Sliding Density-Wave in Sr$_{14}$Cu$_{24}$O$_{41}$ Ladder Compounds

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We used transport and Raman scattering measurements to identify the insulating state of self-doped spin \( \frac{1}{2} \) two-leg ladders of \( \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \) as a weakly pinned, sliding density wave with non-linear conductivity and a giant dielectric response that persists to remarkably high temperatures.

Investigation of the charge and spin dynamics of spin \( \frac{1}{2} \) low-dimensional transition metal oxide materials is attracting attention because of the critical nature of their ground state and the relevance to the phase diagram of high temperature superconducting cuprates \( ^{[1,2]} \). The competition between insulating states at low hole concentrations and superconductive pairing at higher hole densities has emerged as a key feature of the high-\( T_c \) (critical temperature) problem, but the character of the insulating states has remained elusive. Electronically one-dimensional (1D) materials are susceptible to a drastic change of their ground state to an insulator with spontaneous broken symmetry. For example, Peierls ordered states in which the links connecting nearest neighbor sites acquire modulated values for their charge and/or spin densities as well as for the exchange coupling constants are associated with broken translational symmetries and have been extensively discussed in the literature \( ^{[3]} \). In the charge ordered state, collective excitations — such as those seen previously in sliding charge- and spin-density wave (C/SDW) compounds — should dominate the low energy dynamics.

\( \text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} \) is an experimental realization of a two-leg ladder structure (Fig. 1). The planes of the weakly coupled \( \text{Cu}_2\text{O}_3 \) ladders are stacked along the crystallographic \( b \)-axis alternating with 1D \( \text{CuO}_2 \) edge-sharing chain sheets \( ^{[4,5]} \). The Cu-Cu distances in these two subunits are incommensurate but satisfy an approximate relation \( 10c_{\text{chain}} \approx 7c_{\text{ladder}} \). The legs and rungs of the ladders are along the \( c \)- and \( a \)-axes, respectively. Because the average valence of Cu is +2.25, the compound is intrinsically doped with holes believed
to reside mainly in the chain substructure; optical studies have estimated 0.07 holes per ladder Cu site (6).

The self-doped compound Sr$_{14}$Cu$_{24}$O$_{41}$ is an insulator with an Arrhenius temperature dependence of the dc resistivity (7). Microwave (8) and magnetic resonance (9) studies have suggested the possibility of a charge ordering in the ladder planes that leads to insulating behavior. For ladders with higher hole concentrations, $d$-wave like superconductivity was predicted to win the competition with the charge-ordered state (1,10). Superconductivity at 12 K was discovered in doped two-leg ladders by applying both external and chemical pressure (11).

Single crystals of Sr$_{14}$Cu$_{24}$O$_{41}$ were grown as described in (6,12). We have studied the low-frequency charge response by ac transport and Raman scattering experiments. The temperature dependence of the $c$-axis complex dielectric function between 10 and 10$^6$ Hz (Fig. 2A) was measured with a capacitive technique. The dc conductivity was measured by an electrometer (Fig. 3). Raman measurements (Fig. 2B) were performed from the (010) surface of the crystal as described in (13). We also report strong nonlinearity in the $c$-axis conductivity as a function of electric field.

The temperature dependence of the low-frequency Raman response function (Fig. 2B) shows a broad overdamped excitation below 1 meV ($\sim$ 250 GHz). This quasi-elastic scattering peak (QEP) rapidly shifts to lower frequencies with cooling. The data are fit by a relaxational form of the Raman response function

$$\chi''(\omega, T) = A(T) \frac{\omega \Gamma(T)}{\omega^2 + \Gamma(T)^2}. \quad (1)$$

The fit reveals a decrease in the QEP intensity, $A(T)$, with heating and an Arrhenius temperature dependence for the scattering rate $\Gamma(T)$ with an activation gap $\Delta \simeq 2072$ K. The dc conductivity exhibits activated behavior with a break in the activation energy.
around $T^* \simeq 150$ K: $\Delta \simeq 1345$ K for $T < T^*$ and $\Delta = 2078$ K above $T^*$, similar to the activation energy observed for the Raman response function scattering rate $\Gamma(T)$ (Fig. 3). Similar quasi-elastic excitation has also been observed at high temperatures for superconducting Ca doped $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ ($0 < x < 12$) compounds with a higher concentration of holes in the ladder plane (13).

The frequency dependence of complex dielectric constant $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is shown in Fig. 2A for temperatures between 85 and 150 K. The low-frequency response of $\varepsilon_2$ shows overdamped, inhomogeneously broadened peaks at characteristic frequencies $\nu_0(T)$ determined by damping parameters $\Gamma(T) = 2\pi\nu_0(T) = \tau^{-1}$ (where $\tau(T)$ is the relaxation time). Strong relaxational peaks lead to a giant real part of the dielectric response $\varepsilon_1$ below $\nu_0(T)$ observed up to room temperature and even above. Such behavior is incompatible with any single-particle theory as it would imply energy gaps more than six orders of magnitude smaller than the thermal energy and suggests that the low frequency charge dynamics is driven by correlated collective behavior.

In Fig. 4 we scale all the measured complex dielectric functions between 80 and 160 K on one universal generalized Debye relaxational curve,

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + [i\omega\tau(T)]^{1-\alpha}}$$ (2)

where $\varepsilon_0$ and $\varepsilon_\infty$ are low- and high-frequency dielectric constants and the fitted value $\alpha = 0.42$ characterizes the width of the distribution of relaxational times (14). The temperature dependence of the scattering rates $\Gamma(T) = \tau^{-1}$ from ac transport and Raman measurements are compared to the dc conductivity in Fig. 3. The scattering rates $\Gamma(T)$ follow the activated behavior of dc conductivity over 10 decades of frequency.

We now discuss the implications of these observations. First we note that recent microwave experiments by Kitano et al. have reported a relatively small and narrow
peak between 30 and 100 GHz in the c-axis conductivity observed up to moderately high temperatures (3). This resonance is attributed by the authors to a collective excitation of a pinned CDW.

In the charge or spin density state the condensed electrons do not participate in the conduction process for small dc electric fields. The reason for this is the interaction between the condensate and impurities and other lattice irregularities. This pinning shifts the oscillator strength associated with the collective modes to finite frequencies, with no contribution to the dc conductivity that shows an activated behavior and is entirely determined by quasi-particle excitations out of the condensate. The Arrhenius law for the decay constant $\Gamma(T)$ suggests a hydrodynamic origin for the Raman and low-frequency conductivity modes, for which there is considerable precedent in studies of the dynamics of pinned CDW and SDW systems (15, 16, 17, 18, 19, 20), and we compare the Sr$_{14}$Cu$_{24}$O$_{41}$ ladder system to well-established models of CDW dynamics (21). The pinned collective mode can be described by an oscillator making a collective contribution to the ac conductivity

$$\sigma_{\text{coll}}(\omega) = \frac{1}{4\pi} \frac{-i\omega\Omega^2_p}{\Omega^2_0 - \omega^2 - i\gamma_0\omega},$$

where $\Omega^2_p = \rho_c^2/m^*$ is the oscillator strength of the mode with charge density $\rho_c$ and mass density $m^*$, $\Omega_0$ is the pinning frequency, and $\gamma_0$ is an intrinsic damping coefficient. To account for the longitudinal response (relevant for Raman scattering), we must allow for screening of the collective mode. Then the longitudinal response function is

$$\epsilon_L(\omega) = \frac{\Omega^2_p}{\Omega^2_0 - \omega^2 - i\gamma_0\omega - i\omega\Omega^2_p/(4\pi\sigma_{qp} - i\omega\epsilon_{\infty})},$$

where $\sigma_{qp}$ is the dc ”background” conductivity due to quasiparticle transport. Note that at low frequency, Eq. (4) reduces to a relaxational mode, with amplitude $\Omega^2_p/\Omega^2_0$ and decay
constant

$$\Gamma(T) = 4\pi\sigma_{qp} \frac{\Omega_p^2}{\Omega_0^2} = \frac{4\pi\sigma_{qp}}{\epsilon_0 - \epsilon_{\infty}}. \quad (5)$$

The proportionality of $\Gamma(T)$ and $\sigma_{qp}$ arises because the collective charge oscillations are screened by thermally excited and uncondensed quasiparticle carriers on the relevant ladder. Although the longitudinal mode we are discussing is in principle neutral, the effects of disorder in a strongly anisotropic system make it visible — in fact typically dominant — in the transverse response, and therefore it will contribute to ac conductivity. Such was the case in CDW systems (15,16,17,18,19,20). The transfer of spectral weight to the longitudinal channel explains why the oscillator strength in the microwave region (8) is anomalously small.

The plasma edge energy for $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, determined from IR spectroscopy as the peak position of the loss function $\Im[-1/\epsilon(\omega)]$, gives us an estimate for $\Omega_p \simeq 3300$ cm$^{-1}$ (4,22). Using the characteristic pinning frequency $\Omega_0 \simeq 30 - 100$ GHz suggested by microwave measurements (8), we estimate the value of the low-frequency dielectric constant $\epsilon_0 \simeq \Omega_p^2/\Omega_0^2$ to be between $10^6$ and $10^7$, which is consistent with our direct measurements. Following expression (5) and the estimated values for $\epsilon_0$, we calculate the theoretical values for $\Gamma(T)$ using the measured dc conductivity. These calculated values are shown by the shaded green area in Fig. 3. They are in very good agreement with the relaxational energies extracted from the peaks in $\epsilon_2(\omega)$ (see Fig. 4). The overall consistency among the measured temperature dependences of the dielectric response $\epsilon(\omega)$, the relaxation rate $\Gamma(T)$, and the dc conductivity $\sigma_{qp}$ demonstrates the applicability of the hydrodynamic model description for the low-frequency collective charge dynamics in this system. Moreover the broad inhomogeneous response has exactly the character expected for random pinning by disorder of an incommensurate density wave.

The small frequency $\Omega_0$, which describes the oscillation of the collective mode about
the pinned equilibrium position, implies a weak restoring force. Therefore, it is anticipated that a small dc electric field can induce sliding density wave transport by translational motion of the condensate. In the inset of Fig. 3 we show conductivity at 100 K measured as a function of applied electric field. Below a threshold field $E^{(1)}_T \approx 0.2 \text{ V/cm}$, the conductivity obeys Ohm’s law with the Arrhenius temperature dependence discussed above. However, for electric fields above the $E^{(1)}_T$ threshold, the $I-V$ characteristics change from linear to approximately quadratic, indicating an onset for sliding density wave conductivity \(^{(23)}\). In this regime of relatively slow CDW sliding the predominant damping mechanism is the screening of internal electric fields produced by local CDW deformations by backflow currents of uncondensed quasi-particles \(^{(21)}\).

At much higher fields, above 50 V/cm, we observe a second threshold, $E^{(2)}_T$, with a very sharp rise of the current up to the limit of the current generator. The calculated differential conductivity in this regime is enormous, more than $10^5 \text{ } \Omega^{-1}\text{cm}^{-1}$, an estimate limited by contact effects and most likely carried by inhomogeneous filamentary conduction. We attribute this phenomenon to the crossover to a regime of free sliding CDW first proposed by Fröhlich as CDW superconductivity \(^{(24)}\). Such a crossover has been observed in conventional CDWs, and is expected to occur once the density wave reaches velocities at which the background quasiparticles can no longer screen the response \(^{(25)}\). An upper limit of the field at this second threshold may be estimated from the average pinning frequency $E^{(2)}_T \leq (\Omega^2_0/\Omega^2_p)(\rho_c/Q)$, where $\rho_c$ is the collective charge density and $2\pi/Q$ is the period of the density wave. Assuming $2e$ per ladder contributing to the density wave, we obtain $E^{(2)}_T \leq 100 \text{ V/cm}$, again consistent with our measurements. Note that the true threshold for deformable sliding of the density wave is always much lower.

Now we turn to high temperature Raman measurements. The Raman response function is proportional to $\Im \varepsilon_L$. The comparison of the Raman and ac transport data is not
straightforward because only in the Raman data above room temperature $\Gamma(T)$ is large enough for a peak to be observed. Although $\Gamma(T)$ extracted from the Raman data exhibits activated behavior with a gap consistent with dc conductivity above $T^*$, the values for $\Gamma(T)$ are about 50 times the relaxational energies predicted from eq. (5). However, the lowering of the peak intensity with increasing temperature (see Fig. 2B inset) suggests that there is a reduction of the density wave amplitude $\rho_c$ which would produce a concomitant increase in $\Gamma$. Further enhancement in the scattering rate may come from additional relaxation due to the presence of low lying states seen at temperatures above $T^*$ by magnetic resonance (9), high frequency Raman scattering (24) and $c$-axis optical conductivity (22).

All our results have clear quantitative parallels with sliding density wave transport phenomena observed in established C/SDW materials, yet there must be a number of important microscopic differences from conventional weak-amplitude charge- and spin-density waves. The C/SDW correlation in Sr$_{14}$Cu$_{24}$O$_{41}$ is a high-temperature phenomenon that we observe (with diminishing amplitude) up to the highest measured temperature, 630 K. Such high-temperature correlations can not be supported by phonons, which suggests that the charge/spin correlations arise from strong spin exchange interactions with characteristic energy scale $J \approx 1300$ K (24). The magnetic excitations in spin $\frac{1}{2}$ two-leg ladders are resonating valence bond (RVB) quantum states (1, 3, 26, 27), different from the gapless classical spin waves in the SDW systems. Theoretical calculations for a doped two-leg spin ladder suggest that in an RVB environment the holes are paired in a state of approximate $d$-wave symmetry with a few lattice spacings in size (28, 29, 30). The superconducting condensation of bound pairs is competing with a crystalline order of these pairs in a CDW state (14). If the fundamental current-carrying object in the doped singlet ladders is a bound pair of holes, the hydrodynamic mode we have discussed involves local
displacement of “crystallized” pairs, screened by charged excitations across the CDW gap, which would account for the appearance of the conductivity as the relevant parameter to describe backflow. Nevertheless, our observation of a weakly pinned mode — which implies a large stiffness for charged fluctuations of the order parameter — is surprising in the context of models with strong short-range correlations, where one would expect that lattice pinning effects are strong.

References and Notes

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31. We thank A.P. Ramirez for help with ac transport measurements and for discussions.

Figure 1: A 3D sketch of the Sr$_{14}$Cu$_{24}$O$_{41}$ crystal structure. Three neighboring Cu$_2$O$_3$ ladder and CuO$_2$ chain subunits are shown separately. See [4,5] for details.
Figure 2: (A) The temperature dependence of the measured real (open circles) and imaginary (solid circles) parts of the complex dielectric function between 85 and 300 K. The dashed and solid lines are guides for the eye. (B) The temperature dependence of the Raman response function for the polarization of the incident and scattered photons parallel to the legs of the ladders: the data (circles) and the fit to eq. (1) (dashed lines). The spectra were acquired in a backscattering geometry using the 7993 Å excitation. The resonance at about 356 GHz at low temperatures is a phonon. The inset shows the diminishing quasi-elastic scattering intensity, $A(T)$, with heating.
Figure 3: The temperature dependence of the scattering rates (left scale) $\Gamma(T) = \tau^{-1}$ from scaling of the ac dielectric (Fig. 4) and Raman (Fig. 2B) response. The scattering rate follows the activated behavior of the dc conductivity (right scale) over 10 decades of frequencies. The inset shows strong nonlinearity in the dc conductivity as a function of electric field measured at 100 K.
Figure 4: Scaling, measured between 80 and 160 K in the 20 Hz – 1 MHz frequency window, of the complex dielectric function (imaginary part, solid circles; real part, open circles) on the generalized Debye relaxational curve \((2)\). The obtained temperature dependent scattering rate \(\Gamma(T) = \tau^{-1}\) is shown in Fig. 3.