PHYSICAL REVIEW B VOLUME 56, NUMBER 22 1 DECEMBER 1997-II

Far-infrared reflectivity along the c axis in $La_2CuO_{4+\delta}$, $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$, and $Nd_2CuO_{4-x}F_x$ single crystals

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(Received 22 August 1997)

The far-infrared reflectivity along the c axis in $La_2CuO_{4+\delta}$, $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$ (double pyramidal planes), and $Nd_2CuO_{4-x}F_x$ (T' phase) single crystals is measured down to 9 cm^{-1}. All the insulating spectra in the normal states change to show a sharp plasma edge in the superconducting state, which confirms our earlier report of sphere resonance of powder samples [Shibata and Yamada, Phys. Rev. B **54**, 7500 (1996)]. The edge of $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$ is broader than that of $La_2CuO_{4+\delta}$ and $Nd_2CuO_{4-x}F_x$, indicating the existence of a large number of unpaired carriers in the superconducting state. The obtained c-axis penetration depth λ_c is discussed based on the Josephson-coupled layer model. [S0163-1829(97)51746-2]

It is well known that the electronic structure of high-temperature copper oxide superconductors has a strong anisotropy, which is typically shown as the metallic temperature dependence of ρ_{ab} and the semiconductive temperature dependence of ρ_c. In optical measurement, almost-insulating infrared spectra are observed along the c axis in the normal state, in contrast to the metal-like spectra along the ab plane. In the superconducting state, a sharp reflectivity edge is observed along the c axis in the far-infrared region. The reflectivity edge is regarded as the plasma edge of condensed carriers in the superconducting state, and the frequency of the edge is determined by the zero crossing of $\epsilon_1(\omega)$. The plasma edge has been observed in $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{6+\delta}$, $YBa_2Cu_4O_8$, and $Pb_2Sr_2(Y,Ca)Cu_3O_8$ from the c-axis reflectivity measurement of single crystals.[1–5] We have previously measured the sphere resonance of various high-T_c powder samples and have shown that the plasma also exists in $Bi_{1.85}Pb_{0.35}Sr_2Ca_2Cu_{3.1}O_y$ (Bi2223), $La_{1.82}Ca_{1.18}Cu_2O_{6+\delta}$, $(Nd_{0.66}Sr_{0.205}Ce_{0.135})_2CuO_4$ (T* phase), $(Ba_{0.56}Sr_{0.44})_2Cu_{1.1}O_{2.2+\delta}(CO_3)_{0.9}$ (copper-oxycorbonate), $Pr_{1.85}Ce_{0.15}CuO_4$, and $Nd_2CuO_{4-x}F_x$, which means that the plasma exists in most high-T_c cuprates.[6] However, for a detailed investigation of their properties, measurement using single crystals is necessary.

Although it seems quite difficult to grow single crystals of Bi2223, T* phase, and copper-oxycorbonate,[7] high-quality single-crystal growth of $La_{1.82}Ca_{1.18}Cu_2O_{6+\delta}$ and $Nd_2CuO_{4-x}F_x$ have been reported.[8–10] The present paper first reports the measurements of far-infrared reflectivity along the c axis in $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$ and $Nd_2CuO_{4-x}F_x$ single crystals down to 9 cm^{-1}. We also report the measurement of $La_2CuO_{4+\delta}$ single crystal, which did not show a plasma edge down to 30 cm^{-1}.[11] All the spectra show insulating behavior in the normal states, and they change to show a sharp plasma edge in the superconducting state. The plasma is identified as the Josephson plasma oscillation in the weakly Josephson-coupled layer superconductors, and the c-axis penetration depth λ_c is discussed based on this model.

Large single crystals of $La_2CuO_{4+\delta}$ with the dimensions $1\times4\times4$ mm^3 were grown by the traveling-solvent-floating-zone (TSFZ) method and oxidized by high oxygen pressure annealing.[12] The sample showed a bulk superconductivity with T_c=33 K from the magnetic susceptibility measurement, as shown in Fig. 1. It has been revealed that there are two superconducting phases in $La_2CuO_{4+\delta}$, one having δ=0.11–0.12 with T_c=40–45 K and the other δ= 0.06–0.08 with T_c=32–34 K.[13] Although we did not determine the oxygen content, T_c=33 K suggests that the excess oxygen content δ of the sample is about 0.06. The $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$ crystals were grown by the conventional CuO flux method and also oxidized by high oxygen pressure annealing.[8] They showed a bulk superconductivity with T_c= 47 K as shown in Fig. 1. The typical sample size was $3\times3\times0.5$ mm^3. $Nd_2CuO_{4-x}F_x$ crystals with the dimensions $4\times4\times0.4$ mm^3 were also grown by the CuO flux method.[10] These were deoxidized in Ar atmosphere. As shown in Fig. 1, they showed a bulk superconductivity with T_c=21 K.

The polarized reflectivity measurements for $\mathbf{E}\|c$ were carried out down to 9 cm^{-1} using a rapid scan interferometer with a Si bolometer operated at 1.5 and 4 K.[6] In order to obtain sufficient size for the far-infrared measurement along $\mathbf{E}\|c$, three $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$ crystals and ten

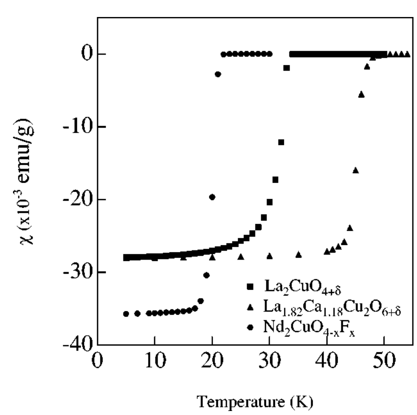

FIG. 1. Magnetic susceptibilities in $La_2CuO_{4+\delta}$, $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$, and $Nd_2CuO_{4-x}F_x$. The measurements were performed under a magnetic field of 5 G, after cooling in zero field, without correction for demagnetization.

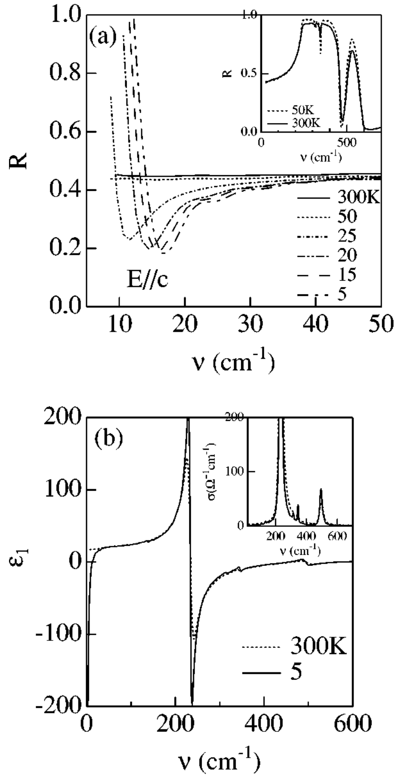

FIG. 2. (a) Infrared reflectivity spectra ($\mathbf{E}\|c$) of $La_2CuO_{4+\delta}$ single crystal. (b) Real part of dielectric function and real part of conductivity (inset) obtained from the Kramers-Kronig transformation of the reflectivity spectra.

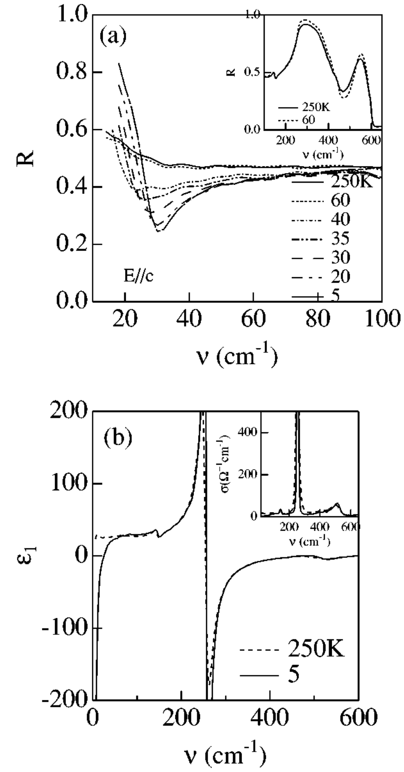

FIG. 3. (a) Infrared reflectivity spectra ($\mathbf{E}\|c$) of $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$ single crystal. (b) Real part of dielectric function and real part of conductivity (inset) obtained from the Kramers-Kronig transformation of the reflectivity spectra.

$Nd_2CuO_{4-x}F_x$ crystals were stacked and bonded, and the side of each stack was polished. After the measurement of the spectra, the sample was coated *in situ* with gold and then the reference spectra were measured.[2] The spectra were calibrated to room-temperature data, which was measured between 250 and 20 000 cm^{-1} using a microscope for unbonded crystals.[14,15]

Figure 2(a) shows the reflectivity spectra for $\mathbf{E}\|c$ of $La_2CuO_{4+\delta}$. The room-temperature spectra agree well with earlier results for undoped La_2CuO_4. However, as the temperature decreases, a very weak structure not observed in the undoped sample appears just below the phonon peak at 512 cm^{-1}. This structure has been more clearly observed in electrochemically oxidized $La_2CuO_{4+\delta}$ with T_c=40 K and δ=0.12, and is attributed to the splitting of the apical oxygen vibration mode along the c axis due to the incorporation of additional oxygen.[11] The observed weaker structure can be explained by the smaller oxygen content in the sample. The reflectivity below 50 cm^{-1} slightly decreases as the temperature decreases, which corresponds to the semiconducting temperature dependence of the dc conductivity. The insulating spectra in the normal state change to show a sharp reflectivity edge in the superconducting state, which is identified as the plasma edge of condensed carriers. As shown in Fig. 2(b), the real part of the dielectric function $\epsilon_1(\omega)$, which is calculated by the Kramers-Kronig transformation, crosses zero below T_c.

Similar spectra for $\mathbf{E}\|c$ are also observed in $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$, as shown in Fig. 3(a). The normal-state reflectivity is dominated by three strong optical phonons at 146, 256, and 512 cm^{-1} and does not show the plasma edge. The reflectivity below 50 cm^{-1} slightly increases as ω approaches 0 cm^{-1}, suggesting the existence of overdamped Drude conductivity, which is consistent with the weakly metallic temperature dependence of $\rho_c (d\rho_c/dT>0)$.[9,16] In the superconducting state, the reflectivity edge due to the plasma of condensed carriers appears, which is confirmed by the zero crossing of $\epsilon_1(\omega)$ in Fig. 3(b). The frequency of the edge well corresponds to the previously observed absorption peak for powder samples.[6] The spectra do not change below 10 K, however, the edge at 5 K is not as sharp as that of $La_2CuO_{4+\delta}$. It suggests the existence of unpaired carriers, which is discussed later.

Figure 4 shows the far-infrared reflectivity spectra for $\mathbf{E}\|c$ of $Nd_2CuO_{4-x}F_x$. As with $La_2CuO_{4+\delta}$ and $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$, the insulating spectra in the normal state change to show a reflectivity edge of condensed carriers in the superconducting state. Again, the frequency of the edge well corresponds to the absorption peak of powder samples.[6] The edge is very sharp, suggesting the absence of residual conductivity in this frequency region.

Usually, the c-axis penetration depth λ_c is directly obtained from the sum rule analysis of $\sigma_1(\omega)$ and/or from $\epsilon_1(\omega)$, which are determined by the Kramers-Kronig transformation. In this case, we determine λ_c by fitting the reflectivity to avoid the error of absolute reflectivity and low-

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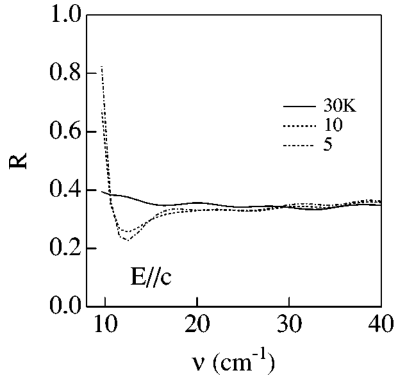

FIG. 4. Far-infrared reflectivity spectra ($\mathbf{E}\|c$) of $Nd_2CuO_{4-x}F_x$ single crystal.

frequency extrapolation in Kramers-Kronig transformation. We assume the low-frequency dielectric function of superconductors at 5 K can be written by the two-fluid model such that

$$\epsilon(\omega)=\epsilon_\infty-\frac{\omega_{ps}^2}{\omega^2}-\frac{\omega_{pn}^2}{\omega(\omega+i\gamma)}, \tag{1}$$

where ϵ_∞, ω_{ps}, ω_{pn}, and γ are the high-frequency dielectric constant, plasma frequency of condensed carrier, plasma frequency, and scattering rate of normal component. In this equation, the Drude formula temporarily expresses the residual conductivity within the superconducting gap region. Assuming the dielectric function of Eq. (1), the reflectivity $R(\omega)$ below 50 cm^{-1} at 5 K in Fig. 2(a) is fitted by the relation

$$R(\omega)=\left|\frac{1-\sqrt{\epsilon(\omega)}}{1+\sqrt{\epsilon(\omega)}}\right|^2. \tag{2}$$

The fit gives $\epsilon_\infty=26.1$ and $\omega_{ps}=75.6$ cm^{-1}, which gives the c-axis penetration depth $\lambda_c=21$ μm although ω_{pn} and γ cannot be simultaneously determined. The details of the above fitting procedure for $La_{2-x}Sr_xCuO_4$ have been discussed by Kim *et al.*[17] The same fitting in Fig. 3(a) gives $\epsilon_\infty=27$ and $\omega_{ps}=160$ cm^{-1}, which gives $\lambda_c=13$ μm for $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$, and the fitting in Fig. 4 gives $\epsilon_\infty=20$ and $\omega_{ps}=50$ cm^{-1}, which gives $\lambda_c=32$ μm for $Nd_2CuO_{4-x}F_x$.

These large c-axis penetration depths can be explained by the Josephson-coupled layer model along the c axis. In the model, λ_c is equal to the Josephson penetration depth λ_J, which is expressed as

$$\lambda_J=\sqrt{\frac{\hbar c^2\rho_c}{4\pi^2\Delta}}, \tag{3}$$

where Δ is the superconducting gap value.[1,4,6] Assuming that $\rho_c=3$ Ω cm and $2\Delta=180$ cm^{-1} for $La_2CuO_{4+\delta}$ and 4 Ω cm and 105 cm^{-1} for $Nd_2CuO_{4-x}F_x$,[18,19] $\lambda_c=21$ μm for $La_2CuO_{4+\delta}$ and $\lambda_c=32$ μm for $Nd_2CuO_{4-x}F_x$ are deduced from Eq. (3). It has been shown that the model also explains the value of λ_c in other cuprates such as $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6+x}$,[1,3,4,6] and it confirms that the observed plasma edge is Josephson plasma oscillation in Josephson-coupled layer superconductors. For the definitive study of the Josephson plasma oscillation, optical measurement under magnetic field is necessary, as has been done for $Bi_2Sr_2CaCu_2O_y$ in the microwave region.[20]

Although the Josephson-coupled layer model well describes the λ_c of many high-T_c cuprates, a significant deviation from the model is observed in the case of $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$. The observed value of $\lambda_c=13$ μm is much longer than the value of $\lambda_c=2.6$ μm expected from the model assuming $2\Delta=200$ cm^{-1} and $\rho_c=0.1$ Ω cm, which was obtained from the transport measurement.[9,16] The discrepancy arises because the model does not take into account the existence of large numbers of unpaired carriers in the superconducting state. Due to these unpaired carriers as shown in Fig. 3(a), the superfluid density in $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$ becomes smaller, and λ_c increases. Numerous unpaired carriers are also observed in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6+\delta}$ in the overdoped region, and their existence has been claimed to be an inherent property of high-T_c cuprates in the overdoped region.[1,3] However, it seems hopeless to explain these unpaired carriers as an inherent property in the overdoped region or to attribute them to thermal excitation of quasiparticles, since $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$ is in the light-doped region and the reflectivity spectra do not change below 10 K.[14,16] In this case, the existence of the large number of unpaired carriers may come from a strong disorder effect in the gap with nodes, since there are La and Ca disorder and oxygen vacancies between two CuO_2 planes in $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$.

The value of λ_c is much longer than the in-plane penetration depth λ_{ab} of 0.42 μm for $La_2CuO_{4+\delta}$ and λ_{ab} of 0.13 μm for $Nd_{1.85}Ce_{0.15}CuO_4$, which were estimated from μSR and microwave absorption measurements.[21,22] The anisotropy λ_c/λ_{ab} for $La_2CuO_{4+\delta}$ is 50, which is almost equal to the value for $La_{1.92}Sr_{0.08}CuO_4$.[1] Since the hole doping level of $La_2CuO_{4+\delta}$ with $T_c=33$ K is almost equal to the level of $La_{1.92}Sr_{0.08}CuO_4$,[13] the present result indicates that the $(La,Sr)_2O_2$ layer and $La_2O_{2+\delta}$ layer have the same insulating nature of a buffer layer between CuO_2 planes. On the other hand, the anisotropy λ_c/λ_{ab} for $Nd_2CuO_{4-x}F_x$ is 250, which means that the insulating nature of the $Nd_2O_{2-x}F_x$ layer is stronger than that of the $La_2O_{2+\delta}$ layer.

In conclusion, we have measured the far-infrared reflectivity for $\mathbf{E}\|c$ in $La_2CuO_{4+\delta}$, $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$, and $Nd_2CuO_{4-x}F_x$ single crystals down to 9 cm^{-1}. All the insulating spectra in the normal states change to show a sharp plasma edge in the superconducting state, which is identified as Josephson plasma oscillation in the Josephson-coupled layer superconductors. In $La_{1.89}Ca_{1.11}Cu_2O_{6+\delta}$, there are a large number of unpaired carriers in the superconducting state. The c-axis penetration depth λ_c has been discussed based on the model.

We would like to thank Dr. A. Matsuda for valuable discussions.

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