Anisotropic Optical Spectra of PrBa$_2$Cu$_4$O$_8$: Possible Tomonaga-Luttinger Liquid Response of the Quasi-One-Dimensional Metallic CuO Double Chains

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The optical spectra of PrBa$_2$Cu$_4$O$_8$ show large in-plane anisotropy. For the a polarization ($\mathbf{E} \perp$ chain), the spectrum is characterized by a gap of 1.4 eV, indicating the charge-transfer insulating nature of the CuO$_2$ planes. For the metallic chain direction ($\mathbf{E} \parallel b$), the spectrum deviates from a simple Drude response; reflectivity $R_b(\omega)$ shows a sharp edge at $\sim$1 eV but it also shows a dip at $\sim$15 meV, which splits the conductivity spectrum into two parts—a zero-energy mode with small weight and a pronounced 40 meV mode. These features are discussed in terms of a Tomonaga-Luttinger liquid in a doped 1D Mott insulator and compared with 1D Bechgaard salts.

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The motivation for the experimental survey of a doped one-dimensional (1D) Mott insulator is twofold. First, it provides an opportunity to study the role of electronic correlation in detail through comparison with the exact theoretical solutions that are available because 1D models are simple. The electronic correlation is essential for various peculiar features of doped Mott insulators, one of which is 2D high-temperature (high-T_c) superconductivity [1]. Second, a 1D metal is theoretically predicted to be a Tomonaga-Luttinger (TL) liquid in which the spin and charge degrees of freedom are separated [2,3]. The physical concept of this non-Fermi liquid state is not only one of the central concerns in the fundamental physics but also a key factor for fabrication of mesoscopic devices [4].

PrBa$_2$Cu$_4$O$_8$ (Pr124) is one of the most useful model materials: (1) It has self-doped CuO double chains with a metallic character, whereas its CuO$_2$ planes are nonsuperconducting and hence considered to be nonmetallic [5,6]. This enables us to investigate directly the charge dynamics of the metallic chains without disturbance from the plane contributions. (2) The CuO chains of Pr124 have the following advantages from a structural view point: (i) They are free of structural transitions and oxygen deficiencies. (ii) The bonding angle of Cu-O-Cu is almost entirely 180°. Generally speaking, oxides are chemically stable and hence appropriate for optical measurements. In addition, carrier filling of oxides is in many cases easy to control by substitution of elements. These are additional merits of oxides.

We show the anisotropic optical spectra of Pr124. The result demonstrates that the CuO$_2$ planes are not sufficiently doped with holes and preserve the electronic structure of a charge-transfer (CT) insulator. The charge dynamics along the metallic CuO chains, on the other hand, drastically deviate from a simple Drude response.

The optical conductivity has two features: a zero-energy mode with only 2% of the spectral weight associated with the chain holes and a finite-energy mode at $\sim$40 meV with the rest of the weight. We discuss these features in terms of an interacting TL liquid in a doped 1D Mott insulator with commensurate carrier filling.

Single crystals of Pr124 were grown by a self-flux method using a MgO crucible under high pressure O$_2$ gas of 11 atm [6]. Typical crystal size was 0.4 mm $\times$ 0.4 mm $\times$ 0.06 mm. The obtained plate crystals were naturally "untwined." Near-normal incident polarized optical reflectivity $R(\omega)$ was measured at room temperature (295 K) on new, flat, shiny, as-grown ab planes using a Fourier-type interferometer (0.005–2.2 eV) and a grating spectrometer (1.2–6.6 eV). The experimental error of reflectivity, ΔR, is less than 1% for the far-IR to visible region and less than 2% for the ultraviolet region.

Figure 1 shows the $R(\omega)$ spectra of Pr124 for two polarizations. The anisotropy is pronounced in the IR region. The spectrum for $\mathbf{E} \parallel b$, $R_b(\omega)$, containing both plane and chain contributions, exhibits a steep rise below 1 eV like a free-carrier plasma. By contrast, the spectrum for $\mathbf{E} \parallel a$, $R_a(\omega)$, is typical of a semiconductor with low reflectivity and manifested optical phonons. Therefore, the edge at $\sim$1 eV in R_b is ascribed to the carriers (excitations) associated with the chains. A weak shoulder just above the edge in R_b is probably due to the CT excitation in the CuO$_2$ plane which yields a peak at $\sim$1.4 eV in R_a (see below). In addition, it is noteworthy that a dip structure is observed in both R_a and R_b ($\sim$15 meV).

In order to make a more detailed discussion, we deduce the optical conductivity $\sigma(\omega)$ from $R(\omega)$ via a Kramers-Kronig (KK) transformation. To do this, appropriate extrapolations are necessary. We assumed a Hagen-Rubens (HR) formula (dashed curves in Fig. 1) below 5 meV and
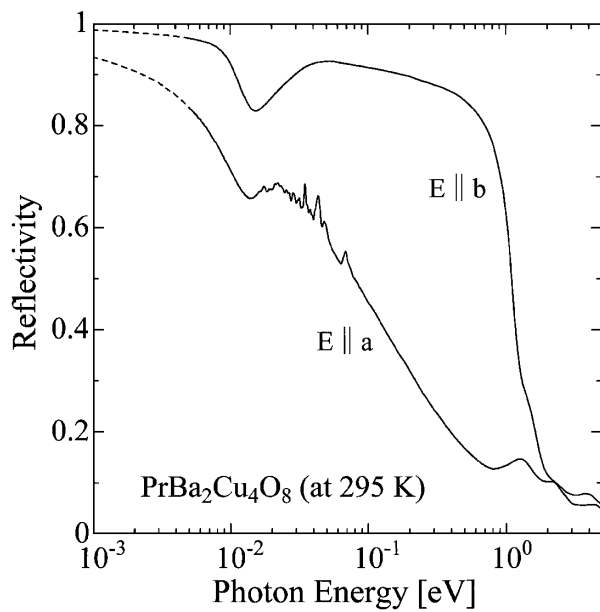
FIG. 1. Reflectivity $R(\omega)$ spectra of PrBa$_2$Cu$_4$O$_8$ at room temperature (295 K) with polarization parallel (**E** $\parallel$ b) and perpendicular (**E** $\parallel$ a) to the CuO chain. Dashed lines represent the extrapolation for a Kramers-Kronig (KK) analysis.

$R \propto \omega^{-4}$ above 6.6 eV. The parameter in the HR extrapolation, $\sigma(0)$, almost coincides with the dc value [6]. Variation of the extrapolation procedure does not affect $\sigma(\omega)$ in the energy range 0.012−2 eV. In the range 5−12 meV, the qualitative ω dependence of $\sigma(\omega)$ does not depend on extrapolations, although the absolute value is slightly affected. Here, one should note that for **E** $\parallel$ a the reflectivity below the edge is rather low and hence the connection with the HR reflectivity is not so smooth as that for **E** $\parallel$ b. This makes the discussion on $\sigma_a(\omega)$ in the lowest energy region, to some extent, ambiguous.

The $\sigma_a(\omega)$ spectrum [Fig. 2(a)] consists of three structures: a weak far-IR mode, a weak mid-IR band, and a pronounced peak at 1.4 eV. The spectrum above the mid-IR region is exactly like that of PrBa$_2$Cu$_3$O$_7$ (Pr123) [7] and is basically similar to that of undoped cuprates such as deoxygenated tetragonal Y123 [8] or La$_2$CuO$_4$ [9]. Therefore, the mid-IR band and the peak at 1.4 eV can be regarded as a contribution from the holes slightly doped onto the planes and as the fundamental absorption of the CT insulating CuO$_2$ plane, the O2$p_\sigma \rightarrow$ Cu3$d_{x^2-y^2}$ (upper Hubbard) excitation, respectively. In high-T_c cuprates this CT absorption is sensitive to carrier doping onto the planes, which transfers the CT oscillator strength to low-energy excitations [8,9]. In Pr124 the peak position shifts slightly to lower energy but the oscillator strength of the CT excitation remains large. This demonstrates that there are insufficient holes doped onto the planes of Pr124. The far-IR mode originating from a dip in R_a at ~15 meV, on the other hand, can hardly be explained by plane contributions and, therefore, can be ascribed to interchain excitations. The calculated σ_a spectrum suggests that this far-IR mode is Drude-like but a conclusive argument is difficult.
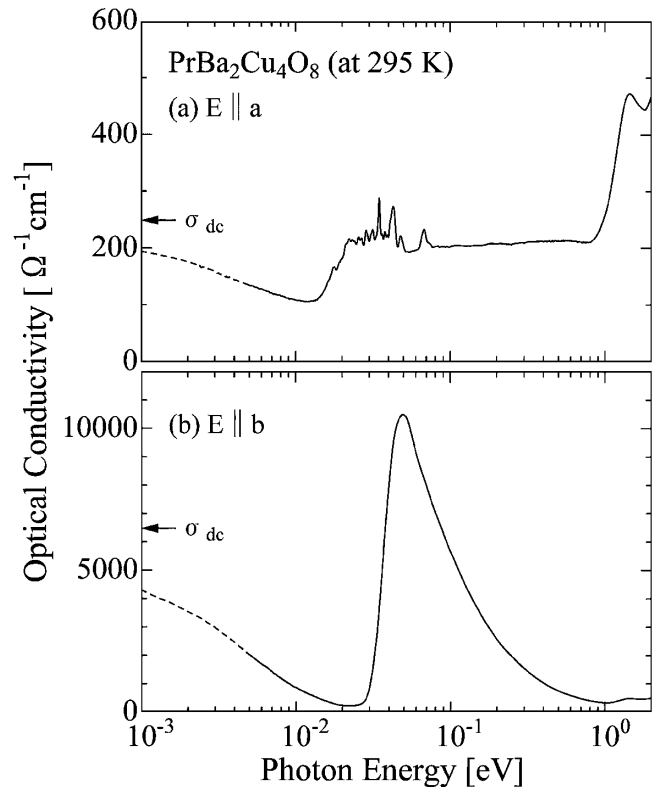

FIG. 2. Optical conductivity $\sigma(\omega)$ spectra of PrBa$_2$Cu$_4$O$_8$; (a) **E** $\parallel$ a and (b) **E** $\parallel$ b. The values of the dc conductivity σ_{dc} are taken from Ref. [6].

The $\sigma_b(\omega)$ spectrum [Fig. 2(b)] is much higher than $\sigma_a(\omega)$ in the IR region below 1 eV and, therefore, the contribution to $\sigma_b(\omega)$ in this region arises mostly from the CuO chains, that is, the CuO chain is metallic whereas the CuO$_2$ plane is insulating. However, the spectrum shows a striking deviation from a simple Drude response. The far-IR dip in the reflectivity has a much more drastic effect on $\sigma_b(\omega)$ than on $\sigma_a(\omega)$; it splits $\sigma_b(\omega)$ clearly into two parts, a Drude-like (zero-energy, ZE) mode with small spectral weight and a pronounced finite-energy (FE) mode centered at ~40 meV.

Integrated spectral weight defined as

$$N_{eff}^{*}(\omega) = \frac{2m_0 V}{\pi e^2} \int_0^\omega \sigma(\omega')\, d\omega' \qquad (1)$$

(m_0: bare-electron mass; V: unit-cell volume) represents an effective density of carriers involved in the optical excitations up to $\hbar\omega$. In Pr124, because the interchain contribution in $\sigma_a(\omega)$ is considered to have much smaller spectral weight compared with the plane contribution in the IR region, $N_{eff}^{*b} - N_{eff}^{*a}$ at $\hbar\omega = 1$ eV can be regarded as the net chain contribution without the plane contribution. It gives about 0.4 [/Cu(1)-atom] or Cu(1)$^{+2.4}$, which is, roughly speaking, coincident with that in Y124 [10,11]. We can conclude that equal amounts of holes are introduced into the chains of Pr124 and of Y124. This is supported by the fact that the chain dc conductivity of Pr124

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[6] is almost the same as that of Y124 [12]. Therefore, the disappearance of superconductivity, or the insulating CuO_2 plane, is primarily attributed to the Fehrenbacher-Rice mechanism [13]; the holes are transferred from the $O2p_\sigma$-$Cu3d$ to the $O2p_\pi$-$Pr4f$ orbitals. The holes doped onto the chains, on the other hand, form the two structures in σ_b. The ZE mode has only 2% of the total spectral weight associated with the chain holes and the rest builds up the FE mode.

The two-component structure in $\sigma_b(\omega)$ resembles $\sigma(\omega)$ of quasi-1D Bechgaard salts [14]. For Bechgaard salts, a model of a 1D Mott insulator with commensurate carrier filling and umklapp scattering is proposed in order to interpret the two-component structure [15]. In this scenario, the metallic state in the doped 1D Mott insulator is unstable when the carrier filling is commensurate and, consequently, a charge gap Δ is formed. The conduction band of a Bechgaard salt is formally 3/4 filled and Δ is 20 meV for the most metallic salt $(TMTSF)_2ClO_4$. In addition, at the in-gap region, a collective mode with small spectral weight is also present and it dominates dc conduction. Because the filling number of the Pr124 chain is close to 1/4 [$Cu(1)^{+2.5}$], a similar argument as Bechgaard salts may be applicable. And/or, the high-frequency structure in $\sigma(\omega)$ may be insensitive to incommensurability.

Within the above theoretical framework, the electronic correlation is numerically expressed as K_ρ, the TL-liquid exponent controlling the decay of all correlation functions [16,17]. K_ρ can be estimated from the power-law exponent γ dominating the higher-energy part ($\hbar\omega > \Delta$) of the conductivity, $\sigma(\omega) \propto \omega^{-\gamma}$, using the relation of $\gamma = 5 - 4n^2 K_\rho$ (n: commensurability). For the present case, γ is estimated to be about 1.2 from $\sigma_b(\omega)$ (Fig. 3). Within
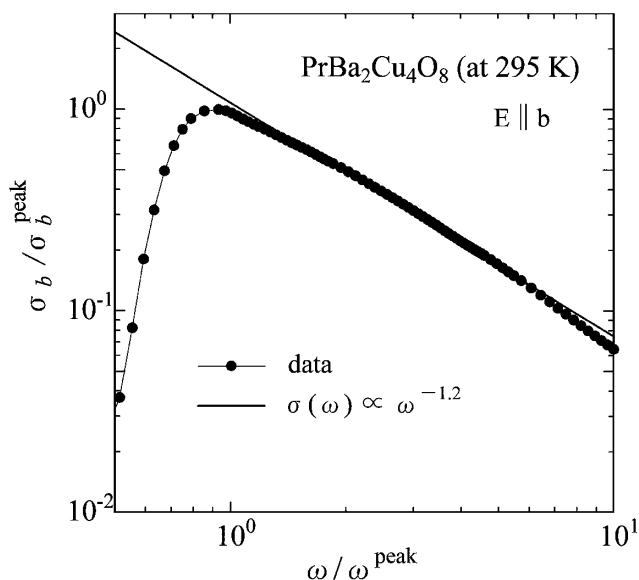

FIG. 3. The normalized conductivity σ_b shown on a log-log scale to demonstrate the power-law frequency dependence of the conductivity above the finite energy peak. The solid line shows a fit of the form $\sigma(\omega) \propto \omega^{-\gamma}$. We find $\gamma = 1.2 \pm 0.1$.

the same framework, the charge gap is expressed as

$$\Delta \sim W \left(\frac{g_{1/2n}}{W} \right)^{2/(\gamma-1)} \qquad (2)$$

(W: band width; $g_{1/2n}$: coupling constant). For the present case, $2/(\gamma - 1) \sim 10$. For the 1/4-filling case, possible commensurabilities are $n = 1$ (1/2-filling umklapp process) and $n = 2$ (1/4-filling umklapp process), which correspond to a phononic (dimerization) and an electronic CDW state, respectively. For $n = 1$, K_ρ is ~ 0.95, corresponding to the weak repulsive regime ($K_\rho = 1$ being the noninteracting point). In this case, $g_{1/2}/W \sim D/W$ depends on the strength of dimerization D and, in general, is expected to be rather small (typically 10^{-2} for Bechgaard salts [17]). Therefore, the large exponent (~ 10) may lead to a physically too small value of Δ. For $n = 2$, on the other hand, K_ρ is ~ 0.24, corresponding to the strong repulsive regime. In this case, $g_{1/4}/W \sim (U/W)^3$ (U: representative value of interaction) can be of the order 1 because U is considered to be much larger than D. Therefore, we may obtain a reasonable value of Δ comparable with the measured value (40 meV). The present optical study seems to support the $n = 2$ case.

However, the above argument, especially on the magnitude of K_ρ, may be too simple. (1) The temperature (T) dependence of the dc resistivity ρ_b shows an exponent larger than 1 [6]. This may be incompatible with the theoretical prediction $\rho(T) \propto T^{2-\gamma}$ (here, $\propto T^{0.8}$). (2) A recent study of angle-resolved photoemission spectroscopy (ARPES) has reported that the spectral weight near the Fermi level is *not* much suppressed [18], suggesting that the Fermi surface exponent $\alpha = (K_\rho + K_\rho^{-1} - 2)/4$ is small, or K_ρ is close to 1. (3) The small value (~ 0.24) of K_ρ suggests a dominant long-range (for example, nearest-neighbor) interaction because a purely local (on-site) repulsion is incompatible with K_ρ below 0.5 [19]. However, it is not self-evident that such a long-range interaction is not screened out in metallic cuprates. These discrepancies may originate from other scattering factors, interactions *within* each double chain, incompleteness of the theoretical framework, especially on analysis of the ARPES data, and so on. Also in the field of Bechgaard salts, similar discrepancies are now under debate.

For Bechgaard salts, the ZE collective mode has been observed when the metallic interchain conduction increases sufficiently to produce the mid-IR plasma edge yielding a pronounced FE mode in the "$E \perp$ chain" spectra [20,21]. However, Pr124 shows a Drude-like in-gap collective mode (at least for $E \parallel b$) without the metallic interchain conduction (or the pronounced FE mode in σ_a). This is probably because the commensurate carrier filling is complete for Bechgaard salts but not for the Pr124 chains. The metallic interchain conduction, which plays the role of effective carrier doping, may be essential for the metallic character (or the ZE collective mode) when the carrier filling is completely commensurate like Bechgaard salts, but may not be a general necessity.

A recent optical study on Ni-doped Y123 [22] shows a peak in σ_b at ~ 300 cm^{-1}, almost the same energy as the charge gap in Pr124. This peak is ascribed to the localization or hopping conduction of the chain carriers. The relation between the present two-component structure in Pr124 and this 300 cm^{-1} peak should be further investigated. However, it is difficult to explain the present two-component structure by the localization effect: (1) A similar structure is also suggested for isostructural pure Y124 [11,23]. (2) $\rho_{\mathrm{chain}}(T)$ of the present Pr124 crystal, which is almost the same as that of Y124, maintains metallic behavior down to the lowest T with small residual resistivity ($\lesssim 12$ $\mu\Omega$ cm) [6]. (3) A Drude-like mode is clearly observed in σ_b in the in-gap region for Pr124 whereas it is absent for Ni-doped Y123 (Ref. [22], Sec. IV-A).

The σ_b (or σ_{chain}) spectrum of a single-chain R(rare-earth)123 system is characterized by the so called "chain peak" at about 0.2 eV [7,11,24], which has been explained by randomness plus a polaronic effect [25]. The present result proposes another possible explanation; the chain peak may be due to the formation of the commensurability charge gap. Also in the R123 chain, the carrier filling is almost $1/4$ [7,22,26]. In addition, the two-band (spinon and holon bands) structure characteristic of the spin-charge separation in the TL-liquid state [27] is observed for Pr123 in the recent ARPES study [26].

The results of spectroscopic studies on the quasi-1D systems are far from completely understood yet. First, for the metallic Bechgaard salt (TMTSF)$_2$ClO$_4$, the energy range of the spectral-weight suppression in the ARPES spectra (~ 0.2 eV) [28] seems too large compared with the charge gap in $\sigma(\omega)$ (~ 20 meV) obtained by the IR spectroscopy [17]. For the CuO chains, on the other hand, the energy scale of the spectral-weight suppression is coincident in the optical and the ARPES spectra. For Pr123 it is about 0.2 eV for both spectra [7,26] and for Pr124 the characteristic energy scale suggested by $\sigma(\omega)$ is so small ($\Delta \sim 40$ meV) that it is not incompatible with the absence of the suppression in the ARPES spectra within the resolution limit [18]. Second, the two-band (spinon and holon bands) structure is not confirmed in the ARPES spectra for Bechgaard salts, whereas it is observed for Pr123 and for a 1D CT insulator SrCuO$_2$ [29]. The ARPES spectra of Bechgaard salts may be quite sensitive to the sample surface [30,31].

In summary, we have reported the polarized optical spectra of PrBa$_2$Cu$_4$O$_8$. The spectrum for $\mathbf{E} \parallel a$ ($\perp$chain) demonstrates that the CuO$_2$ planes preserve the charge-transfer insulating state with a CT gap of 1.4 eV. The spectrum for $\mathbf{E} \parallel b$ ($\parallel$chain), on the other hand, deviates from a simple Drude response and is characterized by two-component conductivity. This is possibly interpreted within the framework of a Tomonaga-Luttinger liquid based on a doped 1D Mott insulator with the commensurability charge gap.

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