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C.J. Jou, R. Kilaas, and J. Washburn

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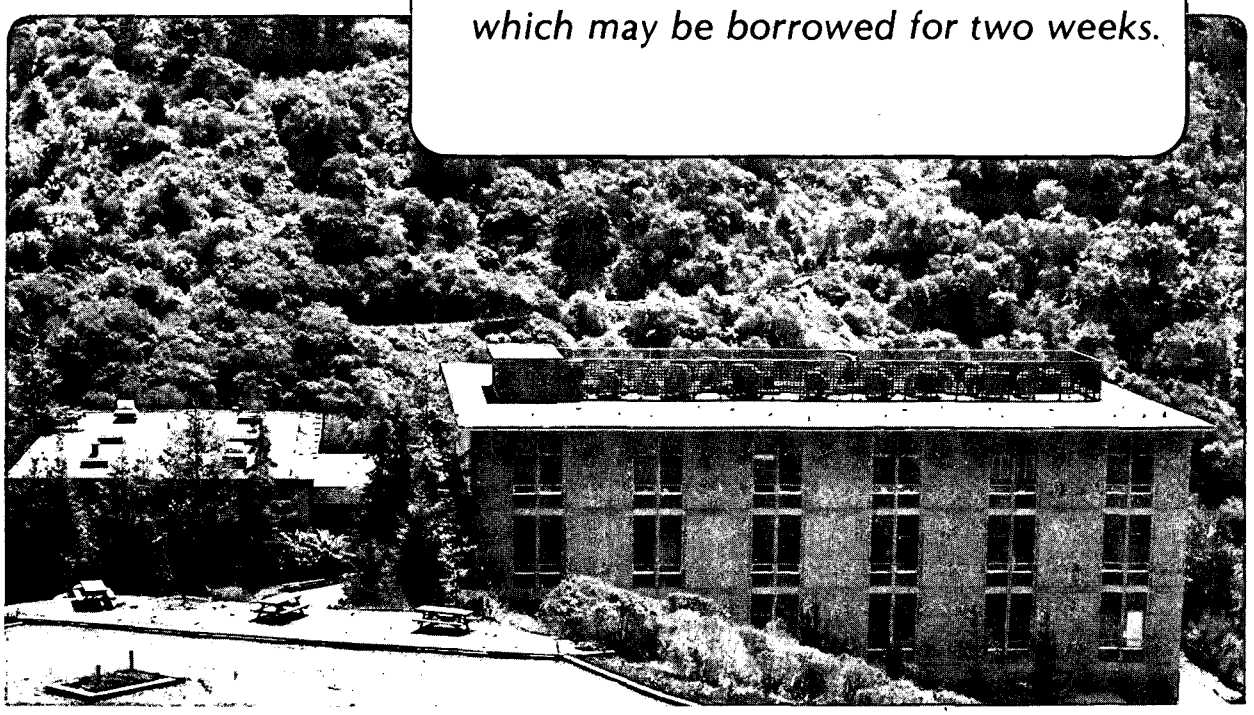

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C. J. Jou, R. Kilaas, and J. Washburn

Department of Materials Science and Mineral Engineering and
Materials and Chemical Science Division and
Center for Advanced Materials and
National Center for Electron Microscopy
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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C. J. Jou,† R. Kilaas,* and J. Washburn†

Department of Materials Science and Mineral Engineering† and
Materials and Chemical Science Division† and
Center for Advanced Materials† and
National Center for Electron Microscopy*
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

ABSTRACT

A model of twin boundaries in $YBa_2Cu_3O_{7-\delta}$ superconductors is proposed. One or more layers of oxygen vacancies at twin boundaries are assumed to exist which avoids strong Coulomb repulsion between close-neighbor oxygen ions at the boundary. The layers of oxygen vacancies would also serve as fast diffusion paths for increases or decreases in oxygen content. One or more layers of oxygen vacancies at twin boundaries can explain the fact that the optimized oxygen stoichiometry, under normal atmospheric pressure processing is less than seven. The maximum number of layers of oxygen vacancies that could exist at twin boundaries of $YBa_2Cu_3O_{7-\delta}$ and still permit tunneling of the current through the boundaries at liquid nitrogen temperature is estimated. Simulations of HREM lattice images based on the model are also found to be consistent with observed lattice images showing that the boundary affected zone is several atomic layers thick.

Since the discovery of the Y-Ba-Cu-O quartary system superconductor[1], the superconducting phase has been identified to be $YBa_2Cu_3O_7$[2] and its structure is an orthorhombic, defected trilayer perovskite with metal atoms ordered and having a deficiency of oxygen.[3,4] Oxygen has been shown to play an important role in determining T_c. The oxygen order-disorder transition has been studied by D. de Fontaine[5] in the two dimensional system. The equilibrium value, x, of oxygen content in $YBa_2Cu_3O_x$ is determined by the processing temperature and oxygen partial pressure in the ambient as experimentally demonstrated by Gallagher et al.[6] Transition temperature as a function of oxygen content x has been determined by Cava et al. with a gettered annealing technique.[7] The effects of fabrication process variables on optimization of T_c have been extentively investigated. The achievable oxygen content under normal pressure, 1 atm O_2 or air, has consistently been found to be less than 7. Another interesting feature of the superconducting orthorhombic low temperature phase is the formation of a high density of coherent twins, during or after the structural transition from tetragonal to orthorhombic. Presumably this is a mechanism for the relaxation of transformation induced stresses. An extended annealing seems to result in higher twin density.[8] A high density of twin boundaries should not only help relieve the internal stress but may also help increase J_c[9] and T_c[10]. A commonly used model[11] for the coherent twin boundaries involves near neighbor oxygen ions which would exert strong Coulomb repulsion and thus increase the twin boundary energy.

The oxygen vacant twin boundary model proposed here (Fig. 1) avoids this high energy state and preserves coherency at the boundaries. The model adopts the usual coherent boundary configuration, except that oxygen sites on Cu-O basal planes between two neighboring Ba-O basal planes are not occupied. The number of oxygen vacant layers are assumed to vary depending on the processing conditions. With higher oxygen partial pressure, slower cooling rate or longer annealing duration, the expected number of vacant oxygen layer should become smaller. Since rapid oxygen diffusion in this material would not be expected to occur along the c axis direction, oxygen vacant twin boundaries may play a role in the diffusion of oxygen into or out of the structure. As pointed out by K. N. Tu[12] the rate limiting step for oxygen flux leaving a specimen is the interfacial reaction rather than the diffusion within the specimen. If twin boundaries increase the rate of internal diffusion, this result becomes more understandable. It is interesting to note that the activation energy, 1.7±0.1 eV, is just half of the oxygen site energy 3.41 eV, determined by Freitas et al.[13] The tetragonal to orthorhombic transformation could be diffusionless (Martensite-like)[14] or diffusion-controlled.[11] However, twins do not appear to form suddenly at the transition temperature.[11] This is an indication that the transformation is diffusion-controlled nucleation-growth process. At the transition temperature, nuclei of the orthorhombic phase apparently form in the tetragonal grains with two perpendicular directions of the b-chain. Initially they probably grow by consuming near-by oxygen atoms and later by incorporating additional oxygen supplied from surfaces in contact with the atmosphere. When neighboring nuclei have the same b-chain

directions, they coalesce during growth to form larger domains. Where domains with perpendicular b-chain directions meet, oxygen vacant twin boundaries are formed. Depending on the processing conditions, further absorption of oxygen from the external environment probably narrows the width of oxygen vacant twin boundaries.

Twins are formed to minimize the distortion energy and to accommodate the volume change. The average twin width, W_t, has been estimated as[15] $W_t \cong ab/(b-a)$ and the twin boundary width, $W_{tb}(j) = 2jab/(a^2 + b^2)^{1/2}$ as illustrated in Fig. (1). Assuming $YBa_2Cu_3O_7$ within the twin domains and $YBa_2Cu_3O_6$ at the twin boundaries, then the average oxygen content, x, in $YBa_2Cu_3O_x$ which is experimentally measured would be $x_j = 6 + \frac{W_t - W_{tb}}{W_t} = 7 - \frac{W_{tb}}{W_t} = 7 - 2j(b-a)/(a^2 + b^2)^{1/2}$. Applying a = 3.822Å, b = 3.891Å of x = 7.0 (j = 0) from the work of Cava et al.,[6] for j = 1 to 10, x_j = 6.975, 6.949, 6.924, 6.899, 6.873, 6.848, 6.823, 6.798, 6.772, 6.747 respectively. These results are consistent with the published data of oxygen content[7,16-22] suggesting that in their samples, near perfect stoichiometric $YBa_2Cu_3O_7$ may form within the twin domains but different numbers of layers of vacant oxygen exist at twin boundaries. The oxygen deficiency study[16] seems indicate that under normal pressure processing, i.e., 1 atm O_2 or air, the ultimate oxygen stoichiometry is about 6.93 or equivalent to the case j = 3. However, there is always a possibility that some oxygen vacancies are dispersed within the twin domains either at random or in an ordered structure,[23] and thus the number of oxygen vacant layers at twin boundaries may be smaller.

One possible mechanism for supercurrent transport across the twin boundaries could be the superconductor - metal - superconductor (S-N-S) tunneling mechanism.[24] Alford et al.[25] have made measurement of the critical current density (J_c) as a function of the oxygen content. Their results are reproduced here as Fig. 2. The oxygen contents of the samples assuming x = 7 within twin domains and various numbers of layers of vacant oxygen at twin boundaries have been added as arrows. When j > 8, supercurrent density drop to zero which could be due to the width of the oxygen vacant twin boundaries or grain boundaries [W_{tb} (j = 9) ~ 49.1Å] being too large, compared to the coherence length[26], for the tunneling mechanism. The maximum number of oxygen vacant layer which could permit tunneling is estimated to be J = 8. However, the oxygen vacant layers along the twin boundaries may not be uniform.[14] Thus tunneling may still be possible at some narrow regions at boundaries with average value of j >8.

When considering the band structure of $YBa_2Cu_3O_7$, twin boundaries are often neglected. Although oxygen vacant twin boundaries may not play an active role in determining T_c, the existence of dense twin boundaries does introduce new symmetry elements into the matrix of the $YBa_2Cu_3O_7$ and the paring potential may thus have a small modification (mini gaps) due to dense, periodic twin structures.[27] This modification may explain why T_c varies slightly when j varies from 1 to 8 even though internally the twin domain may have a constant stoichiometric composition.

Simulated high resolution electron microscope (HREM) images of twin boundaries with various j values, different defocussing conditions and different sample thicknesses are shown in Fig. 3(a) - (c) respectively. The

simulated images of the twin boundaries without oxygen vacancies [(Fig. 3(a) top] show no contrast at all across the twin boundaries regardless the objective lens defocus and sample thickness. However, when various layers of oxygen at twin boundaries are taken away, contrast across twin boundaries appears. The width of the contrast band increases in proportion to j as shown in Fig. 3(a). Contrast at the twin boundaries varies markedly with defocussing conditions as shown in Fig. 3(b). Note that the apparent boundary widths also vary slightly. Contrast at twin boundaries due to sample thickness variation, as shown in Fig. 3(c), is very dramatic. It can vary from almost no contrast to reverse contrast. Various band widths and contrast at twin boundaries in real HREM images are commonly observed[28-31] agreeing with the model proposed here. It has been shown that in HREM in-situ heating and cooling experiments, the orthorhombic, superconducting phase with twin boundaries can transform to the tetragonal phase.[30,32,33] This process can be reversible, but twin boundaries normally reappear at different positions.[30] However, if a significant amount of oxygen evaporates from the sample due to heating by the electron beam, the process becomes irreversible.[34] Furthermore, twin boundaries exposed to a focussed beam for a short time, e.g., 1 minute, show a decrease in contrast.[14] Oxygent atoms in twin domains close to the twin boundaries may gain energy through electron bombardment and diffuse into the twin boundaries. Thus, the contrast at twin boundaries might be expected to smear out as illustrated by the simulated images in [Fig. 3(d)]. Hence, precautions should be taken when using HREM to image the twin boundaries.

In polycrystalline materials, grain boundaries without obstacles, e.g., second phase or segregations, are known to be fast diffusion paths. However, the total surface area perpendicular to the c-axis of the grain boundaries, compared to the total area of the twin boundaries in the grain, is small. Although there may be oxygen deficiency at grain boundaries, a correction of oxygen stoichiometry due to grain boundaries can be neglected. Nevertheless, if the tunneling mechanism is assumed, grain boundaries may still play an important role.

To apply the model of oxygen vacant twin boundaries to the real system, accurate determination of oxygen content as well as microstructure parameters, i.e., lattice constants, twin boundary width and average twin width, is essential. However, the uniformity of the oxygen content in polycrystalline $YBa_2Cu_3O_x$ has been reported to vary from grain to grain.[13][34] An extended annealing of the polycrystalline material is needed to achieve thermal equilibrium. A single crystal specimen eliminating the grain boundary effect would be preferable.

Among the new class of oxide superconductors, e.g., the La-Ba-Cu-O family, the Y-Ba-Cu-O family and the Bi-Ca-Sr-Cu-O family, the Y-Ba-Cu-O family is the only one that is characterized by a high density of twins and Cu-O-Cu chains. The role and microstructure of these twin boundaries have been controversial. However, the newly discovered rare-earth-free superconductor Tl-Ca-Ba-Cu-O (2223 phase)[35] has been reported to exhibit higher T_c (~ 125K) and better reproducibility and chemical stability. An interesting observation is that this system also has a twinned structure with (110) or $(1\bar{1}0)$ twin boundaries.[35] This model may be applicable to this system as well.

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FIGURE CAPTION

Fig. 1. Oxygen vacant twin boundary models for (a) 1 vacant layer (j=1) (b) 3 vacant layers (j=2). (c) 5 vacant layers (j = 3).

Note: The angle at twin boundaries and the length difference between the lattice constants a and b are exaggerated. For simplicity, only oxygen atoms (black dots) are shown.

Fig. 2. Critical current density as a function of oxygen content, x, in $YBa_2Cu_3O_x$ (reproduced from ref. 24). Arrows are added to mark the oxygen contents of the samples assuming x = 7 within twin domains and various numbers of layers of vacant oxygen at twin boundaries.

Fig. 3. Simulated HREM [001] images of twin boundaries. Simulation parameters are chosen to correspond to the operatiang conditions in the JEOL 4000 FX electron microscope. Sample thickness is 100Å and objective lens defocus is -800Å unless specified otherwise. (a) Variation with respect to j from j = 0 (no oxygen depleted layer, top) to j = 3 (bottom). (b) variation with respect to objective lens defocus; -400Å (top) to -1600Å (bottom) in increments of -400Å, j = 3. (c) variation with respect to sample thickness; 50Å (top) to 200Å (bottom) in increments of 50Å, j = 3. (d) Total oxygen atom concentration fixed, but abrupt concentration changes at twin boundaries are gradually relaxed (j = 3).

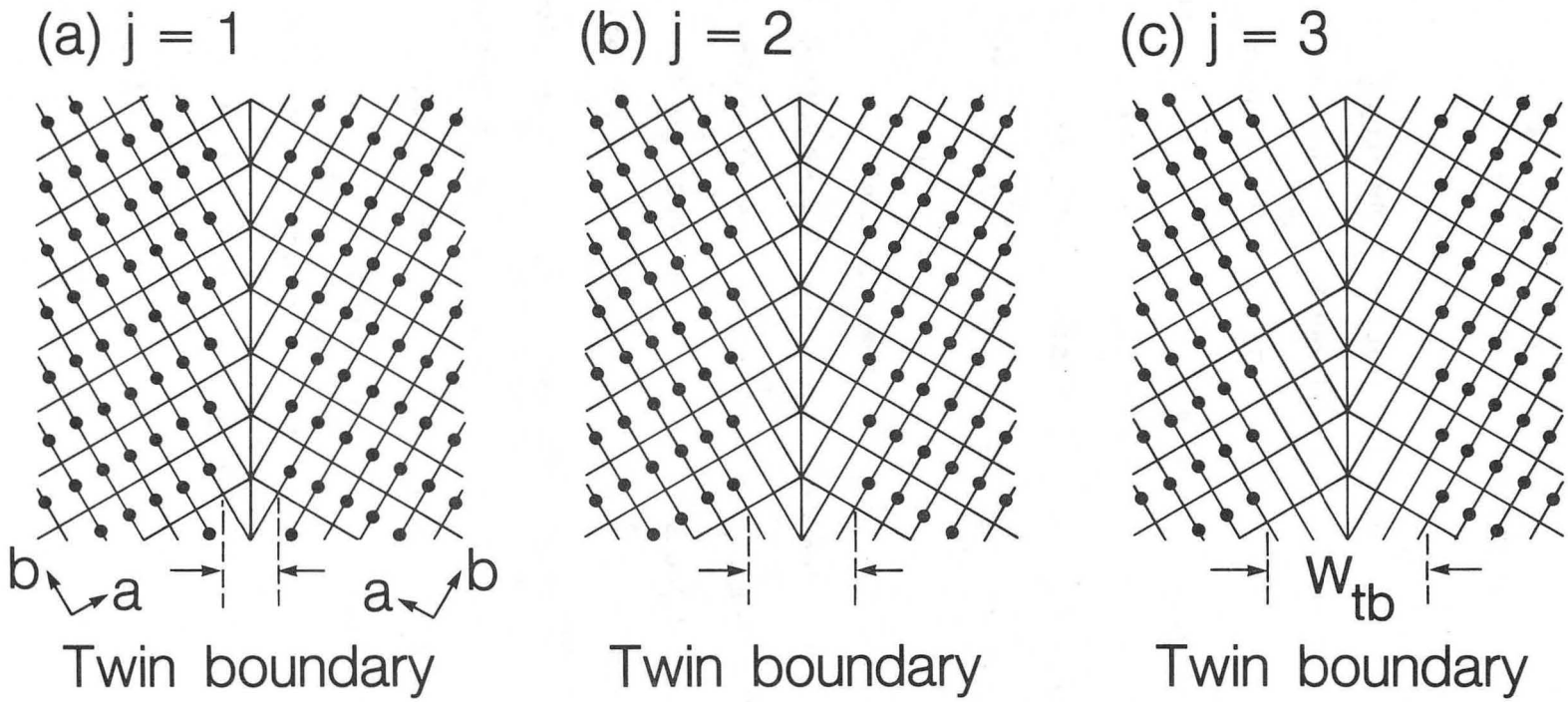

Fig. 1

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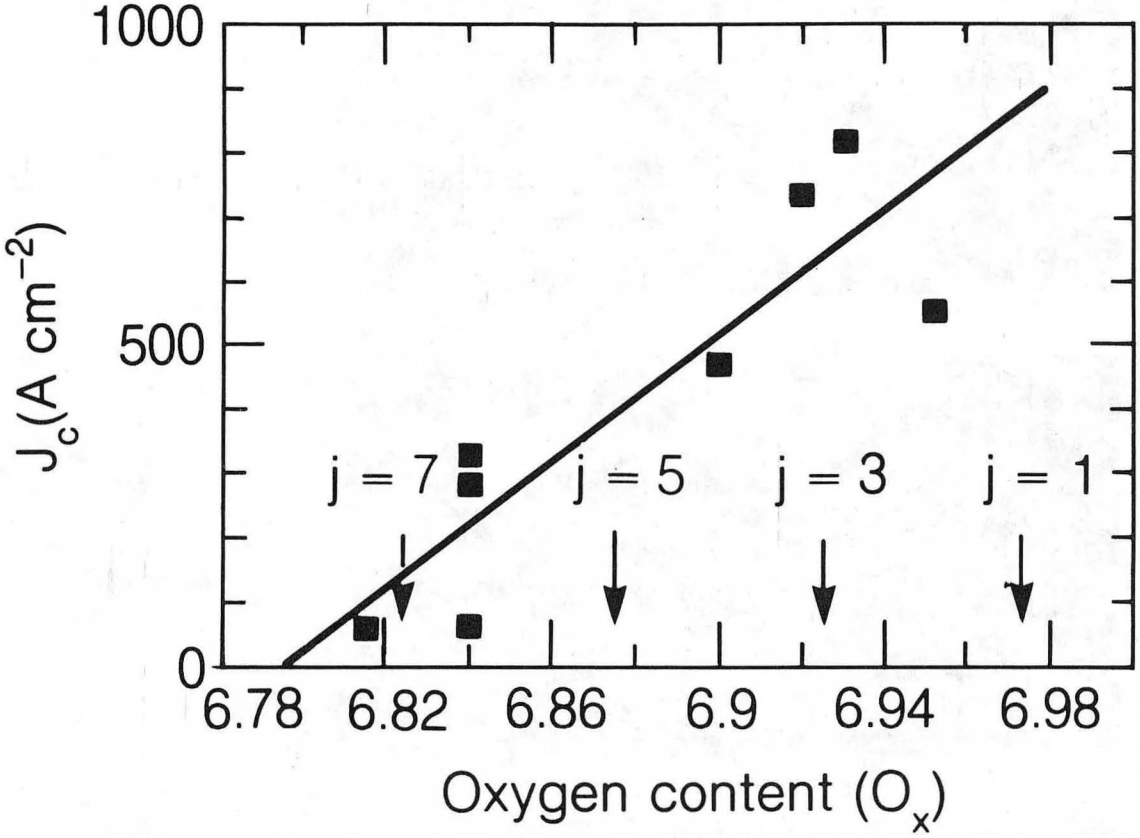

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Fig. 2

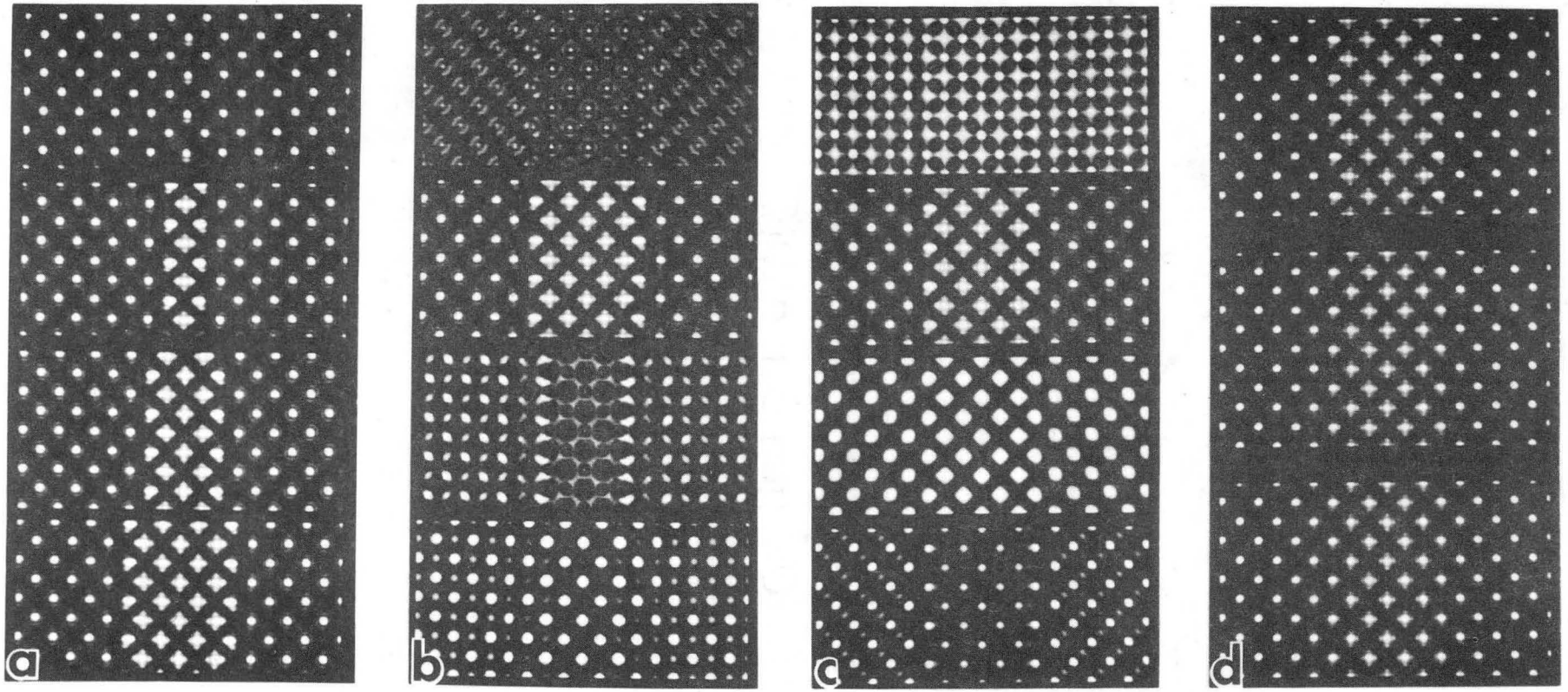

Fig. 3

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