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Soft phonon mode in the high-T_c superconductor Tl-Ba-Ca-Cu-O

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Thermal diffuse scattering due to a transverse phonon (e∥[010]) propagating along the [100] direction was found in electron-diffraction patterns of Tl-Ba-Ca-Cu-O with T_c of 117 K. The scattering has an intensity maximum at the middle between two fundamental spots along the ⟨100⟩ directions and its intensity increases with decreasing temperature. That is, the Tl oxide with high T_c exhibits soft phonon behavior.

Superconductivity in superconducting oxides such as $La_{2-x}M_xCuO_4$ (M=Ba,Sr) and $YBa_2Cu_3O_{7-y}$ is one of the most interesting subjects in solid-state physics. In particular, the discovery of both Bi-Sr-Ca-Cu-O (Ref. 1) and Tl-Ba-Ca-Cu-O (Ref. 2) oxides provides a new group of superconducting oxides in regard to crystal structure. That is, both have layered structures including some CuO_2 layers which are responsible for superconductivity in the oxides.[3-5] It has been pointed out that there is a correlation between the number of CuO_2 layers and a transition temperature.[6]

The mechanism of superconductivity in the superconducting oxides has been discussed, but it is still an open question. On the basis of experimental data of ultraviolet photoemission spectroscopy and x-ray photoemission spectroscopy,[7,8] models based on a strong on-site Coulomb interaction, such as the resonating-valence-bond model,[9,10] seem to be appropriate at present. The isotope effect for oxygen atoms, that is, a small decrease in T_c by substitution of ^{18}O for ^{16}O, has been found, however, in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$.[11,12] This implies that an electron-phonon coupling at least plays an important role in the pairing mechanism. For this reason, so far we have investigated thermal diffuse scattering in $La_{2-x}M_xCuO_4$ (M=Ba,Sr) and $YBa_2Cu_3O_{7-y}$ by means of an electron-diffraction method.[13,14] It is known that thermal diffuse scattering is ascribed to low-frequency lattice vibrations in crystals. We have found characteristic thermal diffuse scattering in each material. As a series of our studies on superconducting oxides, we have examined features of thermal diffuse scattering in Tl-Ba-Ca-Cu-O in the present experiment.

Sheng and Hermann[2] found that one compound in the Tl-Ba-Ca-Cu-O system is a superconductor with the onset temperature near 120 K. Kikuchi *et al.*[5] showed that a crystal structure of the Tl oxide with T_c of about 120 K is a layered structure with lattice parameters a=5.4456 Å and c=35.587 Å. In the layered structure the layer sequence along the c axis is characterized by Tl_2O_2-BaO-CuO_2-Ca-CuO_2-Ca-CuO_2-BaO.

The mechanism of superconductivity in the Tl oxides, of course, remains unsolved, as in other superconducting oxides. In order to understand it, we believe that it is important to examine features of lattice vibrations. Especially, examination of low-frequency lattice vibrations is presumably crucial. This is because the low-frequency lattice vibrations would give rise to the strong electron-phonon coupling. As far as we know, these features have not been examined. In addition, because of T_c near 120 K, it is possible for us to investigate thermal diffuse scattering in the vicinity of T_c by means of electron microscopy, using a low-temperature stage equipped with a liquid-nitrogen reservoir. For this reason, we carried out electron-diffraction observation near T_c in the Tl oxide.

Ceramic powders were obtained by mixing Tl_2O_3, BaO, CaO, and CuO. A starting composition is Tl:Ba:Ca:Cu =2:1.4:2:2. After the powders were pressed into a pellet, it was sintered at 850 °C for 3 h and cooled slowly to room temperature. Electrical resistance of the obtained pellet against temperature is plotted in Fig. 1. The onset temperature and the zero-resistance temperature are found to be about 130 and 117 K, respectively. In this experiment the zero-resistance temperature of 117 K is regarded as T_c. In addition, x-ray powder diffraction gave a tetragonal unit cell with a=5.4579 Å and c=35.704 Å, so that the composition of the pellet is found to be Tl_2Ba_2-$Ca_2Cu_3O_z$ on the basis of data obtained by Parkin *et al.*[6] In order to examine thermal diffuse scattering, electron-diffraction patterns were taken by using a JEM-200CX electron microscope. The low-temperature experiment in this work was made using the low-temperature stage with the liquid-nitrogen reservoir. In the present low-temperature experiment, the lowest specimen temperature is about 95 K, which is higher than the temperature for liquid-nitrogen of 77 K. Flakes obtained by crushing the pellet were used as a specimen for the observation.

Figure 2 represents an electron-diffraction pattern of a Tl-Ba-Ca-Cu-O specimen taken at 100 K. An electron in-

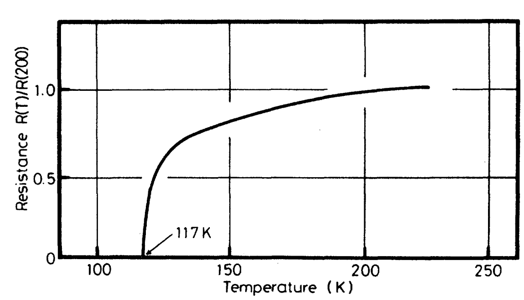

FIG. 1. Electrical resistance vs temperature for the pellet obtained in the present experiment.

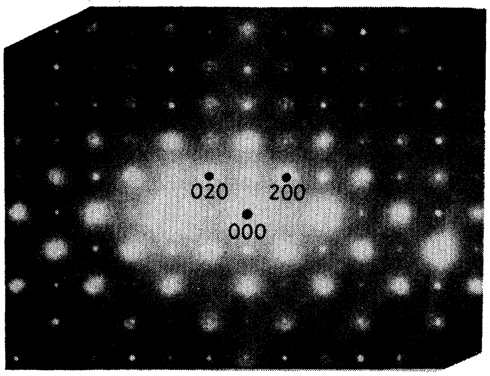

FIG. 2. An electron-diffraction pattern of a Tl-Ba-Ca-Cu-O flake obtained by crushing the pellet, taken at 100 K.

cidence is somewhat tilted from the [001] direction in order to detect diffuse scattering easily. Fundamental spots could be indexed in terms of the tetragonal system with lattice parameters $a=5.4579$ Å and $c=35.704$ Å. That is, the extinction rule for the fundamental spots coincides with that derived from the crystal structure of $Tl_2Ba_2Ca_2Cu_3O_z$ whose space group is $I4/mmm$.[5,6] In the pattern, two kinds of diffuse scatterings, indicated by A and B, are clearly seen. Diffuse scattering A appears around a fundamental spot. The same diffuse scattering has been found by other investigators.[15,16] As they have already discussed the details of the scattering, we shall not deal with them here.

A characteristic feature of the diffuse scattering in the Tl oxide is diffuse scattering B, which is located between two neighboring fundamental spots. Scattering B is observed as a nonradial diffuse streak. It should be noticed that the nonradial streaks have been commonly observed in electron- and x-ray diffraction patterns of many materials such as Al, Si, $BaTiO_3$, and $KNbO_3$.[17–19] In particular, the streaks in both $BaTiO_3$ and $KNbO_3$ are directly related to successive transitions that they undergo. According to the interpretation made by Komatsu and Teramoto,[20] the streak is due to thermal diffuse scattering that is ascribed to low-frequency lattice vibrations, and their polarization vectors are perpendicular to directions of the streaks. The nonradial streak in the Tl oxide is hence interpreted as thermal diffuse scattering due to low-frequency vibrations with polarization vectors parallel to the ⟨100⟩ directions. In addition to this, because an intensity maximum of the streak is found at the middle between two fundamental spots along the ⟨100⟩ directions, the lattice vibration can be identified as a transverse phonon with $\mathbf{q}=[100]$, whose polarization vector is parallel to the [010] direction. That is, this phonon is a phonon mode at a zone boundary of the Brillouin zone (BZ) along the [110] direction of another tetragonal system with lattice parameters $a'=a/\sqrt{2}=3.8593$ Å and $c'=c=35.704$ Å. Directions of the a and b axes in the tetragonal system with a' and c' are rotated by 45° with respect to those with a and c, while the c axis is common to both systems.

An intensity of the streak was found to exhibit a remarkable change with decreasing temperature. Figure 3

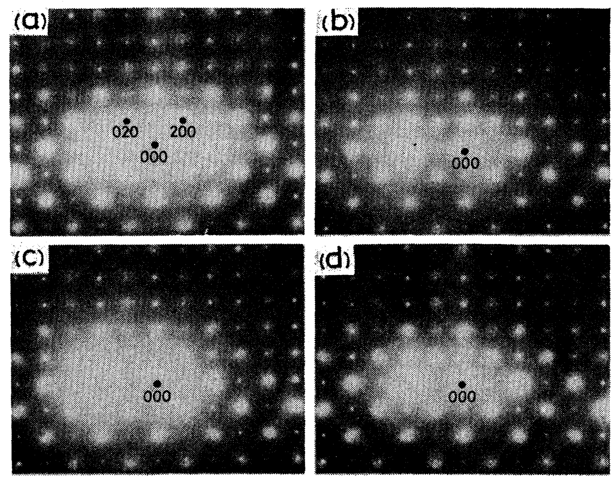

FIG. 3. Electron-diffraction patterns of the $Tl_2Ba_2Ca_2Cu_3O_z$ flake, taken at (a) room temperature, (b) 232 K, (c) 156 K, and (d) 100 K, respectively. An electron incidence is nearly parallel to the [001] direction.

represents a series of electron-diffraction patterns of the $Tl_2Ba_2Ca_2Cu_3O_z$ flake taken at room temperature, 232, 156, and 100 K, respectively. These patterns were taken under the same diffraction conditions in order to compare intensities at various temperatures. The streak at room temperature never had a strong intensity. When the temperature was lowered from room temperature, the intensity of the streak increased. The intensity at the zone boundary along the [100] direction is plotted against temperature in Fig. 4. In the present experiment the intensity at a point, which is marked in each pattern of Fig. 3, was actually measured from 18 diffraction films by photodensitometry and is normalized with respect to that at 100 K. It is found that the intensity approximately increases linearly in the temperature range between room temperature and 110 K with decreasing temperature. The most striking feature is that a remarkable increase occurs near 100 K. Note that the change in the intensity is reversible during a cycle of cooling and heating and is common to all

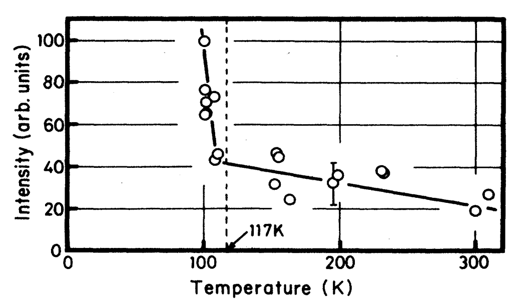

FIG. 4. Temperature dependence of the diffuse intensity at a point, which is marked in each pattern of Fig. 3. The error bar is indicated only for one plotted point because the magnitude of the error is the same for all points. The dashed line represents the zero-resistance temperature of 117 K and the solid line is a visual guide.

the other nonradial streaks. Based on the theory of thermal diffuse scattering, the intensity of the first-order thermal diffuse scattering is inversely proportional to a square of a phonon frequency. Therefore, the increase in the intensity on cooling represents the softening of the transverse phonon. It should be remarked that in the present experiment the increase in the diffuse intensity is, of course, observed in all flakes, showing the same diffraction patterns as those of Figs. 2 and 3.

Let us evaluate an effect of a magnetic field produced by the objective lens of the electron microscope on the superconducting transition. The field is of the order of 1 kOe. Very recently, Iwasaki *et al.*[21] examined upper and lower critical fields in the Tl oxides. According to their results, the coherence length and the penetration depth at 0 K in the Tl oxide are, respectively, 18 and 1400 Å, and the superconducting state under the field of 1 kOe is the vortex line state. In addition, the field makes the superconducting transition broad. That is, the onset temperature at which the rapid decrease in the electrical resistance starts is affected slightly, but the zero-resistance temperature is expected to decrease greatly. Although no intensity below 95 K could be measured in the present experiment because of the use of the low-temperature stage with the liquid-nitrogen reservoir, it seems surprising that the remarkable change in the diffuse intensity occurs in the temperature range where the superconducting transition occurs. Accordingly, the soft phonon mode of the transverse phonon is concluded to occur in a normal state of the high-T_c superconductor Tl-Ba-Ca-Cu-O on the basis of the obtained results.

It is time to discuss possible atomic displacements expected from the coupling of the phonons found in the present experiment in relation to superconductivity. As is well known in materials having the perovskite structure, the condensation of a phonon mode at a zone boundary, that is, R_{25} or M_3 modes, results in the rotation of the O octahedra. In analogy to these materials, it is expected that in the Tl oxide the coupling leads to atomic displacements related to the rotation of the O square surrounding the Cu atom in the CuO_2 layer. Note that this motion is never a unique one because it is impossible to determine an element whose displacements are responsible for the soft phonon mode. If the phonon mode is due to the displacement of the Cu atom instead of the O atom, the Cu-dimerization motion results from the coupling of the phonons. Here, the following remarks should be made. In $SrTiO_{3-x}$ it has been pointed out that soft optical phonons with $q=0$ resulting from the condensation of the R_{25} mode can interact with the conduction electrons.[22] It also seems that the Cu-dimerization motion gives rise to the strong hole-phonon coupling if the hole responsible for the supercurrent exists in the O p orbital. That is, it is possible to relate both the rotation of the O square and the Cu-dimerization motion to superconductivity. Unfortunately, on the basis of the experimental results presented here, the actual motion cannot be determined. We believe, however, that our finding provides an important guide for future studies to elucidate the mechanism of the superconductivity in the superconducting oxides.

In conclusion, we found the soft phonon mode in the normal state of the Tl superconducting oxide. In this material, the phonon mode exhibiting the soft mode is the transverse phonon with a polarization vector parallel to the [010] direction, propagating along the [100] direction. Finally, we have to say that in order to confirm our experimental results, the detailed study of lattice vibrations in the Tl oxide using the neutron-diffraction method is definitely needed.

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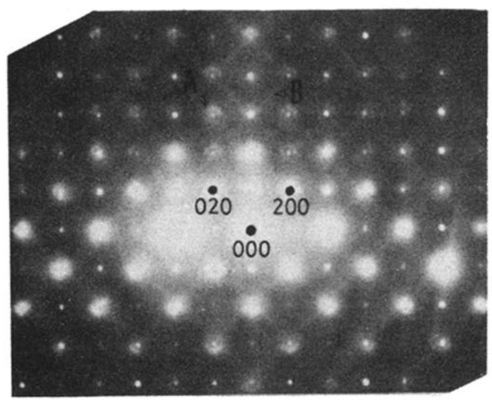

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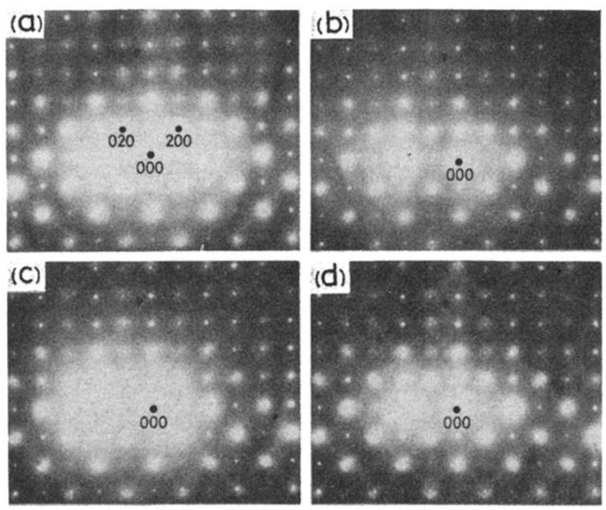

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