Anisotropic optical response of the mixed-valent Mott-Hubbard insulator $NaCu_2O_2$

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Copper oxides with quasi-one-dimensional electronic structure have drawn much attention because of their unusual magnetic properties. Compounds composed of chains of edge-sharing $Cu^{2+}O_4^{2-}$ plaquettes, such as isostructural and isoelectronic $LiCu_2O_2$ and $NaCu_2O_2$, have the peculiar property that the magnitude of the nearest-neighbor hopping matrix element along the chains is anomalously small. The interplay between FM short- and AFM long-range interactions generates spiral magnetism in Mott-insulating compounds and charge density waves in doped compounds. By virtue of their exceptionally narrow electronic bandwidths, these compounds also provide a highly favorable platform for the investigation of the interplay between spin and charge correlations in the cuprates.

The crystal structure of $NaCu_2O_2$ is orthorhombic with the $Pnma$ space group and room-temperature lattice parameters a=6.2087Å, b=2.9343Å, c=13.0648Å. The unit cell (Fig. 1(a)) contains two pairs of $Cu^{2+}O_2^{2-}$ chains running along the b axis and shifted by $b/2$ with respect to each other. The chains are formed by edge-sharing $Cu^{2+}O_4^{2-}$ plaquettes. Two chains within each pair are linked by O^{2-}–Cu^{1+}–O^{2-} dumbbells, which are slightly tilted away from the c axes. A dumbbell and a plaquette share a common O ion, which differs $NaCu_2O_2$ from $YBa_2Cu_3O_{6+\delta}$, in which plaquettes and dumbbells do not overlap, and, as is shown below, has a strong impact on its optical properties. The Cu^{2+}–Cu^{2+} distance along the chains is 2.934Å, and the Cu^{2+}–O^{2-}–Cu^{2+} bond angle is 92.9°. Recent x-ray spectroscopy and neutron diffraction investigations confirmed the superior quality of $NaCu_2O_2$ single crystals which, unlike $LiCu_2O_2$, are not prone to twinning and disorder. Experiments on single crystals of $NaCu_2O_2$ offer the chance to elucidate the intrinsic dielectric anisotropy of this class of compounds.

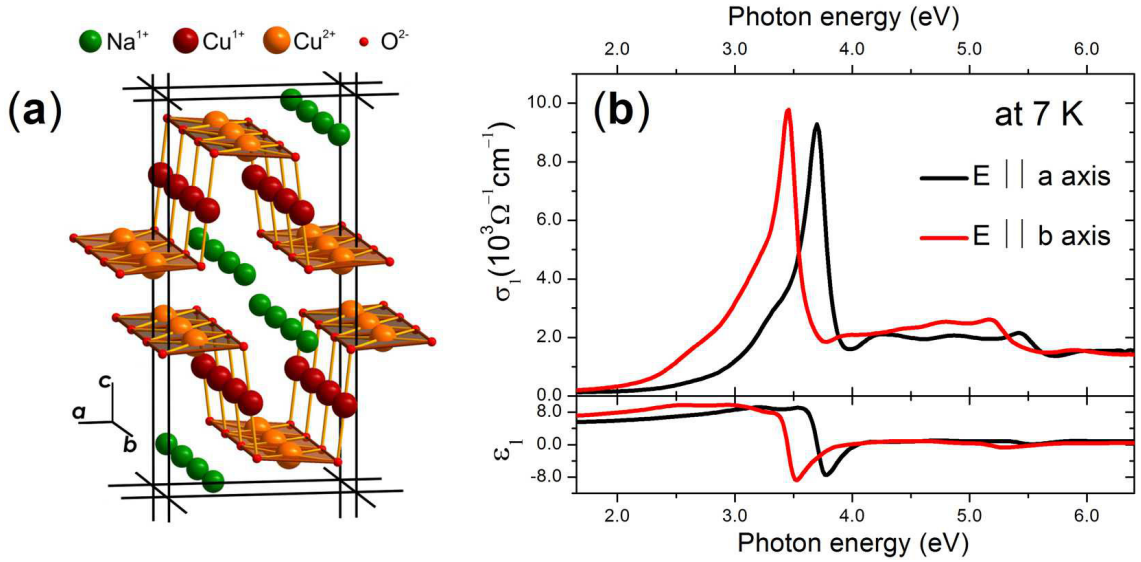

Figure 1: (a) Crystal structure of $NaCu_2O_2$. (b) Real part ε_1 of the dielectric function and real part σ_1 of the optical conductivity of $NaCu_2O_2$ measured at 7K for polarizations along ($E \parallel b$) and perpendicular ($E \parallel a$) to the $Cu^{2+}O_2^{2-}$ chains.

The real parts of the optical conductivity $\sigma_1(\omega)$ and of the dielectric function $\varepsilon_1(\omega)$ derived from ellipsometric data measured for polarizations perpendicular ($E \parallel a$) and parallel ($E \parallel b$) to the $Cu^{2+}O_2^{2-}$ chains in [1] are shown in Fig. 1(b). A remarkable feature of the conductivity spectra is an unusually high and narrow absorption peak observed at 3.45 eV for $\sigma_1^b(\omega)$ and at 3.70 eV for $\sigma_1^a(\omega)$. The anomalous strength of these excitations leads to negative values of ε_1. Below the peak $\sigma_1(\omega)$ gradually decreases with decreasing ω, showing a shoulder ~0.5 eV below the main peak. Above the peak the optical response drops sharply and remains rather featureless up to 5.5 eV. The comparison of the spectra for two polarizations reveals strong optical anisotropy in the ab plane which manifests itself as a shift of the sharp peak and the low energy shoulder of σ_1^a and σ_1^b by 0.25 eV with respect to each other.

In a recent ellipsometry study of $LiCu_2O_2$ Pisarev *et al.* [2] reported a strong and narrow in-plane absorption peak at 3.27 eV and attributed it to excitonic excitation within the $Cu^{1+}O_2$ dumbbells. Although crystallographic

twinning in $LiCu_2O_2$ crystals and Li-Cu chemical inter-substitution obliterate the anisotropy in the ab plane, strong anisotropy of the in-plane and out-of-plane optical responses was reported. The sharp peak at 3.27 eV is completely absent in the $\varepsilon_1^c(\omega)$ spectrum, which reaches its maximum at 4.28 eV. Direct measurements of the optical response along the c axis of the $NaCu_2O_2$ single crystal could not be performed due to the thinness of the sample, but the out-of-plane dielectric function estimated from the ellipsometric data acquired at different angles of incidence resembles closely $\varepsilon^c(\omega)$ measured for $LiCu_2O_2$ [2]. This suggests strong anisotropy of the in-plane and out-of-plane responses also in $NaCu_2O_2$.

In order to explain the observed anisotropy and clarify the origin of the intense peaks of the in-plane absorption, we performed calculations of the band structure and optical response of $NaCu_2O_2$ using the local (spin) density approximation (L(S)DA) as well as the LSDA+U method. The calculations were carried out for the experimental crystal structure of $NaCu_2O_2$ using the linear-muffin-tin orbital method in the atomic sphere approximation.

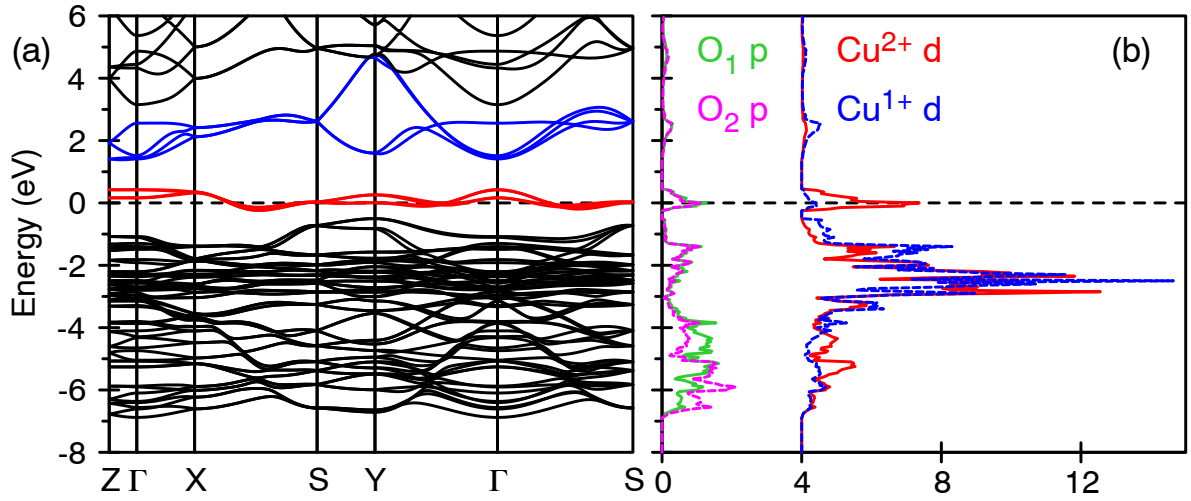

Figure 2: (a) Spin-restricted LDA energy band structure of $NaCu_2O_2$. Partially filled Cu^{2+} d_{xy} bands are shown by red lines. Two lowest Cu^{1+} $p_{x,y}$ bands and two unoccupied bands formed by strongly hybridized Cu^{1+} d_{3z^2-1} – O p_z states are plotted by blue lines. (b) Densities of the O_1 $2p$ (green), O_2 $2p$ (magenta), Cu^{2+} $3d$ (red) and Cu^{1+} $3d$ (blue) states. The Fermi level is at zero energy.

For the sake of clarity, we analyze the theoretical optical conductivity and most important interband transitions on the base of a spin-restricted LDA calculation. The LDA (Fig. 2) results in a metallic state: narrow half-filled bands formed by anti-bonding combinations of Cu^{2+} d_{xy} and O p_x and p_y orbitals produce an intense DOS peak at the Fermi level (E_F). These bands (red lines in Fig. 2(a)) are separated by a small gap of $\sim$0.2 eV from the top of the valence band which is dominated by Cu^{1+} d_{3z^2-1} states hybridized with the p_z states of two O ions forming a $Cu^{1+}O_2$ dumbbell. Bands between -4 eV and -1 eV below E_F are formed by the rest of Cu^{1+} and Cu^{2+} d states hybridized with O p states. Finally, the bottom of the valence band below -4 eV is formed by bonding O p–Cu d states.

The bottom of the conduction band lies 1.4 eV above E_F and is separated by a gap of $\sim$1 eV from the Cu^{2+} d_{xy} bands. Four bands in the range 1.5–2.5 eV (blue lines in Fig. 2(a)) are formed by electronic states of two different types: anti-bonding $Cu^{1+}d_{3z^2-1}$–O p_z states and free-electron like p_x and p_y states of Cu^{1+}. The former are essential for understanding x-ray absorption spectra at Cu $L_{3,3}$ edges, while the latter, together with the partially occupied Cu^{2+} d_{xy} bands act as final states for interband transitions which determine the optical properties of $NaCu_2O_2$ in the 1–6 eV photon energy range.

The calculated optical conductivity is presented in Fig. 3(a)–(c). The optical response below 2.4 eV originates entirely from transitions involving final states of the Cu^{2+} d_{xy} character. The in-plane conductivities show a sharp peak at $\sim$1.5 eV; the $\sigma_1^a(\omega)$ peak being 0.2 eV higher than the $\sigma_1^b(\omega)$ one. The corresponding peak of $\sigma_1^c(\omega)$ is, however, completely suppressed. Although the calculated peaks are found at much lower photon energies, we, as will be discussed below, tend to associate them with the sharp peaks of the experimental spectra. Above 2.4 eV, the calculated conductivity is determined mostly by transitions to the final-state bands formed by the Cu^{1+} $p_{x,y}$ states. Corresponding contributions to the in-plane spectra also exhibit appreciable anisotropy which manifests itself as a shift of $\sigma_1^a(\omega)$ to higher energy as compared to $\sigma_1^b(\omega)$. The average calculated optical conductivity of $\sim 2.5\times10^3$ $\Omega^{-1}\text{cm}^{-1}$ is in agreement with the measured conductivity above the anomalously intense peaks. The intensities of both calculated and experimental spectra are reduced above 5 eV. In order to

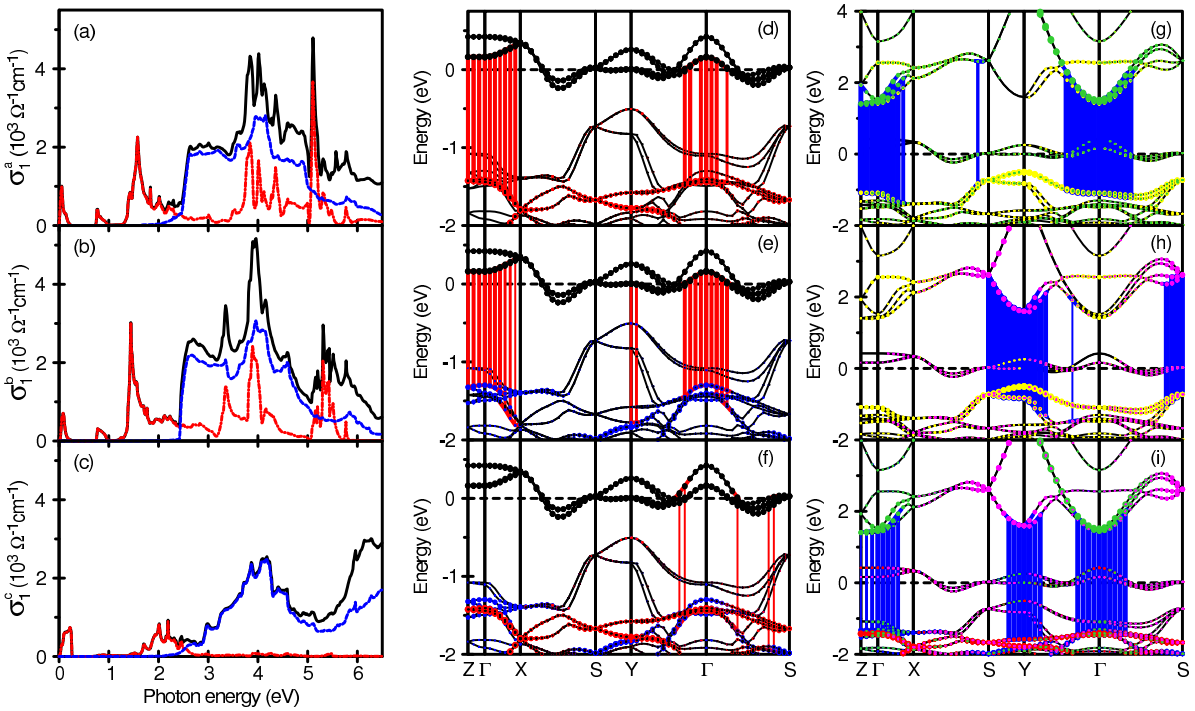

Figure 3: (a)–(c) The real part of the optical conductivity of $NaCu_2O_2$ (black line) calculated for three polarizations with $E \parallel a$, $E \parallel b$, and $E \parallel c$, respectively. Contributions to the conductivity coming from interband transitions to the final bands of Cu^{2+} d_{xy} (red lines in Fig. 2(a)) and Cu^{1+} $p_{x,y}$ (blue lines in Fig. 2(a)) character are shown by red and blue lines. (d)–(f) Most intense interband transitions in the 1.0–2.4 eV energy range are shown by red vertical lines, with the line width being proportional to squared matrix element of the dipole allowed transition with the a, b, or c polarization between two bands connected by the line For clarity, only most intense transitions are plotted. The size of colored circles is proportional to the weight of Cu^{2+} d_{xy} (black) and Cu^{1+} d_{zx} (blue) and d_{yz} (red) states in the wave function. (g)–(i) The most intense transitions (blue lines) in the 2.4–3.5 energy range. Cu^{1+} p_x and p_y contributions are shown by green and magenta circles, while yellow ones mark Cu^{1+} d_{3z^2-1} states.

elucidate the origin of the observed in-plane anisotropy we analyzed interband transitions contributing to the conductivity in two photon energy ranges, 1.0–2.4 eV and 2.4–3.5 eV, in which the anisotropy of the calculated optical response is the strongest.

Let us first turn to the interband transitions associated with the Cu^{2+} d_{xy} final states, giving the sharp peak at ∼1.5 eV in Figs. 3(a) and (b). Figures 3(d)–(f) show band plots which are decorated by vertical lines with the width proportional to the probability of the optical transition between two bands connected by the line. Also shown is the orbital character of the bands involved into the transitions. Comparing Figs. 3(d) and (e) one notices that the 1.5 eV peaks for both polarizations are caused by transitions to the same final-state bands of the Cu^{2+} d_{xy} character. The initial states for two in-plane polarizations are, however, different: Cu^{1+} d_{yz} and Cu^{1+} d_{zx} for σ_1^a and σ_1^b, respectively. The degeneracy of the d_{zx} and d_{yz} states is lifted due to the tilt of $Cu^{1+}O_2$ dumbbells away from the c axis in the ac plane, with the top of the d_{zx} bands lying 0.2 eV higher. As a consequence, the "Cu^{1+} d_{zx}→Cu^{2+} d_{xy}" transitions responsible for the peak of σ_1^b occur at lower photon energies. It should be noted, that although the dominant contribution to the initial-state bands is provided by Cu^{1+} $d_{zx}(d_{yz})$ orbitals, their hybridization with Cu^{2+} states via the O $p_x(p_y)$ results in an appreciable weight of the Cu^{2+} $p_x(p_y)$ states in the corresponding wave functions. This ensures the significant strength of the dipole-allowed transitions, which would be much weaker if O ions were not shared between the $Cu^{2+}O_4$ plaquettes and $Cu^{1+}O_2$ dumbbells. The same Cu^{1+} d_{zx} and d_{yz} bands act also as the initial states for transitions to the Cu^{2+} d_{xy} final bands with $E \parallel c$ (Fig. 3(f)). The probability of these transitions is, however, much lower and $\sigma_1^c(\omega)$ is almost completely suppressed at 1.5 eV.

Similar analysis of dominant transitions in the 2.4–3.5 eV photon energy range (Figs. 3(g) and (h)) reveals that initial bands for both in-plane polarizations are mainly of the Cu^{1+} d_{3z^2-1} character. The final states for a and b polarizations are free-electron-like bands formed by the Cu^{1+} p_x and p_y states, respectively. The bottom of the p_x band is at Γ, whereas the p_y band has a minimum at a Brillouin zone corner (Y). As a consequence, the transitions with two in-plane polarizations occur in different regions of **k**-space and the corresponding absorption edges are shifted by 0.2 eV. Because of the large dispersion of the p_x and p_y states, the transitions give a rather flat

contribution to the optical conductivity up to 5 eV. The same p_x and p_y bands serve as final states for transitions with $E \parallel c$ (Figs. 3(i)). The initial states are Cu^{1+} d_{zx} and d_{yz} bands, instead of d_{3z^2-1} ones, which explains strong anisotropy of the in-plane and out-of-plane responses.

The above analysis of the interband transitions is based on the LDA calculation which gives a metallic solution in contrast to an experimental insulating gap of 2 eV. The discrepancy is not surprising taking into account that electronic correlations in the Cu $3d$ shell are strongly underestimated in the LDA. In LSDA+U calculations with U=6 eV applied to both Cu^{1+} and Cu^{2+} $3d$ states, the on-site Coulomb repulsion splits the half-filled Cu^{2+} d_{xy} bands into occupied lower and unoccupied upper Hubbard bands and opens an insulating gap. As a consequence, the sharp $\sigma_1^a(\omega)$ and $\sigma_1^a(\omega)$ peaks at 1.5 eV, which appear due to the transitions involving the Cu^{2+} d_{xy} final states, are shifted to higher energies improving the agreement with the measured spectra. Nevertheless, the magnitude of the theoretical conductivity remains lower than the experiment one, which indicates that LSDA+U is too crude an approximation to properly account for electronic correlations in $NaCu_2O_2$.

References:

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