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Charge-transfer excitons in underdoped $Ca_{2-x}Na_xCuO_2Cl_2$ studied by electron energy-loss spectroscopy

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Employing electron energy-loss spectroscopy we show that small values of doping in the system $Ca_{2-x}Na_xCuO_2Cl_2$ strongly influence the formation of charge-transfer excitons in the Cu-O plane. We find a remarkable redistribution of spectral weight between the two modes—a bound exciton and a continuum state—seen in the insulator yielding a single sharp feature for nonzero doping accompanied by a strong suppression of the dispersion. Our data may provide evidence for a prominent role of the magnetic background on the dynamics of charge-transfer excitations in underdoped cuprates.

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I. INTRODUCTION

For several reasons $Sr_2CuO_2Cl_2$ (SCOC) or the isoelectronic $Ca_2CuO_2Cl_2$ (CCOC) are of particular interest among the different cuprate families. First, both compounds are considered to be perfect realizations of a two-dimensional (2D) Mott insulator[1]—or charge-transfer (CT) insulator to be more precise[2]—owing to the absence of any distortion of the Cu-O plane. Second, the detection of superconductivity in doped $Ca_{2-x}Na_xCuO_2Cl_2$ (Na-CCOC) with a $T_c \sim 25$ K for $x \sim 0.15$ (Ref. 3) showed the irrelevance of the apical oxygen atoms for the formation of superconductivity in the high-temperature superconductors and it helped to focus the attention to the electronic processes within the Cu-O plane. Third, recently an intriguing type of charge order[4,5] was detected in Na-CCOC which emphasizes the relevance and possible coexistence of several, perhaps competing, order parameters in the region of strong underdoping in the phase diagram of copper-based high-temperature superconductors.

A proper theoretical treatment of these low-energy peculiarities, however, requires a detailed knowledge of the excitations in the energy range of 1–5 eV as well because this part of the spectrum decides whether or not the inclusion of several orbitals is required to develop a well-justified single or multiband model. The processes governing the electronic spectrum in this energy range are mainly caused by charge transfer from oxygen to copper states which results in the formation of electron-hole pairs, CT excitons.[6–8]

Electron energy-loss spectroscopy (EELS) in transmission is a valuable tool for the investigation of materials on all levels of complexity in the electronic-excitation spectrum.[9,10] The EELS cross section is basically proportional to $\mathrm{Im}[-1/\epsilon(\omega,\boldsymbol{q})]$—called loss function (LF)—where $\epsilon(\omega,\boldsymbol{q}) = \epsilon_1(\omega,\boldsymbol{q}) + i\epsilon_2(\omega,\boldsymbol{q})$ is the momentum and energy-dependent complex dielectric function. It is this quantity which provides access to the electronic structure of a solid under investigation. The momentum dependence of the LF allows observation of nonvertical transitions within the band structure of a solid and therefore EELS goes beyond the capabilities of optical experiments. In the present paper we apply EELS to address the question how doped charge carriers within the Cu-O plane influence the CT excitons, in particular, their intensity and propagation behavior, well below optimal doping.

II. EXPERIMENTS AND RESULTS

Single crystals of Na-CCOC ($x=0.05$ and $x=0.1$) were grown by a flux method under high pressure.[11] For the EELS measurements thin films (~100 nm) were cut from these single crystals using an ultramicrotome equipped with a diamond knife. To avoid air exposure caused sample damage this was done under nitrogen atmosphere. In the spectrometer the films were characterized *in situ* with electron diffraction showing the high quality of the investigated samples and allowing for a precise alignment. The measurements were carried out using a dedicated transmission electron energy-loss spectrometer[12] employing a primary electron energy of 172 keV and energy and momentum resolutions of $\Delta E = 80$ meV and $\Delta q = 0.035$ Å^{-1}, respectively.

In Fig. 1 we show how the low-lying CT excitations evolve upon doping the insulating Cu-O plane in the optical limit ($q=0.1$ Å^{-1}). In the undoped case (SCOC) there is a clear double-peak structure. This behavior which is also seen in optical experiments[13,14] is in agreement with reflectivity data for CCOC (Ref. 15) and it emphasizes the equivalent electronic structure of SCOC and CCOC. Upon doping the two features merge into a single sharp structure which is also in agreement with the optical data.[15] This new structure is approximately halfway between the two humps seen in the undoped sample for $x=0.05$ and moves further down for the higher doping value of $x=0.1$. In addition there appears a small shoulder which develops in the tail of the quasielastic line below 1 eV (cf. also Figs. 2 and 3). It has been termed midinfrared peak in the optical literature[16] and it corresponds to the charge-carrier plasmon which is also seen in other cuprates (see, e.g., Ref. 17). The increasing contribution from this component hinders a straightforward subtraction of the quasielastic line responsible for the strong intensity increase below 0.4 eV. Consequently we also did not perform a

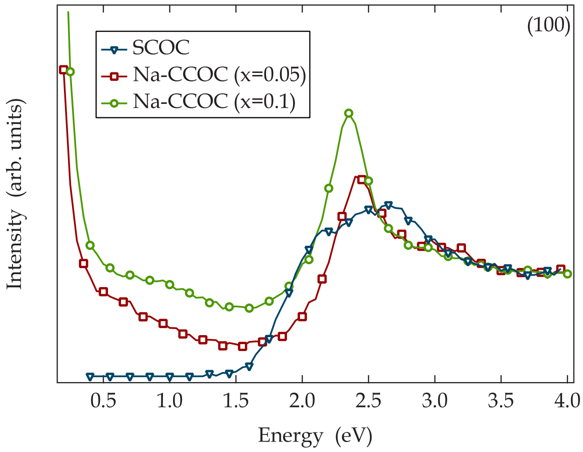

FIG. 1. (Color online) The evolution of the EELS spectra from the Mott insulating SCOC to the doped Na-CCOC ($x=0.05$ and $x=0.1$) for $q=0.1$ Å^{-1} parallel to the Cu-O bonds. The strong intensity increase in the Na-CCOC spectra for $E \leq 0.4$ eV is the quasielastic line, which was not subtracted in this case to avoid any ambiguities (see text). The spectra are normalized to the intensity on the high-energy side at ~4 eV.

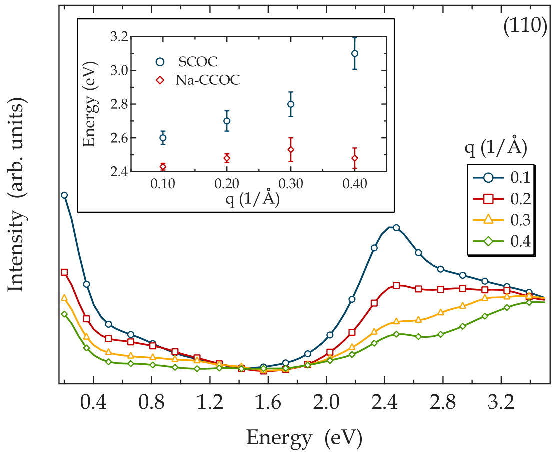

FIG. 3. (Color online) The momentum dependence of the EELS spectra for Na-CCOC ($x=0.05$) for $q \| (110)$. The inset shows the dispersion of the visible feature as extracted from the peak position around 2.5 eV compared to the upper SCOC branch in Fig. 1 (data taken from Ref. 18). The spectra are normalized to the intensity on the high-energy side at ~3.5 eV.

Kramers-Kronig analysis (whose outcome strongly depends on the particular method to fit the zero-energy peak) and show only the plain data for Na-CCOC in Fig. 1. In contrast to that SCOC is an insulator with a well-defined gap of more than 1 eV. Therefore the elastic peak is removed in this case.

In the remainder of the paper we focus entirely on the doping induced modifications between 2 and 3 eV. As the observed effects and the conclusions drawn from them are the *same for both* doping concentrations we present and discuss only the $x=0.05$ data in the following. To investigate them further we measured the LF for different momentum transfers. The resulting spectra are plotted in Fig. 2 for $q \| (100)$ and in Fig. 3 for $q \| (110)$. They have been normalized to the high-energy tail at ~3.5 eV because they appear to be almost momentum independent there. The first interesting observation is the marked reduction in spectral weight, roughly by a factor of 2, upon approaching the zone boundary which is clearly visible for $q \| (100)$ (Fig. 2) and even more pronounced for $q \| (110)$ (Fig. 3). Moreover there is no significant dispersion of the feature at 2.5 eV as can be seen by following the peak position in the LFs starting in the vicinity of the Γ point and moving to the zone boundary. To substantiate this further we extracted the local intensity maximum as a function of q. The resulting curves are shown in Figs. 2 and 3 (insets). For comparison we also plot the dispersion of the feature at ~2.6 eV seen in the SCOC data of Fig. 1 (spectra for higher q values taken from Ref. 18). In contrast to the high-energy feature of the parent compound, which shows a sizable dispersion of several hundred meV (cf. also Refs. 19 and 20), the bandwidth in the doped $Ca_{1.95}Na_{0.05}CuO_2Cl_2$ is strongly reduced. In addition the onset of the feature (for $q=0.1$ Å^{-1}) is substantially raised by ~200 meV. We note that the momentum evolution of the lower branch from the SCOC data cannot be added to the insets of Figs. 2 and 3 because it is not resolved in the spectra for higher q (see also the discussion below).

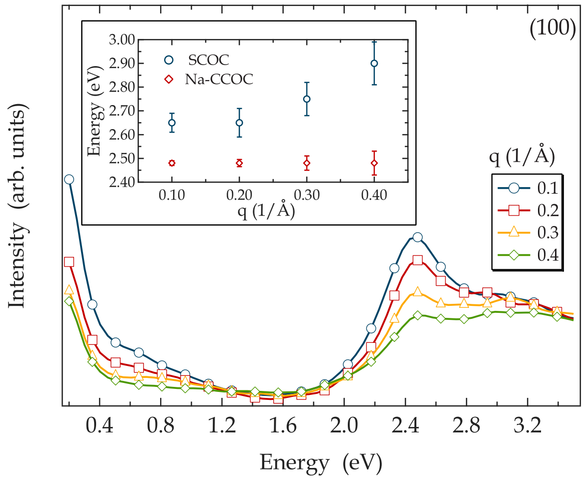

FIG. 2. (Color online) The momentum dependence of the EELS spectra for Na-CCOC ($x=0.05$) for $q \| (100)$. The inset shows the dispersion of the visible feature as extracted from the peak position around 2.5 eV compared to the upper SCOC branch in Fig. 1 (data taken from Ref. 18). The spectra are normalized to the intensity on the high-energy side at ~3.5 eV.

III. DISCUSSION

We mentioned before that the prominent excitations in the considered energy range are formed via CT from oxygen p orbitals to the d shells of adjacent copper sites resulting in a particle-hole pair.[6–8] But there are considerable arguments about the precise nature of these entities in the literature. In particular, the level of delocalization and the number of orbitals, required for a sufficient theoretical description, are a matter of debate.

Previously[8] the upper branch of the SCOC data was attributed to a two-center exciton (2CE), a combination of a Cu d^{10} site bound to a neighboring Zhang-Rice singlet

(ZRS).[21] In addition the theoretical treatment in Ref. 8 suggested a one-center exciton (1CE)—which resides on a single CuO_4 plaquette and involves p_π orbitals on the oxygen sites—for the lower branch. However, there is evidence which motivates to reconsider this approach. The optical data[22,23] for the one-dimensional corner-sharing cuprate Sr_2CuO_3 which (along the chains) is comparable to SCOC provide support for this. For light polarization along the chain axis and parallel to the plaquettes indeed two features are observed around 2 eV. However, the localized 1CE should also be visible perpendicular to the chain, which is not the case. This argues strongly against the possible existence of a 1CE and at the same time emphasizes the importance of correlated states along the chain for the 1D and the participation of more than one CuO_4 plaquette for the formation of the considered CT excitations in the 2D case.

In contrast to the previous reasoning but in agreement with a recent study on Sr_2CuO_3 (Ref. 24) we attribute the low-energy feature seen in the SCOC data of Fig. 1 to an exciton (the 2CE discussed above) and the high-energy structure to a continuum excitation which corresponds to an unbound particle-hole pair. The excitonic mode is theoretically predicted in the extended one-band Hubbard model for $V>2t$ in the 1D and for higher values of V in the 2D case,[25–28] where V and t represent the nearest-neighbor Coulomb interaction and transfer integral. Its existence is experimentally confirmed[26] also for other correlated systems such as Ni halogenides. In the following we argue that this scenario provides a reasonable framework for the understanding of the observed phenomena.

The doping, of course, strongly alters the Coulomb interaction between the particle-hole pair which causes the resulting (screened) Coulomb attraction eventually to fall below the critical value required to bind the particle to the hole. Therefore the exciton is strongly quenched in the doped spectra seen in Fig. 1 and the continuum is strongly enhanced which explains the redistribution of the spectral weight seen in Fig. 1. This is also in agreement with the optical data for Na-CCOC (Ref. 15) where the spectral weight of the lower branch in the optical conductivity seems to be reduced. The same effect is visible for other cuprate families as well: investigations on $La_{2-x}Sr_xCuO_4$ (Ref. 16) and on $YBa_2Cu_3O_{6+x}$ (Ref. 29) show that the lower feature around 2 eV is always more affected by the doping than the higher one. A similar effect is also seen for temperature-dependent data on the optical conductivity in SCOC (Ref. 14) where for increasing temperature, being equivalent to charge-carrier doping by thermal activation, again the effect on the low-energy tail of the CT excitations is more pronounced. We note, however, that in contrast to our data shown in Fig. 1, the mentioned optical studies do not observe a redshift of the continuum upon doping. This seeming contradiction is readily understood by realizing that optics measures, in contrast to EELS, a linear spectral-weight superposition of two transitions. Consider two adjacent transitions in the loss function: reducing the weight for the lower one (the exciton in our case) will shift the higher one (the continuum part) to smaller energies because the zero crossing of $\epsilon_1(\omega)$, required for a peak in $\mathrm{Im}[-1/\epsilon(\omega)]$, will appear at lower energies for nonzero doping.

The exciton-continuum mechanism provides also a straightforward interpretation for the observed dispersion behavior. The undoped case is characterized by a perfectly ordered antiferromagnetic alignment of the spins on the copper sites. Zhang and Ng[6] developed a three-band model for the exciton formation in the copper-oxygen plane. Within this approach the influence of the copper-oxygen hopping t_{pd} and the oxygen-oxygen hopping t_{pp} on the particle-hole dynamics was investigated perturbatively and it was shown that all hopping processes which would eventually disturb the magnetic background are only higher-order corrections. Therefore the propagation of the exciton can be considered to be free with respect to the spin environment. From this we conclude that the nonzero bandwidth of the higher branch in the SCOC data [Figs. 2 and 3 (insets) and Ref. 18] does not reflect the dispersion of the continuum part but is rather caused by the exciton which propagates to higher energies for increasing momentum (in accordance with Ref. 6) thereby merging into the continuum. This will shift the remaining feature which is then a combination of the exciton and the continuum to higher energies and also explains why the low-energy structure disappears for higher momenta in the data for the parent compound.[18]

The breakdown of the dispersion in the doped case may be related to several mechanisms depending on the amount of spectral weight which is still acquired by the exciton. It is well known that the phase diagram of the cuprates exhibits a complicated spin arrangement in the vicinity of the Mott insulator characterized by a highly complex and also fluctuating magnetic order which, at least on a local scale, destroys the perfect antiferromagnetism of the parent compounds. The resulting spin defects will suppress the coherent motion of the particle-hole pair yielding a smaller bandwidth. Another possible scenario might be a disorder-induced localization. The additional holes will form ZRSs which can be understood as randomly distributed scattering centers that can confine the amplitude of the excitonic mode only to a small area of the Cu-O plane, comparable to the conventional disorder-induced metal-insulator transition.[30] If, however, the Coulomb attraction is already below the critical value required to form a pair the dispersion breakdown seen in Figs. 2 and 3 is essentially caused by the magnetic background. In this case the EELS process produces a particle and a hole which are independent from each other. But both strongly interfere with the spins on the copper sites. This is in analogy with the problem of a single hole in an antiferromagnet where the small bandwidth seen in angle-resolved photoemission[31,32] is known to be determined by the exchange instead of the much higher hopping integral.

IV. SUMMARY

To summarize, employing EELS we investigated the doping-dependent low-lying charge-transfer excitations in the system $Ca_{2-x}Na_xCuO_2Cl_2$. We find their behavior to be strongly altered compared to the corresponding data for the parent compound. We observe a considerable redistribution of spectral weight between 2 and 3 eV. The lower of the two modes seen in the undoped case is ascribed to a bound exciton and the higher one to a continuum excitation. The single sharp feature in the spectrum for nonzero doping reflects a strong suppression (perhaps absence) of the excitonic mode. Our data may point to a prominent role of the antiferromagnetic background for the dynamics of the charge-transfer excitations in underdoped cuprates.

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