Variable-range hopping conductivity in the copper-oxygen chains of $La_3Sr_3Ca_8Cu_{24}O_{41}$

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We show that the spin chain/ladder compound $La_3Sr_3Ca_8Cu_{24}O_{41}$ is an insulator with hopping transport along the chains. In the temperature range 35–280 K, dc conductivity $\sigma_{dc}(T)$ follows Mott's law of variable-range hopping conduction; the frequency dependence has the form $\sigma(\nu,T)=\sigma_{dc}(T)+A(T)\nu^s$, where $s\approx 1$. The conduction mechanism changes from variable-range hopping to nearest-neighbor hopping around $T_c = 300$ K. The chain array thus behaves as a one-dimensional disordered system. Disorder is due to random structural distortions of chains induced by irregular coordination of the La/Sr/Ca ions.

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One of the most outstanding properties of the $(La, Sr, Ca)_{14}Cu_{24}O_{41}$ family of quantum spin chain/ladder compounds is the superconductivity (SC) established in $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41}$ at 12 K under pressure.[1] The parent material of this cuprate superconductor $Sr_{14}Cu_{24}O_{41}$ is a charge density wave (CDW) insulator with a spin gap.[2–4] Substituting isovalent Ca for Sr suppresses the CDW insulating phase,[5] while the spin gap remains finite.[4] The latter indicates that SC is driven by the spin-liquid state, in accord with theoretical expectations.[6]

In addition to the two-leg ladders, responsible for the conductivity and superconductivity, the system comprises one-dimensional (1D) CuO_2 chains (c direction) and the (La, Sr, Ca) layers. The chains are charge reservoirs from which holes are transferred into the ladders keeping the average copper valence unchanged. For the fully doped compound $Sr_{14}Cu_{24}O_{41}$, which contains six holes per formula unit, approximately five holes are observed in the chain subsystem. In this case, the antiferromagnetic dimer pattern is created in chains together with the charge order, both inducing gaps in the spin and charge sectors, respectively.[7,8] Spin dimers are formed between those Cu^{2+} spins that are separated by a localized Zhang-Rice singlet (Cu^{3+}), that is, by a site occupied by a localized hole.

No definite understanding has been reached yet on the nature of the spin/charge state and, in particular, on the charge dynamics in the chain subsystem for various doping levels. The $La_{6-y}Sr_yCa_8Cu_{24}O_{41}$ compound provides a good opportunity for such studies since for intermediate doping levels all holes reside on the chain sites[9] and no spin gap is observed.[10] Both susceptibility and dc resistivity, measured on polycrystalline samples, increase with lowering temperature, while their absolute values show a strong decrease on strontium doping.[10] In particular, the absolute value of the susceptibility is directly correlated with the number of Cu^{2+} in chains, indicating that doped holes reside entirely on chains.

In order to understand the nature of the spin/charge state in the spin chains with intermediate hole doping, there is a need to clarify the mechanism of the charge transport. In this paper we present conductivity measurements on single crystalline $La_3Sr_3Ca_8Cu_{24}O_{41}$ in a wide frequency and temperature range. We show that the conductivity measured between 280 and 35 K obeys a true variable-range hopping law as in disordered noncrystalline insulators; in this way we exclude the existence of the charge order pattern found in the fully doped spin chains. In addition, we find no signature of the CDW-related dielectric response; this fact represents definite evidence that the CDW insulating phase observed in $Sr_{14-x}Ca_xCu_{24}O_{41}$ is established in the ladder subunit.[2,5]

dc resistivity was measured between 35 and 700 K. In the frequency range $\nu = 0.1$ Hz–1 MHz the complex conductance was measured. For $\nu < 100$ Hz we used a setup for high-impedance samples while for 20 Hz $< \nu <$ 1 MHz a Hewlett Packard HP4284A impedance analyzer was utilized.[11] The data at the lowest frequency match our four-probe dc measurements. At frequencies $\nu = 6$–$10\,000$ cm^{-1} the complex dielectric function was obtained by a Kramers-Kronig analysis of the reflectivity and by complex transmission measurements[12] at the lowest frequencies 6–20 cm^{-1}. All measurements were done along the crystallographic c axis of a high-quality single crystal.

Figure 1 shows the behavior of dc conductivity in the wide temperature range from 35 K (the lowest temperature obtained in our experiment) up to 700 K. Above $T_c = 300$ K, the dc conductivity follows a simple activation behavior $\sigma_{dc}(T) \approx \exp(-2\Delta/T)$ with $2\Delta = 3200$ K (see inset). As directly seen from the $\log_{10}\sigma_{dc}(T)$ vs $T^{-1/2}$ plot, presented in the main panel, below T_c down to 35 K the con-

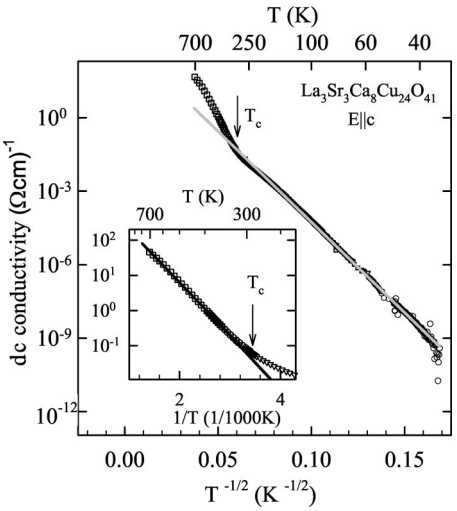

FIG. 1. dc conductivity σ_{dc} of $La_3Sr_3Ca_8Cu_{24}O_{41}$ single crystal along the crystallographic c direction vs $T^{-1/2}$. σ_{dc} follows a simple activation behavior above $T_c=300$ K (full line in the inset) indicating nearest-neighbor hopping. Below T_c the behavior $\sigma_{dc} \propto \exp(T^{-1/2})$ is observed (full line) corresponding to the regime of variable-range hopping in one dimension. T_c is determined by the crossing of extrapolated fitting curves, with an error bar of ± 15 K.

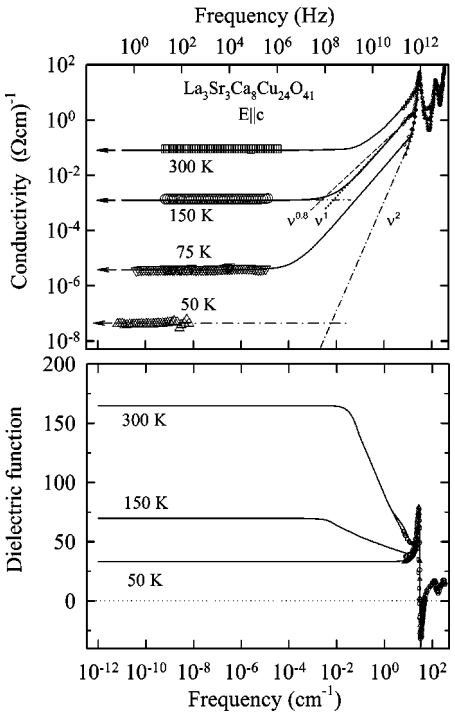

FIG. 2. Upper panel: broad-band conductivity spectra of $La_3Sr_3Ca_8Cu_{24}O_{41}$ single crystal along the c axis for four representative temperatures. Hopping conduction of the form ν^s, $s \approx 1$, is found between 6 and 20 cm^{-1} for $T \geqslant 75$ K, while a frequency independent behavior is found in the radio-frequency range for all temperatures. The arrows denote the dc values. The full lines are fits to the form $\sigma(\nu,T)=\sigma_{dc}(T)+A(T)\nu^1$. A pure power law contributions with $s=0.8$ and 1 are shown for $T=150$ K by a dashed and dotted lines, respectively. At 50 K only a ν^2 contribution (dashed-dotted line) due to the low-energy phonon tail is observed. Lower panel: dieletric function of $La_3Sr_3Ca_8Cu_{24}O_{41}$ single crystals along the c axis (open points). The lines correspond to the fit of the conductivity spectra shown in the upper panel as described in the text. At $T=50$ K, only a phonon contribution to the dielectric function is found.

ductivity perfectly follows the variable-range hopping (VRH) behavior

$$\sigma_{dc}(T)=\sigma_0 \exp[-(T_0/T)^{1/(1+d)}] \tag{1}$$

with the dimensionality of the system $d=1$. These results clearly demonstrate the hopping mechanism of charge transport in one dimension; at $T_c=300$ K it crosses over from nearest-neighbor hopping to variable-range hopping. The cross-over temperature T_c is given by $T_c=\Delta/(2\alpha c)$.[13,14] Here the energy of sites near the Fermi energy available for hops, has an uniform distribution in the range $-\Delta$ to $+\Delta$, c is the distance between the nearest Cu chain sites, and α^{-1} is the localization length. By using $\Delta=1600$ K and $c=2.77$ Å, we find $\alpha^{-1} \approx 1$ Å. Finally, the value of the VRH activation energy $T_0^{exp}=2.9\times 10^4$ K, obtained from the fit of our data to Eq. (1), is very close to the one expected theoretically: $T_0^{th}=8\Delta c \alpha \approx 3.5\times 10^4$ K.

Figure 2 demonstrates the conductivity $\sigma(\nu,T)$ and the dielectric function $\varepsilon'(\nu,T)$ spectra of $La_3Sr_3Ca_8Cu_{24}O_{41}$ over the entire frequency range for different temperatures. We present here only the spectra up to 350 cm^{-1} including a couple of phonon lines. As confirmed by our fit (see below), the kinks in $\sigma(\nu,T)$ and $\varepsilon'(\nu,T)$ on the left side of the lowest-frequency phonon are of electronic (nonphonon) origin and we assign this contribution to the hopping of holes in the chains. Excluding the phonon component, the electronic conductivity can be expressed as the sum of two terms

$$\sigma(\nu,T)=\sigma_{dc}(T)+A(T)\nu^s, \quad s \approx 1, \tag{2}$$

where $\sigma_{dc}(T)$ is given by Eq. (1). We note that the frequency independent behavior is found in the radio-frequency range for all temperatures (open symbols in Fig. 2). Similar dependences have been observed in a variety of disordered systems.[15] The frequency-dependent component $\sigma_{ac}(\nu,T)=A(T)\nu^s$ is found to contain a temperature dependent prefactor $A(T)$. The cross-over frequency ν_{CO} from the frequency independent to the frequency dependent conductivity can be estimated from the condition that the ac hopping length has to be smaller than the dc hopping length in order for $\sigma_{ac}(\nu,T)$ to overcome $\sigma_{dc}(T)$.[13] For one-dimensional VRH, the dc hopping length is given by $R_0=(\Delta c/2\alpha T)^{1/2}$ and the ac hopping length is $R_\nu=\frac{1}{2}\alpha \ln(\nu_{ph}/\nu_{CO})$, where the attempt frequency ν_{ph} depends on the electron-phonon interaction. Assuming $\nu_{ph} \approx 10^{12}$ s^{-1}, we find for the cross-over frequency ν_{CO} the values 0.15, 0.015, and 0.0006 cm^{-1} for $T=300$, 150, and 75 K, respectively. These values coincide nicely with those obtained when the ν^s fits in 6 – 20 cm^{-1} range are extrapolated to lower frequencies (Fig. 2). In particular, the choice of the exponent $s=1$ appears to be the most appropriate. For example, at $T=150$ K we find $\nu_{CO} \approx 0.0027$ and 0.013 cm^{-1}, for $s=0.8$ and 1, respectively. Experimentally we are not able to distinguish between the $\nu^{0.8}$ and ν^1 dependences because of the relatively narrow

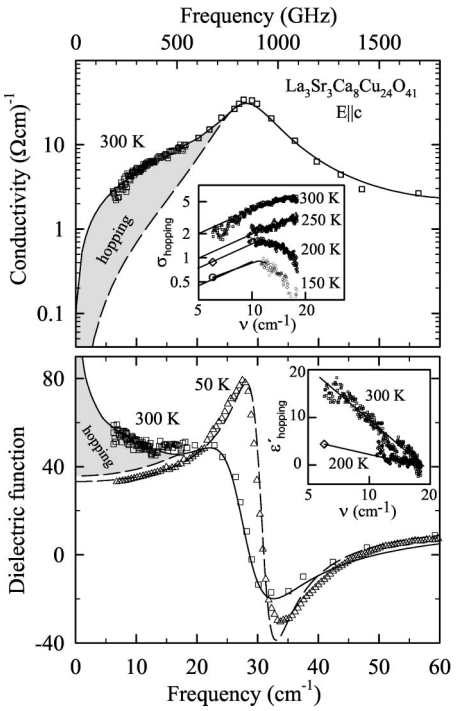

FIG. 3. Optical conductivity (upper panel) and dielectric function (lower panel) of the $La_3Sr_3Ca_8Cu_{24}O_{41}$ single crystal measured along the c axis in the range 6–60 cm^{-1}. The dashed lines are the fits including only the contributions associated to phonon at 28 cm^{-1}. The full lines correspond to the fit which in addition includes an electronic hopping conduction (see text). The insets show (for a few selected temperatures) the conductivity and the dielectric function due to hopping (phonons subtracted) which die out at low temperatures and high frequencies. Full lines are fits to $A(T)\nu^1$. At $T=50$ K, only a phonon contribution is detected.

frequency range in which $\sigma \sim \nu^s$ behavior is detected. At $T \leqslant 50$ K the hopping vanishes because the charge carriers are frozen out, and we observe only the ν^2 contribution to the conductivity associated with the low-energy phonon (Lorentzian) tail.

Next, we estimate the dielectric constant ε' associated with the hopping conduction. In order to do so we fit the conductivity spectra using the Drude term for the frequency independent plateaus below 10^6 Hz and a set of Lorenztians to smoothly describe the increase of $\sigma_{ac}(\nu)$ at higher frequencies. The results are shown by solid lines in Fig. 2; the low-frequency dielectric constant is about 170 at 300 K and decreases with lowering the temperature. We were not able to extract the ε' values from our radio-frequency measurements since the accuracy in determination of ε' is ± 300 for the geometry of the samples used.

Finally, we want to point out that no signature of the CDW-related features of dielectric response in the radio-frequency range is found. Since in this system all holes reside on chains, this result yields definite evidence that the CDW insulating phase observed in $Sr_{14-x}Ca_xCu_{24}O_{41}$ is established in the ladder subunit.[3]

Figure 3 shows a blow-up of the optical conductivity and dielectric function at frequencies 6 – 60 cm^{-1} where a cross-over from hopping to phonon-related response is observed. A contribution due to hopping (shaded) is clearly identified in addition to the phonon part (dashed line). The insets show the difference between the total and the phonon-associated components to the spectra of σ and ε', which is basically the pure hopping contribution. The expected dying out of the hopping contribution becomes more pronounced with lowering the temperature and with increasing the frequency. The latter is—to the best of our knowledge—observed for the first time.

We now comment on the hopping transport found in the chains of $La_3Sr_3Ca_8Cu_{24}O_{41}$ in comparison with disordered noncrystalline insulators. First, for the latter compounds the value of the exponent in Eq. (1) is commonly found to be 1/4, corresponding to hopping in three dimensions; it becomes 1/2 if the electron-electron interaction plays a role.[16] However, electron-electron interactions are expected to have a significant impact on the correlated many-electron hopping only when the temperature T is larger than T_0, which is far from the experimental range since $T_0 = 2.9 \times 10^4$ K.[13,17] The situation is different for systems consisting of parallel chains of finite length where small disorder leads to weakly localized states.[18] This model gives the temperature exponent 1/2 as found in our experiment. We conclude that the exponent 1/2 confirms the one-dimensional nature of the electronic structure of chains in $La_3Sr_3Ca_8Cu_{24}O_{41}$, which is in accord with the crystallographic structure.[19] Second, the obtained value for T_0 indicates the standard regime of the VRH where the hopping distance R_0 is larger than the localization length α^{-1}; the extremely small $\alpha^{-1} \approx 1$ Å shows that the system is far from the metal-insulator transition. Following the usual interpretation of the VRH law, from $T_0 = 16\alpha^3/n(E_F)$ we find the electronic density of states at the Fermi level $n(E_F) \approx 5.5 \times 10^{24}$ eV^{-1} cm^{-3}. Finally, a straightforward consequence of the observed VRH conduction is that its extrapolation indicates a zero conductivity at $T=0$, in accord with the theory developed for disordered noncrystalline insulators.

Generally, a frequency-dependent conductivity varying as $A(T)\nu^s$, where $s \approx 1$, does not necessarily imply hopping conduction.[13] However, we suggest that dc VRH conduction as well as the power-law ac conduction are attributed to the same set of localized states near the Fermi level. The value of the exponent close to one indicates that the observed ac conductivity is due to phonon-assisted hops between spatially distinct sites similarly to the dc contribution, and not to the photon absorption for which $s \approx 2$ is usually found.[13] Note that we did not find the latter in the whole measured frequency range, despite the theoretical prediction that with increasing frequency there is a cross-over from the regime dominated by phonon-assisted $\sigma_{hopping} \approx \nu^s$, $s \leqslant 1$ to that dominated by photon-assisted conduction which varies as ν^s, $s \approx 2$. The conductivity observed at 50 K, which follows a ν^2 behavior, is in our case simply a phonon tail, and is not due to hopping. Further, the observation of a strongly T-dependent $\sigma_{hopping}$ (10 cm^{-1})/σ_{dc} ratio confirms the idea that the hopping transport involves localized states near the Fermi energy. In addition, we find that the prefactor $A(T)$ follows the linear T dependence for $T \geqslant 60$ K. This indicates that the thermal energy k_BT is small compared to the energy

range over which $n(E_F)$ may be taken as the constant,[13] in agreement with the estimates for the bandwidth associated with chains.[20] However, in this case $A(T)=0$ for $T<60$ K which implies no phonon-assisted contribution to $\sigma(\nu)$ at low temperatures. This seems surprising since we observed the VRH law for the dc conductivity down to at least 35 K. The other possibility is that $A(T)$ follows a $T^{1.8}$ law at all temperatures. We note that the exponent $s=1.8$ is larger than $0\leqslant s\leqslant 1$ expected[13] for conventional disordered noncrystalline insulators. Finally, we want to comment on a decrease of the phonon-assisted hopping conductivity observed at high frequencies 6 – 20 cm^{-1} (insets of Fig. 3). In the theoretical two-site hopping model, at frequencies of the order of $\nu_{ph}\approx 10^{12}$ s^{-1}, the frequency dependence of σ_{hopping} saturates due to the fact that the exponent s decreases logarithmically with increasing frequency.[21] Our observation is in line with this theoretical prediction. Moreover, the final fading out of the phonon-assisted hopping at very high frequencies is intuitively expected and deserves more theoretical attention.

At microscopic scale, we propose that strong local distortions of the chains due to irregular coordination of La^{3+}, Sr^{2+}, and Ca^{2+} ions[19] induce a nonperiodic potential in which holes reside. The finding of the VRH law in the measured conductivity can be then viewed as a result of distorted distribution of microscopic conductivities, as predicted in Anderson localization theories. Therefore, copper-oxygen chains in partially doped $La_3Sr_3Ca_8Cu_{24}O_{41}$ can be considered as a system in which disorder, associated with random distribution of holes, causes the Anderson localization. This is in contrast to the observations for a chain subunit in fully doped $Sr_{14}Cu_{24}O_{41}$, where a charge gap opens due to the charge order developed in conjunction with the antiferromagnetic dimer pattern. We propose that the copper-oxygen chain subunit behaves similar to a one-dimensional disorder-driven insulator for the whole range of intermediate hole counts $0<n_h<6$,[22] and crosses over into a charge-ordered gapped insulator at full doping $n_h=6$. Note that the latter phase is established in chains concomitantly with the CDW gapped state in ladders. Moreover, both phases are suppressed by calcium doping at seemingly similar rates, indicating a profound interplay between chain and ladder subunits.[5,8]

In conclusion, the investigations of the frequency and temperature dependent conductivity yield clear evidence for variable-range hopping transport in chains of a spin-chain/ladder system $La_3Sr_3Ca_8Cu_{24}O_{41}$. The absence of holes in ladders for intermediate hole counts eliminates the CDW phase in ladders, and suppresses the charge-ordered gapped state in chains in favor of disorder-driven insulating phase. These results reveal an intriguing possibility for the existence of a phase transition close to $n_h=6$ in the phase diagram of $(La,Sr,Ca)_{14}Cu_{24}O_{41}$ compounds. Further experiments on materials with very low La content, which corresponds to $n_h\lesssim 6$ should elucidate our proposal.

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[22] We have observed the VRH transport with almost unchanged parameters (T_c and activation energy) also in $La_{5.2}Sr_{0.8}Ca_8Cu_{24}O_{41}$ with hole count $n_h=1$ on chains.