Observation of the Josephson plasma reflectivity edge in the infrared region in Bi-based superconducting cuprates

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The far-infrared c-axis optical reflectivity spectra of a heavily Pb-doped Bi2212, $Bi_{1.6}Pb_{0.6}Sr_{1.8}CaCu_2O_y$, single crystal ($T_c=65$ K) were measured in the superconducting state. The crystal was found to be carrier overdoped as the optical phonons are weakly screened by the electronic excitations in the far-infrared region. Below T_c, a sharp reflectivity edge was observed, corresponding to the appearance of the Josephson plasma in the superconducting state. The plasma edge frequency reached 40 cm^{-1} at 8 K, which is comparable with that observed for other cuprates with much less anisotropy. The c-axis penetration depth $\lambda_c=12.6\ \mu m$ was estimated from the unscreened plasma frequency $\omega_{ps}^c=126.2\ cm^{-1}$. This λ_c value is one order of magnitude smaller than that of the optimally doped pure Bi2212, reflecting a drastic enhancement of the interlayer coupling in Pb-doped Bi2212.

It is known that the superconductivity in the high-T_c superconducting cuprates (HTSCs) is two dimensional. This is partly caused by the characteristic crystal structure consisting of alternate stacking of superconducting CuO_2 planes and insulating blocking layers along the c axis. In the superconducting state, carriers move in the c direction by tunneling the blocking layers via the Josephson interlayer coupling, and the superconducting properties of HTSC are strongly affected by the strength of this coupling. Observation of the Josephson plasma reflectivity edge is one of the most powerful probes for evaluation of such interlayer coupling. In general, the c-axis spectra of HTSC compounds are semiconductive in the normal state, reflecting an incoherent carrier dynamics. Below T_c, however, a restoration of the coherency occurs and a sharp reflectivity edge appears in the far-infrared regime.[1,2] The Josephson plasma frequency ω_{ps}^c or the c-axis penetration depth $\lambda_c \equiv c/\omega_{ps}^c$, where c denotes the velocity of the light, is a physical parameter which directly measures the strength of the interlayer coupling and thus gives direct information on the anisotropy in the superconducting state which is essential in understanding the flux-pinning behaviors of HTSC.[3]

$Bi_2Sr_2CaCu_2O_y$ (Bi2212) is the most anisotropic HTSC compounds due presumably to the thick blocking layers consisting of insulating BiO double layers. Therefore, ω_{ps}^c is expected to be very low, far outside the experimentally observable window in the conventional infrared measurements.[4,5] Indeed, microwave measurements have shown an absorption peak in Bi2212 single crystals at less than 10 cm^{-1} under magnetic fields applied parallel to the c axis, and this peak has been identified as the Josephson plasma resonance.[6] Recently, we have found that the anisotropy of Bi2212 in the normal state is drastically reduced by Pb doping through in-plane (ρ_a and ρ_b) and out-of-plane (ρ_c) resistivity measurements.[7] For a heavily Pb-doped $Bi_{1.6}Pb_{0.6}Sr_{1.8}CaCu_2O_y$ single crystal with $T_c=65$ K, the anisotropy parameter $\gamma^2 \equiv \rho_c/(\rho_a\rho_b)^{1/2} \sim 1.2\times 10^3$ was obtained at 100 K; this value is approximately one order of magnitude smaller than that of nominally overdoped Bi2212 without Pb, and is comparable to that of less anisotropic cuprates, such as $La_{2-x}Sr_xCuO_4$ (LSCO) and $YBa_2Cu_3O_y$ (YBCO) in the underdoped regime.[8] However, the measurement of ρ_c for such an extremely anisotropic system is subject to large uncertainty and the effect of Pb substitution is not yet clear. It is also nontrivial if the reduced anisotropy persists in the superconducting state.

In the present study, we have carried out the c-axis reflectivity measurements in the infrared region on a heavily Pb-doped Bi2212 single crystal. We report here that the Josephson plasma edge can be pushed into the observable infrared optical frequency region by the Pb doping even in the extremely anisotropic Bi2212 system.

Bi(Pb)2212 single crystals were grown by the floating zone technique[7,9] from a feed rod with a nominal cation ratio of Bi:Pb:Sr:Ca:Cu=1.6:0.6:1.8:1.0:2.0. These cation compositions of the grown crystals were determined by ICP (inductively coupled plasma) analysis as Bi:Pb:Sr:Ca:Cu $=1.7_6:0.4_6:1.8_9:1.0_2:2.0$. Thin plate crystals with c axis along the shortest dimension were picked up from the grown boule and cleaved to obtain fresh surfaces. The crystals with a typical dimension of $2\times 2\times 0.1\ mm^3$ were treated at 400 °C for 72 h in a sealed quartz tube with pure oxygen gas of the effective pressure $P=2.1$ atm. Magnetization measurements using a superconducting quantum interference device (SQUID) magnetometer showed T_c(midpoint)$=65$ K with $\Delta T_c<5$ K. Since the maximum T_c of the Bi(Pb)2212

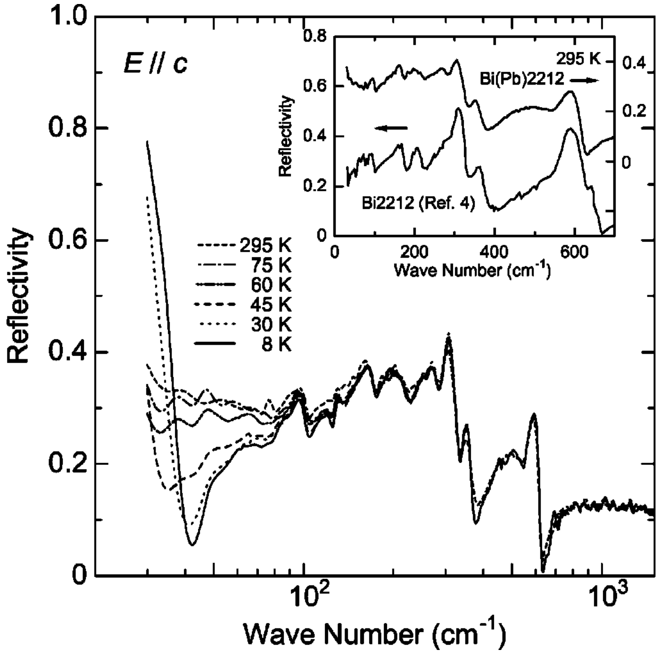

FIG. 1. c-axis reflectivity spectra of $Bi_{1.6}Pb_{0.6}Sr_{1.8}CaCu_2O_y$ single crystal at various temperatures. The inset represents the room-temperature spectra of Bi(Pb)2212 in the present study and pure Bi2212 in Ref. 4.

system is reported to be ~96 K,[10] this significant decrease of T_c is suggestive of carrier overdoping in the present compound. A mosaic sample, which consists of ten pieces of these crystals piled up and molded in an epoxy resin, was prepared and polished along a face parallel to the c axis using alumina powders. Polarized reflectivity measurements were performed using a fast-scan Fourier transform spectrometer (Bruker IFS 113v) in the far- and mid-infrared range ($30-4000\,\mathrm{cm}^{-1}$) and at temperatures between 8 and 295 K. Spectra were taken by detecting the reflection from this mosaic crystal. It should be noted, however, that the reflectance of our sample unavoidably contains small signals from the surrounding epoxy surface. We confirmed that the epoxy resin shows rather featureless structure in its reflectivity with a small absolute value of less than 10% in the whole frequency range of 30–4000 cm^{-1}, and is almost temperature independent between 8 and 295 K. Reflectivity spectra of the crystals were obtained by subtracting contributions of the epoxy resin from the original sample spectra.

Figure 1 shows the c-axis reflectivity spectra of our Bi(Pb)2212 crystal at various temperatures. At 295 K, the spectrum has semiconductive features, i.e., a relatively low reflectivity in the whole frequency range down to 30 cm^{-1} with a few pronounced phonon peaks. The phonon spectrum of the present compound is very similar to that of pure Bi2212 for $E_{\parallel c}$ (Ref. 4) as seen in the inset of Fig. 1. However, in contrast to the spectrum for pure Bi2212, the phonons are screened although still weakly, and a slight rise of the reflectivity toward lower energy is seen in the frequency region below 50 cm^{-1}. These imply an existence of the electronic contribution. No appreciable change is observed in the spectrum down to 75 K except for sharpening of the phonon peaks until the sample is cooled below T_c. An edge structure develops with lowering temperature, and at 8 K, a sharp reflectivity edge is observed at around 40 cm^{-1}. From the similarities of the behavior reported in the c-axis reflectivity of LSCO (Refs. 1,2) and YBCO (Ref. 11) systems, the observed edge here is associated with the c-axis plasma mode of superconducting carriers, presumably corresponding to a Josephson plasmon. Appearance of a sharp edge below T_c indicates that the superconducting gap energy is much larger than this edge energy (=the screened plasmon energy).

In the present study, we thus successfully observed the Josephson plasma reflectivity edge in the present Bi-based cuprate which has the largest electromagnetic anisotropy among the known HTSC compounds. The fact that the Josephson plasma edge appears in the infrared reflectivity spectrum is the most convincing evidence for the remarkably reduced anisotropy of Bi(Pb)2212 in the superconducting state. This feature is quite consistent with our out-of-plane resistivity measurements for $Bi_{2.1-x}Pb_xSr_{1.8}CaCu_2O_y$ single crystals in Ref. 7. The magnitude of ρ_c systematically decreases with increasing Pb content x, whereas no appreciable change has been observed in ρ_a or ρ_b by Pb doping, leading to a rapid decrease of resistivity anisotropy $\gamma^2 = \rho_c/(\rho_a\rho_b)^{1/2}$ with increasing Pb content. Cooper *et al.* have reported in Ref. 12 the ρ_c-T curve of pure Bi2212 single crystal. From the reported T_c and temperature dependence of ρ_{ab} and ρ_c, we believe that the crystal in Ref. 12 is in the optimally carrier-doped state. Their pure Bi2212 shows $\rho_c \sim 12\,\Omega$ cm at 100 K. This value is by a factor of ~60 larger than that of our heavily Pb-doped Bi2212 ($x = 0.6$): $\rho_c = 0.21\,\Omega$ cm at 100 K.

The reflectivity spectra were next transformed into the complex dielectric function $[\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)]$ by Kramers-Kronig (KK) analysis. It was necessary to extrapolate the lowest frequency range between 0 and 30 cm^{-1} for the KK analyses. In the normal state, we applied the Hagen-Rubens formula using the c-axis dc resistivity (ρ_c) measured in Ref. 7. On the other hand, in the superconducting state, it is important to decide how the reflectivity approaches unity. In the previous study for c-axis spectra of LSCO,[2] it was found that the real part of the dielectric function $\epsilon_1(\omega)$ in the superconducting state is well approximated as $\epsilon_1^s(\omega) = \epsilon_\infty - (\omega_{\mathrm{ps}}^c)^2/\omega^2$ in the lowest frequency regime. In the present study, the reflectivity spectrum at 8 K was extrapolated so that this formula was well fitted above and below the detection limit (30 cm^{-1}).[13]

Figure 2 shows the real part of the dielectric function $\epsilon_1(\omega)$ of Bi(Pb)2212 for $E_{\parallel c}$ at various temperatures. In the normal state (295 K and 100 K), $\epsilon_1(\omega)$ was positive and almost constant (~10) below the lowest phonon band at 90 cm^{-1}, whereas at 8 K it rapidly decreased and then changed its sign showing a characteristic of the superconducting state. The reflectivity edge was determined to be 38.4 cm^{-1} by the zero crossing point of $\epsilon_1(\omega)$. This value corresponds to the screened plasma frequency $\omega_{\mathrm{p}}^c = \omega_{\mathrm{ps}}^c/\sqrt{\epsilon_\infty}$ associated with the superconducting carriers along the c axis. On the other hand, $\epsilon_\infty = 11.5$ and $\omega_{\mathrm{ps}}^c = 126.2\,\mathrm{cm}^{-1}$ $(=2.38\times 10^{13}\,\mathrm{s}^{-1})$ were obtained from the $\epsilon_1^s(\omega)$ vs ω^{-2} plot. The value of $\epsilon_\infty = 11.5$ was nearly the same as that of pure Bi2212 ($\epsilon_\infty = 12$) in Ref. 4. The c-axis penetration depth $\lambda_c = c/\omega_{\mathrm{ps}}^c$ is then calculated to be 12.6 μm. For our Pb-doped Bi2212 crystal, we have

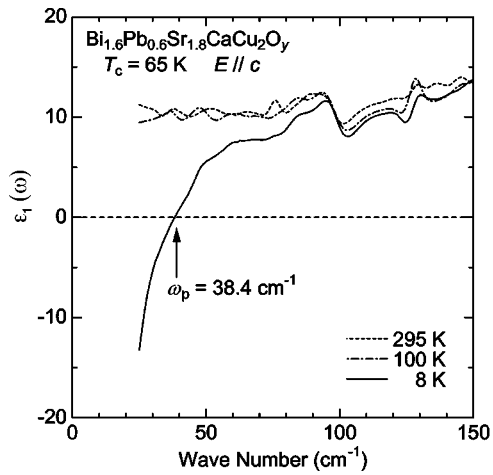

FIG. 2. Real part of the dielectric function of $Bi_{1.6}Pb_{0.6}Sr_{1.8}CaCu_2O_y$ single crystal at 8, 100, and 295 K obtained from Kramers-Kronig analysis on the *c*-axis reflectivity spectra.

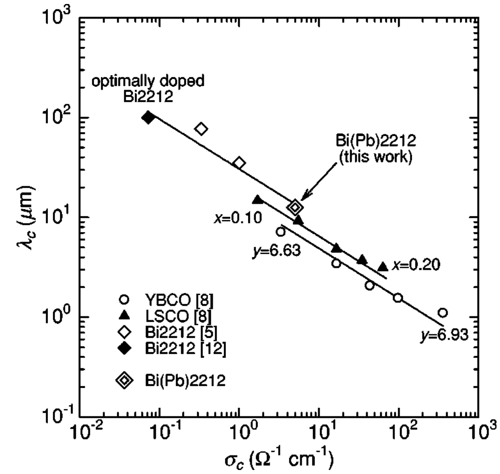

FIG. 3. Correlation between λ_c and σ_c of Bi(Pb)2212 together with the data for Bi2212 (Refs. 5 and 12), LSCO (Ref. 8), and YBCO (Ref. 8). The three lines are guides to the eye, representing $\lambda_c^2 \propto \sigma_c^{-1}$ for Bi2212, LSCO, and YBCO systems.

estimated the in-plane penetration depth from reversible magnetization measurements under high fields as $\lambda_{ab} = 0.20\,\mu$m. This is in good agreement with the reported value for Pb-doped Bi2212,[14] $\lambda_{ab} = 0.19-0.23\,\mu$m. From the measured λ_{ab} value, the superconducting anisotropy parameter γ_s is calculated to be $\gamma_s \equiv \lambda_c/\lambda_{ab} \sim 63$. This value is not so different from the resistivity anisotropy in the normal state, $\gamma_n \equiv \sqrt{\rho_c/\rho_{ab}} \sim 34$ at 100 K.[7]

Basov *et al.*[15] reported that the magnitude of λ_c intimately correlates with the $\omega \rightarrow 0$ extrapolated *c*-axis conductivity (σ_c) just above T_c: λ_c^2 is inversely proportional to σ_c for a variety of HTSC compounds, leading to the universal line in λ_c^2 vs σ_c plot. In Fig. 3, we plot λ_c and σ_c of our Bi(Pb)2212 together with the data for Bi2212,[5,12] LSCO,[8] and YBCO (Ref. 8) with various doping levels in the literature. The present results just follow the universal line. Figure 3 also demonstrates a strong dependence of λ_c on doping in the LSCO and YBCO systems. The data points for LSCO and YBCO in Fig. 3 scan the doping range from $p = 0.10$ to 0.20 and from $p \sim 0.12$ to ~ 0.23, respectively.[8] It is also found that the available data for the Bi2212 system starting from the optimally doped[12] (shown by the closed diamond) to the present overdoped one (double diamond), span nearly the same $\lambda_c^2 - \sigma_c$ range. In this regard, the Pb-doped Bi2212 is heavily overdoped with *p* larger by at least 0.10 than that for the optimally doped sample. However, the T_c of our overdoped crystal is still 65 K, which, if we use the "universal parabola" for T_c vs *p* relation,[16] would correspond to *p* only larger by 0.06 than the optimal carrier density, presumably $p \sim 0.16$ ($T_c = 96$ K).[10] Estimated $p \sim 0.22$ in the present crystal is consistent with the measured values and temperature dependence of the in-plane resistivity (ρ_{ab}).[7,17] The magnitude of ρ_{ab}, transformed into the resistance per CuO_2 plane, is comparable to that for the fully oxygenated YBCO,[18] and the exponent α of the *T* dependence ($\rho_{ab} \propto T^{\alpha}$) is only slightly larger than one ($\alpha = 1.2-1.4$). Therefore, Pb-doped Bi2212 is indeed overdoped but not heavily overdoped, and the observed decrease of λ_c (or the increase of ω_{ps}^c) is more than that expected from the increase in carrier doping. In addition, the overdoped pure Bi2212 with nearly the same T_c (=71 K) in Ref. 5 has much longer λ_c (=35 μm) compared to our Pb-doped Bi2212, $\lambda_c = 12.6\,\mu$m. It is also difficult to explain this difference in λ_c only taking the carrier doping level for each crystal into consideration. We speculate that the Pb substitution would have an additional effect, changing the electronic structure of the BiO double layers so that to enhance the coupling between CuO_2 planes.

It seems that the Josephson plasma edge observed in Bi(Pb)2212 is relatively sharp despite the overdoped state, in contrast to the rather broadened reflectivity edge in the overdoped $La_{1.80}Sr_{0.20}CuO_4$ (Refs. 2,8) and $YBa_2Cu_3O_7$.[19] A broadening of the observed *c*-axis reflectivity edge is considered as a common feature in the overdoped HTSC, and this may be due to residual conductivity in the superconducting gap region. The existence of the residual conductivity is also suggested in our Bi(Pb)2212 from a finite $\sigma_c(\omega \rightarrow 0)$ in the superconducting state as will be mentioned later. However, the magnitude of the *c*-axis conductivity in the normal state is far smaller compared to LSCO and YBCO,[2] reflecting the larger anisotropy of Bi-based cuprates. Therefore, the residual conductivity of Bi2212 in the superconducting state would be still small even in the overdoped crystal, resulting in the relatively smaller broadening effect. As a matter of fact, the edge broadening ($\sim 5\,\mathrm{cm}^{-1}$), defined from the width of a peak in Im$[-1/\epsilon(\omega)]$, was much larger than the width of the Josephson plasma resonance observed for an optimally doped Bi2212 in the microwave region.[6]

The optical conductivity $\sigma_c(\omega)$ spectra are shown in Fig. 4. In the normal-state spectra at 295 and 100 K, a Drude component is hardly seen and the phonon peaks dominate down to 100 cm^{-1}, evidencing weak electronic contribution along the *c* axis even in the present overdoped crystal. However, the conductivity below the lowest phonon band (~ 90 cm^{-1}) is finite, and $\sigma_c(\omega \rightarrow 0)$ is in good agreement with the dc resistivity value at 295 and 100 K. This indicates that the relatively small ρ_c and metallic feature of the spectrum are bulk properties, and not caused by an extrinsic factor such as an imperfection of the grown crystals. At 8 K, disappearance of a part of spectral weight is seen in the low-frequency region below $\sim 250\,\mathrm{cm}^{-1}$, and this must be due to

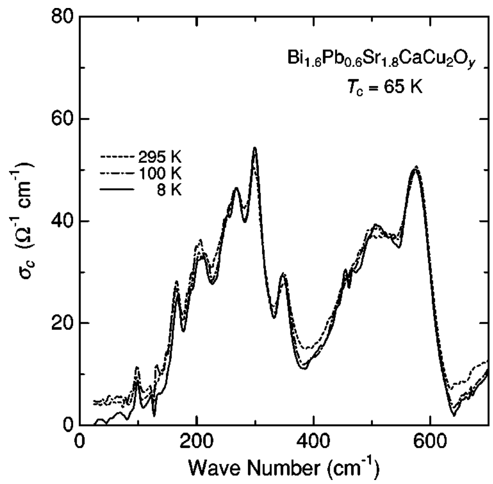

FIG. 4. *c*-axis optical conductivity spectra of $Bi_{1.6}Pb_{0.6}Sr_{1.8}CaCu_2O_y$ single crystal at 8, 100, and 295 K obtained from Kramers-Kronig analysis on the *c*-axis reflectivity spectra.

the opening of a superconducting gap. A small but finite conductivity ($\sim 2\ \Omega^{-1}\,cm^{-1}$) remains even in the superconducting state. Thus, the Pb-doped Bi2212 shares a common feature with the other cuprates in the overdoped regime.

Finally, we comment on the anomalous bump seen around $400\,cm^{-1}$ for other bilayer cuprates. In the previous studies of the *c*-axis reflectivity measurements for an underdoped YBCO and the other bilayer cuprates, an anomalous bump was found to develop at around $400-450\,cm^{-1}$ with decreasing temperature and particularly below T_c.[11,20] In the overdoped regime of YBCO, however, it was far from clear whether or not similar feature develops in the *c*-axis spectrum in the superconducting state, since the spectrum was dominated by a coherent (Drude) term which make the feature around 400 cm^{-1} indiscernible. The overdoped Bi(Pb)2212 is interesting in this respect as it maintains fairly large anisotropy even in the overdoped regime and hence the electronic contribution is not large enough to smear out the features around $400-450\,cm^{-1}$. In Fig. 4, very weak features appear to develop between 400 and 500 cm^{-1} below T_c. Some of these features might correspond to the 400 cm^{-1} bump in the underdoped YBCO,[11,20] but the spectral change is too weak to conclude whether this anomaly has the same origin as in the YBCO system.

In summary, we have successfully prepared carrier-overdoped Bi-based cuprates and observed a *c*-axis Josephson plasma edge in the far-infrared optical frequency region for the first time. The overdoping was made by heavily Pb-doping into Bi2212 single crystal and by annealing it in oxygen atmosphere. The reflectivity edge is pushed up to 40 cm^{-1} well above the lower detection limit for the conventional infrared reflectivity measurement. From the observed Josephson plasma frequency at 8 K, the *c*-axis penetration depth $\lambda_c = 12.6\,\mu m$ is estimated. This λ_c value is being reduced by almost one order of magnitude compared with that for the optimally doped pure Bi2212. The plasma frequency or λ_c is well correlated with the value of the dc conductivity just above T_c and follows a universal relationship between λ_c and $\sigma_c(T_c)$. We find that the reduction of λ_c is more than that expected from the increase of carrier doping in the CuO_2 planes and hence the Pb doping must have an additional effect in reducing the anisotropy in the Bi-based cuprates.

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