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Bound Excitons in Sr_2CuO_3

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We investigated temperature dependent optical spectra of the one-dimensional chain compound Sr_2CuO_3. The charge transfer transition polarized along the chain direction shows a strongly asymmetric line shape as expected in one-dimensional extended Hubbard model. At low temperature, the charge transfer peak shows a large blueshift and reveals additional sharp peaks at the gap. Even though many spectroscopic studies suggest that this material cannot have a bound exciton based on the one-dimensional extended Hubbard model, we attribute the additional sharp peaks to excitons, which come to exist due to the long-range Coulomb interaction.

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The physics of Mott insulators is still a subject of great interest due to a possible link with high temperature cuprate superconductors and its own physical properties. One-dimensional (1D) Mott insulators, in particular, have attracted a lot of attention not only for their unique physical properties such as spin-charge separation, but also as good candidates for an optical switching material thanks to their large optical nonlinearity [1–5]. Ni-halogen bridged 1D materials and 1D cuprates of Sr_2CuO_3 and Ca_2CuO_3 show comparable or even larger optical nonlinear property than well-known nonlinear materials such as conjugated polymers [1,2]. In these materials, the optical gap has a charge transfer character. That is, the optical gap is determined by the occupied halogen (oxygen) p-orbitals and empty Ni (Cu) d-orbitals. But they should be metallic without strong on-site Coulomb repulsion. Their nonlinear behavior has been explained by the one-dimensional extended Hubbard model (1D EHM), of which Hamiltonian is

$$H = -t\sum_{l,\sigma}(c^{\dagger}_{l+1,\sigma}c_{l,\sigma} + \text{H.c.}) + U\sum_{l} n_{l,\uparrow}n_{l,\downarrow} + V\sum_{l} n_l n_{l+1} \quad (1)$$

where $c^{\dagger}_{l,\sigma}(c_{l,\sigma})$ is the creation (annihilation) operator for a spin $\sigma = \uparrow, \downarrow$ electron at site l, $n_{l,\sigma} = c^{\dagger}_{l,\sigma}c_{l,\sigma}$, $n_l = n_{l,\uparrow} + n_{l,\downarrow}$, t is the hopping integral between nearest neighbor sites, and U (V) is the on-site (nearest neighbor) Coulomb interaction. In this model, a bound exciton is formed when $V > 2t$ [6]. Among them, Ni-Br-Br compound and Sr_2CuO_3 are believed to be on the verge of forming a bound exciton which should affect their nonlinear properties [2]. For Ni-Br-Br compound, it is clearly demonstrated by the low temperature measurements that there is a bound exciton [5]. However, for Sr_2CuO_3 no clear evidence for a bound exciton has been provided yet.

Sr_2CuO_3 has one-dimensional chain with CuO_4 plaquettes, which is a basic building block of the high temperature cuprate superconductors. It is believed that the physical properties of this material can be explained with 1D EHM. Ono *et al.* have pursued thorough studies on this material, and from electro-reflectance and photoconductivity measurements, they argued that this material should have a bound exciton [2]. However, electron energy loss (EELS) spectra and optical spectra have been well explained with parameters which expect no bound exciton [7–9].

In this Letter, we show clear evidence of bound excitons in Sr_2CuO_3 from temperature-dependent optical spectra, which appears as sharp peaks. Even though the overall line shape of optical spectra could be understood with 1D EHM, we notice that those sharp features are beyond 1D EHM. We propose that the long-range Coulomb interaction should be taken into account as a missing ingredient to explain those sharp features.

Single crystalline samples were grown using the traveling-solvent floating zone method. Temperature dependent polarized reflectivity spectra were carefully measured over a wide energy range. In a low energy region of 30 to 24 000 cm^{-1} (4 to 3 eV) an *in situ* evaporation technique was adopted in the overfilling method on Bruker 66 v/S Fourier transform spectrometer. In 4000–50 000 cm^{-1} (0.5 to about 6 eV), Cary5 grating spectrometer was used in the underfilling method. High energy spectra in 6–30 eV were measured at room temperature utilizing synchrotron radiation from the normal incidence monochromater beam line at Pohang Light Source (PLS). All measurements were done on freshly cleaved surfaces. More careful measurements were performed in the visible region where the strongly anisotropic charge transfer response is. For a better polarization, two polarizers (a polarizer-analyzer configuration) were used. The polarization for measurements was kept close to s-polarization to minimize possible rotation of polarization after reflections on the sample and mirrors. And those angles of incidence from the sample and mirrors between

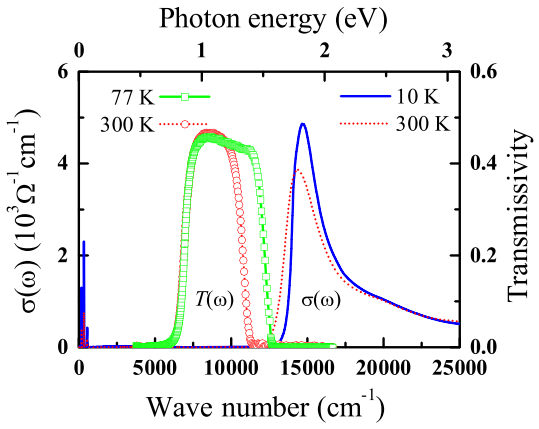

FIG. 1 (color online). Optical conductivity and transmission spectra along the chain direction of Sr_2CuO_3. Transmission was measured on a piece cleaved to be about 200 μm thick.

two polarizers were less than 10 degrees. The complex optical conductivity spectra $\tilde{\sigma}(\omega)$ were obtained from Kramers-Kronig transformation of reflectivity $R(\omega)$.

Because of interesting properties of this material as described above, optical spectra have already been reported many times [1–4]. They agree with each other in general features that it has strong asymmetric charge transfer peak at 1.5–2.5 eV along the chain as shown again in Fig. 1 and no apparent feature along other axes perpendicular to the chain in that energy region. As temperature is lowered, this peak moves to higher energy and becomes narrower. But it should be noted that there is a distinct difference between our spectra and reported data. Most of the previous reports show a long tail into the gap region. But as shown in Fig. 1, Sr_2CuO_3 is fairly transparent in the gap region, which dictates that the optical conductivity should not have that long tail into the gap region. Thanks to high quality large single crystals and accurate measurements over a wide energy range, we could get reasonable optical spectra with a sharp gap edge.

This strong charge transfer peak can be well explained within 1D EHM, parameters of which expect no bound exciton [6,8]. The temperature dependent change of this peak has been attributed to electron-phonon coupling as in other insulating cuprates [2,10,11]. However, there is another distinctive change at low temperature. Figure 2 shows temperature dependent $R(\omega)$ and derivative spectra of $\sigma(\omega)$. There are clear additional sharp features only at low temperature. Note that the strong charge transfer peak which steeply increases just above the gap overwhelms those features. As a result, these sharp peaks in reflectivity seem to be hidden in $\sigma(\omega)$. However, its derivative also clearly reveals their sharp nature. The loss function in Fig. 3 also shows that there is a separated small feature (open triangle) below the strong charge transfer peak [12]. These sharp peaks have been also observed in a photoluminescence (PL) measurement with a finite Stokes

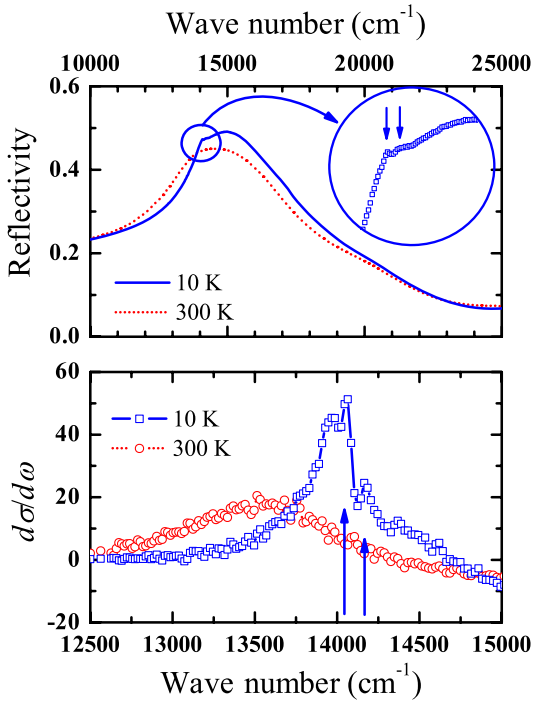

FIG. 2 (color online). Reflectivity and derivative spectra of $\sigma(\omega)$ along the chain direction. Sharp peaks at 10 K are marked with arrows. The reflectivity spectra were measured by 1 nm resolution and the instrumental error is smaller than the line thickness (symbol size) in this energy region.

shift of about 600 cm^{-1} [2]. The energy difference ($\sim$130 cm^{-1}) of the two peaks marked as arrows in Fig. 2 is same with that of peaks in PL spectra. The inset of Fig. 3 shows the loss function by longitudinal optic (LO) phonons. It is clear that the observed Stokes shift in PL

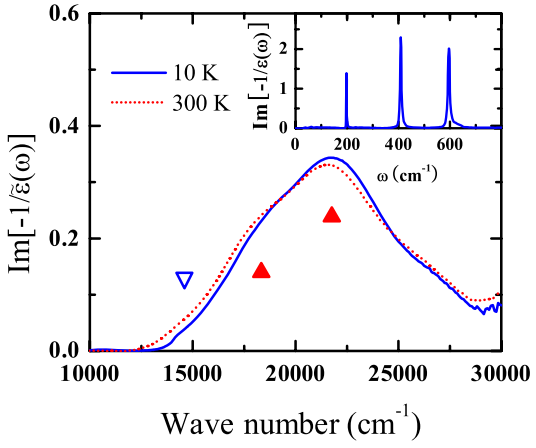

FIG. 3 (color online). Loss function of Sr_2CuO_3 along the chain direction. The solid triangles indicate peaks observed in the EELS measurement, and the open triangle indicates the excitonic response at 10 K. The inset shows a 10 K spectrum in phonon region, peaks of which correspond to LO phonon modes.

spectra is by the highest LO phonon, which corresponds to the Cu-O breathing mode.

Ono *et al.* argued that this material has a bound exciton from photoconductivity and electro-reflectance spectra [2]. However, EELS and $\sigma(\omega)$ require the system not to have a bound exciton within 1D EHM [7,8]. It should be noted that the observed sharp peaks are different from the exciton in 1D EHM. The line shape of $\sigma(\omega)$ in 1D EHM depends on the strength of the intersite Coulomb interaction V. As V increases, more spectral weight shifts to lower energy and $\sigma(\omega)$ has a strongly asymmetric shape like spectra shown Fig. 1 [6]. Note that any finite V can result in a bound exciton at zone boundary, which has been manifested in EELS spectra of this material [8,13]. If $V > 2t$, a holon (a hole without spin) and a doublon (a doubly occupancy site) form a bound exciton even at zone center and more spectral weight is accumulated to the exciton, resulting in a strong narrow peak just above the gap. Although there could be other peaks corresponding to continuum excitation or multiple excitons, they are much weaker and should come at higher energy than that of the exciton. Therefore, according to 1D EHM with appropriate parameters, there is only one strong peak expected at just above the gap in Sr_2CuO_3 regardless of forming a bound exciton. However, the sharp peaks observed here come right at the gap and have much smaller weight compared to the main charge transfer peak, which cannot be explained by 1D EHM.

Moskvin *et al.* proposed a weak one-center transition localized within one CuO_4 plaquette should come at slightly lower energy than the two-center transition between neighboring plaquettes, which corresponds to the strong charge transfer peak observed at 1.8 eV in Fig. 1 [14]. It was argued that this one-center peak should be observed both along the chain and perpendicular to the chain directions, which correspond to b and a axes, respectively. Figure 3 shows the loss function at zone center. There are clearly two peaks at both temperatures marked with solid triangles which were observed in EELS spectra. But both peaks turned out to have the two-center transition character, and the small feature appears additionally only at low temperature (open triangle) [12]. Note that no feature has been observed in an absorption measurement along a direction in this energy region [3]. Therefore, the one-center transition cannot explain the observed sharp peaks [12]. As another candidate for these peaks, on-site d-d transitions should be discussed. In many insulating cuprates, on-site d-d transitions have been observed in this energy region [15–17]. In materials with CuO_2 planes, these d-d transitions are usually very weak. Interestingly, in CuB_2O_4 with 0 dimensional CuO_4 plaquette, these d-d transitions appear as very sharp peaks even at room temperature [15]. However, the featureless absorption along a axis also eliminates this possibility for the sharp peaks. If there were on-site d-d transitions, they are expected to be stronger (sharper) in a axis (0D CuO_4 plaquette) than in b axis (1D chain of CuO_3), which is contrary to the observations here. As being discussed later, the observed strength of these peaks is even stronger than that of 0D case of CuB_2O_4. Note that any localized phenomena within a CuO_4 plaquette cannot reconcile the lack of absorption along a axis of Sr_2CuO_3.

Even though these sharp peaks are not discussed carefully, it has been noticed that there could be more than one transition in the charge transfer peak in Sr_2CuO_3 [2,18]. Matsueda *et al.* proposed that a strong electron-phonon interaction should be considered to understand the charge transfer peak in Sr_2CuO_3 [18]. They argued that the effect of electron-phonon interaction is enhanced by on-site Coulomb interaction, and it could result in splitting of the charge transfer peak. Not only in this system, but also in many insulating cuprates, the electron-phonon interaction could play an important role [2,11]. However, the observed sharp peaks are qualitatively different from what is expected due to the electron-phonon interaction. Note that the calculated spectra always have the strongest peak just above the gap with expected parameters for Sr_2CuO_3 in 1D EHM [3,7,8]. Another point which has to be noticed is that the energy difference ($\sim$130 cm^{-1}) of the two peaks cannot be explained by any phonon observed in this system [19].

Interestingly, quite a similar behavior has been observed in a Ni-Br-Br compound which is also supposed to be close to the boundary of $V = 2t$ within 1D EHM. Its reflectance at 77 K shows a narrow peak on top of the strong charge transfer peak [2], which looks similar to that of Sr_2CuO_3 at 10 K. Even though this multipeak structure does not show up as separated two peaks in ϵ_2, it is clear that there has to be more than one peak [1,2]. The spectrum at 4.2 K clearly shows a few peaks with most of the spectral weight accumulated at the first peak, which is an exciton [5]. This similarity of two materials suggests that such a small peak observed just above the gap could be a unique phenomenon in an 1D system with $V \sim 2t$, which is close to the boundary of forming a bound exciton in 1D EHM.

An exciton in semiconductor is a hydrogen-like bound state of electron and hole due to the long-range Coulomb interaction [20]. On the other hand, most theoretical studies of the 1D EHM have usually considered on-site and nearest-neighbor Coulomb interactions instead of the long-range interaction, which expect one strong exciton at the gap. There have been reported a few theoretical studies on 1D EHM with the long-range Coulomb interaction [13,21]. Interestingly, it is agreed that even in strongly correlated systems with large U, the long-range interaction gives rise to hydrogen-like bound states as in semiconductors. Such a Wannier exciton could be formed with a smaller nearest-neighbor interaction than the case without the long-range interaction. In 1D EHM of Eq. (1) with $U \gg t$, the binding energy of a bound exciton is $V - 4t + 4t^2/V$ and its size is

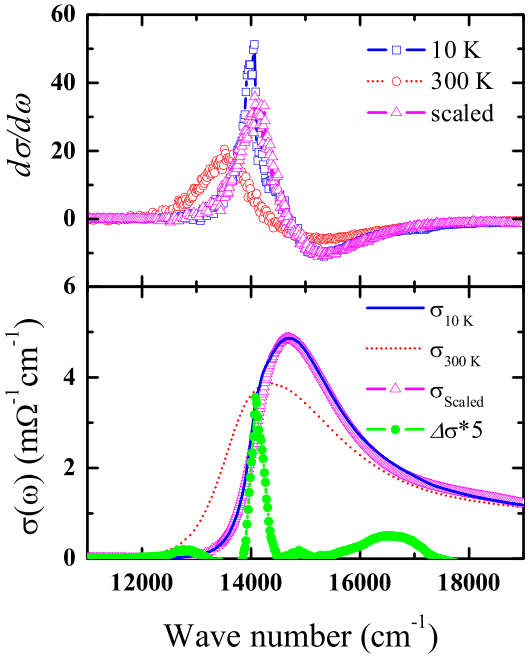

FIG. 4 (color online). Scaling of $d\sigma/d\omega$ and $\sigma(\omega)$ by peak height and width. The 10 K spectra and the scaled 300 K spectra agree with each other except the sharp peaks.

$V^2/(V^2-4t^2)$ (unit cell lattice parameter $=1$) when $V > 2t$ [6]. It is clear that as V approaches $2t$ the size diverges, which is natural for an exciton with small binding energy. This situation is still the same in the case with a finite U [6]. In this limit of $V \sim 2t$, there should be significant correlation between holon and doublon at distance larger than 1 unit cell. Therefore, the long-range Coulomb interaction could play an important role. Although there is no consensus whether there is a bound exciton or not, Sr_2CuO_3 must be closely located to the boundary of $V = 2t$ within the 1D EHM. Therefore, the observed sharp peaks at low temperature could be responses of Wannier-like excitons with the help of the long-range Coulomb interaction.

The optical spectra at 10 and 300 K look quite similar to each other except the sharp peaks at 10 K. Figure 4 shows $d\sigma/d\omega$ and $\sigma(\omega)$ at 10 and 300 K and the scaled 300 K spectra simply by peak height and width. The scaled spectra remarkably agree with 10 K spectra except the sharp exciton peaks. As in other insulating cuprates, such a temperature dependence could be attributed to an electron-phonon coupling [2,10,11]. Assuming the overall response modulated by temperature and electron-phonon coupling could be counted by the scaling, the excitonic response was estimated from the difference spectrum as shown in Fig. 4. Note that the excitonic feature is much stronger than the absorption by on-site d-d transitions in 0D cuprate CuB_2O_4 [15], which supports its correlated nature along the chain.

In summary, we presented carefully measured optical spectra of Sr_2CuO_3. A strong charge transfer peak polarized along the chain direction shows a strongly asymmetric shape with a clear gap edge. At low temperature, the main charge transfer peak shows a large blueshift and additional sharp peaks appear. The overall temperature dependence of the main peak, which is mainly attributed to the electron-phonon coupling, could be scaled by its peak height and width. And the additional peaks were attributed to Wannier-like excitons. Such an excitonic behavior is expected with the long-range Coulomb interaction, which should be important when $V \sim 2t$ in one-dimensional extended Hubbard model.

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