclase."