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Layer-rigidity model and the mechanism for ion-diffusion-controlled kinetics in the bismuth cuprate 2212-to-2223 transformation

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Recent transmission electron microscopy (TEM) experiments have shown that the transformation of the Bi cuprate 2212 phase to 2223 phase consists of fast growth of Ca/CuO$_2$ planes in the Bi-2212 matrix. A theory is proposed which considers the cylindrical void created by the edge dislocation due to the insertion of a Ca/CuO$_2$ plane to be a channel for fast ion diffusion. A layer-rigidity model is used to estimate the size of the void for Bi-2212/Bi-2223, as well as that for the stacking fault created by heavy-ion irradiation in YBa$_2$Cu$_3$O$_7$ (YBCO) compounds. We find the predictions of the model to agree quantitatively with TEM measurements of the structures of ion-irradiated YBCO systems. The calculated void size for Bi-2212/Bi-2223 compounds is consistent with the existence of fast ion diffusion along the *ab* plane. The experimentally observed time dependence of the volume fraction of Bi-2223 during the transformation is found to be consistent with a one-dimensional diffusion-controlled transformation mechanism, as predicted by our model.

I. INTRODUCTION

The Bi cuprate 2223 phase is one of the most promising high-T_c superconductors for large-scale and high-current applications because of its high superconducting transition temperature (≈ 110 K), high critical current density due to the lack of weak links in the bulk material, and the relative ease with which it can be made into wires and tapes. On the other hand, the superconducting properties of Bi-2223 depend sensitively on its microstructure, which in turn depends on the fabrication processes.

The most widely used method of making Bi-2223 materials is to mix Bi-2212, CaPbO$_3$, and CuO powder and to anneal the mixture in a sealed tube at about 830 °C for 10–100 h. The factors which affect the rate of conversion from Bi-2212 to Bi-2223 have been studied extensively. An understanding of the formation mechanism and reaction kinetics is obviously important for the efficient preparation of Bi-2223 superconductors.

Several attempts have been made recently[1–3] to analyze the kinetics of Bi-2223 formation using the Avrami equation

$$\ln\left(\frac{1}{1-C}\right)=K_0\exp(-E/RT)t^{\alpha}, \tag{1}$$

where C is the fraction of Bi-2223 transformed at time t, T is the temperature, E is the activation energy, $K_0=1.71\times10^{-22}$ is the rate constant, R is the universal gas constant, and α is the Avrami exponent. It is generally agreed upon that the Avrami exponent obtained from experimental data can provide some insight into the reaction mechanism. Interestingly, although almost all the above-mentioned authors conclude that their data supports a diffusion-controlled, two-dimensional transformation, the Avrami exponents they obtained vary greatly, ranging from 0.5 (Ref. 1) to close to $1-1.5$,[2,3] which seem to be more consistent with one-dimensional diffusion-controlled transformation mechanism with a varying nucleation rate.[4]

Recent transmission-electron microscopy (TEM) experiments have shown that during the annealing process, the Bi-2212/Bi-2223 system consists of fast-growing intercalating Ca/CuO$_2$ bilayers instead of compact Bi-2223 domains.[5] Unlike the conventional nucleation-and-growth mechanism, where a reactant diffuses from grain boundaries into the interior of the bulk materials, leading to a compact advancing "front" of the products, the transformation from Bi-2212 to Bi-2223 appears to be accomplished via the layer-by-layer intercalation of the extra Ca/CuO$_2$ planes into the Bi-2212 matrix. Figure 1 shows the (002) lattice image from a sample annealed at 825 °C for 30 h and 150 hours, respectively (the

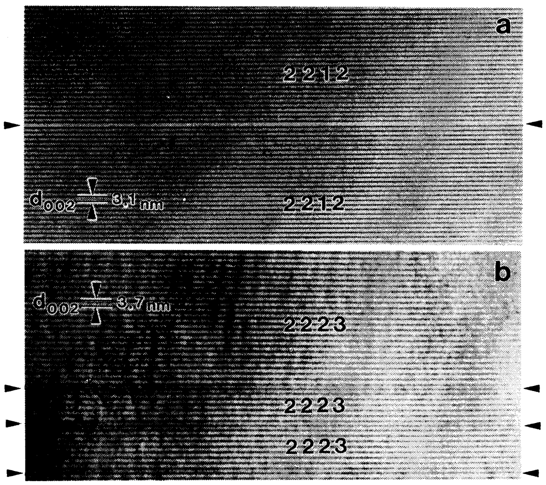

FIG. 1. (a) A (002) lattice image from a sample annealed at 825 °C for 30 h. The crystal matrix was dominated by the 2212 phase. A pair of arrowheads indicates the insertion of a Ca/CuO$_2$ bilayer which forms a half unit-cell of the 2223 phase. (b) A (002) lattice image from a sample annealed at 825 °C for 150 h. The majority of the crystals had completed the transformation from the 2212 phase to the 2223 phase. The remaining 2212 phase are marked by the arrowheads.

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experimental detail is described in a separate paper.[5]) From the lattice image of the system at the very early stage of the transformation [Fig. 1(a)] to the stage where the transformation is almost completed [Fig. 1(b)], we did not observe any edge dislocation inside the 2212 grain formed by inserting the extra Ca/CuO$_2$ planes. It is clear that the fast intercalation of individual Ca/CuO$_2$ plane into the 2212 matrix, rather than the nucleation and growth of compact 2223 domain, is the path for 2212 to 2223 transformation.

The growth of the intercalant Ca/CuO$_2$ planes is much faster than the bulk cation diffusion rate seems to allow, which lead us to propose that a different diffusion mechanism is at work in the Bi-2212/Bi-2223 system. We believe that the mechanism of cation diffusion is by the way of pipe diffusion through the cylindrical void created by the edge dislocation which accompanies the insertion of a Ca/CuO$_2$ plane. These voids are located at the "interfaces" between Bi2212 and Bi-2223 where the reaction takes place. As the transformation progresses, these voids move with the Bi-2212/Bi-2223 "interface;" thus, the reaction progresses uninhibited. It should be noted that the term "interface" in this paper denotes the edge-dislocation caused by the intercalation of extra Ca/CuO$_2$ planes in Bi-2212 matrix. Since the Bi-2223 is formed by the intercalation of individual Ca/CuO$_2$ plane rather than the nucleation and growth of compact 2223 domain, there is no Bi-2212/Bi-2223 interface *plane* in the traditional sense. We will show in the following sections that pipe diffusion via voids created by edge dislocations in Bi-2212/Bi-2223 is indeed plausible. We will calculate the size of the voids using a layer-rigidity model[6,7] modified for Bi-2212/Bi-2223 systems, with its parameters calculated from a shell-model simulation and show the results of our model are consistent with the existing experimental data for the time dependence of the volume fraction of Bi-2212 converted to Bi-2223.

In Sec. II we will describe the cation diffusion model constructed using the microstructure of the Bi-2212/Bi-2223 system observed by TEM as a guide. In Sec. III we will calculate the size of the voids using a layer-rigidity model. In Sec. IV we will analyze the experimental data in the framework of our model.

II. EDGE DISLOCATIONS AS CHANNELS FOR FAST ION DIFFUSION

The transformation from Bi-2212 to Bi-2223 can be regarded as a chemical reaction between the Bi-2212 precursor and the secondary phases such as CaPbO$_3$ and CuO, to provide the necessary extra Ca and Cu. As shown in Fig. 2, the only structural difference between Bi-2212 and Bi-2223 is a pair of extra Ca/CuO$_2$ planes inserted in the case of Bi-2223 and the associated lattice expansion. It is therefore convenient to divide the layered structure of Bi-2212 into two parts: the block layers (also called "host layers" below), which consist of BiO, SrO, and the Ca/CuO$_2$ plane in Bi-2212, and the "gallery layers" into which the extra Ca/CuO$_2$ planes are inserted in the case Bi-2223. In this context, we can regard the Bi-2223 as a stacking fault of Bi-2212. The interfaces in a transforming system between Bi-2212 and Bi-2223 layers can then be regarded as an edge dislocation. The approximately cylindrical void created at the extra half plane of this dislocation is a line of vacancies which can be an easy path for the extra Ca, Cu, and oxygen ions to diffuse from the surface (or grain boundary) into the bulk material provided that the size of the void is large enough. The size of the voids will depend on the rigidity of the block layer as well as the compressibility of the Ca/CuO$_2$ plane along the *c* axis. Obviously the more rigid the layer is, the larger the void will be. In the limit of infinite layer rigidity, the size of the void will be infinite. The size of the void in the Bi-2212/Bi-2223 system will be evaluated in the next section. We will see that the size of the void is about twice the size of the biggest ions (oxygen), thus indicating that the dislocations at the Bi-2212/Bi-2223 interface can be easy paths for the reactant ions to diffuse into the bulk.

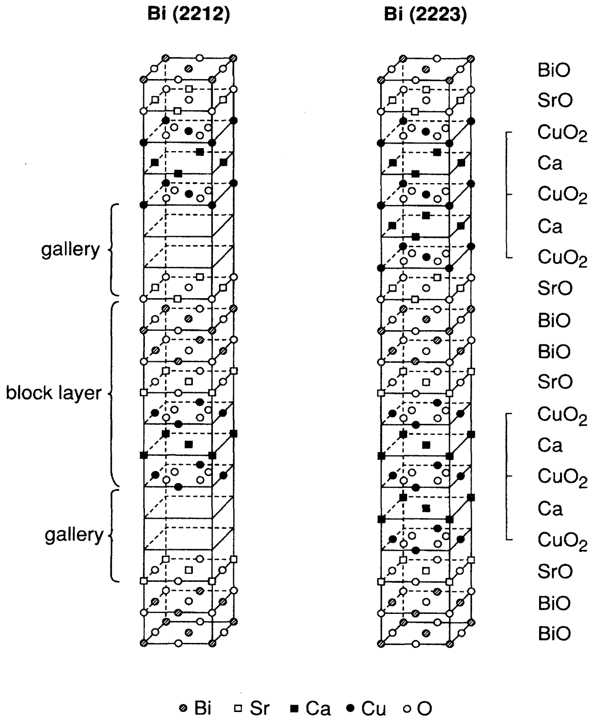

FIG. 2. The unit cells of Bi-2212 and Bi-2223. The layered structure of Bi-2212 can be divided into block layers and galleries for intercalation of the extra Ca/CuO$_2$ plane to form Bi-2223. The "gallery height" in the 2212 structure is shown here expanded from its normal value for clarity of comparison of the two structures.

At the annealing temperature (~830 °C) both CaPbO$_3$ and CuO are liquid. The grinding and mixing prior to the annealing make sure that this liquid phase is evenly coated around each Bi-2212 grain. As a Ca/CuO$_2$ plane nucleates near the surface of the Bi-2212 grain (grain boundary), the void created by the partially inserted Ca/CuO$_2$ plane then opens up a channel for the reactant ions to diffuse into the bulk, thus permitting the edge dislocation to climb and the reaction to proceed rapidly at this location. Since the void moves into the bulk as the edge dislocation climbs, the reactants are always in contact with the Bi-2212/Bi-2223 "interface." The growth of the Ca/CuO$_2$ plane can therefore be very fast. The transformation from Bi-2212 to Bi-2223 is likely then to be limited by the nucleation rate of the Ca/CuO$_2$ plane near the 2212 grain boundary and the diffusion of reactant ions along the moving dislocation lines. This mechanism will give rise to the intercalation of individual Ca/CuO_2 planes in the Bi-2212 matrix, as we observed in TEM experiments,[5] instead of compact Bi-2223 domains one would expect from conventional nucleation and growth theory.

III. THE LAYER-RIGIDITY MODEL

To address the question of the volume expansion at the cores of the edge dislocations (extra atomic half-planes) produced during the Bi-2212 to Bi-2223 transformation, it is important to consider the large anisotropy in physical properties in these layered systems. It is reasonable to assume that the major expansion takes place along the direction perpendicular to the layers, denoted as the c axis. In fact, it has been shown by diffraction experiments that the lattice parameters along the a or b axis change very little during Bi-2212 to Bi-2223 transformation, while the lattice parameter along the c axis increases from 30.9 to 37.8 Å.

Since the only structural difference between Bi-2212 and Bi-2223 compounds is the extra layers of Ca and CuO_2 and the associated c-axis expansion, it is reasonable to regard the the extra Ca and CuO_2 layer in Bi-2223 phase as "intercalants" and the rest of the structure as "host layers." Therefore we can regard the Bi-2212/Bi-2223 compound as a type of intercalation compound in the form of $A_{1-x}B_xL$, with $0 \leqslant x \leqslant 1$, where B is the intercalant (extra Ca and CuO_2 layer in Bi-2223 phase), A is a vacant (but collapsed) layer in the Bi-2212 phase (see Fig. 2), which will be regarded as an intercalant of a smaller size, and L denotes the host layer which represents the rest of the structure. Therefore the single phase Bi-2212 (AL) and Bi-2223 (BL) can be regarded as the limiting cases for $x=0$ and $x=1$, respectively. The dislocation at the interface of Bi-2212/Bi-2223 can be modeled as an intercalation compound with B occupying the semi-infinite plane, as shown in Fig. 3.

In the past, several attempts have been made to study the c-axis expansion of intercalation compounds within the framework of two quite distinct types of models.[6,7] It is assumed in these models that the host layers have finite transverse as well as bending rigidity while the intercalants have finite compressibilities as well as different sizes. The first model,[6] referred to as bilayer model, assumes that the compressibility of the host layer is much smaller than that of the intercalant, so that the correlation between different galleries can be ignored. The second model,[7] referred to as the multilayer model, assumes that the compressibility of the host layer is much larger than that of the intercalant, so that the correlation between different galleries can be mapped into an Ising-type model. In the case of Bi-2212/Bi-2223 compound, we believe that the first type of model is more suitable. Since the compressibility of the host layer is inversely proportional to its thickness, and in the case of Bi-2212/Bi-2223 system, the host layer thickness is much larger than the average gallery height, we find the compressibility of the host layer is about 10% of that of the intercalant. In this paper we set up a spring model that describes both the layer rigidity and the size and stiffness of the intercalant species. The model can be solved analytically if the compressibilities of the intercalants A and B are the same.

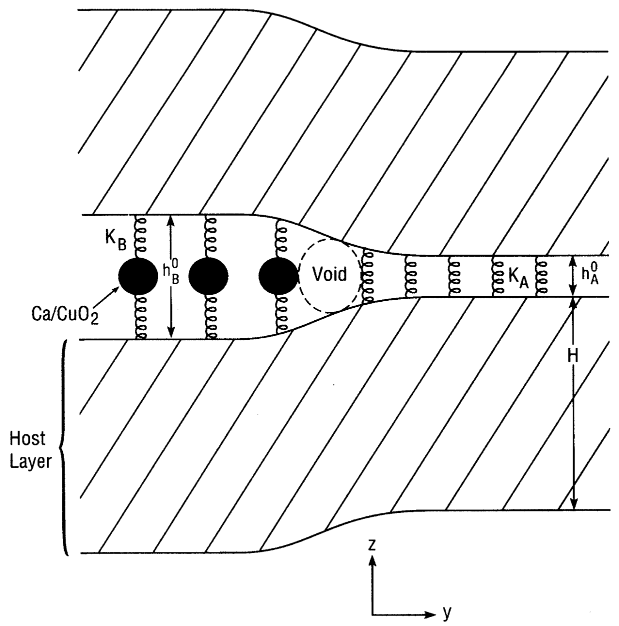

FIG. 3. Side view of the intercalants in the transforming Bi-2212/Bi-2223 system. The extra Ca/CuO_2 plane is shown schematically as large intercalant "atoms." The rest of the structural features are shown schematically as the "host layer." The separation between the host layers are given by the local gallery height h_i.

Consider a layered system with composition $A_{1-x}B_xL$ where L represents the host layer of thickness H which consists of BiO, SrO, and Ca/CuO_2 plane in the Bi-2212 phase. A and B are two different types of intercalants which are assumed to occupy a set of well-defined lattice sites. The total energy of the system can be approximated by a sum of two major contributions; one associated with the interaction between the intercalants and the host atoms and the other between host atoms themselves. We assume the intercalants to be frozen into the ordered structure (i.e., the time it takes to nucleate the Bi-2223 phase is much shorter than the time it takes for the Ca, Cu, and O ions to diffuse from the grain boundary to the bulk). Therefore the direct interaction energy between the intercalants does not play any role in the layer distortion. As discussed in the introduction, the compressibility of the host layer is much smaller than the intercalant, so that the interlayer correlation is mostly related to the various thickness of the host layer instead of the correlation between intercalants of different galleries. Since the variation of the host layer thickness ΔH is very small compared to H, we can neglect the interlayer correlation and consider a single gallery bounded by two host layers with intercalants occupying the lattice sites inside the gallery.

The total energy of the host layer-intercalant system can be written as

$$E=\frac{1}{2}\sum_i K_i(h_i-h_i^0)^2+\frac{1}{2}K_T\sum_{\langle i,\delta\rangle}(h_i-h_{i+\delta})^2+\frac{1}{2}K_F\sum_i\left[\sum_\delta (h_i-h_{i+\delta})\right]^2, \qquad (2)$$

where h_i is the local gallery height at the site i where an intercalant either (A or B) sits. h_i^0 is the gallery height for the pure system (AL or BL). It can be obtained from the diffraction measurements that for Bi-2212 (AL) $h_A^0=2.21$ Å, for Bi-2223 (BL) $h_B^0=6.18$ Å. K_i is the spring constant representing the compressibility of the local intercalant i. The terms involving the spring constants K_T and K_F describe, respectively, the transverse and bending rigidity of the host layers.[6] K_T and K_F are related to the elastic constants of the Bi-2212 compound by the following relations:

$$K_T=\frac{H}{a_0}\,c_{44}, \tag{3}$$

$$K_F=\frac{H^3}{12a_0^3}\left[\frac{(c_{11}+c_{33})c_{33}-2c_{13}}{c_{33}}\right], \tag{4}$$

where $a_0=3.8$ Å is the lattice constant in the ab plane and $H=14.35$ Å is the thickness of the host layer.

The compressibility $K_A=K_i(A)$ of the intercalant A (the vacancy) can also be obtained from the elastic constants given the relationship

$$K_A=\frac{a_0}{h_A^0}\,c_{33}. \tag{5}$$

The compressibility $K_B=K_i(B)$ of the intercalant B (the Ca and CuO_2 plane) cannot be calculated due to the lack of data for the elastic properties of Bi-2223. However it is reasonable to assume that $K_B>K_A$. Here we will calculate the gallery height for the case of $K_B=K_A$ so as to estimate the minimum size of the void.

The relevant elastic constants for Bi-2212 were calculated by Baetzold[8] using a suitable shell-model potential. They are found to be

$$c_{11}=24.08\times10^{11}\ \text{dyn/cm}^2,\quad c_{13}=6.71\times10^{11}\ \text{dyn/cm}^2,$$
$$c_{33}=14.59\times10^{11}\ \text{dyn/cm}^2,\quad c_{44}=6.18\times10^{11}\ \text{dyn/cm}^2. \tag{6}$$

Minimizing E in Eq. (2) with respect to the h_i, we find

$$\mathbf{M}\mathbf{h}=\mathbf{\Phi}, \tag{7}$$

where $\mathbf{M}$ is a tridiagonal matrix with

$$\begin{aligned}M_{ii}&=K_i+2K_T+6K_F,\\ M_{i,i\pm1}&=-K_T-4K_F,\\ M_{i,i\pm2}&=K_F,\end{aligned} \tag{8}$$

and $\mathbf{h}$ and $\mathbf{\Phi}$ are two column vectors

$$\mathbf{h}=\begin{pmatrix}h_1\\ h_2\\ \vdots\\ h_N\end{pmatrix},\quad \mathbf{\Phi}=\begin{pmatrix}K_1h_1^0\\ K_2h_2^0\\ \vdots\\ K_Nh_N^0\end{pmatrix}. \tag{9}$$

One can then obtain the h_i's by diagonalizing the $\mathbf{M}$ matrix. In the case of $K_A=K_B=K$, the dispersion relation for the system is given by

$$\lambda_q=K+2K_T[1-\cos(qa_0)]+4K_F[1-\cos(qa_0)]^2 \tag{10}$$

and the expanded form of $(\mathbf{M}^{-1})_{nm}$ can be expressed as

$$(\mathbf{M}^{-1})_{nm}=\frac{1}{N}\sum_q\frac{\exp[iqa_0(n-m)]}{\lambda_q} \tag{11}$$

with $q=2\pi r/Na_0$ where $r=1,2,\ldots,N$ and λ_q being the eigenvalue of the matrix $\mathbf{M}$. Then we have

$$h_n=\frac{1}{N}\sum_m(\mathbf{M}^{-1})_{nm}\Phi_m=\frac{1}{N}\sum_q\frac{K}{\lambda_q}\sum_m e^{iqa_0(n-m)}h_m^0. \tag{12}$$

Taking a system with half of the $y-z$ plane occupied by intercalant B (i.e., Bi-2223 phase), we assume the dislocation is at $y=z=0$ and the equilibrium height h_n^0 is defined by

$$h_n^0=\begin{cases}h_B^0, & \text{for } n=-\frac{N}{2}+1,-\frac{N}{2}+2,\ldots,-1\\[1ex] h_A^0, & \text{for } n=1,\ldots,\frac{N}{2}-1,\frac{N}{2}.\end{cases} \tag{13}$$

Taking the limit of $N\to\infty$ and changing the summation over q to integral, we find that

$$h(y)=\frac{h_A^0+h_B^0}{2}+\frac{h_A^0-h_B^0}{4\pi}\int_0^{\pi}\frac{K\sin\left[\theta\left(\frac{y}{a_0}-\frac{1}{2}\right)\right]}{\lambda_\theta\sin(\theta/2)}\,d\theta, \tag{14}$$

where $\theta=qa_0$ and $\lambda_\theta=K+2K_T(1-\cos\theta)+4K_F(1-\cos\theta)^2$ as defined in Eq. (10).

The solid line in Fig. 4 shows the profile of h_n for $K_A=K_B$ and the values of parameters defined in Eqs. (3)–(5). Since no high-resolution TEM image of the stacking fault of Bi-2212/Bi-2223 system is currently available, we performed calculation on a similar system to verify the accuracy of the results we obtained using this model. A space profile of the gallery height h_n is measured from the high-resolution TEM image of the stacking fault near the columnar defect produced by heavy-ion irradiation in $YBa_2Cu_3O_7$.[9] The stacking fault consists of an extra CuO plane in the $YBa_2Cu_3O_7$ matrix. The theoretical profile of h_n is calculated using the elastic constants obtained from the atomistic simulation of $YBa_2Cu_3O_7$ using the shell-model potential suitable for this material.[10] The calculated as well as measured h_n for the stacking fault of $YBa_2Cu_3O_7$ system are plotted along with the calculated h_n for Bi-2212/Bi-2223 system in Fig. 4. We can see that the calculated results agree very well with the experimental data, indicating that our assumption of $K_A=K_B$ is reasonable in this type of system.

Of the three types of reactant ions (Ca^{2+}, Cu^{2+}, and O^{2-}), the largest is O^{2-}, which has a diameter of about 2.9 Å. We can see from Fig. 4 that the lateral size of the void is about twice as large as the oxygen ion diameter, if we consider the the void to be the region where $h_n\geqslant3$ Å for $y\geqslant0$. Therefore we have confirmed that the dislocation line is indeed likely to be an easy path for reactant ions to diffuse from the liquid phase at the 2212 grain boundaries into the

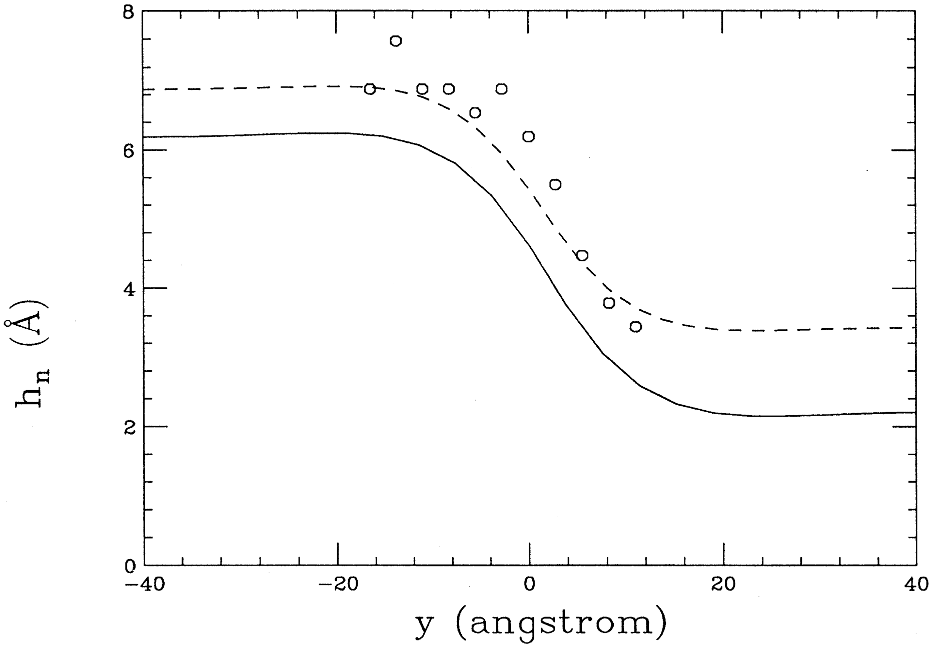

FIG. 4. The spatial profile of the gallery height h; Solid line: Bi-2212/Bi-2223 systems for $K_A = K_B = K$; Dashed line: $YBa_2Cu_3O_7/YBa_2Cu_4O_8$ system for $K_A = K_B = K$; open circle: Experimental data for the $YBa_2Cu_3O_7/YBa_2Cu_4O_8$ system. Note the units of both h and y are angstroms.

bulk, causing the edge dislocation (the extra Ca/CuO_2 plane) to rapidly climb into Bi-2212.

IV. ANALYSIS OF THE TIME DEPENDENCE OF Bi-2212 CONVERSION TO Bi-2223

Since the reactant is always in contact with the Bi-2212/Bi-2223 interface, the reaction rate of Bi-2212 to Bi-2223 perpendicular to the dislocation line is independent of the volume fraction of Bi-2223 and the growth in this direction is very fast. We therefore need to consider only the diffusion along the dislocation line and assume that the reactants are consumed immediately upon reaching the Bi-2212/Bi-2223 interface, since the diffusion is probably a much slower process than any local rearrangements of atoms which might be required. Thus the rate of growth of the product layer along the dislocation line is given by

$$dl/dt = D/l, \tag{15}$$

where l is the distance from the grain boundary measured along the dislocation line and D is the effective diffusion coefficient of the reactant ions. Since the diffusion coefficient and the size of the void (see the previous section) are independent of the volume fraction of Bi-2223, integrating the above equation yields

$$l = \sqrt{2Dt}. \tag{16}$$

The volume of the reactant ions consumed by the formation of the product phase is given by

$$R = S\sqrt{2D}t^{1/2}, \tag{17}$$

where S is the size of the void. For a Bi-2212 grain, the number of Ca/CuO_2 planes nucleated at the grain boundary in the time interval between t' and $(t'+dt')$ is $I(t')Vdt'$ where $I(t')$ is the nucleation rate per unit area of the grain boundary. Therefore the total volume of reactant ions consumed at time t (assuming the nucleation can occur everywhere at the grain boundary, including the transformed region) is given by

$$V_e^C = A\int_0^t I(t')R(t-t')dt' = S\sqrt{2D}A\int_0^t I(t')(t-t')^{1/2}dt', \tag{18}$$

where A is the total area of the grain boundary. It should be pointed out that V_e^C is different from the actual volume of reactant consumed since it assumes that the nucleation can occur in the transformed region and it treats all regions as though they continued growing irrespective of other regions. To correct this problem, we assume the volume of the transformed region is V^C and work out the relationship between V^C and V_e^C. Consider a small region of which a fraction $[1-(V^C/V)]$ remains untransformed (where V is the total volume of the grain). During the time interval dt, of the total transformed volume dV_e^C, a fraction $[1-(V^C/V)]$ on the average will lie in previously unreacted material, and thus contribute to dV^C while the reminder of the dV_e^C will be in already transformed material. Therefore we obtain

$$dV^c = \left(1 - \frac{V^C}{V}\right)dV_e^C, \tag{19}$$

or

$$V_e^C = -V\ln\left(1 - \frac{V^C}{V}\right). \tag{20}$$

Let $[1-(V^C/V)] = 1 - C$ where C is the volume fraction of the Bi-2223 and substitute Eq. (20) into Eq. (18), we have

$$\ln\left(\frac{1}{1-C}\right) = \frac{S\sqrt{2DA}}{V}\int_0^t I(t')(t-t')^{1/2}dt'. \tag{21}$$

The volume fraction of Bi-2223 depends sensitively on the nucleation rate $I(t)$. It is often assumed that the time dependence of the number of nucleation sites is a classical first-order rate process, i.e.,

$$dN(t)/dt=-fN(t), \tag{22}$$

where f is the frequency of an empty gallery in Bi-2212 turns into a nucleation site for Bi-2223 and $N(t)$ is the number of such nucleation sites at time t. Integrating the above equation yields

$$I(t)=fN(t)=fN_0\exp(-ft), \tag{23}$$

where N_0 is the number of empty galleries in the Bi-2212 grain at $t=0$. Substituting Eq. (23) into Eq. (21) yields

$$\ln\left(\frac{1}{1-C}\right)=\frac{S\sqrt{2D}N_0A}{V}\left[t^{1/2}+\frac{i}{2}\sqrt{\frac{\pi}{f}}\exp(-ft)\mathrm{erf}(i\sqrt{ft})\right], \tag{24}$$

where $\mathrm{erf}(z)$ is the error function with complex variable z. We can then obtain the Avrami exponents for various values of f.

In the limiting case that ft is very small, i.e., the time it takes to produce a Bi-2223 nuclei is much longer than the time it takes to grow the Ca/CuO$_2$ across the sample, we can expand Eq. (24) in terms of ft

$$\ln\left(\frac{1}{1-C}\right)=\frac{S\sqrt{2D}N_0A}{V}\left(\frac{2}{3}ft^{3/2}-\frac{4}{15}f^2t^{5/2}+\cdots\right). \tag{25}$$

Comparing the above equation with Eq. (1) we have $\alpha\approx1.5$ which agrees well with the experimental results in Refs. 2 and 3 for the preheated sample. It should be pointed out that the assumption in this limiting case is valid only if the reactants (Ca, Cu, and O) are evenly coated around the Bi-2212 grains and the Bi-2212 grains are small enough. The prediction of our model is therefore more consistent with experiments with small precursor powder which are heat treated before annealing to ensure the even distribution of the reactants.

On the other hand, if ft is very large, i.e., the time it takes to produce a Bi-2223 nuclei is much shorter than the time it takes to grow the Ca/CuO$_2$ plane across the sample, we can consider that all the empty galleries in Bi-2212 have turned into nucleation sites for Bi-2223 before the Ca/CuO$_2$ planes begin to grow. In that case we find from Eq. (17)

$$\ln\left(\frac{1}{1-C}\right)=\frac{N_0AR}{V}=\frac{S\sqrt{2D}N_0A}{V}t^{1/2}, \tag{26}$$

i.e., $\alpha=0.5$. We can see that this will be the case if there is local shortage of reactant ions which will leads to the slow growth of Ca/CuO$_2$ plane. Experiments in Ref. 1 apparently fall into this situation. As we can see from Fig. 4 in Ref. 1, the Avrami exponent α increases as the temperature rises, from 0.5 at 840 °C to 0.79 at 870 °C. The small value of Avrami exponents in Ref. 1 is either due to the large Bi-2212 grain size as indicated by the high porosity ($\sim$40%) or the uneven distribution of the reactant ions.[1] When the temperature rises, the growth of the Ca/CuO$_2$ plane accelerates due to the increase of ion diffusion constant D and the reactant ions distribute more evenly around the Bi-2212 grain due to the decreased viscosity of the ionic liquid of Ca, Cu, and oxygen.

V. SUMMARY

In conclusion we have proposed a microscopic kinetics and diffusion mechanism for the Bi-2212 to Bi-2223 transformation. The layer-rigidity model yields the local gallery height which is in good agreement with experimental observations. We propose that the Bi-2212 to Bi-2223 transformation is a one-dimensional diffusion-controlled nucleation and growth process with edge dislocations at the Bi-2212/Bi-2223 interface acting as channels for fast ion diffusion. The Avrami exponent depends sensitively on the nucleation rate of the Bi-2223 (the extra Ca/Cu$_2$ plane) in the Bi-2212 matrix and varies between 0.5 to 1.5.

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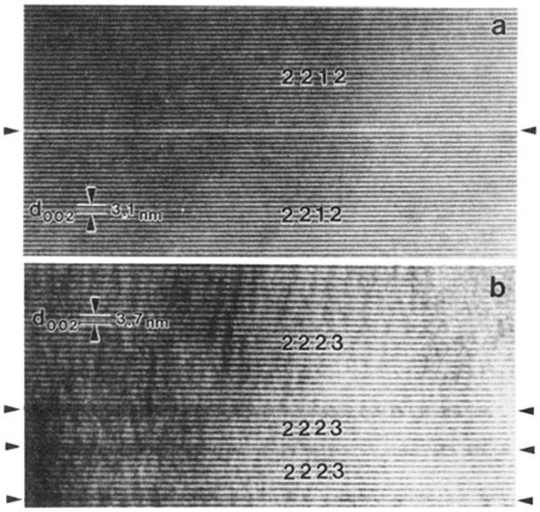

FIG. 1. (a) A (002) lattice image from a sample annealed at 825 °C for 30 h. The crystal matrix was dominated by the 2212 phase. A pair of arrowheads indicates the insertion of a Ca/CuO_2 bilayer which forms a half unit-cell of the 2223 phase. (b) A (002) lattice image from a sample annealed at 825 °C for 150 h. The majority of the crystals had completed the transformation from the 2212 phase to the 2223 phase. The remaining 2212 phase are marked by the arrowheads.