Direct observation of a structural-fluctuation enhancement in a superconducting state of $Tl_2Ba_2Ca_2Cu_3O_{10}$ by electron diffraction

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Features of temperature-dependent diffuse scattering showing a structural fluctuation in $Tl_2Ba_2Ca_2Cu_3O_{10}$ have been investigated in detail in a temperature range between about 20 K and room temperature by means of electron diffraction. As the temperature is lowered, the intensity of diffuse scattering increases remarkably below about 130 K, which is taken to be the onset temperature of superconductivity. Because the scattering is obviously due to a structural fluctuation, $Tl_2Ba_2Ca_2Cu_3O_{10}$ is understood to exhibit an enhancement of the fluctuation in a superconducting state. In addition, a careful analysis of the features in the scattering suggests that a dynamic displacement of an apical O atom in the CuO_5 pyramid along the c axis is responsible for the structural fluctuation in the superconducting state.

It was reported in our previous paper[1] that in $Tl_2Ba_2Ca_2Cu_3O_{10}$ with a T_c of about 130 K a structural fluctuation detected as diffuse scattering in electron diffraction is enhanced in the vicinity of T_c. However, because the previous experiment was limited to a temperature range between about 100 K and room temperature, the results obtained were insufficient to establish a correlation between the fluctuation and superconductivity. With the aid of a low-temperature stage with a liquid-helium reservoir, we have reexamined features of the structural fluctuation in $Tl_2Ba_2Ca_2Cu_3O_{10}$ by means of electron diffraction.

In this paper, we report the intensity distribution of diffuse scattering in reciprocal space and describe the details of the change in this intensity, which was obtained by using the low-temperature stage with the liquid-helium reservoir. Then, we identify atomic displacements corresponding to the structural fluctuation and briefly discuss a mechanism of the superconductivity in $Tl_2Ba_2Ca_2Cu_3O_{10}$ on the basis of the present results.

Both the procedure of the sample preparation and the details of the observation method were already described in the previous paper.[1] Sample pellets used in the present experiment were found to have an onset temperature of about 130 K and zero resistivity at about 117 K on the basis of electrical resistivity measurement. In this paper, the onset temperature is taken to be T_c. X-ray powder diffraction also gave the tetragonal system with lattice parameters of $a = 3.8593$ Å and $c = 35.704$ Å. A structural fluctuation was observed as diffuse scattering in electron-diffraction patterns by using an H-800-type electron microscope equipped with a low-temperature stage with the liquid-helium reservoir. The low-temperature experiment was carried out in the temperature range between about 20 K and room temperature.

In electron-diffraction patterns of $Tl_2Ba_2Ca_2Cu_3O_{10}$, there exists characteristic diffuse scattering, whose intensity is temperature dependent, in addition to ring-shape scattering around a fundamental spot. The ring-shape scattering has been already understood to be due to static displacements of Tl and O atoms in the Tl-O layer and is independent of temperature.[2,3] Hence, an important feature of the diffraction pattern is the existence of the temperature-dependent diffuse scattering. Figure 1 shows electron-diffraction patterns of $Tl_2Ba_2Ca_2Cu_3O_{10}$,

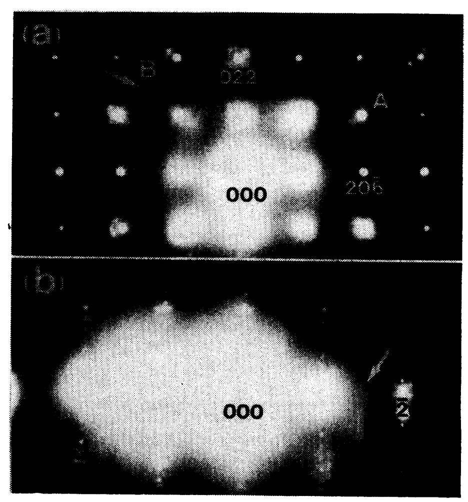


FIG. 1. Electron-diffraction patterns of $Tl_2Ba_2Ca_2Cu_3O_{10}$ at 23 K.

taken at 23 K. An electron incidence of Fig. 1(a) is nearly perpendicular to the $(3\bar{1}1)$ plane in reciprocal space. When the pattern of Fig. 1(b) was taken, a specimen was slightly rotated about the $[1\bar{1}0]$ direction from the [110] electron incidence in order to avoid double diffraction. In Fig. 1(a), the ring-shape scattering indicated by A is found around a fundamental spot. The temperature-dependent diffuse scattering is observed as a diffuse streak B connecting between two neighboring fundamental spots and an intensity maximum exists in the middle between them, as indicated by an arrow in Fig. 1(a). In addition, the scattering is seen as a diffuse streak along the [001] direction in Fig. 1(b). This implies that there are diffuse rods along the [001] direction in reciprocal space and the intensity maximum in Fig. 1(a) is a cross section of the diffuse rod. The most important feature of the diffuse rod is that no intensity can be detected around $l=0$, as shown by an arrow in Fig. 1(b).

As described in the previous paper,[1] the intensity of diffuse scattering increases remarkably around T_c on cooling. Figure 2 shows electron-diffraction patterns taken at 96 and 37 K. Electron incidences of these patterns are nearly parallel to the [110] direction. The diffuse streak is hardly detected at room temperature. When the temperature is lowered, the streak appears around T_c [Fig. 2(a)], and its intensity increases remarkably on further cooling [Fig. 2(b)]. In order to see this interesting change in the intensity easily, the intensity at each temperature was measured from an electron-diffraction pattern by photodensitometry. A change in the intensity of the diffuse streak at a position indicated by an arrow in Fig. 2(a) is shown in Fig. 3. Surprisingly, the remarkable increase in the intensity occurs in a temperature range between about 130 K (T_c) and about 40 K, and the intensity seems to reach a constant value below about 40 K. Note that the present experiment shows a reversible change in the intensity during the cooling and subsequent heating cycle. Because of the reversible change in addition to other features of the streak, the diffuse scattering is presumably thermal diffuse scattering due to low-frequency lattice vibrations, as described in the previous paper.[1] However, it is difficult to rule out the possibility that the scattering can be ascribed to static displacements of atoms. Anyhow, the structural fluctuation is understood to enhance in a superconducting state of $Tl_2Ba_2Ca_2Cu_3O_{10}$.

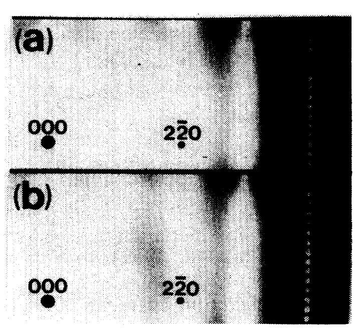


FIG. 2. Electron-diffraction patterns taken at (a) 96 K and (b) 37 K, respectively.

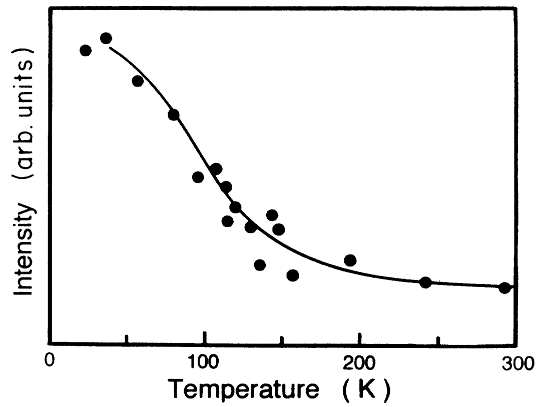


FIG. 3. Change in an intensity of the diffuse streak as a function of temperature. A signal ratio of the diffuse streak to the background, obtained by photodensitometry, is plotted as an intensity. The solid line is a visual guide.

The present experiment clearly shows that $Tl_2Ba_2Ca_2Cu_3O_{10}$ exhibits an enhancement of the structural fluctuation in the superconducting state. In order to understand the details of the structural fluctuation, we first identify atomic displacements for the fluctuation in $Tl_2Ba_2Ca_2Cu_3O_{10}$. In reciprocal space, the diffuse rod indicating the fluctuation exists along the c axis. This implies that atomic displacements corresponding to the fluctuation have a two-dimensional character. That is, only atoms in one layer are displaced coherently. Further, because the rod appears along a $(h/2)(k/2)$-type line with odd integer h and k, a two-dimensional fluctuation can be basically characterized as a transverse wave with $\mathbf{q}=\frac{1}{2}\langle 1,1,0\rangle$. In addition to these, the missing of the diffuse rod around $l=0$ shows that a polarization vector of the wave is parallel to the [001] direction; this involved a mistake, now corrected, on the specification of the polarization vector in our previous paper.[1]

Atomic displacements corresponding to the fluctuation are more concretely specified here. Note that the polarization vector of the wave is parallel to the [001] direction. On the basis of the x-ray-diffraction analysis of $Tl_2Ba_2Ca_2Cu_3O_{10}$ made by Kajitani *et al.*,[4] the mean-square displacement along the c axis u_{33} is found to be large for the apical O(3) atom of the CuO_5 pyramid, the O(2) atom in the Cu-O layer and the O(4) atom in the Tl-O layer. Because of both a remarkable increase in u_{33} on cooling as well as for a reason to be given later, a dynamic displacement of the apical O(3) atom along the c axis should be primarily responsible for the fluctuation in the superconducting state if the displacement has a dynamic nature. Then, a pattern for the displacements of the apical O(3) atoms, Fig. 4, is obtained from the two-dimensional wave with $\mathbf{q}=\frac{1}{2}\langle 1,1,0\rangle$. As is seen in the figure, the O(3) displacements are just antiferroelectric-type displacements in the Ba-O layer. In addition, the x-ray-diffraction analysis also indicates the existence of two sites along the c axis for the apical O(3) atoms.[4] Because of the existence of these two sites, the structural fluctuation found in the present work can be understood to be

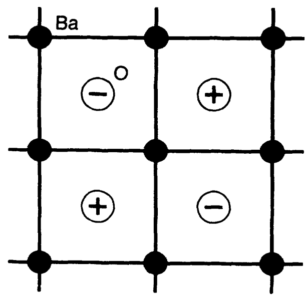


FIG. 4. Schematic representation for O(3) displacements in the Ba-O layer, predicted from features of the diffuse rod. The + and − signs indicate perpendicular displacements of oxygen atoms toward and away from the Tl-O layer, respectively.

directly related to the double-well potential for the O(3) atom. In other words, the structural-fluctuation enhancement in the superconducting state of $Tl_2Ba_2Ca_2Cu_3O_{10}$ seems to be the same phenomenon as the lattice instability proposed for both $YBa_2Cu_3O_7$ and $TlBa_2Ca_3Cu_4O_{11}$.[5-8] As for the O(4) atom in the Tl-O layer, displacements compatible with the features of the diffuse rod are also antiferroelectric-type ones, just as in the case of the apical O(3) atom. On the other hand, for the O(2) atom, the features predict a pattern of O(2) buckling, which is identical to that near and below T_c in $Tl_2Ba_2CaCu_2O_8$.[9] In the present work, it is impossible to determine whether or not all above-mentioned displacements actually take place.

We briefly describe a mechanism of the superconductivity in $Tl_2Ba_2Ca_2Cu_3O_{10}$ in terms of the structural fluctuation in the superconducting state. First of all, we have to say that the present results seem to be entirely consistent with the scenario proposed for both $YBa_2Cu_3O_7$ and $TlBa_2Ca_3Cu_4O_{11}$.[6,8] That is, the fluctuation related to the motion of the apical O(3) atom along the c axis could be coupled to the charge transfer between the Tl and apical O(3) atoms. The charge-transfer excitations reflect the dynamic polarizability along the c axis, which could then enhance the pairing of two holes in the Cu-O layer. Further, it was pointed out that a strong anharmonic O(3) motion derives large-amplitude Jahn-Teller or buckling modes. This buckling mode seems to be consistent with the O(2) buckling predicted in the present work. In addition, the charge transfer might result in the antiferroelectric-type displacements for the O(4) atom in the Tl-O layer as a polarizable layer. In other words, there is no essential discrepancy between the scenario mentioned above and the atomic displacements predicted on the basis of the present results if the dynamic displacement of the apical O(3) atom is responsible for the structural fluctuation. Eventually, the fluctuation found in the present work is expected to be directly related to the superconductivity in $Tl_2Ba_2Ca_2Cu_3O_{10}$.

In summary, we have examined the details of the structural fluctuation in $Tl_2Ba_2Ca_2Cu_3O_{10}$ by means of electron diffraction. As a result, the present experiment establishes the existence of the structural-fluctuation enhancement in the superconducting state of $Tl_2Ba_2Ca_2Cu_3O_{10}$. We suggest that the atomic displacement for the fluctuation is mainly due to the dynamic displacement of the apical O(3) atom in the CuO_5 pyramid along the c axis.

[1] Y. Koyama and H. Hoshiya, Phys. Rev. B **39**, 7336 (1989).

[2] J. D. Fitz Gerald, R. L. Withers, J. G. Thompson, L. R. Wallenberg, J. S. Anderson, and B. G. Hyde, Phys. Rev. Lett. **60**, 2797 (1988).

[3] S. Iijima, T. Ichihashi, Y. Shimakawa, T. Manako, and Y. Kubo, Jpn. J. Appl. Phys. **27**, L1061 (1988).

[4] T. Kajitani, K. Hiraga, S. Nakajima, M. Kikuchi, Y. Syono, and C. Kabuto, Physica C **161**, 483 (1989).

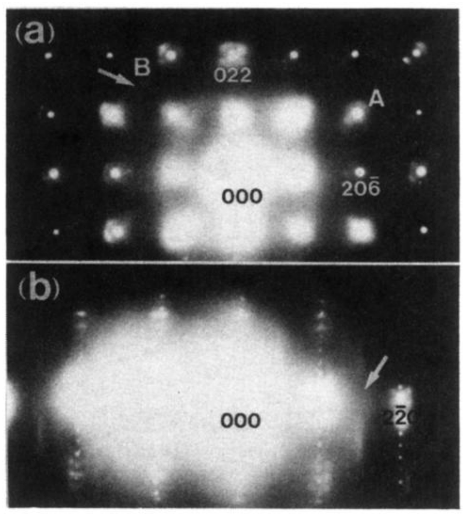
[5] S. D. Conradson and I. D. Raistrick, Science **243**, 1340 (1989).

[6] S. D. Conradson, I. D. Raistrick, and A. R. Bishop, Science **248**, 1394 (1990).

[7] J. M. de Leon, S. D. Conradson, I. Batistić, and A. R. Bishop, Phys. Rev. Lett. **65**, 1675 (1990).

[8] P. G. Allen, J. M. de Leon, S. D. Conradson, and A. R. Bishop, Phys. Rev. B **44**, 9480 (1991).

[9] B. H. Toby, T. Egami, J. D. Jorgensen, and M. A. Subramanian, Phys. Rev. Lett. **64**, 2414 (1990).



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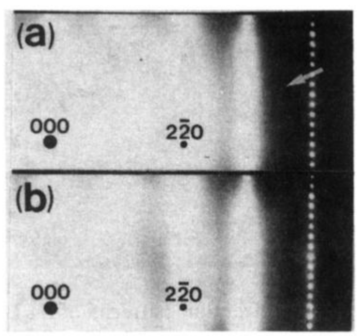

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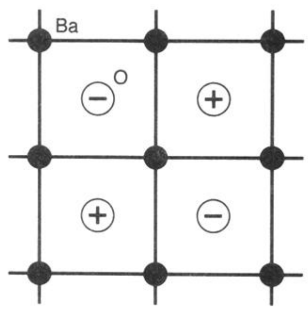

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