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Microwave collective transport in single-crystal Eu_2CuO_4

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We measured the complex conductivity of single crystals of Eu_2CuO_4 from 3 to 15 GHz and observed collective transport with a sample-independent spectral weight. An unusual activated temperature dependence for the spectral weight, and anomalous temperature dependence of the Eu Mössbauer line, indicate magnetic effects well above the Néel temperature. The collective transport is similar to that observed in a spin-density wave compound where charged, massive solitons are the suspected source of the transport.

Collective electronic modes are present in superconductors,[1] charge-density-wave[2] (CDW) systems, and spin-density-wave (SDW) systems at frequencies well below the single-particle gap. In superconductors, the collective mode is unpinned and undamped, while in the density-wave systems, the damped and pinned mode occurs at microwave frequencies. Important information about these collective electronic states has been obtained by measurements of the complex conductivity at microwave frequencies.[2] We report here microwave observations of a collective mode with an activated spectral weight in Eu_2CuO_4, a semiconductor that shares the Cu-O planar structure seen in La_2CuO_4 and $RBa_2Cu_3O_7$ (R=rare earth), and Mössbauer observations of related but unidentified magnetic effects.

We grew Eu_2CuO_4 as large single-crystal plates (0.3 $cm^2 \times 0.005$ cm) from a PbO flux. The a axes are in the plane of the plates. X-ray-diffraction measurements indicate a single phase with lattice constants $a=3.91$ Å, $c=11.93$ Å. It is characterized by an optical gap[3] which, in light of the half-filled orbital with degenerate spin states expected from simple charge-count arguments, must arise from electron-electron interactions. Also observed is an activated dc conductivity with activation energy an order of magnitude lower than the gap. Weak features in the resistivity near 240 K are observed[4] and from susceptibility measurements are interpreted as indicating a Néel temperature (T_N). Hall measurements[4] on samples from the same batch we studied yield a carrier density $n=10^{18}/cm^3$ at 300 K with an activation energy of 700 K. We found our samples to have a resistivity of 3 Ω cm at 300 K with an activation energy of 1310 K over the temperature range of 80 to 300 K. Because the dc conductivity is a measure of the product of mobility and carrier density, the mobility must be activated as well, suggesting that electronic transport is governed by a hopping process.

The optical spectrum is remarkably clean with an ir-active carrier density[3] $n \lesssim 10^{18}/cm^3$. Such a low ir-carrier density leaves the origin of dc conductivity in question because carrier sources such as impurity levels would require $10^{19}/cm^3$ impurity sites to provide 10^{18} carriers/cm^3 at 300 K if the carriers are activated as above. But all 10^{19} impurities/cm^3 would be observed with ir. Another oxide superconductor $BaPb_{1-x}Bi_xO_3$ has the same spectroscopic anomaly, dc conduction with an activation energy much lower than the gap, and insufficient extrinsic carrier sources.[5] We suggest below a mechanism for this unusual transport.

The planar cuprates La_2CuO_4, Eu_2CuO_4, and oxygen-deficient $R_1Ba_2Cu_3O_{7-x}$ ($x>0.5$) all share an optical gap[3] of ~ 1.7 eV and magnetic transitions[4] near 240 K indicating identical intrinsic excitations. The observation of superconductivity at 95 K in many compounds with Cu-O planes also confirms that the Cu-O planes are responsible for the important physical properties. The Eu_2CuO_4 compound differs[4] from the La_2CuO_4 analog[6] in that it is tetragonal rather than orthorhombic and its out-of-plane oxygens are in another location. In addition, Eu_2CuO_4 grows more easily and has a much lower conductivity. It therefore appears to have a lower impurity concentration, making intrinsic processes obscured in La_2CuO_4 visible in Eu_2CuO_4.

Microwave conductivity measurements were made using a unique coaxial microwave bridge. This technique for waveguide bridges is described elsewhere.[7] Our method differs only in that it is implemented in a coaxial line and is therefore tunable over a full decade, from 2 to 20 GHz. The sample chamber of the bridge is mounted in a flow cryostat where Chromel-Constantan thermocouples and an electronic controller could maintain the sample at temperatures from 9 to 300 K with an accuracy of 2 K and stability of 0.1 K. The samples to be measured were mounted directly across one open coaxial arm of the bridge using evaporated Cu contacts and silver paint. At the frequencies of interest, capacitive coupling reduced the contact impedance to less than 2% of the sample impedance. The samples were typically $0.14 \times 0.02 \times 0.005$ cm^3. The c faces were as they came from the melt. Four-wire resistivity measurements in the a plane were made in the same cryostat as the microwave measurements.

The ^{151}Eu Mössbauer effect was measured for $1.2<T<475$ K. Mössbauer measurements were made from unoriented powder obtained by grinding the crystals, with the sample acting as the absorber, and with both the source and sample kept at the same temperature. The gross absorber thickness was only 6.5 mg cm^{-2} so no temperature-dependent saturation line broadening was expected. The temperature dependence of the recoil-free fraction f, determined from the integrated absorption corrected for the f values of the $^{151}SmF_3$ source, was well represented by a Debye model with $\Theta_D = 220$ K. The linewidth at high temperatures is 2.0 mm s^{-1}; one expects some quadrupole broadening. The isomer shift corresponds to Eu^{3+}. The significant line shape change with decreasing temperature has been interpreted as a transferred magnetic hyperfine field from negative Cu sites acting on the (nonmagnetic) Eu^{3+} sites. The temperature dependence of the hyperfine field is shown in Fig. 1. Note the unusual linearity of the hyperfine field for $1.2 < T < 350$ K. We see no anomaly associated with the reported Néel temperature.[4] The Mössbauer effect measures the hyperfine field averaged over the 1.4×10^{-8} s lifetime of ^{151m}Eu so a static field is not necessarily implied; however, the results imply spin correlations to $T > 400$ K.

The microwave complex conductivity of Eu_2CuO_4 at 300 K is displayed in Fig. 2 for two samples. At 9 GHz, sample No. 1 displays its peak real conductivity, which is 9 times larger than at dc. The peak imaginary conductivity of both samples is much lower than the real part, indicating a resonance. The resonant frequency of sample No. 1 is within the range of the bridge while for sample No. 2 it is close to our upper frequency limit. We note that the peak imaginary conductivity of sample No. 2 is half the peak real conductivity of sample No. 1. For a simple harmonic oscillator, the peak imaginary conductivity is half the peak real conductivity. Thus, the curves in Fig. 2, which are fits to a harmonic oscillator model,[2] correspond to the same oscillator strength for both samples, where

$$\sigma = \sigma_{dc} + \frac{ne^2\tau}{m^*} \frac{i\omega}{i\omega + (\omega_0^2 - \omega^2)\tau} + \frac{i\omega\epsilon_\infty}{4\pi} , \qquad (1)$$

and the fit parameters are $ne^2\tau/m^* = 2.5$ $(\Omega\,\text{cm})^{-1}$, $\sigma_{dc} = 0.3$ $(\Omega\,\text{cm})^{-1}$, $(2\pi\tau)^{-1} = 35$ GHz in all cases. The mode frequency ω_0 is 6 GHz and the infinite frequency dielectric constant ϵ_∞ is 100 for sample No. 1; ω_0 is 18 GHz and ϵ_∞ is neglected for sample No. 2. The fits to

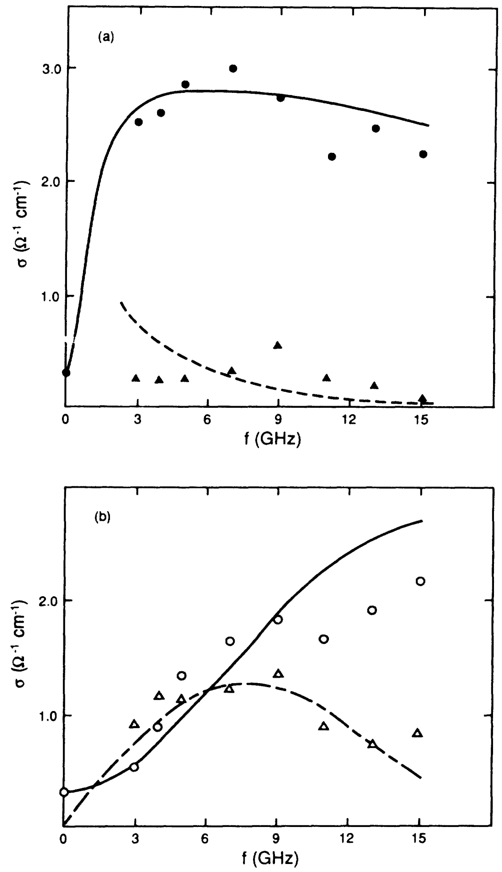

FIG. 2. Frequency-dependent complex conductivity for two single-crystal samples of Eu_2CuO_4. (a) sample No. 1; (b) sample No. 2; ○, real conductivity; △, imaginary conductivity. The fits are to Eq. (1), solid lines, Re(σ); dashed lines, Im(σ).

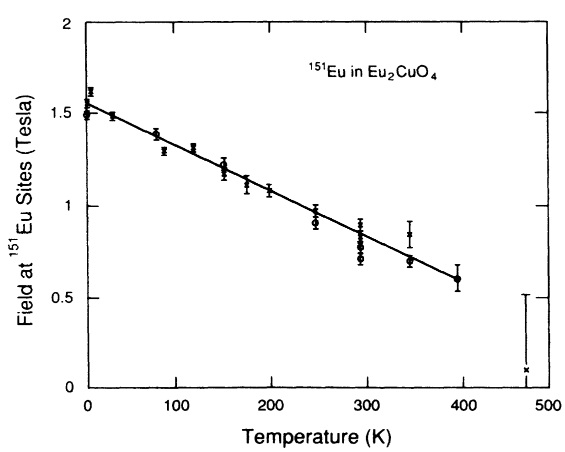

FIG. 1. The temperature dependence of the hyperfine field at the ^{151}Eu sites in Eu_2CuO_4 determined from the Mössbauer spectra (×, sample No. 1; ○, sample No. 2). The solid line is $1.57\,(1 - T/655\ \text{K})$.

$\sigma(\omega)$ with Eq. (1) are in good agreement with the experimental results, except for Imσ of sample No. 1. The weak peak in Imσ occurs when Reσ is large and a small phase shift, perhaps at a contact, results in part of the current response being out of phase with the driving field leaving Imσ containing a small fraction of Reσ. Such an effect is difficult to avoid when Reσ is much larger than Imσ. The slightly different values of ϵ_∞ for the two samples would then be an artifact. The spectral weight of the resonance is strongly temperature dependent so that by 150 K, the peak conductivity is only 0.5 $(\Omega\,\text{cm})^{-1}$. We note that the temperature dependence of the resonant frequency and width is weak and not detectable, a quality observed in CDW and SDW systems where the frequency is determined only by the defect density, which provides pinning sites for microwave conduction. The different pinning frequencies for the two samples may be due to different impurity concentrations. In CDW's, the resonance width is also observed to be temperature independent, but the mechanism for this is not understood. The temperature dependence of the peak real conductivity, $\sigma_{dc} + ne^2\tau/m^*$ (proportional to spectral weight), is displayed in Fig. 3. From this plot, we obtain an activation energy of 630 K, about the same as for the Hall carriers. The effective mass m^* of the mode may be estimated from our 300-K

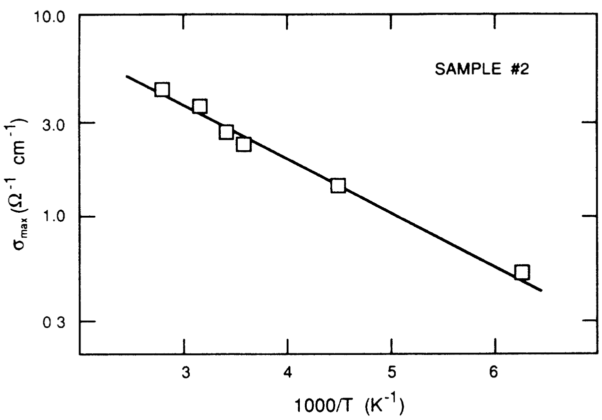

FIG. 3. The peak real conductivity derived from fits to Eq. (1) vs 1000/T. The solid line is a fit to $\exp(-T_0/T)$, with $T_0=630$ K.

microwave data and from the Hall carrier density because of the apparent thermal correspondence between the Hall and microwave carriers. Note that the microwave electric fields are not sufficient to cause hopping for the hopping mobility we observe, thus, we expect the Hall and microwave activation energies to agree. Using σ_{dc}, $ne^2\tau/m^*$, τ, and n, we find $m^* \approx 500 m_e$. The mass estimate is only reliable at an order of magnitude level due to the use of a Hall carrier density and an imprecise measurement of τ.

We note that the dc dielectric constant of Eu_2CuO_4 deduced from Fig. 2 is of order 10^3 at 300 K, ensuring complete screening of Coulomb interactions. Such effects may also be present at low temperatures in the doped material as we discuss below.

A frequency-dependent microwave conductivity may result from a number of phenomena. Low-lying modes, such as in a ferroelectric,[8] may contribute a frequency-dependent microwave conductivity, but they occur only in a narrow range of temperatures near a transition, unlike what is observed here. Antiferromagnetic resonances should show a temperature-dependent frequency because the Mössbauer data show a temperature-dependent field, but we observe a fixed frequency. Single-electron processes may contribute where disorder and low-dimensionality exist[9] but are characterized by a single-electron scattering rate several orders of magnitude larger than we observe. The unit cell is too small to allow optical phonons at this frequency.

In contrast, the coherence in modes derived from electronic collective states results in scattering times and pinning frequencies of order 20 GHz for CDW's and SDW's (comparable to our result) and zero for both quantities in superconductors. We see a temperature-dependent peak conductivity inconsistent with that of a CDW (Ref. 10) where far below T_c the spectral weight saturates. Our results are, however, similar to observations[11] in $(TMTSF)_2PF_6$ where TMTSF denotes tetramethyltetrathiofulvalene, and where a microwave collective mode is observed below the SDW transition at 12 K with damping and pinning frequencies comparable to those observed here. The mode in $(TMTSF)_2PF_6$ also displays a similar thermally activated spectral weight which was interpreted as arising from charged solitonlike excitations of the SDW. In a one-dimensional commensurate SDW Horovitz[12] has shown that charged, spinless solitons are the lowest charged excitations above the ground state. Our system is quasi two dimensional. Fermi surface nesting, however, may imply that the cuprates have quasi-one-dimensional characteristics. The mode appears both above and below T_N, therefore, some form of long-range order is not important. The lack of long-range order ensures that localized states are responsible for the microwave conduction, even though the ground state is not well understood.

Our results place an important constraint on the ground state because we see charged excitations at energies 25 times lower than the 1.7-eV single-electron gap. Such excitations are not possible in a Mott-Hubbard system, with on-site repulsions much larger than transfer energies, where all the low-energy excitations are spin waves. Instead, we require substantial itinerant character leading, qualitatively, to "holes" spread over an area of approximately 25 lattice sites with a creation energy estimated to be $B=1.7/25$ eV ~ 800 K. The itinerant character is also clearly displayed in NMR studies[13] of La_2CuO_4, where the temperature dependence of the sublattice magnetization is *not* consistent with a local moment ordering.

We propose that the 630 K activation energy indicates that localized states are thermally excited as a positive-negative pair (because the total localized-state charge must be conserved up to single-electron excitation energies of 1.7 eV) from a ground state much like a commensurate SDW but with shorter-range order. The microwave response results from translation of the localized states, which have a metal-like mobility. The dc conduction arises from the same carriers, but with a much lower hopping mobility, explaining the anomalous dc properties. In the superconductors, if a similar ground state existed, such localized states, the lowest charged excitations, could also form through doping of the Cu-O planes with positive charges. The charged, perhaps spinless, localized states would then exist in the ground state of the doped material at $T=0$ K. Observations[14] of similar collective modes in the $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$ superconductors support this.

Thus, we find that Eu_2CuO_4 exists with some type of magnetic order unrelated to the reported T_N and has a collective mode of the type seen in SDW systems, but the identification of the ground state is inconclusive. The collective mode is thermally activated suggesting that charged, massive, localized states thermally created above the ground state are responsible.

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