### Title
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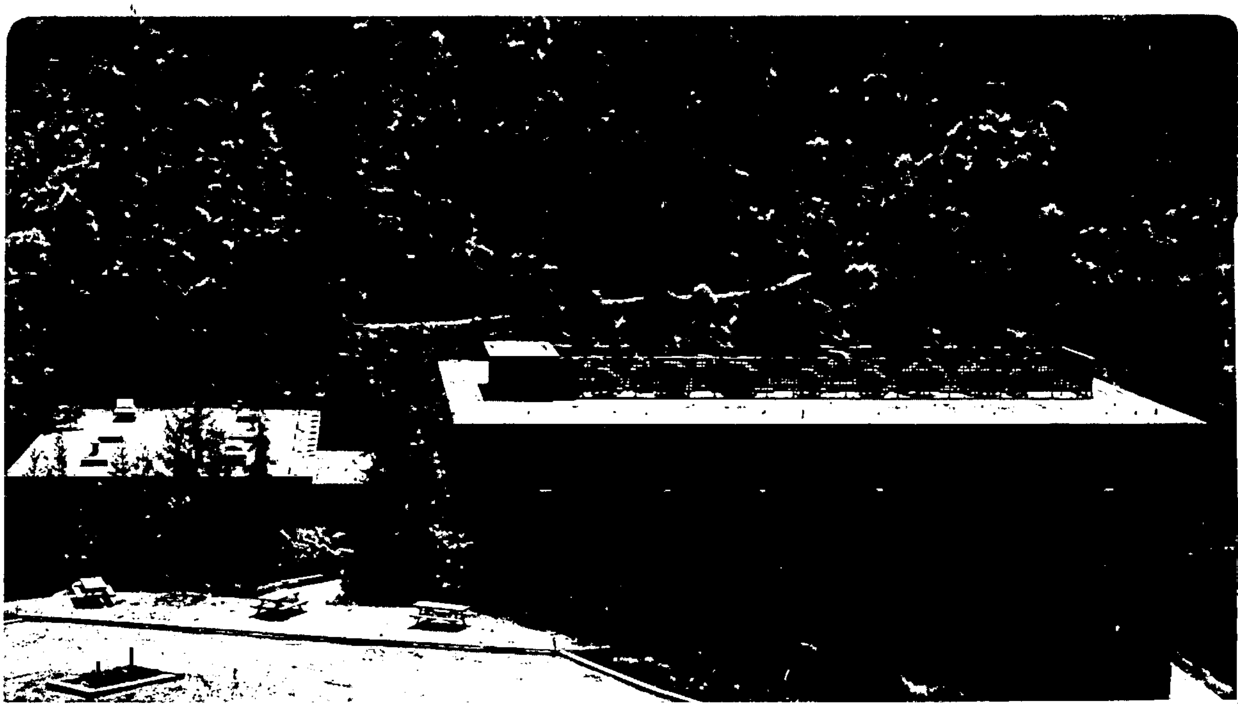



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# DISCLAIMER

# DIRECT OBSERVATION OF STRUCTURAL DEFECTS IN LASER DEPOSITED SUPERCONDUCTING Y-Ba-Cu-O THIN FILMS

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The defect structure of in-situ pulsed laser deposited, thin films of Y-Ba-Cu-O high $T_c$ superconductor has been observed directly by atomic resolution electron microscopy. In a thin film with nominal composition $YBa_2Cu_3O_7$(123), stacking defects corresponding to the cationic stoichiometry of "248", "247" and "224" have been observed. Other defects observed include edge dislocations and anti-phase boundaries. These defects, which are related to the non-equilibrium processing conditions, are likely to be responsible for the higher critical currents observed in these films compared to single crystals.

**INTRODUCTION** : The most important question concerning the potential of the new high $T_C$ cuprate superconductors for large scale applications is whether there is an intrinsic limitation to their ability to carry large currents with little or no loss at temperatures that are greater than or equal to $T_C/2$. A recent news report[1] outlines some of the evidence which is the basis for pessimism. On the other hand, the fact that thin films of $YBa_2Cu_3O_7$("123") have very high critical currents[2,3] with losses many orders of magnitude less than Cu metal when measured only a few degrees below $T_C$, is, we believe, a convincing proof that there is no intrinsic limitation.

There are several key questions regarding the origin of the high critical currents in these thin films. In earlier work[4] the lower $J_C$ of ceramic samples was attributed to the presence of grain boundaries. Since these oxide superconductors are type II materials with a very small value of $H_{C1}$, a flux lattice, either in the ordered form or disordered form, is very likely to exist. Indeed, the flux lattice has been observed in single crystals of $YBa_2Cu_3O_7$[5]. Thus, if the thin film is to carry a large critical current, it is essential that the fluxoids be pinned. Pinning of the flux lattice can, in general, be accomplished by the introduction of structural defects into the lattice. In the case of Y-Ba-Cu-O thin films , the atomic nature of defects, resulting from the deposition process, is still not known, although structural defects in bulk samples have been characterized using atomic resolution imaging(see for example, refs.6,7). The atomic structure of defects in thin films is the focus of this report. Defects in typical epitaxial films deposited on single crystal MgO have been examined using high resolution transmission electron microscopy at a resolution of 1.6Å. These films exhibit a sharp (≤1K) resistive transition at 88-90K and possess critical currents of the order of $10^6 A/cm^2$ at 77K.

Details of the thin film laser deposition process have already been reported elsewhere[2]. Cross-section samples were prepared and were ion milled for a few minutes prior to examination so as to reduce the degradation due to moisture in the atmosphere. High resolution electron microscopy (HREM) was carried out in the Berkeley Atomic Resolution Microscope(ARM) at a point-to-point resolution of 1.6Å. HREM images were obtained under conditions close to Scherzer defocus such that the projections of the atomic columns appear black on a white background. Images were obtained within a few minutes of exposure to the electron beam to reduce the beam induced damage. The interpretation of the experimental images was verified by carrying out simulations using the MacTempas®[8] software.

Planar sections of the thin film samples revealed that these films contained transformation twins. Most of the stacking defects are associated with the layered structure of these oxides. In Fig.1, the HREM image shows a local region where the $YBa_2Cu_3O_y$ (123) structure is observed. This structural interpretation is confirmed by the simulated image shown in the inset. The most common defect observed is the intergrowth of the $YBa_2Cu_4O_8$ structure, i.e., one which has two CuO chains rather than one. As shown by Zandbergen et.al[6], the two CuO chains are related by either a 1/2[100] or a 1/2[010] glide symmetry, both of which were observed in this study. This structure was subsequently detected by X-ray diffraction and electron diffraction in thin films of Y-Ba-Cu-O[9] and was found to have a $T_c$ of 81K. In the HREM image in Fig.2 the "248" structure with the 1/2[010] glide symmetry is presented. The interpretation of the image contrast in terms of the extra CuO layer is confirmed by the results of the image simulations, shown in the inset to Fig.2 for the 1/2[010] shift.

Two other types of stacking defects observed are illustrated in the image in Fig.3. The experimental image in Fig.3 shows in addition to the "perovskite block" consisting of the sequence "BaO-$CuO_2$-Y-$CuO_2$-BaO", another unit consisting of three rows of black dots. To identify the cationic species in these sites, detailed image simulations were carried out using different combinations of the cations. The best fit of the experimental image to the simulated image, shown in the inset to Fig.3, was obtained for the unit consisting of two CuO chains between which a Y atom is located with eight-fold oxygen coordination. There are four oxygen atoms in the Y plane and two each in the two CuO chains above and below the Y layer. The stereochemistry of Y in this site is different from that of the Y ion in the perovskite block, details of which are deferred to a later paper. This structure, with the stoichiometry of $Y_2Ba_2Cu_4O_9$, is charge balanced when the formal charges are used and is likely to be insulating. Since doping and the type of conductivity depends upon the oxygen content, there is always the possibility of altering the oxygen content to induce charge carriers and possiby superconductivity in this structure. The same structure has also been observed as an isolated defect in bulk samples of nominal cationic composition corresponding to "123"[7]. Defects in the "perovskite block" have also been observed, (although less frequently than the defects discussed above), one of which is identified by arrows in the structural image in Fig.3. This unit cell shows a contrast that is different from that of other perovskite blocks. The intensity at this position suggests that an extra Ba layer has been intercalated, which is glide related to the Y layer. Such a defect has not been reported before in the Y-Ba-Cu-O system.

The lower magnification HREM image in Figure 4 illustrates the complex inter-mixed defect structure of these films. This image also shows two anti-phase boundaries(APB), planar defects that are frequently observed in these films. On either side of the boundary the film is in the same orientation, i.e., [100], but the cationic layers in the two sides are out of phase due to the difference in stacking sequence. In addition, several of the stacking defects described above in Figs.2&3 are intimately mixed in this local region. Transformation of one structure to another takes place via the introduction or the removal of the corresponding cationic layer(s) during growth. In a general sense, this corresponds to the introduction of an edge dislocation with the Burger's vector along the c-direction. For example, the "123" stacking sequence could be converted into the "224" stacking, Fig.3, in two stages. First, in a very local region, shown by arrows in Fig.3, the "248" structure (containing two Cu-O chains) is observed. Subsequently, an extra Y-layer appears between the two Cu-O layers of the "248" structure to give the "224" structure. Thus, different polytypoidic variants form in order to accommodate local changes in composition along the a-b plane and along the c-direction.

The larger variety and density of defects found in thin films, compared to bulk, is a consequence of the non-equilibrium growth involved in the deposition process. Since only short range diffusion and atomic rearrangement is permissible under the deposition conditions, the in-coming species in the laser plume are "frozen" into a relatively metastable configuration. It is interesting to note that the basic perovskite block (defined earlier) is rarely disturbed. The structural changes mainly take place in the layers between two such units. These layers are also the doping centers in the Y-Ba-Cu-O system and hence there is a definite possibility of changes in superconducting properties, as exemplified by the "248" structure. The observation of the new stacking sequences in the atomic images also suggests that the relatively non-equilibrium laser deposition process can be used to produce new metastable structures with novel properties. The "224" structure is one such example. The fact that these defects are associated with the layered nature of these cuprates suggests that these defects are likely to be a generic feature of all in-situ deposited thin films. Indeed, the defects presented in this paper have also been observed in thin films deposited on $SrTiO_3$, although the density of the various defects appears to be different.

The connection between the flux pinning, leading to higher critical currents and smaller magnetic field induced resistive broadening compared to single crystals, and the defects remains to be established. As in the low $T_c$ superconductors, flux pinning by structural defects, with superconducting properties different from that of the matrix, is likely to play an important role. In the bulk form some of these defects such as the "248" or the "247" structures are superconducting with a $T_c$ lower than the "123" phase and thus may be suitable pinning sites in the thin films. Although there is no information available on transport properties of the "224" phase, based upon formal charge balance considerations, it is likely to be insulating and hence may also be a source of flux pinning. The inter-conversion of the stacking defects along the a-b plane to accommodate local changes in composition, as discussed above, could also provide the pinning required to resist vortex motion in the a-b plane. More quantitative studies through the control of the defect density are required in order to establish the relationships. Ultimately, this will assist in designing superconductors with better transport properties.

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10. We wish to acknowledge stimulating discussions with and the support of P.L.Key, J.H.Wernick, J.M.Tarascon, M.J.Bowden, P.F.Liao and J.M.Rowell. The assistance of the staff of the National Center for Electron Microscopy is greatly appreciated. The work at Lawrence Berkeley Laboratory is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S.Department of Energy under contract No. DE-AC03-76SF00098. The work at Stanford is supported in part by the Center for Materials Research under the NSF-MRL program.

# FIGURE CAPTIONS

Figure 1: [100] zone axis atomic resolution image showing the $YBa_2Cu_3O_7$(123) structure ; inset shows the simulated image for a foil thickness of 20Å and defocus of -450Å, confirming the interpretation of the experimental image.

Figure 2: [100] zone axis atomic image revealing the cationic positions of the $YBa_2Cu_4O_8$(248) structure, in which the two Cu-O layers are related by a 1/2[010] glide ; inset shows the simulated image corresponding to the experimental image for a foil thickness of 20Å and defocus of -450Å.

Figure 3: [100] zone axis atomic resolution image of the $Y_2Ba_2Cu_4O_9$ (224) defect ; inset shows the simulated image for a foil thickness of 20Å and defocus of -450Å, confirming the interpretation of the image. Note also two unit cells in which an extra Ba layer is intercalated in the perovskite block.

Figure 4: A typical [100] zone axis HREM image showing the complex inter-mixed defect structure of the film. The "123", "248" and "224" structures are arrowed. Two anti-phase boundaries are also observable in this image.

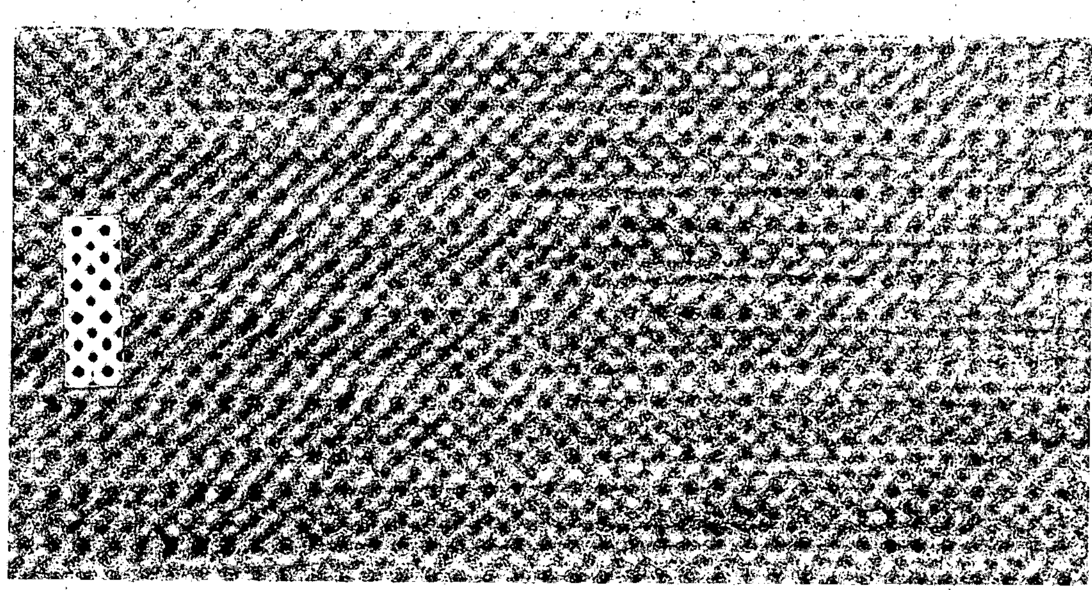

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Fig. 1

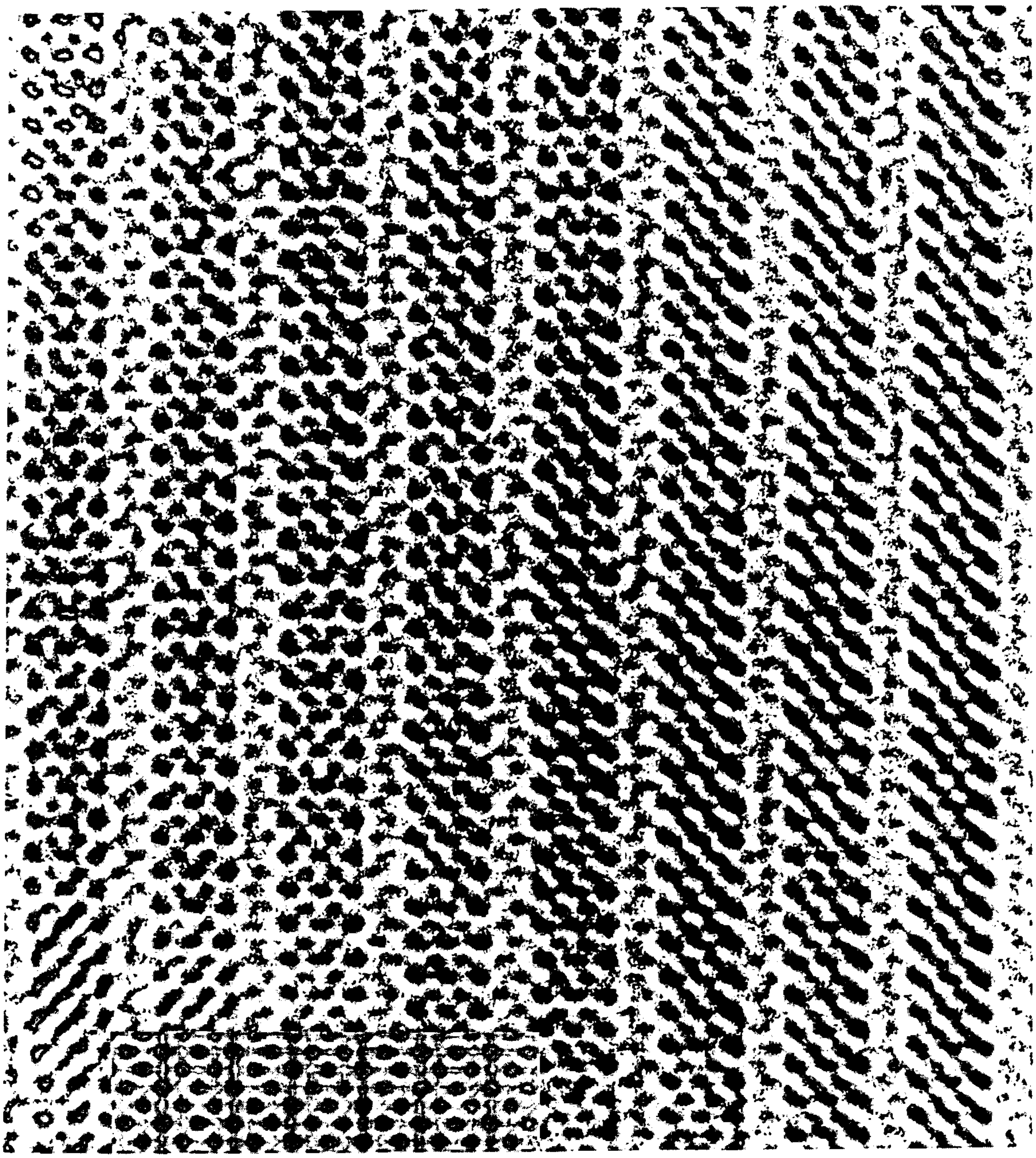

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Fig. 2

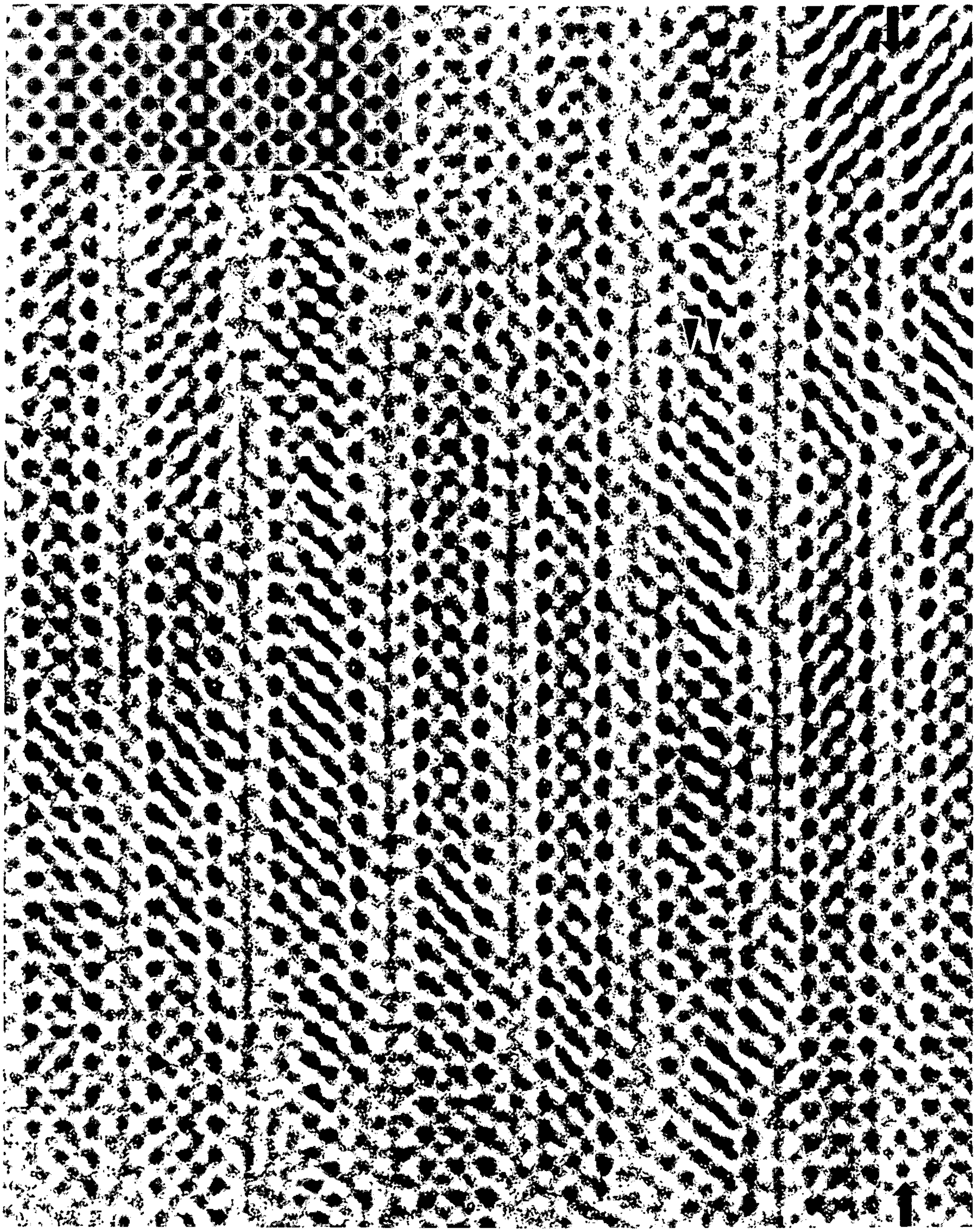

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Fig. 3

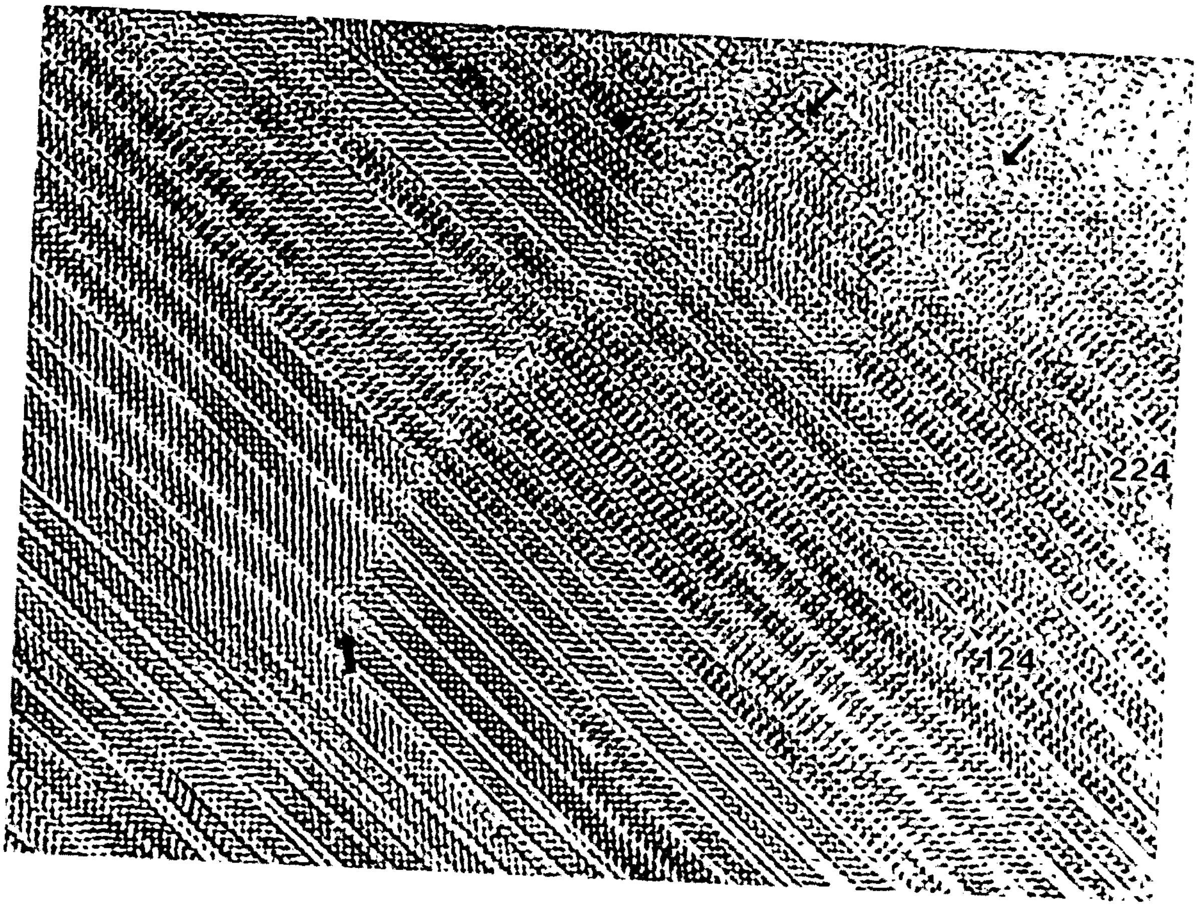


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Fig. 4

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