Temperature-dependent optical conductivity of undoped cuprates with weak exchange

J. Málek,1,2 S.-L. Drechsler,1,* U. Nitsche,1 H. Rosner,3 and H. Eschrig1
1Leibniz-Institut für Festkörper-und Werkstoffsforschung Dresden, P.O. Box 270116, D-01171 Dresden, Germany
2Institute of Physics, ASCR, Na Slovance 2, CZ-18221 Praha 8, Czech Republic
3Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

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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 rather dramatic dependence of $\sigma(\omega)$ on the ratio of the first to second neighbor exchange integrals is predicted. On the basis of these results, information about exchange interactions for frustrated edge-sharing cuprates can be obtained from $T$-dependent optical spectra. Our results are also relevant for magnetically weakly coupled wide-gap insulators in general.

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Standard wisdom on wide-gap insulators says that their optical spectra above 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). Here, we present exact theoretical results qualitatively valid for several cuprates to be specified below which prove just the opposite in all these respects. Our study is based on the fact that different magnetic states with different symmetries obey different selection rules, which—in the case of soft magnetic materials—can lead to sizable $T$ dependence of the optical spectra. For systems with small 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. This will cause a strong $T$ dependence of various response functions, here presented for the case of the optical conductivity $\sigma(\omega)$. For an illustration of our approach we consider Li$_2$CuO$_2$ being of current interest,1–12 structurally simple, and most importantly, where single-crystal data are available in a broad $\omega$ range.12 This system stands for a class of frustrated spin-1/2 chain materials with both small ferromagnetic (FM) NN Cu-Cu exchange coupling $J_1$ and antiferromagnetic (AFM) next-nearest-neighbor (NNN) in-chain exchange $J_2$ (Ref. 1 and 3) in terms of a 1D spin-1/2 Heisenberg model

$$\mathcal{H}_S = \sum_i J_1 s_i s_{i+1} + J_2 s_i s_{i+2} + J_3 s_i s_{i+3} + \ldots$$ (1)

In Li$_2$CuO$_2$ chains running along the $b$ axis are formed by the edge-sharing of CuO$_4$ plaquettes. The most exciting puzzle addressed here is the missing of the Zhang-Rice singlet peak (ZRS) in reflectivity and electron energy-loss spectroscopy (EELS) data at $T=300$ K.1,12 Its detection in resonant inelastic x-ray scattering (RIXS) spectra is under debate, too.4,45 There is also no consensus on the role of two scenarios for the FM in-chain order below the Néel temperature $T_N=9$ K. Scenario I is given by a dominant FM $J_1$ (Ref. 9) defined by the inequality $a=-J_1/J_2<\alpha_c=0.25$, if $J_2$ is weak,13 where $\alpha_c$ marks the transition from a high-spin FM to a low-spin spiral-like ground state. While in scenario II it stems from a specific AFM interchain coupling and a single chain would be at $a>\alpha_c$.1,4,14

A first microscopic theoretical description1 of the magnetic susceptibility $\chi(T)$ and of $\sigma(\omega)$ at zero temperature on the basis of a Cu $3d_{xy}$–O $2p_x$ Hubbard model ($x$ and $y$ along the $b$ and $c$ axes, respectively, see Figs. 1 and 2 of Ref. 1) predicts charge-transfer excitation of a Cu hole into a ZRS near $\omega_{ZRS}=2.25$ eV. Its missing observation (at $T=300$ K) was ascribed to poor resolution,1 or to uncoupled CuO$_4$ units.2 We show, that a ZRS visible at low $T$ would be strongly suppressed at 300 K. However, if the Hamiltonian parameters are chosen to improve the description of O 1s x-ray absorption (XAS),7 optical,1 EELS,2 and RIXS data,3 then the ZRS absent at $T=0$ appears with rising $T$ but is accompanied by a Zhang-Rice triplet (ZRT) contribution at $\omega_{ZRT}=4$ eV in $\sigma(\omega)$ (superimposed with further transitions). The $\sigma(\omega)$ data are well described this way.

The used Hubbard Hamiltonian reads (cf. also Ref. 1)

$$\mathcal{H}_H = \mathcal{H}_k + \mathcal{H}_C + \mathcal{H}_{\text{ex}}.$$ (2)

Its kinetic, Coulomb, and exchange contributions are

$$\mathcal{H}_k = \sum_i e_n i + \sum_{i,j,s} t_{ij}^s c_{i,s}^\dagger c_{j,s}, \quad n_{is} = c_{i,s}^\dagger c_{i,s},$$ (3)

$$\mathcal{H}_C = \sum_i U_{ni} n_{i} + \sum_{i,j,s} V_{ij} n_{i} n_{j}, \quad n_i = \sum_s n_{is},$$ (4)

$$\mathcal{H}_{\text{ex}} = \frac{1}{2} \sum_{i<j,s,s'} K_{ij} (c_{i,s}^\dagger c_{j,s'}^\dagger c_{i,s'} c_{j,s}) \quad (5)$$

where $i$ and $j$ run over all Cu-$3d_{xy}$ and O-$2p_x$ orbitals and $s$ is the spin index. Except for the $e_{t}$, the Hamiltonian parameters are the same as in Ref. 1: $U_{ji}=8.5$ eV, $U_{ij}=4.1$ eV for the intraorbital and $V_{ij}=-2K_{ij}=2.9$ eV for the O-site interorbital repulsion, where $K_{ij,p}=0.6$ eV is the FM Hund’s rule coupling. As in Ref. 1 isotropy of the FM Cu-O exchange integrals $K_{ij}=K_{ji}=K_{ij,p}=0.05$ eV was used for the sake of simplicity. Polarized O 1s XAS measurements7 with the electric-field vector in $x$ and $y$ direction, respec-
Additionally, a nearly isotropic O 2p-hole distribution in the xy plane. This indicates a condition \( n_p = n_p \) within XAS error bars for the O 2p hole occupation numbers in the GS. In order to achieve this despite the anisotropic CuO\(_4\) plaqutte geometry, \( e_p = e_p = 0.2 \) eV was taken as distinct from Ref. 1 where \( e_p = e_p \) was assumed. In order to reproduce the first strong peak in \( \sigma(\omega) \) near 4.4 \( \pm 0.2 \) eV (Figs. 1 and 2), the mean O onsite energy \( \Delta_{\text{on}} = (e_p + e_p)/2 - e_g \) has additionally been up shifted by 0.5 to 3.7 eV. To demonstrate the strikingly distinct \( \sigma(\omega) \) caused by these moderate changes, calculations were performed with the \( e_p \)-values of Ref. 1, too. Hereafter, these two models [Eq. (2)] are called M\(_1\) and M\(_2\) (above choice). We will show that they lead to different magnetic GS yielding different \( T \) behavior of \( \sigma(\omega) \).

Naturally, the dominating 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 \( H \), the optical conductivity \( \sigma(\omega,H,T) \) of Eq. (2) is obtained from the \( \sigma(\omega) \) with the initial spin states \( |\nu\rangle \) of Eq. (2):\(^15\)

\[
\sigma(\omega,T) = \sum_\nu w_\nu(T) [1 - \exp(-\hbar\omega/k_B T)] \sigma_\nu(\omega),
\]

where \( H=0 \) the spin degeneracy is \( g_s = 2S + 1 \). For instance, for the largest cluster, Cu\(_6\)O\(_{14}\), which can still be handled by the exact diagonalization of the Hamiltonian (2) there are \( 2^6=64 \) low-energy spin states: \( 5 \times (S=0), 9 \times (S=1), 5 \times (S=2), \) and \( 1 \times (S=3) \) multiplets. Due to the large optical transition energies \( h\omega_\nu \gg k_B T \), the thermal occupation of the final states in Eq. (6) can be ignored. In case of an applied external magnetic field \( H \) the \( S=0 \) states with finite \( S \) are Zeeman split which affects the Boltzmann probability \( w_\nu = w_\nu(T,H) \) to find a cluster in a given spin state \( (S_\tau,S_\pi,S) \). In this case the \( g_s \) are replaced by

\[
g_s(\nu,T,H) = 1 + 2 \sum_{\nu'} \cosh \left( \frac{(2\nu' - 1) g_s H}{2k_B T} \right),
\]

for even and odd chains, respectively, where \( g_s \) denotes the Landé factor. All response functions reported below were calculated using exact diagonalizations and the common continued fraction method for Cu\(_6\)O\(_{2n+2}\) clusters. The \( \delta \) functions of the calculated \( \sigma(\omega) \) spectra are convoluted with a Lorentzian broadening of \( \gamma_{\text{L}} = 0.35 \) eV at half width to compare them with optical data.

Generally, the calculated \( \sigma(\omega) \) for Cu\(_6\)O\(_{2n+2}\) chain clusters at \( H=0 \) exhibit a multiplet peak structure: two well-pronounced peaks near 4 and 5 to 5.5 eV as shown in Fig. 1. Remarkably, there are marked differences in the exciton starting from dimers \( n=2 \) to \( n=5 \) and 2 clusters. The \( \delta \) functions of the calculated \( \sigma(\omega) \) spectra are convoluted with a Lorentzian broadening of \( \gamma_{\text{L}} = 0.35 \) eV at half width to compare them with optical data.
sitting mainly on O (similar to a ZRS state on a CuO$_4$ unit). This transition is usually denoted as a ZRS excitation. In the FM case the excited state may contain a triplet (ZRT) of two holes on one plaquette, which in the optical excitation process occurs slightly below the main peak near 4 eV. The intensities of the ZRS and ZRT transitions exhibit some positive finite-size effect $\propto 1/n$ reflecting mainly the number of available plaquettes for an interplaquette transition. For a dimer with $J_1<0$ the GS is always a triplet since $J_2$ is involved for $n\geq 3$, only. A detailed finite-size analysis will be given elsewhere. The ZRT excitation $\approx 4$ eV found above is in excellent agreement with $4.1$ eV reported in a recent RIXS study but in sharp contrast with the assignment given in Ref. 5.

FIG. 3. (Color online) $T$-dependent optical conductivity at $H = 0$ (upper) and at $H \neq 0$ (lower) within the regions of ZRS and ZRT transitions for clusters within a low-spin (M1) and a high-spin GS (M2). “$T=\infty$” means $k_BT \gg |J_1|$, but still $\omega \approx 10^4$ K $\gg k_BT$.

Exact diagonalization of the Hamiltonian (2) yields excitation energies $\omega_{ZRS} = 2.7$ eV, $\omega_{ZRT} = 4$ eV for M2 and $\omega_{ZRS} = 2.25$ eV, $\omega_{ZRT} = 3.7$ eV for M1. For both models this is consistent with $\Delta_{ZRT} = 1.3$ eV obtained as the distance between the lowest $S=0$ and the $S=1$ levels in a single CuO$_5$ plaquette with two holes. The $\sigma(\omega,T)$ obtained from Eq. (6) for both models are shown on Fig. 3. At 300 K M1 and M2 yield the same qualitative behavior: the ZRS is largely suppressed. The main peak position of the experiment at $\approx 4$ eV is, however, much better reproduced by M2. We studied also the field dependence of $\sigma(\omega,T)$ (Fig. 3, lower panel) and found it similar in both models. To repeat it, M1 results in $-J_2/J_1 = \alpha > \alpha_c$ when projected onto the spin Hamiltonian (1) and hence in a low-spin GS; while M2 resulting in $\alpha < \alpha_c$ and hence in a FM GS. The reason for the reduced $\alpha$ is mainly a reduced superexchange due to the enhanced $\Delta_{pl}$ value. As is clearly seen from Fig. 3, whether $\alpha < \alpha_c$ or $\alpha > \alpha_c$ can directly experimentally be decided by low-$T$ studies of $\sigma(\omega)$ and such measurements are strongly encouraged. In this context we stress once more that our main result is not simply the determination of an improved parameter set M2 in a literal sense, but the demonstration of a unique correlation between the magnetic nature of the GS and the $T$ dependence of $\sigma(\omega)$. A refinement of M2 when low-$T$ and field data will be available, a generalization of the Hamiltonian (2) to include further orbitals or interactions, its application to other cuprates with a different set will not change this fundamental interrelation.

To compare the $J_i$ with those from another method, density-functional theory (DFT) calculations for Li$_2$CuO$_2$ 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 was employed. The on-site Coulomb integral for a Cu 3$d_{yz}$ hole was taken to be $U = 8$ eV and an onsite exchange integral $J = 1$ eV was used. The LSDA+$U$ yields quite reliable results for total-energy differences of different spin structures from which the $J_i$ values of Eq. (1) can be extracted. Table I shows the $J_1$ and $J_2$ values we found in comparison with similar results given in Refs. 9 and 14 including a quantum chemistry study of dianion trimers, with those from projecting the models M1 and M2 onto Eq. (1). The small $J_3$ values justify a description of Li$_2$CuO$_2$ in terms of a $J_1$-$J_2$ model. There is an almost perfect agreement of three independent approaches to be close to $\alpha_c = 0.25 (J_3 = 0)$ of a quasi-1D situation. Moreover, model M2, the LSDA+$U$ as well as the QC calculations point to

![Figure 3](image1.png)

![Figure 3](image2.png)

**TABLE I.** In-chain exchange integrals $J_i$ and the frustration ratio $\alpha = -J_2/J_1$ obtained from exact diagonalizations of the Hubbard model (2) on CuO$_4$chain clusters with sets M2 (ED2) and M1 (ED1) as well as from independent DFT+$U$ calculations [DFT1: LSDA+$U$ (FPLO) $U = 8$ eV, $J = 1$ eV; DFT2: GGA+$U$; WIEN2k]; $U_{eff} = U - J = 8$ eV, see Ref. 14 and a quantum chemistry (QC, Table II of Ref. 9). study.

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<th>Other work</th>
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<tr>
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<td>ED2</td>
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<tr>
<td>$J_1$ (K)</td>
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<td>$-161$</td>
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<td>$J_2$ (K)</td>
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\( \alpha < \alpha_c \), i.e., to a FM chain. This holds in our LSDA+U, if 7 eV \( \leq U \leq 9 \) eV.

To conclude, we have shown that the model many-body Hamiltonian (2) with parameters M2 is capable of consistently describing XAS, EELS, RIXS, and \( \sigma(\omega) \) of \( \text{Li}_2\text{CuO}_2 \) at 300 K. The main issue, however, is that the magnetic GS and the spin excitation spectrum strongly affect the \( T \) dependence of \( \sigma(\omega) \) in the visible range. The reason for is the thermal population of excited spin states which differ magnetically much from the GS. This qualitatively new effect, irrespectively on details of the relevant microscopic parameters for a particular compound, has been overlooked so far in the cuprate optics literature. Our findings allow a quick qualitative magnetic classification of cuprates by optical measurements: if the AFM (FM) exchange is dominant, \( \sigma(\omega) \) in the ZRS energy region increases (decreases) lowering \( T \).

In the 1D FM−AFM−1/2 Heisenberg model e.g., triplets independently on the value of \( J_1 > 0 \) follows from the Bethe-ansatz solution of the related 1D-AFM spin-1/2 Heisenberg model.

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\*Corresponding author; drechsler@ifw-dresden.de


15 Similar finite T-approaches have been used for the t-J model e.g. by J. Jaklič and P. Prelovšek, Adv. Phys. 19, 1 (2000); for spinless fermions by X. Zotos and P. Prelovšek, Phys. Rev. B 53, 983 (1996); and for single-band Hubbard models at \( U > > t \) by H. Onodera, T. Tomyama, and S. Maekawa, ibid. 69, 245117 (2004). With an approach equivalent to Eq. (6) the optical sum rule was evaluated by M. Aichhorn, P. Horsch, W. van der Linden, and M. Cucu, Phys. Rev. B 65, 201101 (2002) to obtain T-dependent weights from the \( \omega \)-integrated partial \( \sigma(\omega,T) \).

16 This notation reflects properly only the excitation energies. There is no change of \( S \), or \( \Delta S \) of a chain (cluster) as the term “triplet” excitation might suggest.


