JOURNAL OF SOLID STATE CHEMISTRY 87, 308–320 (1990)

Study of the Ordering of Sc and Ta Atoms in Pb_2ScTaO_6 by X-Ray Diffraction and High Resolution Electron Microscopy

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Received February 13, 1989; in revised form March 1, 1990

Single crystals of Pb_2ScTaO_6 were grown by slow cooling of the melt. X-ray single crystal methods led to a cubic structure with a primitive unit cell with $a = 4.07$ Å. X-ray powder diffraction on crushed crystals reveals weak lines indicating some degree of ordering. High resolution electron microscopy (HREM) has been done along the [110] direction: ordered and disordered domains actually exist, with a domain size between a few angstroms and roughly 1000 Å. In the present case ordered domains were just at the limit of detection by X-ray methods. It has been shown that high resolution electron microscopy is a powerful method for the study of ordering, especially in the case of small domains.

Introduction

The $A_2^{2+}B^{3+}B^{0.5+}O_6$ perovskite-type structure compound Pb_2ScTaO_6 is one of the numerous ferroelectric compounds which are "relaxor" ferroelectrics. These materials exhibit a broad dielectric permittivity peak versus temperature, and dielectric dispersion at low frequencies. Careful X-ray and dielectric studies (*1*) have shown that the broad dispersive response is associated with a disordered structure and the relaxation behavior is significantly reduced by ordering of the Sc and Ta atoms on the perovskite B sites (Figs. 1a and 1b). Dark field images of transmission electron microscopy (*2*) show the existence of large ordered microdomains (35–120 nm in size). On this basis it has been postulated that the relaxation behavior is due to the presence of microscopic regions (microdomains) of slightly different compositions (and hence with different Curie temperatures).

As Goodenough and Longo stated (*3*), the cationic radius ratio of Sc(3+) and Pb(2+) is roughly 0.59 (<0.8): the radius of Sc(3×) in 6-coordination is 0.885 Å and the radius of Pb(2+) in 12-coordination is 1.50 Å (*4*). The relative difference between Sc and Ta radii: [r(Sc)-r(Ta)]/r(Sc) is approximately 0.12 (>0.09), the radius of Ta(5+) in 6-coordination is: 0.78 Å (*4*). Therefore, a strong ordering tendency is present in Pb_2ScTaO_6. According to Refs. (*2*) and (*5*) the ordered

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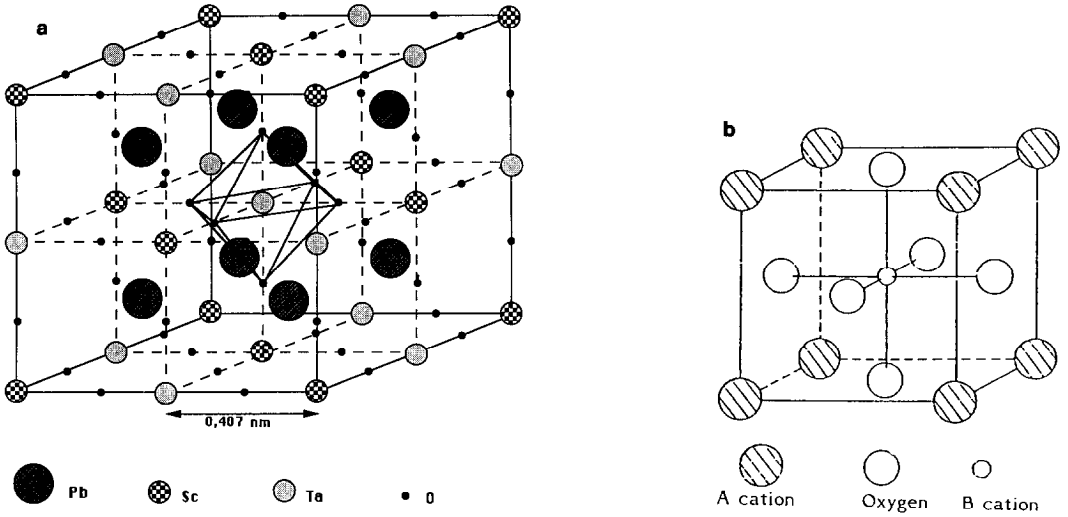

FIG. 1. (a) Structure of ordered perovskite Pb_2ScTaO_6 crystal (after Galasso). (b) Structure of disordered perovskite Pb_2ScTaO_6 crystal (classical perovskite).

structure should be the $(NH_4)_3FeF_6$ structure (Fig. 1a) which consists of discrete $(B'X_6)$ octahedra separated by A and B cations and which has the space group $Fm3m$; here B cations are in $4(b)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, fcc positions; A cations, in $8(c) \pm (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, fcc positions; B' cations in $4(a)(0, 0, 0)$, fcc positions; and X anions in $24(e) \pm (u, 0, 0; 0, u, 0; 0, 0, u)$, fcc positions, with $0.2 < u < 0.25$. A movement of the A cation along the [111] axes may occur, destroying the cubic symmetry, so that it is important to check the symmetry of the compound in the [100] orientation.

For very small domains the resolution provided in dark-field images or diffraction contrast images would not be sufficient for display of domain structures. We will show here that HREM can be a very powerful tool in this case.

Experiments

Pb_2ScTaO_6 crystals were prepared by the mixed oxide technique, and were grown by slow cooling of the melt. Single crystals are

TABLE I

X-RAY POWDER DATA FOR Pb_2ScTaO_6

$d_{(hkl)}$ (Å)	I	(hkl) P a = 4.07 Å	(hkl) F a' = 8.14 Å
4.67	w′		111
4.07	w	100	200
2.86	s	110	220
2.45_5	w′		311
2.34	w	111	222
2.03	s	200	400
1.87	w′		331
1.82	w	210	420
1.66	s	211	422
1.57	w′		511,333
1.44	s	220	440
1.28_5	s	310	620
1.17_5	s	222	444
1.09	s	321	642
1.01	s	400	800
0.96	s	411,330	822,660
0.91	s	420	840
0.89	w	421	842
0.87	s	332	664
0.83	s	422	844
0.80	s	431,510	862,10.20

Note. $\lambda CuK\alpha$ = 1.54178 Å.

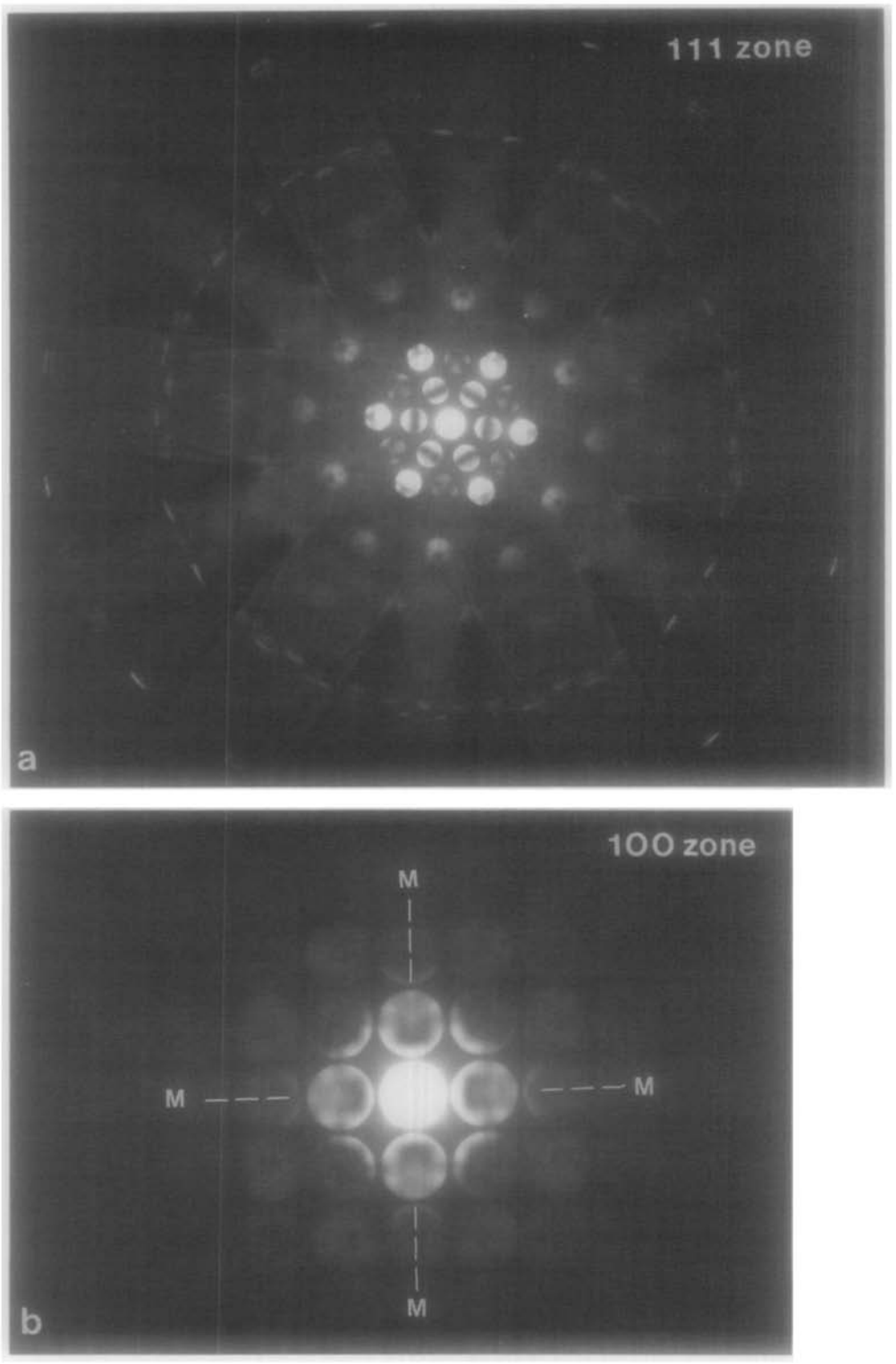

FIG. 2. (a) CBED pattern in the [111] orientation. The threefold symmetry is visible in the whole pattern. (b) CBED pattern in the [100] orientation. The fourfold symmetry is visible in the pattern.

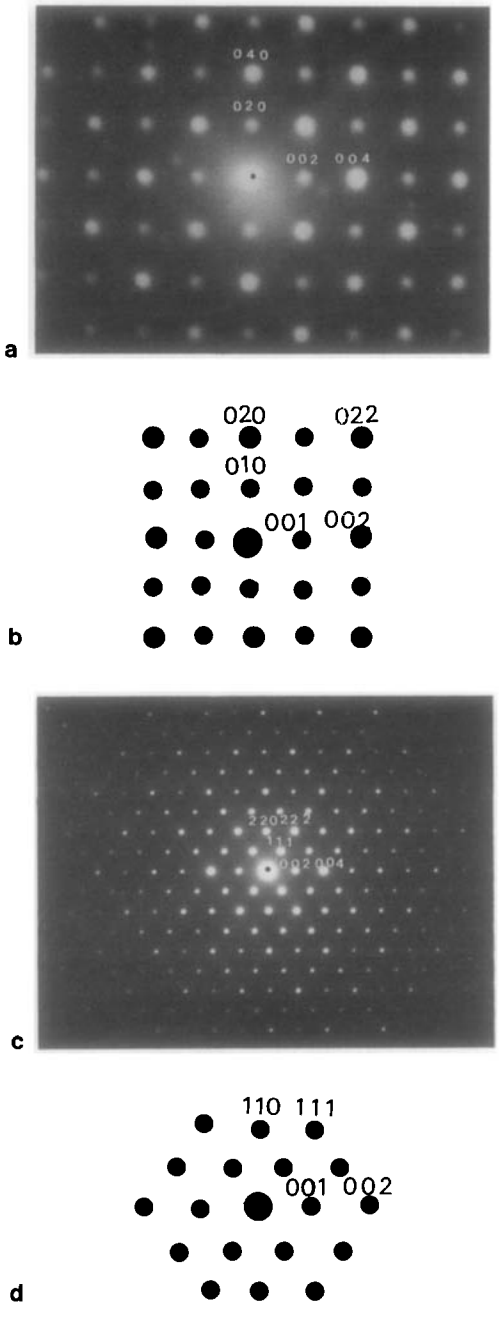

FIG. 3. (a) Diffraction pattern of the [100] zone indexed in the ordered structure; (b) indexing in the disordered structure; (c) diffraction pattern of the [110] zone indexed in the ordered structure; 111_0 spots of the ordered structure (and homologous spots) cannot be indexed in the disordered structure; (d) indexing of the disordered structure.

cubic in shape, with a few small twins, and are rose pink in color. One crystal has been studied by the rotation method. Another single crystal and ceramics were studied after crushing by powder X-ray diffraction in a Debye-Scherer camera. HREM and CBED (convergent beam electron diffraction) have also been carried out in two different JEOL 2000FX instruments, with and without high angle EDX detector. The electron probes used were about 500—1000 Å in diameter (4L spot, ×300K, 50-μm condensor aperture).

X-Ray Diffraction

Rotation photograph and precession methods on a single crystal using λ Cu$K\alpha$

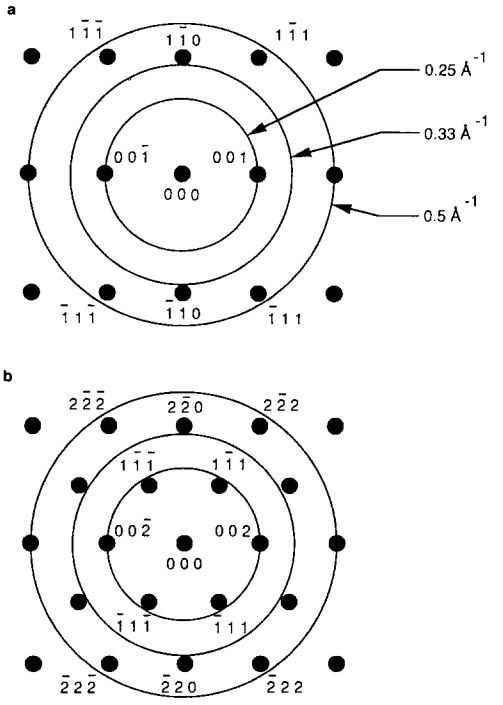

FIG. 4. Different positions of the objective lens apertures in the [110] direction corresponding to about 2, 3, and 4 Å resolutions for respectively larger, mean, and smaller apertures: (a) for the disordered structure; (b) for the ordered structure.

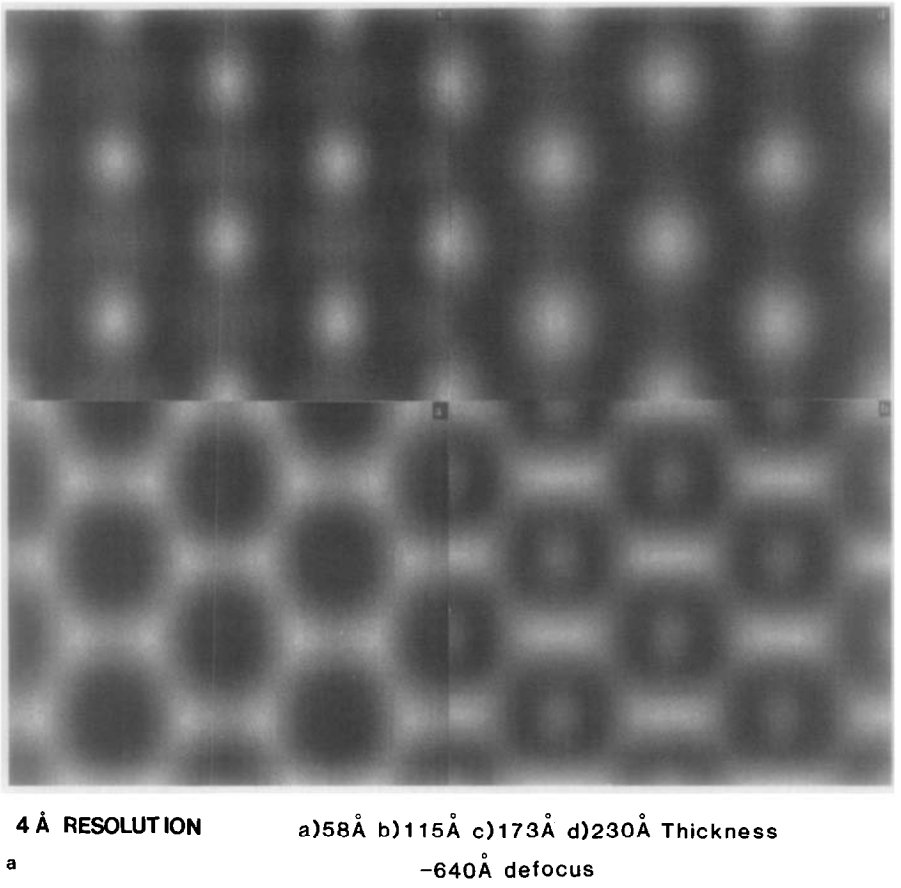

FIG. 5. (a) Calculated high resolution images in the [110] zone for the ordered structure and for different thicknesses (resolution: 4 Å). (b) Calculated high resolution images in the [110] zone for the disordered structure and for different thicknesses (resolution: 4 Å).

radiation indicate a primitive cubic structure with $a = 4.07$ Å. This corresponds to the case of disorder for Sc and Ta atoms (Fig. 1b). These methods indicate that at room temperature there is only the single cubic structure. X-ray powder studies on crystallites (a crushed crystal) less than 1 μm in size are summarized in Table I: 13 strong reflections appear on the film (labeled s) with four weak reflections (labeled w), which fit with a primitive unit cell $a = 4.07$ Å, in agreement with the previous results. But the film also contains four very weak lines (labeled w′) which can correspond only to the 111, 311, 331, and 333-511 reflections of the ordered $(NH_4)_3FeF_6$-type structure ($a = 8.14$ Å). This leads us to suppose that there are in fact two coexisting phases, corresponding to ordered and disordered domains. These small domains could have not be detected in single crystals because of the heavy X-ray absorption for these compounds (especially due to the lead), which masks the weak lines corresponding to the ordered structure. For powder, the absorption is reduced for domains near the surface, which explains why the lines for the ordered structure can be observed at the limit of detection of the ordered domains by X-ray methods. The maximum size of these do-

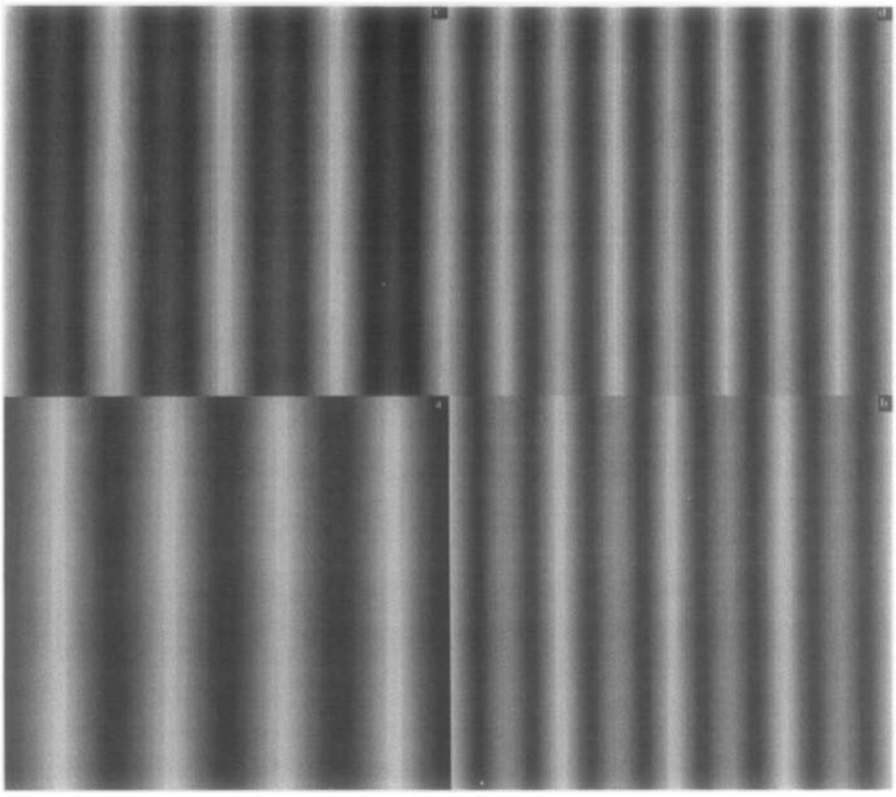

FIG. 5—*Continued*

mains is roughly 1000 Å. Very small ordered domains (less than 100 Å) would certainly not have been detected by X-ray methods. Electron microscope dark field images by diffraction contrast (generally used in this kind of studies) would not be much more definitive. However, HREM does provide more precise results, and was used in the present study. CBED has also been done to check the cubic structure.

Electron Diffraction and CBED Studies

CBED (*6, 7*) and electron diffraction studies have been carried out on the crystal studied previously by X-ray diffraction. For these investigations the crystal is broken into small pieces by a special technique so as to present thin regions that can be used for different kinds of electron microscope studies.

Figures 2a and 2b show CBED patterns obtained along the [111] and [100] axes. In the first case the entire pattern (zone axis pattern) is displayed. The threefold symmetry is clearly visible (the zero layer looks like a sixfold coordination pattern but upper Laue layers reveal the threefold symmetry). In the second case only the zero layer is visible, each diffraction spot becomes a disk, in which the G–M lines reveal the fourfold symmetry. From these two patterns we

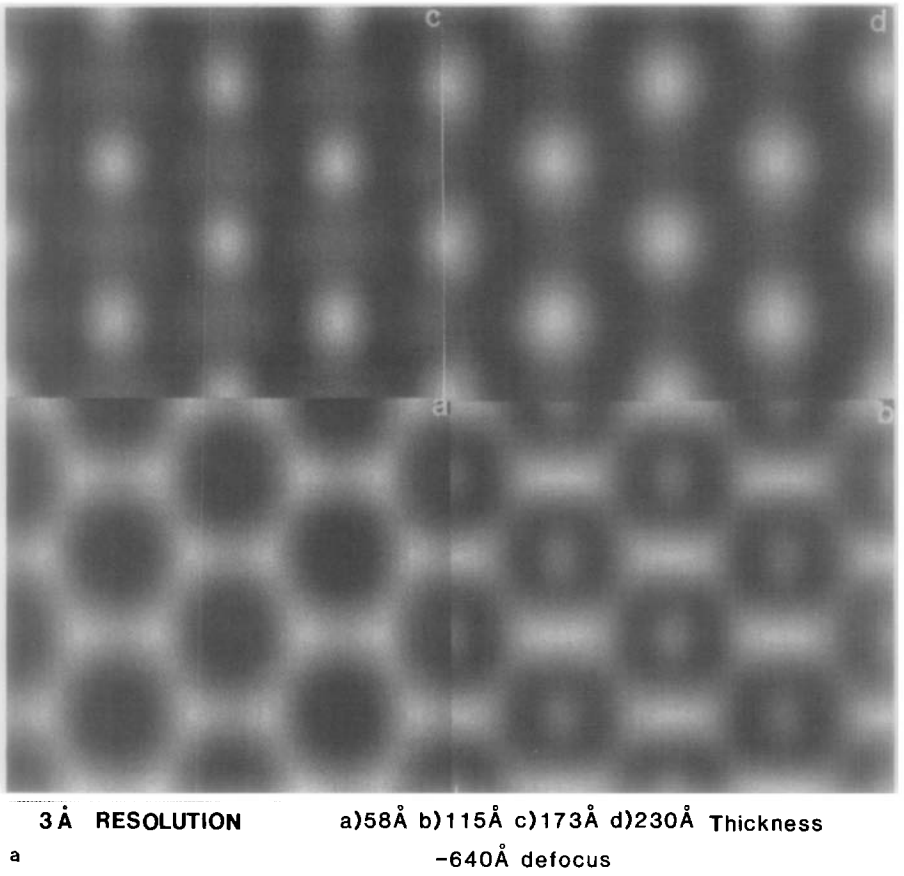

FIG. 6. (a) Calculated high resolution images in the [110] zone for the ordered structure and for different thicknesses (resolution: 3 Å). (b) Calculated high resolution images in the [110] zone for the disordered structure and for different thicknesses (resolution: 3 Å).

can be certain that the structure is cubic, in agreement with X-ray diffraction results.

Figures 3a, 3b, 3c, and 3d show the diffraction patterns in the [100] and [110] zones and their indexing in the ordered and disordered unit cells. Nothing concerning ordering can be deduced from the diffraction pattern along the [100] axis which remains identical for ordered and disordered structures. However, the 111 spots of the ordered structure do not appear in the disordered structure. The existence of such spots in electron diffraction, along the [110] axis, reveals the ordering in the crystal. These spots are visible on the electron diffraction pattern and may be strong due to the dynamical scattering effect (see Fig. 3c). These spots cannot arise in a disordered structure, even through multiple diffraction processes. The existence of these spots clearly indicates that some regions are ordered. This is in agreement with the X-ray results if very small ordered domains are involved. This point was checked by HREM studies.

HREM Studies

Ordered and disordered regions are generally distinguished by dark field images of spots which are not present in the disor-

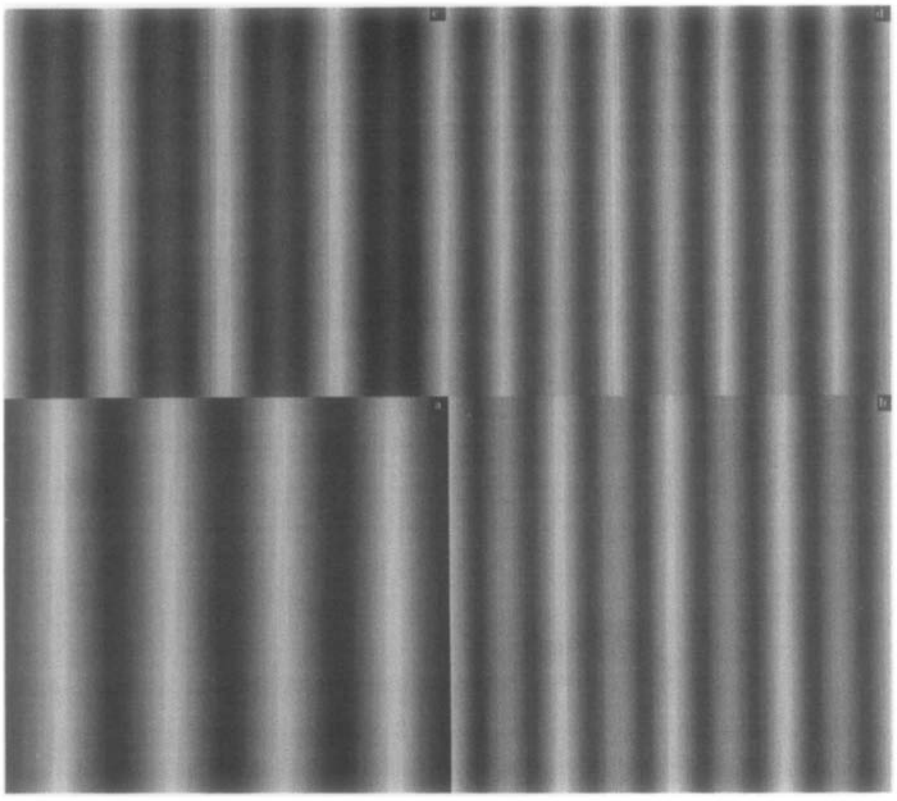

FIG. 6—*Continued*

dered structure. In the present case, this technique did not lead to significant results, probably because the ordered domains are too small. Thus, high resolution electron microscopy was used for the [110] zone, for three different diameters of the objective lens aperture (Fig. 4), corresponding to different image resolutions. We always use an objective aperture such that the 111 and 002 spots of the ordered phase are included, so that the images should be different for the ordered and disordered structure. Figures 5a and 5b show the calculated image for ordered and disordered structures for which the image resolution is roughly 4 Å (smaller aperture, Fig. 4). Figures 6a and 6b show the calculated images for image resolution of approximatly 3 Å resolution (mean aperture, Fig. 4). Figures 7a and 7b show the calculated images for all image resolutions of roughly 2 Å (larger aperture, Fig. 4). These calculated images clearly demonstrate the difference between the ordered and disordered phases. In all cases the disordered phase has a fringe image except in the case of the 2 Å resolution where the fringes turn into a tetragonal net; the ordered phase always gives rise to a white or black dot pattern.

Figures 8a and 8b show respectively the experimental images at 4 and 2 Å resolutions. The existence of disordered and or-

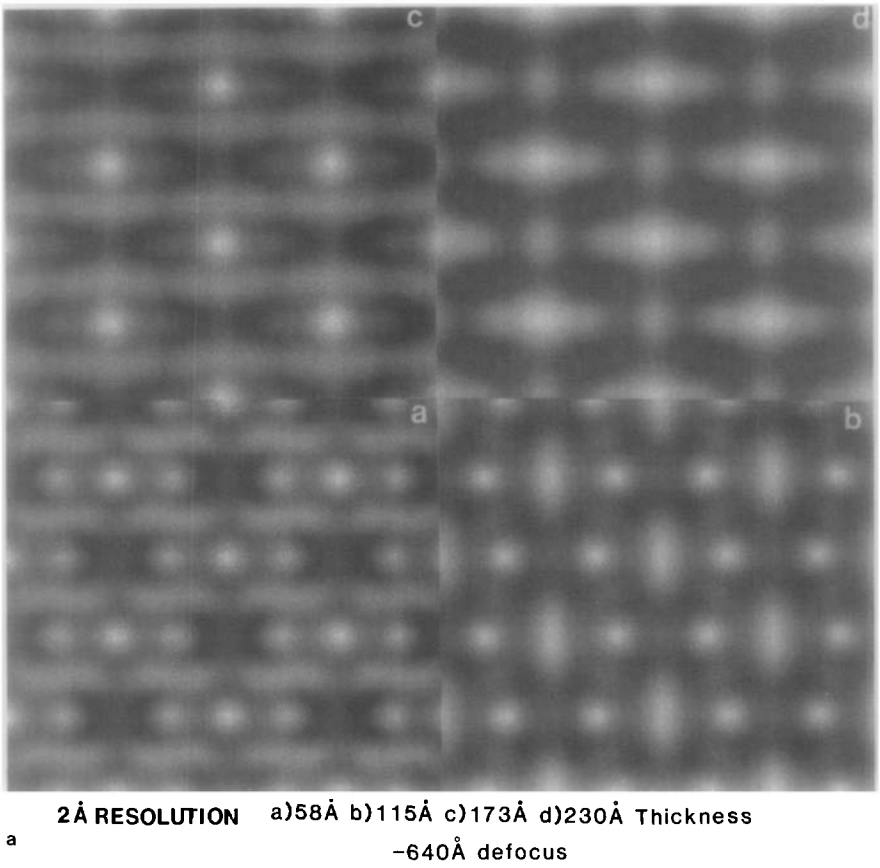

FIG. 7. (a) Calculated high resolution images in the [110] zone for the ordered structure and for different thicknesses (resolution: 2 Å). (b) Calculated high resolution images in the [110] zone for the disordered structure and for different thicknesses (resolution: 2 Å).

dered domains is clearly shown by comparison with calculated images. The difference in the images is clearer at the smaller resolution, which can be understood by the smaller number of diffraction spots included for the image formation (but always with inclusion of the 111 spots of the ordered structure). On Fig. 8b optical diffraction patterns are exhibited for expected ordered and disordered regions; they clearly correspond to the calculated diffraction patterns of each kind, confirming the high resolution identification of ordered and disordered domains. Optical diffraction patterns can be taken on regions no larger than 50 Å in diameter. Figure 9 shows the same condition as in Figs. 8a and 8b but at higher magnification. According to the calculated results the white or black dot regions correspond to the ordered phase and the tetragonal or fringe regions correspond to the disorded phase. Domains of ordered or disordered phases can have dimensions ranging from a few angstroms to several hundred angstroms in diameter. Boundaries between ordered and disordered regions are completely coherent; the interface between them is irregularly stepped. A few unit cells (sometimes even just one) of ordered regions occur in disordered regions and vice versa. Thus, the so-

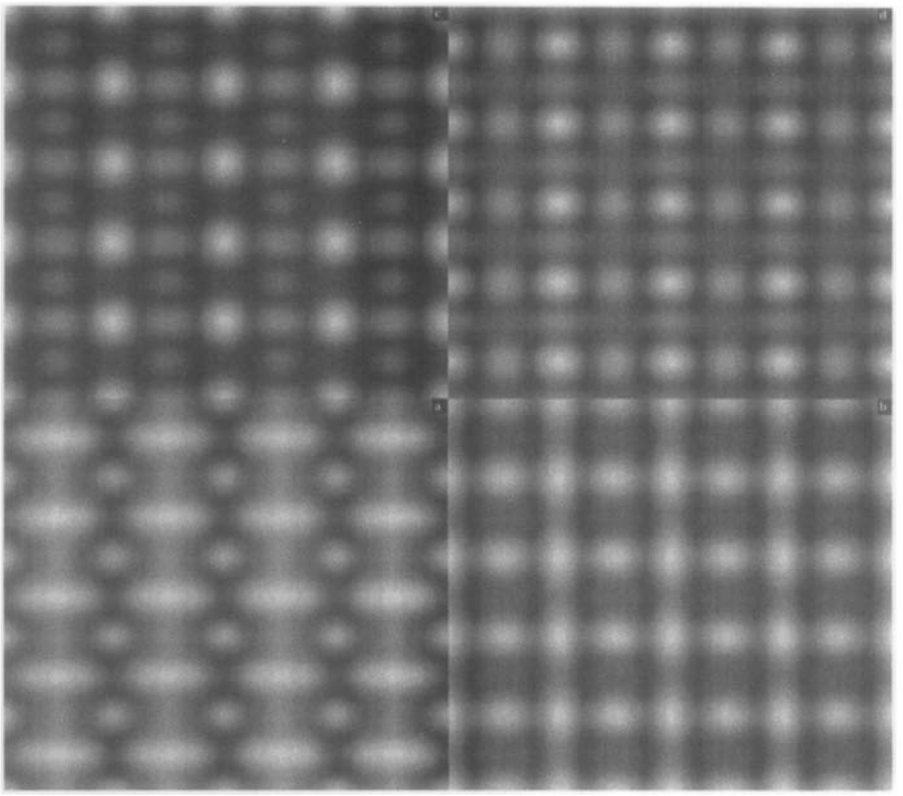

FIG. 7—*Continued*

called degree of ordering really represents simply the occurrence of a percentage of ordered region inside the entire specimen. The degree of ordering very likely does not occur at the atomic scale and represents only a macroscopic concept.

Microanalysis and Chemical Analysis

The JEOL 2000FX microscope with high angle EDX detector can detect the composition of a small area (about 500 Å in diameter) where the image can also be taken. For a quantitative analysis the K-factor must be calibrated by a standard sample, but for a qualitative analysis, to detect some compositional variations, this step is not necessary. We used one region as a standard for all microanalyses. EDX spectra from different areas clearly show that the Ta/Sc ratio is not constant and that it can change by more than 10%. A problem of the electric charge balance may then arise. It would be interesting to analyze more carefully small regions to assertain if this fact is related to variations of the structure, but this has as yet not been done.

A chemical analysis has been carried out for this sample, yielding the following atomic ratios: [Sc]/[Pb] = 0.50, [Ta]/[Pb] = 0.47 (instead of 0.50), and [Ta]/[Sc] = 0.95 (instead of 1.00). This means that the

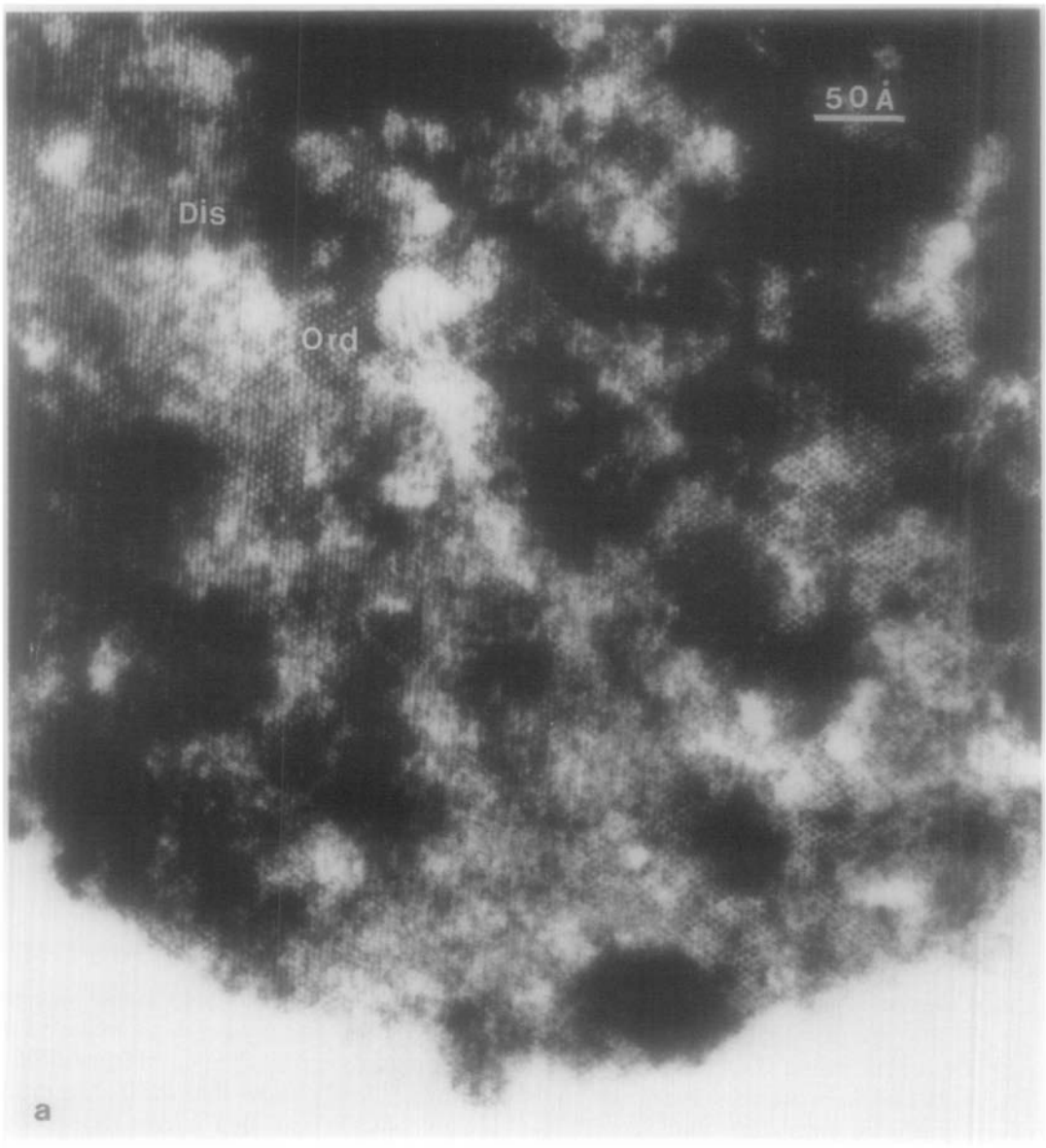

FIG. 8. (a) Experimental high resolution images with roughly 4 Å resolution. Ordered and disordered structures are labeled Ord and Dis. (b) Experimental high resolution images with roughly 2 Å resolution, with optical diffraction patterns for ordered and disordered regions, respectively, labeled on the image by Ord and Dir.

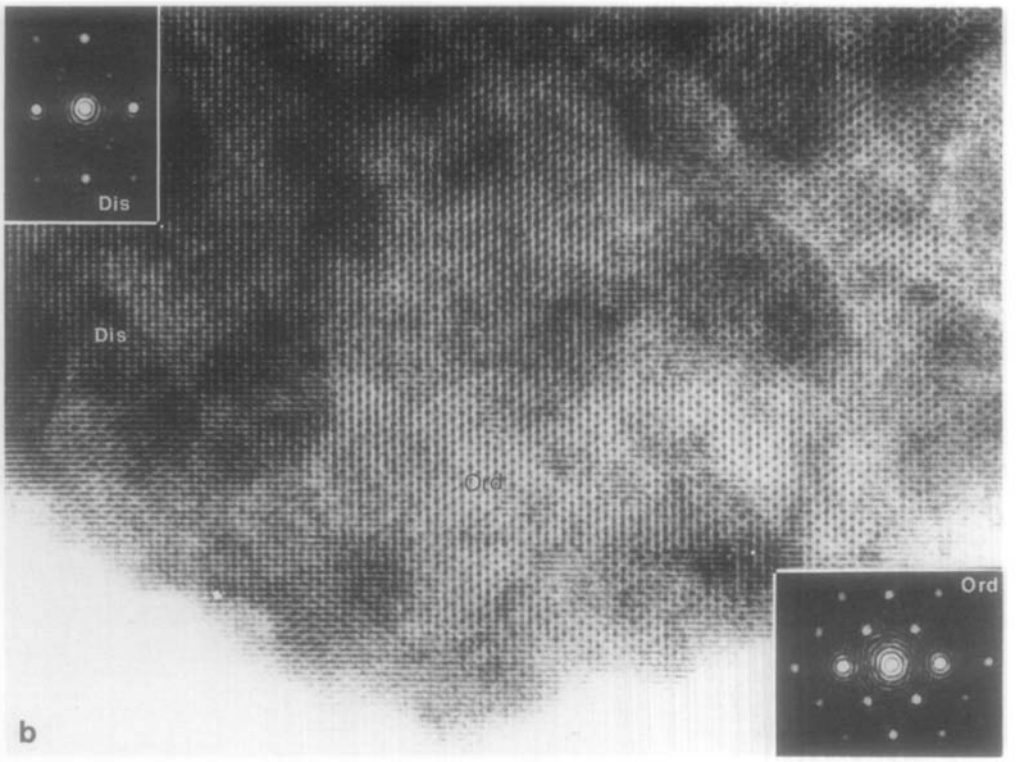

FIG. 8—*Continued*

general chemical formula of the compound shows a small deficit in tantalum.

Conclusion

The X-ray diffraction methods, the CBED microdiffraction, and high resolution images definitely reveal or confirm the following facts:

(i) Pb_2ScTaO_6 crystals are cubic at room temperature and have ordered domains of the $(NH_4)_3FeF_6$-type structure. However, the single crystal X-ray diffraction does not reveal ordering, probably because it was masked by X-ray absorption.

(ii) Both ordered and disordered regions exist and are interleaved, the boundary between them being irregularly stepped. The size of ordered domains varies from a few angstroms to roughly 1000 Å, the largest being detected by X-ray diffraction on powders.

(iii) The degree of order here corresponds to the fraction of ordered regions in the sample. There is no intermediate state at the atomic scale. This concept at least in this case is a macroscopic one.

Microanalysis shows that the Ta/Sc ratio is not uniform in the sample. A chemical analysis shows a small deficit of tantalum.

HREM appears to be a very powerful method for the study of ordering, specially when we deal in the range of small domains.

Acknowledgments

The authors are grateful to the CRMC2 for the use of the 2000 FX Jeol electron microscope, and to Mr. S. Nitsche for his help. The authors also thank Dr. A. Bourret for very useful comments.

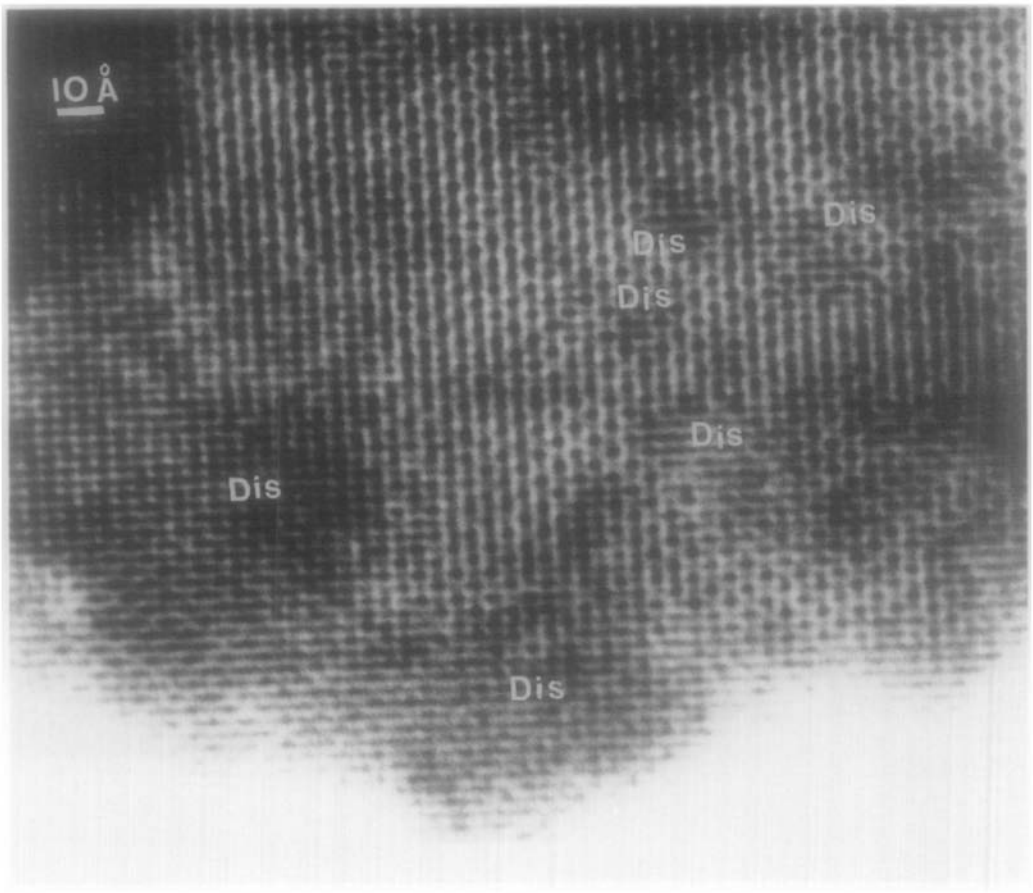

FIG. 9. High magnification image of the same region of the experimental high resolution image. Disordered regions are labeled Dis.

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