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Character of charge transfer excitons in $Sr_2CuO_2Cl_2$

A. S. Moskvin
Department of Theoretical Physics, Ural State University, 620083 Ekaterinburg, Russia

R. Neudert, M. Knupfer, J. Fink, and R. Hayn
Institut für Festkörper- und Werkstofforschung (IFW) Dresden, D-01171 Dresden, Germany
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High resolution electron energy loss spectroscopy (EELS) measurements of the insulating, layered cuprate compound $Sr_2CuO_2Cl_2$ have been performed with a transferred momentum near $\mathbf{k}=0$ and in a wide energy range up to 20 eV. To interpret the data a semiquantitative embedded cluster approach is applied to describe the electron-hole excitations in insulating cuprates. The theory includes the complete set of Cu $3d$ and O $2p$ orbitals and predicts a rather wide ($2 \div 13$ eV) spectral range of the main dipole-allowed one- and two-center charge transfer (CT) transitions whose positions are in good quantitative agreement with the experimental spectra. Both, theory and the experimental data show that the CT gap is determined by a superposition of nearly degenerate one-center, localized CT excitations and two-center CT excitons with sizable dispersion.

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The nature of the electron-hole excitations in parent quasi-2D cuprates such as La_2CuO_4, $Sr_2CuO_2Cl_2$, $YBa_2Cu_3O_6$, and their 1D counterparts like Sr_2CuO_3, Sr_2CuO_2, Li_2CuO_2 represents one of the most important, challenging issues both for the high T_c problem and, in general, for strongly correlated oxides. It is now believed that the most intense low-energy electron-hole excitations in insulating copper oxides correspond to the transfer of electrons from O to Cu in the CuO_2 layer, hence these materials are charge transfer (CT) insulators.[1] However, there is much ambiguity concerning the nature of this spectral feature. Sometimes, only the intense band near 2 to 3 eV is connected with the O $2p$ - Cu $3d$ charge transfer, and higher-lying structures are assigned to Cu $4s$, Cu $4d$, Sr $5d$ or La $5d/4f$ states depending on the actual chemical structure. The band structure calculations, including LDA+U, fail to clarify the situation since they cannot reproduce the important effects of intra-atomic correlations which are important both for the ground and the excited state. Moreover, the electron-hole excitations of Mott insulators cannot be treated as independent excitations of single-particle states.

One of the most ideal model compounds of a 2D CT insulator is $Sr_2CuO_2Cl_2$ on which we will concentrate the following discussion. Studying this compound using angle resolved photoemission spectroscopy (ARPES) it was found that the lowest excitation consists of a Zhang-Rice (ZR) singlet with a small dispersion of the order of $2J$ (J being the in-plane exchange integral), i.e., with a high effective mass.[2] Different from ARPES where an electron is emitted, the excitations in electron energy-loss spectroscopy (EELS) represent electron-hole pairs. The first analysis[3] of excitons in $Sr_2CuO_2Cl_2$ revealed a surprisingly large energy dispersion of about 1.5 eV along [110] which was interpreted in terms of a small exciton moving freely through the lattice without disturbing the antiferromagnetic spin background, in contrast to the single hole motion. This model of Zhang and Ng (ZN) is restricted to the Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals and the elementary excitation consists of a Cu^+ and a neighboring Zhang-Rice singlet-like excitation in Cu and O orbitals.[4] Already a shorthand inspection of the original experimental data,[3] and especially of the high-resolution EELS spectra[5] for this system point to some essential shortcomings of the ZN-model. In particular, the nature of several dispersionless narrow bands (one of them with a small binding energy of only about 2 eV) is not explained. Moreover, the high-resolution measurements reveal a very rich multi-excitonic nature of the EELS spectra.

In order to get a better experimental basis of electron-hole excitations in $Sr_2CuO_2Cl_2$ we present here high resolution EELS data in a wide energy range up to 20 eV and not restricted to 8 eV as in Refs. 3 and 5. We limit ourselves to a momentum transfer near zero where only dipole allowed transitions are visible. For its interpretation an embedded cluster method is applied which extends the ZN-theory with respect to two points. It includes the complete set of Cu $3d$ and O $2p$ orbitals of the CuO_4 plaquette and it distinguishes two types of excitons, namely localized one-center excitations and two-center excitons extending over two CuO_4 plaquettes.

For the EELS measurements, films of about 100 nm thickness were cut from a $Sr_2CuO_2Cl_2$ single crystal using an ultramicrotome equipped with a diamond knife. EELS spectra were recorded in transmission using a spectrometer described in detail elsewhere.[6] The energy and momentum resolution were chosen to be 115 meV and 0.05 $Å^{-1}$, respectively. Prior to the measurements, the crystal structure and the orientation of the films were characterized by electron diffraction.

In Fig. 1 we show the imaginary part of the dielectric function, ϵ_2, for a small momentum transfer in the a-b plane of 0.1 $Å^{-1}$ which corresponds to the optical limit. The dielectric function has been derived from the measured loss function via a Kramers-Kronig analysis. Also shown in Fig. 1 is an assignment of the individual features in ϵ_2 which will be presented in detail below.

To analyze the data we apply the embedded molecular cluster method. It is an effective method to describe excitonic states in strongly correlated Mott-Hubbard insulators

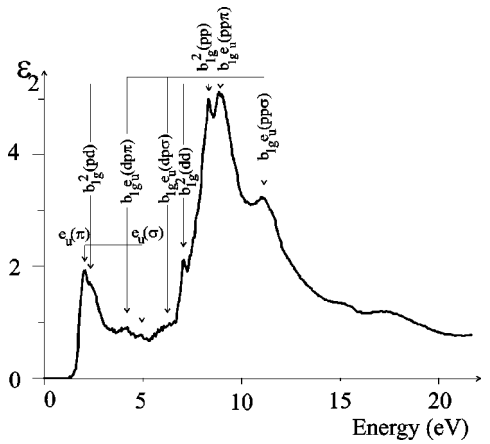

FIG. 1. The spectral dependence of the imaginary part of dielectric function $\epsilon(\omega)$ for $Sr_2CuO_2Cl_2$. Arrows mark the predicted energy position of one-center, two-center b_{1g}^2 channel, and $b_{1g}e_u$ channel CT transitions.

especially with small effective electron-hole separation. In the present context we use one or two neighboring CuO_4 plaquettes embedded into the CuO_2 plane.

One-center excitons. Beginning from 5 Cu $3d$ and 12 O $2p$ atomic orbitals for a CuO_4 cluster with D_{4h} symmetry, it is straightforward to form 17 symmetrized even a_{1g}, a_{2g}, b_{1g}, b_{2g}, e_g and odd a_{2u}, b_{2u}, $e_u(\sigma)$, $e_u(\pi)$ orbitals. The even Cu $3d$ a_{1g} $(3d_{z^2})$, b_{1g} $(3d_{x^2-y^2})$, b_{2g} $(3d_{xy})$, and e_g $(3d_{xz},3d_{yz})$ orbitals hybridize due to strong Cu $3d$–O $2p$ covalency with the even O $2p$ orbitals of the same symmetry, thus forming appropriate bonding γ^b and antibonding γ^a states.

Fig. 2 represents a realistic single-hole energy spectrum for a CuO_4 plaquette embedded into an insulating cuprate like $Sr_2CuO_2Cl_2$. For illustration we show also a step-by-step formation of the cluster energy levels from the bare Cu $3d$ and O $2p$ levels with the successive inclusion of the crystalline field (CF) effects, the O $2p$–O $2p$ and the Cu $3d$–O $2p$ covalency. We used typical values for the different energy parameters in accordance with several estimates in the literature that can be summarized as follows (in eV): $\epsilon_p-\epsilon_d\approx 2-3$, $\Delta_p=\epsilon_{p\sigma}-\epsilon_{p\pi}\approx 1-3(\epsilon_{p\pi}<\epsilon_{pz}<\epsilon_{p\sigma})$, $t_{pd}\approx 1.0-1.5$, and $t_{pp\sigma}\approx 0.8$, $-t_{pp\pi}\approx 0.2-0.4$, where ϵ_i denote on-site energies of the corresponding orbitals and t_i denote the special transfer integrals.[7,8] The energies ϵ_d and ϵ_p are the centers of gravity for the Cu $3d$ and O $2p$ manifolds, respectively.

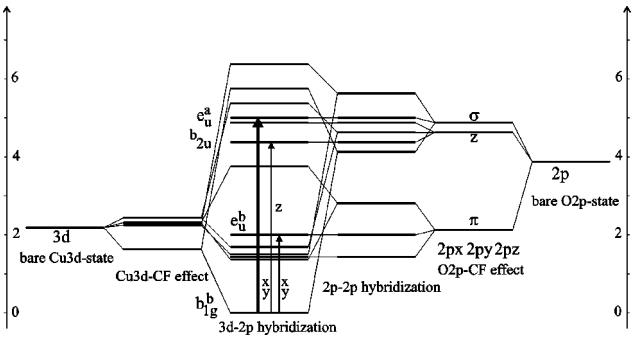

FIG. 2. Model single-hole energy spectra for a CuO_4 plaquette based on simple cluster model with parameters relevant for $Sr_2CuO_2Cl_2$ and a number of other insulating cuprates. Only the ground state and the nonbonding orbitals that are final states of dipole-allowed CT transitions are denoted and transitions marked by arrows. The other orbitals from bottom to top are given as b_{2g}^b, a_{2g}, a_{1g}^b, e_g^b, b_{2g}^a, a_{2u}, e_g^a, b_{1g}^a, and a_{1g}^a.

Among the numerous one-center electron-hole CT excitations the first candidates for dipole-active excitons are CT transitions from the ground state b_{1g}^b to the purely oxygen doublet O $2p_\pi$–O $2p_\sigma$ hybrid states $e_u^{a,b}$, which are allowed in "in-plane" polarization $\vec{E}\perp C_4(x,y)$. The transition to a purely oxygen O $2p_z$-like state b_{2u} is allowed in "out-of-plane" polarization $\vec{E}\|C_4(z)$ which is however not measured in Fig. 1. The two excitations to e_u^b and e_u^a differ by the oxygen hole density distribution: the former has predominantly O $2p_\pi$ character, while the latter is O $2p_\sigma$ dominated. Discussing shortly the dipole inactive excitons one should note the a_{2g} excitation with purely oxygen O $2p_\pi$ holes. In accordance with the model energy spectrum (see Fig. 2) its energy should be of the order of 1.5–1.8 eV, or in other words appears to be lower than the optical gap. This circumstance draws specific attention to this exciton, despite it is dipole forbidden.

Consequently, we predict two one-center excitons to be visible in the experimental spectra shown of Fig. 1: namely the $e_u(\pi)$ and $e_u(\sigma)$ excitons with predominantly $2p_\pi$ and $2p_\sigma$ orbital weight, respectively. Its energy separation and also its relative intensity are determined by the level of the p_π-p_σ mixing characterized by the mixing angle $\alpha_e\approx-(t_{pp\sigma}+t_{pp\pi})/\Delta_p$. The respective one-center excitons may be represented rather simply as a hole rotating on the four nearest oxygens around an electron dominantly localized in the Cu $3d_{x2-y2}$ state with a minimal electron-hole separation $R_{eh}\approx R_{CuO}\approx 4$ a.u. [see Fig. 3(a)]. This low distance leads to a considerable Coulomb attraction such that we estimate the energy of the $e_u(\pi)$ exciton to be about 2 eV. The final $e_u(\pi)$ and $e_u(\sigma)$ states are unstable with regard to the formation of Jahn-Teller (or pseudo-Jahn-Teller) centers with a resulting self-localization of the appropriate CT excitation. This effect is especially important for the $e_u(\pi)$ exciton due to the predominantly O $2p_\pi$ nature of the hole state resulting in small transfer integrals and relatively large effective mass for the exciton.

For the relative intensities of the $e_u(\pi)$ and $e_u(\sigma)$ excitons it is easy to obtain $I[e_u(\pi)]/I[e_u(\sigma)]=\tan^2\alpha_e$ with the mixing angle α_e. We find this ratio to be about 0.1 resulting in small but nonzero intensity for the $e_u(\pi)$ exciton. The high-energy $e_u(\sigma)$ exciton is expected to manifest significant higher intensity both in optical and EELS spectra.

Two-center excitons. The local two-atomic O $2p$–Cu $3d$ charge transfer generates not only intra-center excitations within one CuO_4 plaquette but also inter-center excitons. These inter-center transitions between two CuO_4 plaquettes may be considered as quanta of the disproportionation reaction

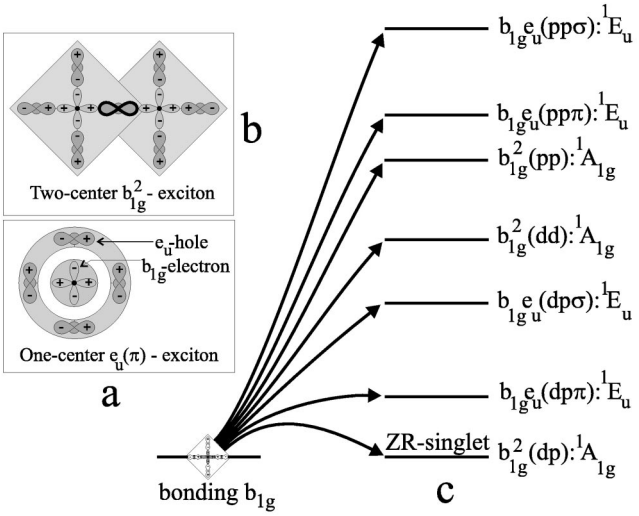

FIG. 3. (a) Simplified illustration of the one-center exciton and (b) the two-center exciton of $b_{1g}^2(pd)$, i.e., ZR-singlet type. (c) Classification of the important two-center excitons together with an energy scheme.

$$CuO_4^{6-} + CuO_4^{6-} \rightarrow CuO_4^{7-} + CuO_4^{5-}$$

with the creation of electron CuO_4^{7-} and hole CuO_4^{5-} centers. The former correspond to completely filled Cu $3d$ and O $2p$ shells, or the vacuum state for holes, while the latter may be found in different two-hole states.

All the two-center excitons may be classified by the two hole configuration of the CuO_4^{5-} center. Restricting to charge transfer processes which are governed by the strongest σ bond, one has to distinguish three different channels $b_{1g}^2, b_{1g}a_{1g}, b_{1g}e_u$, respectively, in accordance with the symmetry of the final two-hole state. The $b_{1g}a_{1g}$ channel has zero matrix elements at the Γ point and can be neglected. The b_{1g}^2 channel consists of 3 wave functions with different Cu or O character. The lowest one is the famous Zhang-Rice (ZR) singlet

$$|b_{1g}^2(dp)\rangle = |ZR\rangle = -0.25|d^2\rangle + 0.95|dp\rangle - 0.19|p^2\rangle,$$

with an energy $E_1 = 3.6$ eV on the CuO_4 cluster. For the estimate we used standard parameters (in eV): $U_d = 8.5$, $U_p = 4.0$, $V_{pd} = 1.2$, $\epsilon_d = 0$, $\epsilon_p = 3.0$, $t_{pd} = 1.3$.[7] The two excited states are 5.2 and 6.7 eV higher in energy and are described by the wave functions

$$|b_{1g}^2(dd)\rangle = 0.95|d^2\rangle + 0.21|dp\rangle - 0.22|p^2\rangle,$$

$$|b_{1g}^2(pp)\rangle = -0.17|d^2\rangle - 0.24|dp\rangle - 0.96|p^2\rangle.$$

Due to the smallness of our cluster we expect the ZR-singlet energy (3.6 eV) to be overestimated, larger clusters give 2 to 3 eV. Nevertheless, the energy separation to the excited states is expected to be of the right order of magnitude. In a similar way one can also estimate the $b_{1g}e_u$ channel. As it was mentioned above, we have two types of purely oxygen e_u orbitals: $e_u(\sigma)$ and $e_u(\pi)$ with σ and π directions of the O $2p$ lobes, respectively. These orbitals hybridize with each other due to the oxygen transfer. As a result we obtain four ^1E_u terms for the $b_{1g}e_u$-like two-hole configurations, namely $b_{1g}^b e_u(\pi)$ which can also be denoted as $b_{1g}e_u(dp\pi)$, and further $b_{1g}e_u(dp\sigma)$, $b_{1g}e_u(pp\pi)$, and $b_{1g}e_u(pp\sigma)$. They form the final states of the $b_{1g}^b e_u$ channel of the two-center CT transitions. An overview about all two-center excitons is given in Fig. 3(c).

All the two-center excitons could be divided into even and odd excitons. For 2D cuprates these excitons generate four A_{1g}, B_{1g}, E_u plane modes ($S, D, P_{x,y}$ modes)[4] that are visible in the EELS spectra away from the Γ-point. The transition matrix elements have a rather complicated **k** dependence and the simple dipole approximation is not sufficient. In the matrix element analysis which shall be presented in a forthcoming publication[9] we find at Γ for the b_{1g}^2 channel two important excitons with an energy separation ≈ 7 eV in between, and a less intense exciton, blue-shifted to ≈ 5 eV with regard to the first one. The low-lying exciton with ZR-singlet character has a rather unusual **k** dependence of intensity along the [110] direction with a sharp decrease, or even a compensation point, when going to the BZ boundary. The high-energy exciton with the final ZR-singlet-like $^1A_{1g}$ state of predominantly O $2p$ nature, is likely to manifest the largest intensity for the b_{1g}^2 channel. Within the $b_{1g}e_u$ channel we predict four important excitons, generated by CT to $e_u(\pi)$ and $e_u(\sigma)$ orbitals with smaller and larger weight of O $2p_\sigma$ orbitals, respectively. These weights would determine the relative intensity of the appropriate excitons. The photoemission data[10,8] predict the energy separation between the low-lying $b_{1g}e_u(dp\pi)$ and $b_{1g}^2(dp)$ excitations to be of the order of 1.5 eV. The $b_{1g}e_u$ excitons manifest a rather simple dispersion of intensity along both main directions in the BZ zone with gradual interchange between dipole allowed and forbidden modes.

Interpretation of the excitation spectrum. Having classified all the dipole-allowed one- and two-center excitons, one can assign the significant peaks of Fig. 1. The lowest one at around 2 eV has clearly a double peak structure which was not resolved in Ref. 3. Furthermore, inspecting the **k** dependent spectra of Ref. 5, one observes that the lower peak has no dispersion and loses intensity away from Γ. The other one has a strong dispersion in agreement with the data and the analysis of Ref. 3. Therefore, we assign that double peak structure to the one-center $e_u(\pi)$ and the two-center (ZR-singlet) $b_{1g}^2(pd)$ exciton, respectively. This interpretation is also supported by an angle-resolved EELS study of the 1D cuprate Sr_2CuO_3.[11] Such chain materials provide an unique opportunity to separate one- and two-center excitons, thereby to verify our main proposal. This is possible due to different polarization properties for both excitons. Indeed, the one-center CT transitions are allowed both in longitudinal ($\vec{E}\parallel$ chain direction) and in transversal ($\vec{E}\perp$ chain direction) polarizations, whereas the two-center CT transitions appear only in the former. Therefore, the weak dispersionless peaks in transversal polarization[11] can be attributed to one-center excitons, whereas the EELS spectra in longitudinal polarization[11,12] can be understood as a superposition of one-

and two-center excitations. The one-center excitons provide small additional peaks on the dominant structures given by the two-center excitons.

Having positioned the lowest one- and two-center excitons, the higher states are fixed by the chosen parameter values (see Fig. 1). Remarkably, all the excitations which were analyzed before correspond to visible features in ϵ_2. The highest intensity is found at about 9 eV and it is connected with the two-center excitons $b_{2g}^2(pp)$ and $b_{1g}e_u(pp\pi)$ of dominantly oxygen character. This shows that important spectral information is contained in the region above 8 eV. The highest excitation at about 12 eV is interpreted to be $b_{1g}e_u(pp\sigma)$, and then the spectral intensity decreases. The peak at about 18 eV is likely to be attributed to transitions with O $2s$ initial state.

A close examination of other materials shows that the two-component structure of the CT gap appears to be a commonplace for many parent cuprates.[13–15] The dipole-allowed localized $b_{1g}\rightarrow e_u^b$ excitation within the CuO_4 plaquette related essentially to the $e_u(\pi)$ state is distinctly seen in optical and EELS spectra for different insulating cuprates as a separate weak feature or a low-energy shoulder of the more intense band near 2.5 eV assigned to the inter-center CT transition associated with the Zhang-Rice singlet-like excitation $b_{1g}^2(dp)$.[9] The small intensity of the one-center $e_u(\pi)$ exciton is explained by the dominantly O $2p_\pi$ nature of the final state and by the strong tendency to self-localization (trapping).

One may wonder why such a double-peak structure of the lowest excitation is not seen in the corresponding ARPES spectra of $Sr_2CuO_2Cl_2$. There, the lowest excitation is clearly connected with the ZR-quasiparticle,[2] and the nonbonding oxygen p_π orbitals appear with 1.5 eV higher binding energy (see Refs. 8 and 10). The reason is that EELS (or optical absorption) creates electron-hole pairs and the smaller extent of the one-center exciton leads to a Coulomb contribution to the exciton binding energy which compensates the ZR-singlet binding energy. On the other hand, comparing the different two-center excitons, the energy difference between ZR-singlet and nonbonding oxygens is seen in the difference between $b_{1g}^2(pd)$ and $b_{1g}e_u(dp\pi)$ (roughly 1.7 eV in Fig. 1).

In conclusion, we measured and interpreted the electron-hole excitations of $Sr_2CuO_2Cl_2$. We extended the Zhang-Ng model by considering the complete set of Cu $3d$ and O $2p$ orbitals and by introducing one-center and two-center excitons. Instead of one $d-p_\sigma$ CT transition of the ZN-model with an energy ≈ 2.5 eV (Γ point) we arrive at a set of one- and two-center excitons generated by $d-p_\sigma$ charge transfer, and occupying a very broad energy range from ≈ 2 up to ≈ 13 eV. The EELS data shows a double-peak structure of the CT gap which is determined by nearly degenerate intra-center and inter-center excitons.

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