Peculiar temperature-dependent charge response of frustrated chain cuprates near a critical point

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Abstract. The optical conductivity $\sigma(\omega)$ is calculated at finite temperature $T$ for CuO$_2$ chain clusters within a $pd$-Hubbard model. Data at $T = 300$ K for Li$_2$CuO$_2$ are reanalyzed within this approach. The relative weights of Zhang-Rice singlet and triplet charge excitations near 2.5 and 4 eV, respectively, depend strongly on $T$, and a dramatic dependence of $\sigma(\omega)$ on the ratio of the 1$^{st}$ to 2$^{nd}$ neighbor exchange integrals is predicted. Information about exchange interactions for edge-shared cuprates can be obtained from $T$-dependent optical spectra. A reduced intensity of the ZRS-transition with increasing $T$ is also relevant for unfrustrated cuprates in general.

Usually the optical spectra of wide gap insulators at $\hbar \omega > 1$eV excitation energy are hardly affected by temperature $T$, magnetic fields $H$, and by the magnetic nature of their ground state (GS). Moreover, spin and charge degrees of freedom are often decoupled in one dimension (1D). We present theoretical results qualitatively valid for several cuprates which prove just the opposite in all these respects. Our study bases on the fact that different magnetic states with different symmetries obey different selection rules, which can lead to sizable $T$-dependence of the optical spectra. Especially, for systems with small (large) exchange integrals, the energy difference between the GS and the excited magnetic states of the system will be small enough so that they can be thermally populated, causing a strong (weak) $T$-dependence for $\sigma(\omega)$. For an illustration we consider Li$_2$CuO$_2$ being of current interest [1–7]. In Li$_2$CuO$_2$ chains running along the $b$-axis are formed by the edge-sharing of CuO$_4$ plaquettes. This system stands for a class of frustrated spin-1/2 chain systems with both small ferromagnetic (FM) nearest-neighbor (NN) Cu-Cu exchange coupling $J_1$ and antiferromagnetic (AFM) next-nearest neighbor (NNN) in-chain exchange $J_2$ [1,3] in terms of a 1D spin-1/2 Heisenberg model

$$H_S = \sum_i J_1 S_i S_{i+1} + J_2 S_i S_{i+2} + J_3 S_i S_{i+3} + ...$$

(1)

The lack of the Zhang-Rice singlet peak (ZRS) in reflectivity and electron energy loss spectroscopy (EELS) data at $T = 300$ K [1, 2] is a challenge. There is also no consensus on the role of two scenarios for the FM in-chain ordering below $T_N = 9$ K. Scenario 1 is given by a dominant FM $J_1$ [7] according to $\alpha = -J_2/J_1 < \alpha_c \approx 1/4$, if $J_3 \approx 0$, where $\alpha_c$ marks the transition from a high-spin FM to a low-spin spiral-like ground state (GS). In scenario 2 it stems from a specific AFM inter-chain coupling and a single chain would be at $\alpha > \alpha_c$ [1,8].
The theoretical description [1] of the optical conductivity $\sigma(\omega)$ at $T=0$ on the basis of a Cu $3d_{xy}$ O $2p_{x,y}$ Hubbard model (model M1; $x$ and $y$ along the $b$- and $c$-axes, respectively, see Ref. 1) predicts charge transfer excitation into a ZRS near $\omega_{ZRT} = 2.25$ eV. Its missing observation (data at $T=300$ K) was ascribed to poor resolution [1], or to uncoupled CuO$_4$ units [2]. We show, that a ZRS present at low-$T$ would be strongly suppressed at 300 K. However, if the Hamiltonian parameters (model M2) are chosen to improve the description of O 1 s x-ray absorption (XAS) [6], optical [1], EELS [2], and RIXS data [4], then a weak ZRS appears at finite $T$, only, but is accompanied by a Zhang-Rice triplet (ZRT) absorption at $\omega_{ZRT} \approx 4$ eV.

The used five-band Hubbard $pd$-Hamiltonian reads (cf. also Ref. 1)

$$H_H = \sum_i \varepsilon_i n_i + U_i n_i \langle n_i \rangle + \sum_{ij,s} t_{ij} c^\dagger_{ij,s} c_{ij,s} + \frac{1}{2} \sum_{i \neq j} V_{ij} n_i n_j + \sum_{s,s'} K_{ij} \left( c^\dagger_{ij,s} c_{ij,s'} c_{ij,s} + c^\dagger_{ij,s} c_{ij,s'} c_{ij,s} \right),$$

(2)

where $n_{is} = c^\dagger_{is} c_{is}$ and $n_i = \sum_s n_{is}$. The indices $i$ and $j$ run over all Cu-$3d_{xy}$ and O-$2p_{x,y}$ orbitals and $s$ is the spin index. Except for the $\varepsilon_i$ the Hamiltonian parameters are the same as in Refs. 1. Polarized O 1 s XAS studies [6] show a nearly isotropic O 2p-hole distribution in the $xy$-plane, i.e. $n_{ps} \approx n_{py}$. To achieve this despite the anisotropic CuO$_4$ plaquette geometry, $\varepsilon_{py} - \varepsilon_{px} = 0.2$ eV was taken as distinct from $\varepsilon_{py}$ in Ref. 1. To get a strong peak in $\sigma(\omega)$ near 4.4 eV (Fig. 2), $\Delta_{pd} = (\varepsilon_{py} + \varepsilon_{px})/2 - \varepsilon_d$ has been up-shifted by 0.5 eV. To show the very distinct $\sigma(\omega)$ caused by these slight changes, calculations were performed for the set M1, too.

The leading exchange integrals $J_1$ and $J_2$ determine the spectrum of low-energy excited states $|\nu\rangle$ (spin excitations) of the spin model (1). We found the $J$-values from projecting the Hamiltonian (2) onto (1). At a given $T$ and possibly in the presence of a magnetic field $H$, $\sigma(\omega,H,T)$ of (2) is obtained from the $\sigma_\nu(\omega)$ with the initial spin states $|\nu\rangle$ of (2) [9]:

$$\sigma(\omega,T) = \sum_\nu w_\nu(T) [1 - \exp(-\hbar \omega/k_B T)] \sigma_\nu(\omega), \quad w_\nu = \frac{g_\nu \exp(-E_\nu/k_B T)}{\sum_\nu' g_{\nu'} \exp(-E_{\nu'}/k_B T)},$$

(3)

where for $H=0$ the spin degeneracy is $g_\nu = 2S_\nu + 1$. E.g., for the largest cluster, Cu$_8$O$_{14}$, which can still be handled by the exact diagonalization (ED) of Eq. (2) there are $2^8$=64 spin states. Due to $\hbar \omega \gg k_B T$ the thermal occupation of the final states in (3) can be ignored. In case of $H \neq 0$ the $S \neq 0$ states with nonzero $S_z$ are Zeeman split which affects the probability $w_\nu = w_\nu(T,H)$ to find a cluster in a given spin state $(S_\nu, S_{z,\nu})$. Then the $g_\nu$ are replaced by

$$g_\nu(H,T) = 1 + 2 \sum_{\nu'=1}^{\nu_{\text{max}}} \cosh \left[ \frac{\nu'/g_{\nu} \mu_B H}{k_B T} \right], \quad g_{\nu}(H,T) = 2 \sum_{\nu'=1}^{\nu_{\text{max}}} \cosh \left[ \frac{(2\nu'-1)g_{\nu} \mu_B H}{2k_B T} \right],$$

(4)

for even (odd) chains, respectively, $g_L$ denotes the Landé-factor. The $\sigma(\omega)$ has been found using ED and the continued fraction method for Cu$_n$O$_{2n+2}$ clusters as well as the DMRG-technique [10] for clusters with $n > 6$. The $\delta$-functions of the spectra are convoluted with a Lorentzian broadening of $\gamma_L = 0.35$ eV at half width for comparison with experimental data.

The $\sigma(\omega)$ for Cu$_n$O$_{2n+2}$ chain clusters at $H = T = 0$ exhibit a multiple peak structure: two peaks near 4 and 5 to 5.5 eV (see Fig. 1). There are marked differences in $\sigma(\omega)$ between 2 and 4 eV depending the GS is low-spin (i.e. a helical state) or a high spin state (i.e. a FM state ). For the chains of Li$_2$CuO$_2$, due to their closeness to $\alpha_c$, the issue depends sensitively on the $J$-values governed by the parameters $\varepsilon_i$. A main issue is that while the $\varepsilon_i$ values of M1 lead to a low-spin GS ($\alpha > \alpha_c$) M2 results in a high-spin GS ($\alpha < \alpha_c$). $\sigma(\omega)$ for a Cu$_4$O$_{14}$ chain with a high-spin GS ($S=3$) or a low-spin GS ($S=0,1$) are shown on Fig. 1. The height of the feature between 2 and 3 eV depends on the cluster size and on the total spin of the GS. Peaks caused by inter-plaquette transitions may occur starting from dimers $n = 2$. If their GS is an
Figure 1. (Color online). Finite size effect for $\sigma(\omega)$. Left: GS in the lowest spin state. The curves for various $n$ are shifted by $(n-1) \times 100 (\Omega \text{cm}^{-1})^{-1}$. Right: Experimental and theoretical optical conductivities of (2) for $T = 0$ and $T = 300$ K using a low-spin ($S = 0.1$) GS (M1) and a high-spin ($S = 3$) GS (M2).

$S = 0$ or a low-spin state for larger clusters a peak appears between 2 and 3 eV. This transition is forbidden, if the GS is a FM state. Since in the optical transition $S$ and $S_z$ are conserved, the final state for an excited dimer in the former case is again a singlet (low-spin state) with two holes at one of the two CuO$_4$ units, one sitting mainly on Cu and one sitting mainly on O. This transition is usually denoted as a ZRS excitation. In the FM case the excited state contains a ZRT of two holes on one plaquette, which occurs slightly below the main peak near 4 eV. The energy of a ZRT $\approx 4$ eV found above is in accord with 4.1 eV reported in a recent RIXS study [4]. Results for $\sigma(\omega, T)$ from (3) for the sets M1 and M2 are shown on Fig. 2. At 300 K both sets M1 and M2 yield a strong suppression of the ZRS feature. The main experimental

Figure 2. (Color online). $T$-dependent optical conductivity at $H = 0$ (upper) and at $H \neq 0$ (lower) within the typical energy regions of ZRS and ZRT transitions for clusters within a low-spin (M1) and a high-spin GS (M2). '$T = \infty$' means $k_B T \gg | J_i |$, but $\hbar \omega \geq 10^4$ K $\gg k_B T$ is still fulfilled.
Table 1. Exchange integrals $J_i$ and their ratio $\alpha = -J_2/J_1$ from ED of the Hubbard model (2) with sets M2 and M1 as well as from DFT+$U$ and a quantum chemistry (QC, Ref. 9, Tab. II) study.

|     | ED (M2) | PRESENT WORK DFT (LSDA+$U$, FPLO) | ED (M1) | OTHER WORK DFT (GGA+$U$, WIEN2k) | QC |
|-----|---------|----------------------------------|---------|-------------------------------|----|
| $J_1$, K | -146    | -187                             | -215    | -103                          | -126 | -142 |
| $J_2$, K | 33      | 43                               | 67      | 49                            | 52   | 22   |
| $J_3$, K | -0.5    | -                                | -       | -2                            | -    | -    |
| $\alpha$ | 0.23    | 0.23                             | 0.31    | 0.47                          | 0.41 (U = 8eV, $J=0$) | 0.15 |

peak at $\gtrsim 4$eV is, however, better reproduced by set M2. We also studied the field dependence of $\sigma(\omega, T, H)$ (Fig. 2, right panel) and found it similar for both sets M1 and M2. Set M1 results in $-J_2/J_1 = \alpha > \alpha_c$ and hence in a low-spin GS, while set M2 results in $\alpha < \alpha_c$ and hence in a FM GS. The main reason for the smaller $\alpha$-value of set M2 is a reduction in superexchange due to the enhanced $\Delta_{pd}$-value. As is clearly seen from Fig. 2, whether $\alpha < \alpha_c$ or $\alpha > \alpha_c$ can directly experimentally be decided by low-$T$ studies of $\sigma(\omega)$ and such studies are highly desirable.

To compare the $J_i$ with those from other methods, density functional theory (DFT) calculations using the structural data of Ref. 5 were performed in the local spin density plus Hubbard $U$ (LSDA+$U$) approach. The full-potential local-orbital (FPLO) code [11] was employed. In addition to the onsite Coulomb integral $U$ for the Cu 3$d_{xy}$ hole also an onsite exchange integral $J = 1$ eV was used. Table I shows the obtained values for $J_1$ and $J_2$ and a comparison with similar results given in Ref. 8, by a quantum chemistry (QC) study [7], and with values obtained from a projection of the models M1 and M2 onto the Hamiltonian (1). The small obtained values of $J_3$ justify the use of a $J_1$-$J_2$ model for Li$_2$CuO$_2$. Note the agreement of three independent approaches to be near $\alpha_c = 1/4$ ($J_3 = 0$) of a quasi-1D situation.

We have shown that the $pd$-Hamiltonian (2) with the set M2 consistently describes EELS and optical data of Li$_2$CuO$_2$ at 300 K. The main issue, however, is that the magnetic GS and the low energy spin excitations strongly affect the T-dependence of $\sigma(\omega)$ in the visible range caused by the thermal population of excited spin states which differ magnetically from the GS. This allows a classification of cuprates by optical studies between 300 K and low-$T$: if the AFM (FM) exchange is dominant, $\sigma(\omega)$ in the ZRS energy region increases (decreases) lowering $T$. For a 1D FM-J$_1$–AFM-J$_2$ system it shows directly its location relative to $\alpha_c$. For Li$_2$CuO$_2$ this can be decisive to elucidate the intra-chain exchange and the reason for the FM in-chain order at low $T$. If $\alpha_c > \alpha$ would be true and the FM in-chain order below $T_N$ would be due to weak inter-chain exchange, a non-monotonic behavior of $\sigma(\omega, T)$ for $T > T_N$ is predicted. Near $\alpha_c$ as in Li$_2$ZrCuO$_4$ [12] in addition also the magnetic field effect becomes an issue.

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