

## Changes of the dimensionality and $T_c$ through the iodine intercalation and oxidation in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ single crystals

Akihiko Fujiwara,\* Yoji Koike,<sup>†</sup> Takashi Noji, and Yoshitami Saito<sup>‡</sup>

*Department of Applied Physics, Faculty of Engineering, Tohoku University, Aramaki Aoba, Aoba-ku, Sendai 980-77, Japan*

Terukazu Nishizaki and Norio Kobayashi

*Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-77, Japan*

Akio Yamanaka

*Research Institute for Electronic Science, Hokkaido University, Kita-ku, Sapporo 060, Japan*

Shunji Takekawa

*National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba 305, Japan*

Fujio Minami

*Department of Physics, Faculty of Science, Tokyo Institute of Technology, 2-12-1 Oh-Okayama, Meguro-ku, Tokyo 152, Japan*

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The effects of stage-one iodine intercalation and oxidation on the dimensionality of the physical properties and on the superconducting transition temperature  $T_c$  have been investigated in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  single crystals. Both intercalation and oxidation change the dimensionality of the normal-state properties from pseudo-two-dimensional to three-dimensional, decrease  $T_c$  and also change the magnetic-field dependence of the activation energy in the flux creep. The broadening of the resistive superconducting-transition under magnetic fields is suppressed through only the oxidation. These changes through the intercalation and oxidation have been found to be explained by the multilayer model, where a high- $T_c$  superconductor is regarded as an alternating stack of the  $\text{CuO}_2$  layer ( $S$  layer) and the block layer ( $N$  layer), taking account of the proximity effect and of the redistribution of carriers to the  $S$  and  $N$  layers. We have arrived at the conclusion that the multilayer model can be one of the candidates for the model of high- $T_c$  superconductors.

### I. INTRODUCTION

Since the discovery of high- $T_c$  superconductivity in the La-based cuprate,<sup>1</sup> many kinds of high- $T_c$  superconductors have been found. Their crystal structures are layered perovskite ones including the two-dimensional  $\text{CuO}_2$  layer in common. In consequence, these materials exhibit anisotropic or pseudo-two-dimensional behaviors in the physical properties, e.g., the electrical resistivity and thermoelectric power in the normal state and also the upper critical field  $H_{c2}$  and the activation energy in the flux creep in the superconducting state. Another feature of the high- $T_c$  superconductivity is the parabolalike dependence of the superconducting transition temperature  $T_c$  on the carrier concentration per Cu,  $p$ . However, the material dependence of the maximum value of  $T_c$  at the optimum concentration has not yet been understood clearly. It may be related to the two dimensionality of the material. Therefore, understanding of the correlation between the large anisotropy or two dimensionality of the physical properties and the occurrence of high- $T_c$  superconductivity is expected to be crucial to elucidate the mechanism of high- $T_c$  superconductivity.

Formerly, anisotropic or pseudo-two-dimensional behaviors were studied vigorously for layered conventional superconductors such as transition-metal dichalcogenides ( $\text{NbS}_2$ ,  $\text{NbSe}_2$ ,  $\text{TaS}_2$ ,  $\text{TaSe}_2$ ) and their intercalation compounds,<sup>2-10</sup> graphite intercalation compounds<sup>11,12</sup> and artificial multilay-

ers ( $\text{Nb/Ge}$ ,  $\text{Nb/Cu}$ ,  $\text{V/Ag}$ ,  $\text{V/Ni}$ ).<sup>13-16</sup> For example,  $H_{c2}$  versus  $T$  in transition-metal dichalcogenides was found to change from anisotropic three-dimensional to more anisotropic pseudo-two-dimensional through intercalation, and the dimensionality of the superconducting properties in artificial multilayers was found to change depending on the thicknesses of the component layers. These experimental results were well explained by the so-called multilayer model, where a layered superconductor was regarded as a multilayer made of an alternating stack of superconducting layers ( $S$  layers) and nonsuperconducting normal layers ( $N$  layers).<sup>17-19</sup> That is to say, the dimensionality could be understood in terms of the actual extent of the  $S$  layer (controlled by the thickness of the  $S$  layer  $d_S$ ) and the coupling between the adjacent  $S$  layers (controlled by the thickness of the  $N$  layer  $d_N$ ), and superconductivity became more three-dimensional with an increase in  $d_S$  or with a decrease in  $d_N$  and became more two-dimensional in the opposite case. In this way, it was found that the dimensionality of the physical properties was strongly affected by the structural dimensionality determined by both  $d_S$  and  $d_N$ .

Several kinds of study with respect to the anisotropy (dimensionality) have been reported for the high- $T_c$  superconductors, too. One is an investigation using artificial superlattices. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO)/ $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (PBCO) multilayers, for example, the occurrence of superconductivity, the value of  $T_c$  and the Kosterlitz-Thouless transition

have been investigated by controlling the thicknesses of YBCO and/or PBCO layers.<sup>20,21</sup> In this case, YBCO and PBCO layers are regarded as  $S$  and  $N$  layers, respectively, and the dimensionality depends on the respective numbers of unit cells of YBCO and PBCO along the  $c$  axis. Other examples are on the intrinsic pinning effect<sup>22</sup> and intrinsic Josephson coupling,<sup>23</sup> which have been proposed theoretically. In these cases, the unit cell of a high- $T_c$  superconductor is divided into the superconducting  $\text{CuO}_2$  layer ( $S$  layer) and the nonsuperconducting block layer ( $N$  layer), and the high- $T_c$  superconductor is regarded as an alternating stack of the  $S$  layer and  $N$  layer. The dimensionality is dependent on the two-dimensional arrangement of atoms in high- $T_c$  materials. So, it can be called intrinsic structural dimensionality and may play an important role in the occurrence of high- $T_c$  superconductivity. Accordingly, intercalation, which is able to change the intrinsic structural dimensionality, is expected to be a good approach to understanding of the correlation between the two dimensionality and high- $T_c$  superconductivity.

The Bi-based cuprates of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$  ( $n = 1, 2, 3$ ) and  $\text{Bi}_2\text{Sr}_2(\text{Gd}_{0.82}\text{Ce}_{0.18})_2\text{Cu}_2\text{O}_{10+\delta}$  are known to form intercalation compounds by accepting halogen ( $\text{I}_2$ ,  $\text{Br}_2$ ,  $\text{IBr}$ ) or metal halide ( $\text{AgI}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ) between the weakly coupled BiO-BiO double layers.<sup>24-29</sup> Among these intercalation compounds, the stage-one iodine intercalation compound  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}\text{I}_x$  has been studied most vigorously because of its relatively high stability and quality. We also studied the effects of stage-one iodine intercalation on  $T_c$  for sintered samples of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}$  and  $\text{Bi}_{1.6}\text{Pb}_{0.5}\text{Sr}_{1.9-x}\text{La}_x\text{Cu}_{1.05}\text{O}_{6+\delta}$ <sup>30,31</sup> and found that  $T_c$  is affected by both the structural change and charge transfer from intercalated iodine to the host material through the intercalation. In some reports, a role of the anisotropy (dimensionality) in the high- $T_c$  superconductivity has been discussed, but the correlation between the anisotropy (dimensionality) of the physical properties and  $T_c$  has not yet been understood clearly. In this paper, in order to clarify this problem, we investigate variations of the crystal structure, the anisotropy in the electrical resistivity and thermoelectric power, and the resistive superconducting transition under magnetic fields through the stage-one iodine intercalation and oxidation, using  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  single crystals. The variations through the oxidation are studied in order to know the effects of only charge transfer to the host material and to extract the effects of the structural change through the iodine intercalation.

This paper is organized as follows: In Sec. II, the processes of crystal growth, intercalation and oxidation are shown, and the methods of measurements are also described. In Sec. III, the experimental results and discussion are presented. In this section, we also present the multilayer model to explain the experimental results and discuss the applicability of the multilayer model to high- $T_c$  superconductors. The summary and conclusions are given in Sec. IV.

## II. EXPERIMENTAL

Single crystals of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  were grown by the floating-zone method.<sup>32</sup> The as-grown crystals were used as host for the intercalation and oxidation. The stage-one iodine intercalation was achieved by sealing the as-grown host crys-

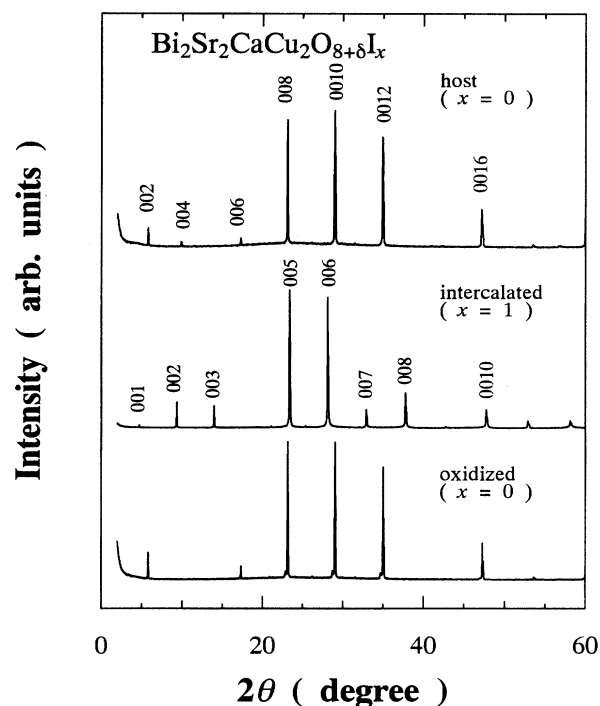


FIG. 1. X-ray-diffraction patterns using  $\text{Cu } K_\alpha$  radiation for the as-grown host, iodine-intercalated, and oxidized crystals.

tals with elemental iodine separately in an evacuated glass tube and annealing at  $180^\circ\text{C}$  for 330 h. The oxidation was performed by annealing the as-grown host crystals under 10 atm of oxygen at  $550^\circ\text{C}$  for 140 h or under 600 atm of oxygen at  $400^\circ\text{C}$  for 320 h. The crystal structure was characterized by x-ray diffraction.

Resistivity measurements were carried out by the standard dc four-probe method. The thermoelectric power was measured by the conventional dc method with a temperature gradient of  $\sim 0.5$  K across the crystal. For resistivity measurements under magnetic fields, a split-type superconducting magnet was used, combined with a sample-rotation system using a computer-controlled stepping motor. The current flowed in the  $ab$  plane, and magnetic fields up to 9.0 T were applied always perpendicular to the current direction. In this paper,  $\theta$  is defined as the angle between the magnetic-field direction and the  $ab$  plane. The finest step of  $\theta$  was  $0.72^\circ$ .

## III. RESULTS AND DISCUSSION

### A. Crystal structure

Figure 1 shows x-ray-diffraction patterns for the as-grown host, iodine-intercalated, and oxidized crystals. The patterns of the as-grown host and oxidized crystals are almost the same and accord with that of the Bi2212 structure reported in the literature.<sup>33</sup> No structural change is observed through the oxidation, though the lattice constants change a little. On the other hand, the diffraction pattern of the iodine-intercalated crystal does not accord with that of the Bi2212 structure but accords with that of the stage-one iodine-intercalated  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}\text{I}_x$ ,<sup>24</sup> meaning the achievement of stage-one

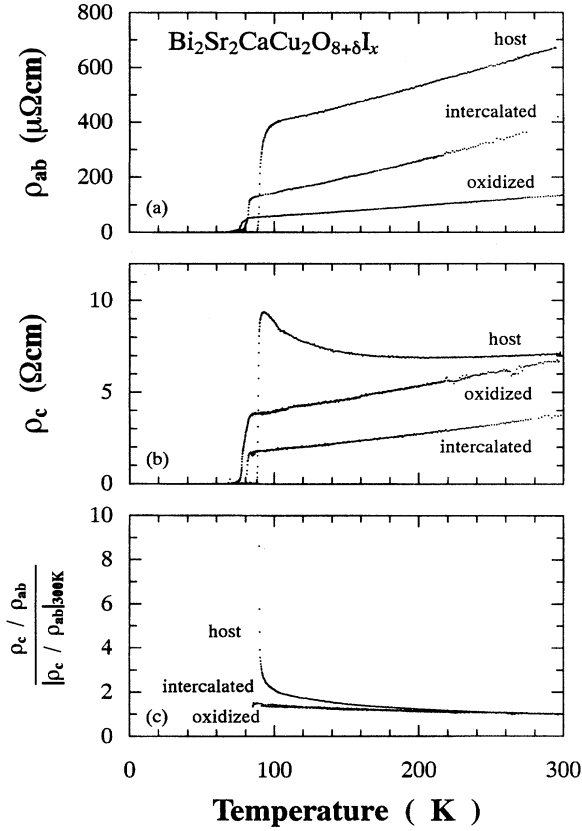


FIG. 2. Temperature dependence of (a) the in-plane resistivity  $\rho_{ab}$ , (b) the out-of-plane resistivity  $\rho_c$  and (c) the anisotropy in resistivity  $\rho_c/\rho_{ab}$  for the as-grown host, iodine-intercalated, and oxidized crystals. The  $\rho_c/\rho_{ab}$  is normalized at 300 K.

intercalation. As a result of the introduction of iodine between the BiO-BiO double layers, the block layer becomes thicker and the distance between  $\text{CuO}_2$  layers across the block layer increases by  $3.5 \text{ \AA}$ .<sup>34</sup> In other words, the  $\text{CuO}_2$  planes are diluted in the crystal structure along the  $c$  axis. From the viewpoint of structural dimensionality, the two dimensionality is enhanced through the stage-one iodine intercalation. Therefore, it may be said that the stage-one iodine intercalation is a modification of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  accompanied with a change of the structural dimensionality and that the oxidation is a modification without the structural change.

### B. Normal-state properties

Figure 2 displays the temperature dependence of the electrical resistivity for the as-grown host, iodine-intercalated, and oxidized crystals. The in-plane resistivity  $\rho_{ab}$  shows metallic behavior above  $T_c$  for the as-grown host crystal, while its out-of-plane resistivity  $\rho_c$  shows semiconductorlike behavior. Accordingly, anisotropy in the resistivity  $\rho_c/\rho_{ab}$  increases with decreasing temperature, as shown in Fig. 2(c). If the material is an anisotropic three-dimensional conductor,  $\rho_c/\rho_{ab}$  should be generally independent of temperature. Therefore, the electrical conduction of the as-grown host crystal is concluded to be pseudo-two dimensional. On the contrary,  $\rho_c$  of the iodine-intercalated and oxidized crystals

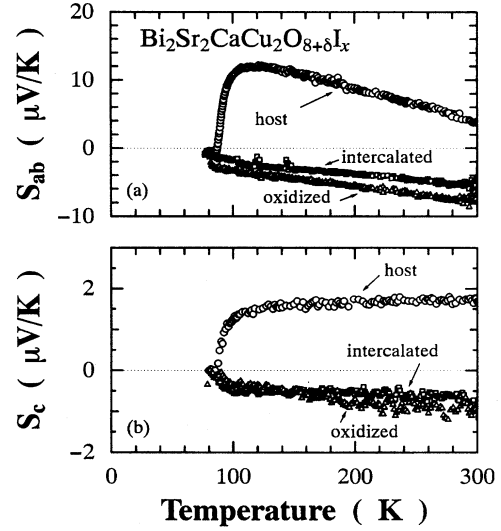


FIG. 3. Temperature dependence of (a) the in-plane thermoelectric power  $S_{ab}$  and (b) the out-of-plane thermoelectric power  $S_c$  for the as-grown host, iodine-intercalated, and oxidized crystals.

gets to show metallic temperature dependence like  $\rho_{ab}$ , which is consistent with the reports presented before.<sup>35–37</sup> As a result, the temperature dependence of  $\rho_c/\rho_{ab}$  is weakened. This means that the electrical conduction changes from pseudo-two-dimensional to three-dimensional through the intercalation and oxidation. The similar dimensional crossover has been observed in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  also, where the dimension changes from pseudo-two-dimensional to three-dimensional with increasing  $x$ , namely, with increasing  $p$ .<sup>38</sup> So, the dimensional crossover through the intercalation and oxidation seems to be mainly due to the increase in  $p$ , owing to charge transfer from the intercalated iodine and the excess oxygen to the host material, respectively.

Figure 3 shows the temperature dependence of the thermoelectric powers for the as-grown host, iodine-intercalated, and oxidized crystals. The in-plane and out-of-plane thermoelectric powers for the host crystal exhibit temperature dependences similar to those reported in the literature.<sup>39</sup> As proposed by Tanaka *et al.*,<sup>40</sup> the in-plane thermoelectric power  $S_{ab}$  can be expressed as

$$S_{ab} = AT + \frac{BT^\alpha}{(T + \Theta)^\alpha}, \quad (1)$$

where  $A$  is rather insensitive to  $p$ , and  $B$  gives the  $T$  independent part of  $S_{ab}$  at high temperatures ( $T \gg \Theta$ ) and decreases monotonically with increasing  $p$ . The present results of  $S_{ab}$  can be understood on this line, too. That is, the  $T$ -linear part of  $S_{ab}$  at high temperatures makes an almost parallel shift in the negative direction through the intercalation and oxidation, meaning that  $A$  changes little and that  $B$  decreases through the intercalation and oxidation. This is reasonably understood as being due to the increase in  $p$  through the intercalation and oxidation. On the other hand, the out-of-plane thermoelectric power  $S_c$  exhibits not only a shift but also a change of the temperature dependence through the intercalation and oxidation. The sign of  $dS_c/dT$

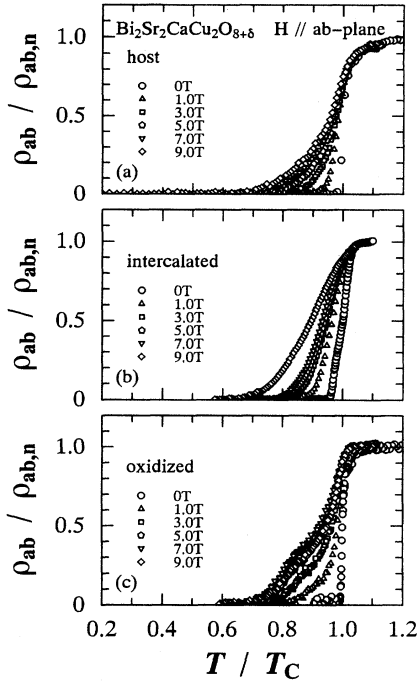


FIG. 4. Resistive superconducting-transition under magnetic fields parallel to the  $ab$  plane ( $\theta=0^\circ$ ) up to 9 T for (a) the as-grown host crystal, (b) the iodine-intercalated crystal and (c) the oxidized crystal. The in-plane-resistivity  $\rho_{ab}$  is normalized by the normal-state resistivity in zero field  $\rho_{ab,n}$ . Temperature is normalized by  $T_c$ , defined as the midpoint of the superconducting transition in zero field. The values of  $T_c$  are 86.0, 80.7, and 81.7 K for the as-grown host, iodine-intercalated, and oxidized crystals, respectively.

changes from plus to minus through the intercalation and oxidation. Although the origin of this change in  $S_c$  is not clear, it is suggested that the electronic structure changes from pseudo-two-dimensional to anisotropic three-dimensional through the intercalation and oxidation. This is because the sign of  $dS_c/dT$  becomes the same as that of  $dS_{ab}/dT$  through the intercalation and oxidation, though there still remains large anisotropy in  $S$ .

After all, the normal-state properties of these crystals can be understood as follows. Signs of  $d\rho_{ab}/dT$  and  $dS_{ab}/dT$  are different from those of  $d\rho_c/dT$  and  $dS_c/dT$ , respectively, for the as-grown host crystal, owing to the pseudo-two-dimensional electronic structure. Both intercalation and oxidation change the electronic structure from pseudo-two-dimensional to anisotropic three-dimensional, so that the temperature dependences of  $\rho$  and  $S$  are independent of the direction.

### C. Superconducting properties

Figure 4 displays the resistive superconducting-transition under magnetic fields  $H$  parallel to the  $ab$  plane ( $\theta=0^\circ$ ) for the as-grown host, iodine-intercalated, and oxidized crystals. In a highly anisotropic superconductor, the resistive superconducting transition under magnetic fields is very sensitive to  $\theta$ , especially around  $\theta=0^\circ$ . Therefore, taking into account

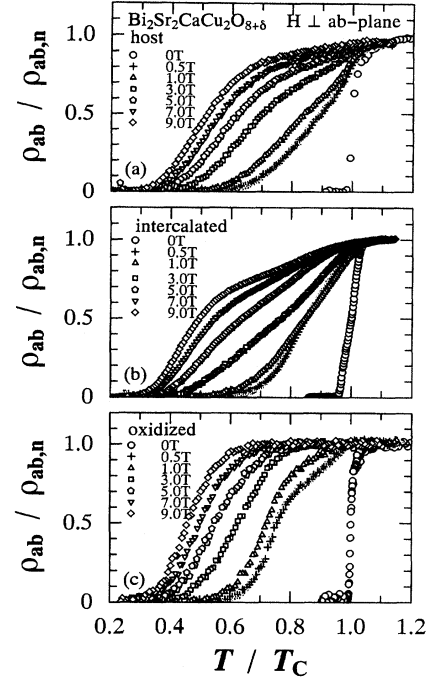


FIG. 5. Resistive superconducting transition under magnetic fields perpendicular to the  $ab$  plane ( $\theta=90^\circ$ ) up to 9 T for (a) the as-grown host crystal, (b) the iodine-intercalated crystal, and (c) the oxidized crystal. The in-plane resistivity  $\rho_{ab}$  is normalized by the normal-state resistivity in zero field  $\rho_{ab,n}$ . Temperature is normalized by  $T_c$ .

the misorientation in the crystal setting, we cannot find any clear difference among three kinds of crystals.

Figure 5 shows the resistive transition under magnetic fields perpendicular to the  $ab$  plane ( $\theta=90^\circ$ ). The resistive transitions of the iodine-intercalated crystal exhibit behavior similar to that of the as-grown host crystal. That is, the superconducting onset temperatures  $T_c^{\text{onset}}$  under different magnetic fields are located close to each other. In contrast to  $T_c^{\text{onset}}$ , the zero-resistance temperature  $T_c^0$  decreases with increasing magnetic-field strength. In consequence, the transition width  $\Delta T_c (\equiv T_c^{\text{onset}} - T_c^0)$  increases, namely, the transition becomes broad as  $H$  increases. On the other hand, a clear difference is observed for the oxidized crystal. That is, both  $T_c^{\text{onset}}$  and  $T_c^0$  decrease as  $H$  increases, and  $\Delta T_c$  does not increase so much in spite of the increase in  $H$ . The broadening of the resistive transition under magnetic fields has been discussed theoretically by Ikeda, Ohmi, and Tsuneto<sup>41</sup> in terms of the superconducting fluctuation enhanced by the low dimensionality. According to their idea, the superconducting fluctuation becomes striking under magnetic fields perpendicular to the  $ab$  plane in two-dimensional systems and decreases the resistivity in the high-temperature regime of the superconducting transition, leading to broadening of the resistive transition. In the present results, the broadening of the resistive transition is suppressed through only the oxidation. Therefore, it is suggested that the dimensionality of the electronic structure in the superconducting state changes from pseudo-two dimensional to anisotropic three dimen-

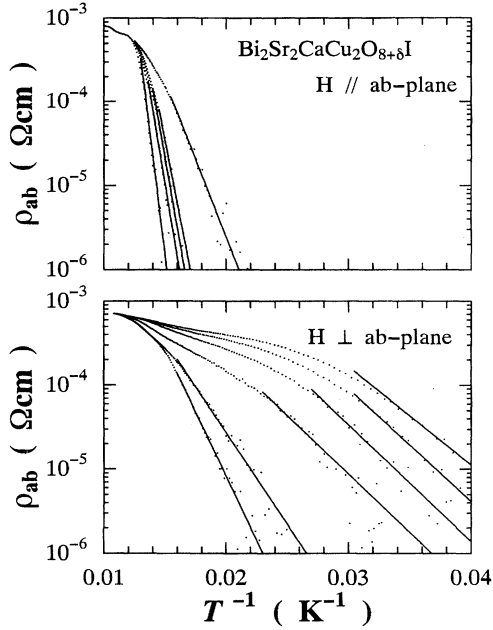


FIG. 6. Arrhenius plots of the data shown in Figs. 4(b) and 5(b) for the iodine-intercalated crystal. (a)  $H \parallel ab$  plane ( $\theta=0^\circ$ ) and (b)  $H \perp ab$  plane ( $\theta=90^\circ$ ). The solid lines are fits to the data using Eq. (2) with adjustable parameters  $\rho_0$  and  $U_0(H, \theta)$ .

sional through the oxidation, but remains pseudo-two dimensional through the intercalation. This is different from dimensional crossover in the normal state as mentioned in Sec. III B, in which the dimensional crossover is observed through both intercalation and oxidation.

In the low-temperature regime of the superconducting transition, on the other hand, the flux motion plays an important role. In this regime, the broadening of the resistive superconducting transition has been interpreted as due to the thermally activated flux creep.<sup>42</sup> The resistivity is generally given by

$$\rho(T, H, \theta) = \rho_0 \exp\left(\frac{-U_0(H, \theta)}{T}\right), \quad (2)$$

where  $\rho_0$  is constant and  $U_0(H, \theta)$  is the activation energy in the flux creep. Detailed studies indicate that  $U_0$  depends on not only  $H$  and  $\theta$ , but also the  $T$ .<sup>43</sup> In the present work, however, we disregard the temperature dependence of  $U_0$ , because our discussion is rough and hardly influenced by this disregard. Arrhenius plots of the resistivity for the iodine-intercalated crystal are shown in Fig. 6. The solid lines are fits to the data using Eq. (2) with adjustable parameters  $\rho_0$  and  $U_0(H, \theta)$ . The slope of the lines corresponds to the activation energy  $U_0(H, \theta)$ . The values of  $U_0(H, \theta)$  obtained thus are shown for three kinds of crystals in Fig. 7. It is reasonable that  $U_0$  in the case of  $H \parallel ab$  plane is larger than that in the case of  $H \perp ab$  plane for all the crystals. This is because the intrinsic pinning effect, where the block layer is considered to operate as a pinning center, is valid for  $H \parallel ab$  plane.<sup>22</sup> The power dependence of  $U_0$  on  $H$  in the case of  $H \parallel ab$  plane is more striking than in the case of  $H \perp ab$  plane for the as-grown host crystal, as reported previously.<sup>44</sup> How-

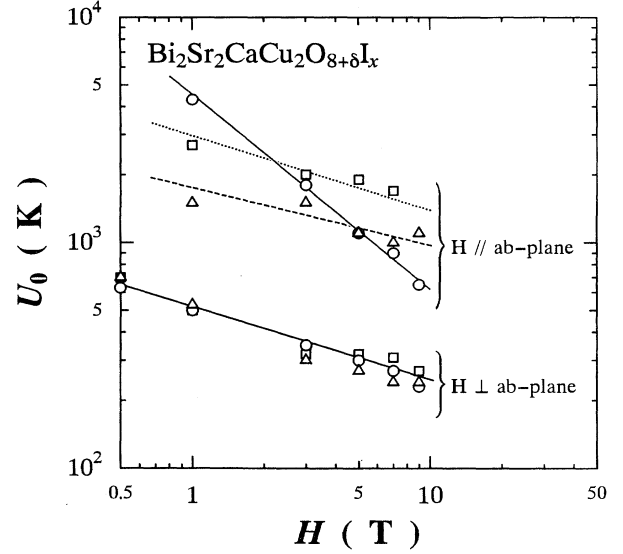


FIG. 7. Magnetic-field dependence of the activation energy  $U_0$  in the case of  $H \parallel ab$  plane and  $H \perp ab$  plane for the as-grown host ( $\circ$ ), iodine-intercalated ( $\square$ ), and oxidized ( $\triangle$ ) crystals. The lines are guides to the eye.

ever, it is remarkable that the power dependences of  $U_0$  on  $H$  in both cases become almost the same through the intercalation and oxidation, though there still remains large anisotropy in  $U_0$ . This suggests that the dimensionality of the flux motion also changes from pseudo-two-dimensional to anisotropic three-dimensional through the intercalation and oxidation.

#### D. Multilayer model

Here, we try to explain the various physical properties of the as-grown host, iodine-intercalated, and oxidized crystals, presented in this work, by the multilayer model mentioned in Sec. I. According to the multilayer model,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  is simply regarded as an alternating stack of the  $S$  layer (consisting of two neighboring  $\text{CuO}_2$  layers and a  $\text{Ca}$  layer sandwiched by them) and the  $N$  layer (consisting of  $\text{SrO}$ - $\text{BiO}$ - $\text{BiO}$ - $\text{SrO}$  layers).

First, we discuss the normal-state properties. The temperature dependence of  $\rho_{ab}$  shows metallic behavior for all the crystals. This is explained as being due to parallel connection of metallic  $S$  layers and  $N$  layers. Taking account of the semiconductorlike behavior of  $\rho_c$  for the as-grown host crystal, the  $N$  layer should be a semiconductor with a low carrier concentration. Then, the semiconductorlike behavior of  $\rho_c$  can be attributed to serial connection of metallic  $S$  layers and semiconductorlike  $N$  layers. According to the band calculation,<sup>45</sup> the carrier number in the  $N$  layers is as small as about 10% of that in the  $S$  layers, supporting our speculation. The metallic behavior of  $\rho_c$  for the iodine-intercalated and oxidized crystals is understood as being due to metallization of the  $N$  layers, which may be caused by carrier doping into the  $N$  layers through the intercalation and oxidation. That is, the alternating stack of the metallic  $S$  layers and the semiconductorlike  $N$  layers seems to change

to the alternating stack of the metallic  $S$  layers and the metallic  $N$  layers through the intercalation and oxidation. As a result, the pseudo-two-dimensional conductor, which is metallic in the  $ab$  plane and semiconductorlike along the  $c$  axis, changes to a three-dimensional conductor, which shows metallic behavior in all the directions. The dimensional crossover in resistivity through the intercalation and oxidation can be qualitatively explained in this way. This explanation is not so unreasonable, because the carrier doping into the  $N$  layers through oxidation was observed in the angle-resolved-photoemission experiment on  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .<sup>46</sup> As for the thermoelectric power, we cannot make a clear discussion, because the temperature dependence of the thermoelectric power has not yet been understood clearly for the high- $T_c$  superconductors. However, it is guessed that the dimensional crossover in thermoelectric power through the intercalation and oxidation also occurs in the same way as the dimensional crossover in  $\rho$ .

Secondly, we discuss the resistive superconducting transition under magnetic fields. The difference in the broadening of the resistive transition is considered to be due to the degree of coupling between the adjacent  $S$  layers, namely, the overlap along the  $c$  axis of the superconducting order parameter in each  $S$  layer. According to the theory on the proximity effect,<sup>47</sup> the penetration of the order parameter into the  $N$  layers depends on the carrier concentration in the  $N$  layers, and the overlap depends on the penetration as well as the distance between the adjacent  $S$  layers, namely,  $d_N$ . The suppression of the superconducting fluctuation through the oxidation may be due to more three-dimensional nature originating from large penetration of the order parameter in the  $N$  layers owing to an increase of the carrier concentration in the  $N$  layers. The maintenance of the large superconducting fluctuation through the intercalation despite an increase of the carrier concentration in the  $N$  layers is understood as being due to more two-dimensional nature originating from the increase in  $d_N$ . It seems that the delicate competition between the carrier concentration in the  $N$  layers and  $d_N$  dominates the superconducting fluctuation enhanced by the low dimensionality. As for the flux motion, the intrinsic pinning effect, based on the two-dimensional stack of the  $\text{CuO}_2$  layer and the block layer, is essentially a two-dimensional effect and weakened through the penetration of the superconducting order parameter into the  $N$  layers owing to an increase of the carrier concentration in the  $N$  layers.<sup>22</sup> As the intrinsic pinning energy is related to the rate of the spatial variation of the order parameter, the carrier concentration in the  $N$  layers influences the intrinsic pinning more than  $d_N$ . Therefore, the dimensional crossover in the flux motion through both intercalation and oxidation is explained as being due to the suppression of the two-dimensional intrinsic pinning effect.

Next, we focus the discussion on  $T_c$ , using the multilayer model. When the superconducting coherence length  $\xi$  is much larger than  $d_S$  and  $d_N$ , the proximity effect is effective on  $T_c$ . Taking account of the proximity effect, de Gennes<sup>47</sup> derived the formula of the effective BCS coupling constant,  $[N(0)V]_{\text{eff}}$ , for a multilayer system as

$$[N(0)V]_{\text{eff}} = \frac{N_N^2 V_N d_N + N_S^2 V_S d_S}{N_N d_N + N_S d_S}, \quad (3)$$

where  $N_S$  and  $N_N$  are the densities of states for  $S$  and  $N$  layers, respectively.  $V_S$  and  $V_N$  are the attractive potentials between electrons for  $S$  and  $N$  layers, respectively. In this case, the superconducting transition temperature of the multilayer system,  $T_c^{\text{ML}}$ , is expressed as

$$T_c^{\text{ML}} \approx \Theta_D \exp \left[ -1 \left/ \left( \frac{N_N^2 V_N d_N + N_S^2 V_S d_S}{N_N d_N + N_S d_S} \right) \right. \right]. \quad (4)$$

This formula is based on the weak-coupling BCS theory and  $\Theta_D$  is the Debye temperature. Although, at present, it is not clear that the high- $T_c$  superconductivity can be treated in this category or not, Eq. (4) may be applied to high- $T_c$  superconductors by assuming following two conditions. (i)  $\Theta_D$  is replaced by some characteristic temperature  $T_a$  which is not limited to the Debye temperature. (ii)  $V$  is an attractive potential due to an unknown attractive force between electrons. As it is believed that  $V_N$  vanishes in the  $N$  layer for high- $T_c$  superconductors, Eq. (4) is rewritten as

$$T_c^{\text{ML}} = T_a \exp \left[ -1 \left/ \left( \frac{N_S V_S d_S}{(N_N/N_S) d_N + d_S} \right) \right. \right]. \quad (5)$$

In the first step, it is necessary to estimate various parameters. In the as-grown host crystal of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ,  $d_S$  and  $d_N$  are 3.0 and 12.0 Å, respectively. Those in the oxidized crystal are almost the same as those in the as-grown host one, on account of no structural change through the oxidation. Through the intercalation, on the other hand,  $d_N$  increases to be 12.0 Å + 3.5 Å = 15.5 Å. The carrier concentration per Cu  $p$  can be approximately estimated from the value of thermoelectric power at 290 K,  $S(290 \text{ K})$ , by using the universal relation between  $S(290 \text{ K})$  and  $p$  presented by Obertelli, Cooper, and Tallon.<sup>48</sup> The ratio of the carrier concentration per Cu in the  $S$  and  $N$  layers,  $p_S:p_N$ , is determined to be 10:1 for the as-grown host crystal by the band calculation,<sup>45</sup> as mentioned above. In such a two-dimensional system as the  $S$  layer and  $N$  layer, the density of states is proportional to the carrier concentration, namely, the carrier number divided by the volume. After all, the ratio of the densities of states,  $N_N/N_S$ , is estimated as  $(p_N/d_N)/(p_S/d_S)$ . When Eq. (5) is applied to the as-grown host crystal, two parameters,  $T_a$  and  $N_S V_S$  have not yet been estimated. Therefore, our discussion on  $T_c$  is developed in two ways. In the first way (case A), the attractive force between electrons is assumed to be due to electron-phonon interaction. Then,  $T_a$  corresponds to the Debye temperature. As the Debye temperature of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  has not yet been reported, we use the Debye temperature of YBCO, 400 K, reported in the literature.<sup>49</sup> Using parameters listed in Table I,  $N_S V_S$  is estimated from Eq. (5) to be 0.739 and  $[N(0)V]_{\text{eff}}$  is estimated from Eq. (3) to be 0.672. As Eqs. (4) and (5) are valid in the case of  $[N(0)V]_{\text{eff}} \ll 1$ , it seems that these estimated values are not so exact. In the second way (case B),  $[N(0)V]_{\text{eff}}$  is assumed to be 0.3, which is approximately the upper limit of the reasonable value for the use of Eqs. (4) and (5). Using parameters listed in Table I,  $T_a$  is estimated from Eq. (5) to be 2535 K. In this case, the attractive potential is expected to be no longer caused by the phonon-mediated mechanism but by another mechanism due to a rather high-energy driving force. It attracts interest that the experimental

TABLE I. Parameters used for the calculation. The values of  $p$  are estimated from the experimental values of  $S(290\text{ K})$  by using the relation between  $S(290\text{ K})$  and  $p$  presented by Obertelli, Cooper, and Tallen (Ref. 48). For parameters of  $T_a$ ,  $N_S V_S$ , and  $[N(0)V]_{\text{eff}}$ , two values are shown in correspondence to case *A* and case *B*. The value of  $T_c^{\text{ML}}$  for the as-grown host crystal is an experimental one.

Parameter	Host	Intercalated	Oxidized
$S(290\text{ K})$	4.19	-5.35	-7.67
$p$	0.143	0.219	0.224
$p_S$	0.130		
$p_N$	0.013		
$\Delta p$		0.076	0.081
$d_N$ (Å)	12.0	15.5	12.0
$d_S$ (Å)	3.0	3.0	3.0
$T_a$ (K)	400/2535	400/2535	400/2535
$N_S V_S$	0.739/0.330		
$[N(0)V]_{\text{eff}}$	0.672/0.300		
$T_c^{\text{ML}}$ (K)	90.4		

values of  $T_c$  for the iodine-intercalated and oxidized crystals can be approximately reproduced from the calculation of Eq. (5) in both case *A* and case *B*, by well distributing the additional carriers ( $\Delta p$  per Cu) through the intercalation and oxidation into the *S* and *N* layers. The results of the calculation are listed in Table II. In the long run, the decrease in  $T_c$  through the intercalation and oxidation is understood as being due to enhancement of the proximity effect by an increase of the carrier concentration in the *N* layers and due to an increase in  $d_N$  only in the case of intercalation.

Last, we discuss the applicability of the multilayer model to general high- $T_c$  superconductors. Here, we try to explain the parabolalike dependence of  $T_c$  on  $p$ , which is one of the important features of high- $T_c$  superconductors, by the multilayer model. The increase in  $T_c$  with increasing  $p$  in the so-called underdoped region is naturally understood to be due to an increase of carriers in the *S* layers ( $\text{CuO}_2$  layers), because carriers are indispensable to superconductivity. On the other hand, the decrease in  $T_c$  with more increasing  $p$  in the so-called overdoped region is explained as follows. That is to say, additional carriers cannot enter only the *S* layers but also the *N* layers (block layers). The carriers introduced

TABLE II. Results of the calculation of  $T_c$  by using parameters listed in Table I.

Experimental data	$T_c$ (K)	Intercalated	Oxidized
		81.7	80.7
case <i>A</i>	$T_a$ (K)	400	400
	$\Delta p_N : \Delta p_S$	0.662:0.338	0.662:0.338
	$[N(0)V]_{\text{eff}}$	0.630	0.629
	$T_c^{\text{ML}}$ (K)	81.8	81.6
case <i>B</i>	$T_a$ (K)	2535	2535
	$\Delta p_N : \Delta p_S$	0.626:0.374	0.626:0.374
	$[N(0)V]_{\text{eff}}$	0.291	0.291
	$T_c^{\text{ML}}$ (K)	81.7	81.5

TABLE III. Results of the calculation of  $T_c$  at  $p=0.3$ .

	case <i>A</i>		case <i>B</i>	
$p_S$	0.15	0.10	0.15	0.10
$p_N$	0.15	0.20	0.15	0.20
$p_N/p_S$	1	2	1	2
$T_c^{\text{ML}}$ (K)	38.3	2.0	13.3	0.02

into the *N* layers no longer contribute to the occurrence of superconductivity and operate to decrease  $T_c$  on account of their enhancement of the proximity effect. The vanishment of superconductivity around  $p \approx 0.3$  in the overdoped region is also explained by the multilayer model, adjusting the distribution of carriers to the *S* and *N* layers. In  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  for example,  $T_c$  is calculated as 38.3 K in case *A* and to 13.3 K in case *B*, supposing  $p_S = p_N = 0.15$ . Supposing  $p_S = 0.1$  and  $p_N = 0.2$ ,  $T_c$  is 2.0 and 0.02 K in cases *A* and *B*, respectively. Parameters used for the calculation and the results are summarized in Table III. Thus, the parabolalike dependence of  $T_c$  on  $p$  is reasonably explained by the multilayer model. Furthermore, it may be worthwhile pointing out that the material dependence of the maximum value of  $T_c$  at the optimum concentration is also able to be explained by the multilayer model. Ohta, Tohyama, and Maekawa<sup>50</sup> found that the maximum value of  $T_c$  is related to the difference in the Madelung potential between the in-plane oxygen site and the apical oxygen site. That is, the maximum value of  $T_c$  tends to increase, as the potential difference increases. In the multilayer model, the in-plane oxygen and apical oxygen belong to *S* and *N* layers, respectively. Therefore, the increase of the maximum value of  $T_c$  with the increase of the potential difference is explained by the multilayer model as being due to the suppression of the proximity effect owing to the decrease of carriers in the *N* layers.

After all, it is understood by the multilayer model that  $T_c$ 's of high- $T_c$  superconductors are determined by the intrinsic value of  $T_c$  of the *S* layers and by the proximity effect between the *S* and *N* layers. However, there still remains an unsettled big problem "what is the mechanism of the intrinsic superconductivity of the *S* layers?"

#### IV. SUMMARY AND CONCLUSIONS

The effects of stage-one iodine intercalation and oxidation on the dimensionality of the physical properties and on the  $T_c$  have been investigated in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  single crystals. Both intercalation and oxidation change the dimensionality of the normal-state properties from pseudo-two-dimensional to three-dimensional, decrease  $T_c$  and also change the magnetic-field dependence of the activation energy in the flux creep. The broadening of the resistive superconducting transition under magnetic fields is suppressed through only the oxidation. These changes through the intercalation and oxidation have been explained by the multilayer model, where a high- $T_c$  superconductor is regarded as an alternating stack of the  $\text{CuO}_2$  layer (*S* layer) and the block layer (*N* layer), taking account of the proximity effect and of the redistribution of carriers to the *S* and *N* layers. The parabolalike dependence of  $T_c$  on  $p$ , which is a general feature of the high- $T_c$  superconductors, is also explained adjusting the distribution of carriers to the *S* and *N* layers in this

model. In the multilayer model, the material dependence of the maximum value of  $T_c$  at the optimum concentration is understood as difference of the proximity effect owing to the difference in the Madelung potential between the in-plane oxygen site in the  $S$  layer and the apical oxygen site in the  $N$  layer among the materials. Thus,  $T_c$ 's of high- $T_c$  superconductors are determined by the intrinsic value of  $T_c$  of the  $S$  layers and by the proximity effect between the  $S$  and  $N$  layers in the multilayer model, though the mechanism of the intrinsic superconductivity of the  $S$  layers remains unsettled. We have arrived at the conclusion that the multilayer model can be one candidate for the model for high- $T_c$  superconductors.

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- \*Present address: Department of Physics, School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan.
- †Author to whom correspondence should be addressed.
- ‡Present address: Aomori Polytechnic College, Iizume, Goshogawara 037, Japan.
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