Bound Excitons in Sr$_2$CuO$_3$

K. W. Kim, G. D. Gu, C. C. Homes, and T. W. Noh

Department of Physics, University of Fribourg, Chemin du Musée 3, CH-1700 Fribourg, Switzerland
Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA
School of Physics and Research Center for Oxide Electronics, Seoul National University, Seoul 151-747, Korea
(Dated: October 26, 2008)

We investigated temperature dependent optical spectra of the one-dimensional chain compound Sr$_2$CuO$_3$. 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 blue shift and reveals additional sharp peaks at the gap. Even though many spectroscopic studies suggest that this material can not 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.

PACS numbers: 71.27.+a, 71.35.-y, 78.20.-e, 78.67.-n

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 lots of attention not only from unique physical properties such as spin-charge separation but also as a good candidate for an optical switching material thanks to their large optical nonlinearity. Ni-halogen bridged 1D materials and 1D cuprates of Sr$_2$CuO$_3$ and Cu$_2$CuO$_4$ show comparable or even larger optical nonlinear property than well known nonlinear materials such as conjugated polymers. In those materials the optical gap has 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 onsite Coulomb repulsion. Their nonlinear behavior has been explained with one-dimensional extended Hubbard model (1D EHM), of which Hamiltonian is

$$H = -t \sum_{l, \sigma} \left( c_{l+1, \sigma}^\dagger c_{l, \sigma} + h.c. \right) + U \sum_{l} n_{l, \uparrow} n_{l, \downarrow} + V \sum_{l} n_{l} n_{l+1}$$

where $c_{l, \sigma}^\dagger$ ($c_{l, \sigma}$) is the creation (annihilation) operator for a spin $\sigma = \uparrow, \downarrow$ electron at site $l$, $n_{l, \sigma} = c_{l, \sigma}^\dagger c_{l, \sigma}$, $n_l = n_{l, \uparrow} + n_{l, \downarrow}$, $t$ is the hopping integral between nearest neighbor sites, and $U$ ($V$) is the onsite (nearest neighbor) Coulomb interaction. In this model, a bound exciton is formed when $V > 2t$. Among them, Ni-Br-Br compound and Sr$_2$CuO$_4$ are believed to be on the verge of forming a bound exciton which should affect their nonlinear properties. For Ni-Br-Br compound, it is clearly demonstrated by the low temperature measurements that there is a bound exciton. However, for Sr$_2$CuO$_3$ no clear evidence for a bound exciton has been provided yet.

Sr$_2$CuO$_3$ 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. However, electron energy loss (EELS) spectra and optical spectra have been well explained with parameters which expect no bound exciton.

In this letter, we show a clear evidence of bound excitons in Sr$_2$CuO$_3$ 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 24000 cm$^{-1}$ (4 meV to 3 eV) an in situ evaporation technique was adopted in the overfilling method on Bruker 66v /S Fourier transform spectrometer. In 4000-50000 cm$^{-1}$ (0.5 eV 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 two polarizers were less than 10 degrees. The complex optical conductivity spectra $\sigma(\omega)$ were obtained from Kramers-Kronig transformation of reflectivity $R(\omega)$.

Because of interesting properties of this material as described above, optical spectra have been already reported many times [1, 2, 3, 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 direction. Sharp peaks at 10 K are marked with arrows. Figure 2 is same with that of peaks in PL spectra. The inset of fig. 2 shows the loss function by longitudinal optic (LO) phonons. It is clear that the observed Stokes shift in PL 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 double 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$_2$CuO$_3$ 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 can not 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 can not explain the observed sharp peaks [12]. As another candidate for these peaks, onsite $d$-$d$ transitions should be discussed. In many insulating cuprates, onsite $d$-$d$ transitions have been observed in this energy region [15, 16, 17]. In materials with CuO$_2$ planes, these $d$-$d$ transitions are usually very weak. Interestingly in CuB$_2$O$_4$ with 0 dimensional CuO$_4$ plaquette, these $d$-$d$ transitions appear as very sharp peaks even at room temperature [18]. However, the featureless absorption along $a$ axis also eliminates this possibility for the sharp peaks. If there were onsite $d$-$d$ 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$_2$O$_4$. Note that any localized phenomena within a CuO$_4$ plaquette can not reconcile the lack of absorption along $a$ axis of Sr$_2$CuO$_3$.

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$_2$CuO$_3$ [2, 18]. Matsueda et al. proposed that a strong electron phonon interaction should be considered to understand the charge transfer peak in Sr$_2$CuO$_3$ [18]. They argued that the effect of electron phonon interaction is enhanced by onsite 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 have always the strongest peak just above the gap with expected parameters for Sr$_2$CuO$_3$ in 1D EHM [2, 7, 8]. Another point which has to be noticed is that the energy difference ($\sim$130 cm$^{-1}$) of the two peaks can not be explained by any phonon observed in this system [10].

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$_2$CuO$_3$ at 10 K. Even though this multi-peak structure does not show up as separated two peaks in $\epsilon_2$, it is clear that there has to be more than one peak [12]. 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 [2]. 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 onsite 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.
strongly correlated systems with large action [13, 21]. Interestingly, it is agreed that even in other except the sharp peaks.

The 10 K spectra and the scaled 300 K spectra agree with each other except the sharp peaks.

FIG. 4: 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.

action [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 $V^2/(V^2 - 4t^2)$ (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 one 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$_2$CuO$_3$ 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 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 onsite d-d transitions in 0D cuprate CuB$_2$O$_4$ [12], which supports its correlated nature along the chain.

In summary, we presented carefully measured optical spectra of Sr$_2$CuO$_3$. 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 blue shift 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.

K. W. Kim acknowledges discussions with D. Baeriswyl, E. Jeckelmann, C. Bernhard and A. Dubroka. This work is supported by the Schweizer Nationalfonds (SNF) with grant 200020-119784, by the Department of Energy under contract No. DE-AC02-98CH10886, by the Creative Research Initiatives (Functionally Integrated Oxide Heterostructure) of KOSEF, and by the Brain Korea 21 Project in 2002. The experiments at PLS was supported by MOST and POSCO.

* Electronic address: kyungwan.kim@gmail.com

[1] H. Kishida et al., Nature. 405, 929 (2000).
[2] M. Ono et al., Phys. Rev. B 70, 085101 (2004).
[3] H. Kishida et al., Phys. Rev. Lett. 87, 177401 (2001).
[4] T. E. Kidd et al., Phys. Rev. B 77, 054503 (2008).
[5] M. Ono, H. Kishida, and H. Okamoto, Phys. Rev. Lett. 95, 087401 (2005).
[6] E. Jeckelmann, Phys. Rev. B 67, 075106 (2003).
[7] H. Benthien and E. Jeckelmann, Phys. Rev. B 75, 205128 (2007).
[8] R. Neudert et al., Phys. Rev. Lett. 81, 657 (1998).
[9] Note that ref. [3] is often cited as data showing $V > 2t$ which is an unscreened $V$ value. It is mentioned that the screened $V$ for 1D EHM is smaller than $2t$.
[10] J. P. Falck, A. Levy, M. A. Kastner, and R. J. Birgeneau, Phys. Rev. Lett. 69, 1109 (1992).
[11] K. M. Shen, et al., Phys. Rev. B 75, 075115 (2007).
[12] K. W. Kim, G. D. Gu, cond-matt/08081382.
[13] F. B. Gallagher and S. Mazumdar, Phys. Rev. B 56, 15025 (1997); W. Barford, ibid 65, 205118 (2002).
[14] A. S. Moskvin et al., Phys. Rev. Lett. 91, 037001 (2003).
[15] R. V. Pisarev, I. Sänger, G. A. Petrukovskii, and M. Fiebig, Phys. Rev. Lett. 93, 037204 (2004).
[16] S. Pagliara, F. Parmigiani, P. Galinetto, A. Revcolevschi, G. Samoggia, Phys. Rev. B. 66, 024518 (2002).
[17] H. S. Choi et al., Phys. Rev. B. 60, 4646 (1999).
[18] H. Matsueda, A. Ando, T. Tohyama, and S. Maekawa,
[19] O. V. Misochko, S. Tajima, C. Urano, H. Eisaki, S. Uchida, Phys. Rev. B 53, R14733 (1996).
[20] Jacues I. Pankove, *Optical processes in semiconductors* (Dover, New York, 1975).
[21] J.-P. Gallinar, Phys. Rev. B 48, 5013 (1993).