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Antiferromagnetic resonance in La_2CuO_{4+y}

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Our attempts to observe the antiferromagnetic resonance (AFMR) modes in La_2CuO_{4+y} in both single-crystal and small-particle forms have been unsuccessful. An argument based on a magnetic-susceptibility sum rule shows that the resonance previously identified with the AFMR in polycrystalline La_2CuO_{4+y} [R. T. Collins *et al.*, Phys. Rev. B **37**, 5817 (1988)] is too strong to be compatible with a magnetic spin-wave mode. No evidence of an AFMR mode is found in our single-crystal La_2CuO_{4+y} transmission measurements versus magnetic field. Additional measurements on small particles show that the broad resonant feature observed around 8 cm^{-1} is produced by an electric-dipole-active superconducting sphere resonance of the La_2CuO_{4+y} particles.

The recent discovery of superconductivity[1] at temperatures above 30 K in $La_{2-x}Ba_xCuO_{4+y}$ has brought much attention to the parent compound La_2CuO_{4+y}. Early magnetic susceptibility measurements[2] on La_2CuO_{4+y} showed anomalies around 250 K which suggested antiferromagnetism in this compound. The antiferromagnetic ordering on the Cu sites was confirmed by elastic neutron scattering.[3] Moreover, inelastic neutron scattering[4] and two-magnon Raman-scattering measurements[5] showed that the intraplanar antiferromagnetic exchange interaction in La_2CuO_{4+y}, as well as in $YBa_2Cu_3O_{6+y}$, is quite strong. Collins *et al.*[6] have reported a very broad antiferromagnetic resonance (AFMR) feature at 9 cm^{-1}. Using neutron scattering together with the results of Ref. 6, Peters *et al.*[7] reported in-plane and out-of-plane spin-wave excitations at energies of 8 ± 2 and 20 ± 4 cm^{-1}, respectively. The identification of the modes would appear complete were it not for the fact that we find the measured strength of the reported AFMR mode to be more than an order of magnitude larger than the value required by the measured dc susceptibility.

In this paper, we first show that the far-infrared line strength[6] of the reported AFMR in powder samples is not consistent with the measured dc magnetic susceptibility. Next we demonstrate with single-crystal samples that an absorption line of the same strength is not observed. To identify the origin of the observed resonance we have made additional far-infrared measurements on La_2CuO_{4+y} in small particle form. Our study shows that the resonant feature observed by Collins *et al.*[6] is most likely a superconducting sphere resonance similar to that previously observed in $La_{2-x}Sr_xCuO_{4+y}$.[8]

To show that the resonance feature reported by Collins *et al.*[6] is not consistent with AFMR, we use a susceptibility sum rule[9] which relates the magnetic absorption strength of the AFMR to the dc magnetic susceptibility for linearly polarized light, namely

$$\Delta\chi_{\perp i}(0) = \frac{1}{4\pi^3 n}\int_0^\infty \frac{\Delta\alpha_i}{\omega^2}d\omega \,. \tag{1}$$

Here $\chi_{\perp i}(0)$ is the contribution to the dc magnetic susceptibility in emu/cm^3 produced by the ac response of magnetic mode i. Both $\Delta\alpha_i$ and ω are given in cm^{-1}, and n is the low-frequency index of refraction produced by the electric dipole active TO modes of the lattice vibration spectrum; n is assumed to be a constant over the FIR frequency region of interest.

In this orthorhombic crystal the two spin sublattices are aligned mainly along the diagonal direction in the *ab* plane with a small canting ($\sim 0.17°$) along the c axis, which is also the hard uniaxial anisotropy direction.[7] For such an easy plane anisotropy configuration[10] it can be shown that the "in-plane mode" which has the oscillating dipole moment in the *ab* plane along the perpendicular direction to the diagonal determines $\chi_{\perp 1}(0)$ with the "out-of-plane mode" determining $\chi_{\perp 2}(0)$ in the c direction.[11]

Usually, for a particular AFMR mode, the width is small compared to the center frequency so Eq. (1) simplifies to

$$\chi_{\perp i}(0) = S_i/(4\pi^3 n\omega_{0i}^2) \,, \tag{2}$$

where S_i is the line strength in cm^{-2} in the mode $i=1$ or 2 and $\omega_{0i} = \lambda_{0i}^{-1}$ is the corresponding AFMR resonant frequency in cm^{-1}. For a randomly oriented pressed powder sample[11] at $T=0$ K,

$$\chi_{pi}(0) = \chi_p(0)/2 = \chi_\perp(0)/3 \,, \tag{3}$$

and since only one third of the grains have the sublattice magnetizations correctly oriented to interact with a specific far-ir polarization, the powder strength is $S_{pi} = S_i/3$. Substituting this result and Eq. (3) into Eq. (2) yields

$$\chi_p(0)/2 = S_{pi}/(4\pi^3 n\omega_{0i}^2) \,, \tag{4}$$

the relation between the susceptibility and mode strength in the powder sample.

For the first comparison of the strength to the susceptibility we use the values quoted in Ref. 6: $S_{p1} = 2$ cm^{-2},

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$\omega_0 = 9$ cm^{-1}, and with $n = 6.6$ (Ref. 12), Eq. (4) gives $\chi_{p\mathrm{FIR}}(0) = 6.0 \times 10^{-5}$ emu/cm which is more than an order of magnitude larger than the measured dc value $\chi_p(0) = 1.4 \times 10^{-6}$ emu/cm^3, assuming that the 0-K value of $\chi_{\perp 1}(0)$ is equal to the value at the Néel temperature, as expected from simple theoretical considerations. [A more precise estimate[13] for the broad line, using Eq. (1), gives $\chi_{p1}(0) = 1.0 \times 10^4$ emu/cm^3 or $\chi_{p\mathrm{FIR}}(0) = 2.0 \times 10^{-4}$ emu/cm^3, which is now compared with the more recent experimental value obtained for a single crystal. For a twinned crystal with the dc magnetic field in the *ab* plane, the Néel temperature value is 2.2×10^{-6} emu/cm^3.[14] Since this is the same as the 0-K value of $\chi_{\perp 1}(0)$, then $\chi_{\perp 1}(0) = 2.2 \times 10^{-6}$ emu/cm^3 so $\chi_p(0) = 1.5 \times 10^{-6}$ emu/cc $\approx \chi_{p\mathrm{FIR}}(0)/130$.] Clearly with either analysis the observed absorption line is too strong to be identified with an AFMR mode.

To identify the source of the low-frequency resonant feature, we have measured the far-infrared transmission spectra of single-crystal and polycrystalline La_2CuO_{4+y} using a lamellar grating (2–40 cm^{-1}) interferometer in conjunction with a 0.3-K ^{3}He-cooled Ge bolometric detector. The sample temperature was varied between 4 and 70 K, and the applied magnetic field was varied between 0 and 6 T.

La_2CuO_{4+y} crystals were grown from a CuO-based flux.[14] To remove any trace of the superconducting phase, the crystals were annealed in vacuum for 24 h at 700 °C and slowly cooled to room temperature. In order to get the *ab*-plane index of refraction of La_2CuO_{4+y} for the sum rule, we polished a crystal down to 100 ± 10 μm and observed the interference fringes in transmission. These data are shown in Fig. 1(a). From the measured fringe spacing and the known thickness of the sample we obtain $n_{ab} = 5.75 \pm 0.5$, slightly smaller than the value of 6.7 which has been derived from the infrared mode residues in a single-crystal reflectivity study.[12]

To look for the antiferromagnetic resonance at 8 cm^{-1}, we used a crystal with dimensions of about $1.15 \times 0.6 \times 0.15$ cm^3. The out-of-plane mode cannot be examined in this arrangement. Because of low-temperature hopping conduction the transmission along the *c* axis is very small, less than a percent in the region from 5 to 25 cm^{-1} at 4.2 K, and decreases rapidly as the temperature is raised. This high absorptivity and temperature dependence are in agreement with the measured dc resistivity.[15] Because of this background temperature dependence, it is not feasible to look for the AFMR by temperature-dependent measurements.

The change in the far-infrared absorption coefficient α at 1.2 K has been studied as a function of magnetic field between 0 and 6 T. As shown in Fig. 1(b) (solid line), no change in α is observed within our experimental uncertainty. This result differs strongly from the field dependence of α that has been reported for a polycrystalline sample,[6] shown with a dashed line in Fig. 1(b).

Given the known dc susceptibility, could an AFMR line be observed in our experiment? If the in-plane spin-wave excitation is located at 8 cm^{-1} with a 1-cm^{-1} linewidth and the dc susceptibility is $\chi_{\perp 1}(0) = 2.2 \times 10^{-6}$ emu/cm^3, then the maximum absorption coefficient is about 0.10 cm^{-1}, a value somewhat smaller than the experimental uncertainty in Fig. 1(b). Before such a weak resonance can be located, it is necessary first to reduce the hopping conductivity so that thicker crystals can be used.

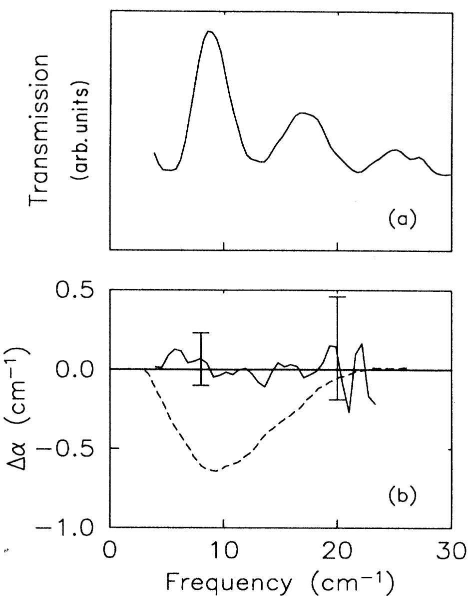

FIG. 1. Transmission measurements on La_2CuO_{4+y} single crystals. (a) Transmission spectrum of a thin La_2CuO_{4+y} single crystal, with thickness 100 ± 10 μm. The spacing between the Fabry-Perot fringes and the known thickness of the sample yield the value of the *ab*-plane index of refraction, $n_{ab} = 5.75 \pm 0.5$. (b) The difference in absorption coefficient, $\Delta\alpha$, between 0 and 6 T. The solid line is our measured value for a La_2CuO_{4+y} single crystal. The solid bars indicate our experimental uncertainty at 8 and 20 cm^{-1}. The dashed line is the measured value for a polycrystalline sample from Collins *et al.* (Ref. 6).

To investigate the apparent discrepancy between the polycrystalline and single-crystal results shown in Fig. 1(b), we prepared polycrystalline samples of pure La_2CuO_{4+y} by the solid-state reaction of CuO and La_2O_3. Well-mixed powder was ground and fired in air. The fired powder was reground and refired, typically two times, until the material became single phase, as determined by x-ray diffraction. This material was pressed into pellets, fired at 1050 °C for 12 h in a flowing O_2 atmosphere, and slowly cooled to 500 °C. After being annealed for 5 h at 500 °C, the pellets were slowly cooled to room temperature. The sample prepared in this way has a broad superconducting transition with a midpoint at around 30 K, similar to the observation of Grant *et al.*[16] The temperature-dependent resistivity is shown by the solid curve in Fig. 2(a).

To produce a nonsuperconducting sample of pure La_2CuO_{4+y}, we annealed it in vacuum for 1 h at 700 °C. As shown by the dashed line in Fig. 2(a), the dc resistivity is consistent with semiconducting behavior, growing with decreasing temperature. Even though the temperature dependence before and after heat treatment is very different, the room-temperature resistivity is almost the

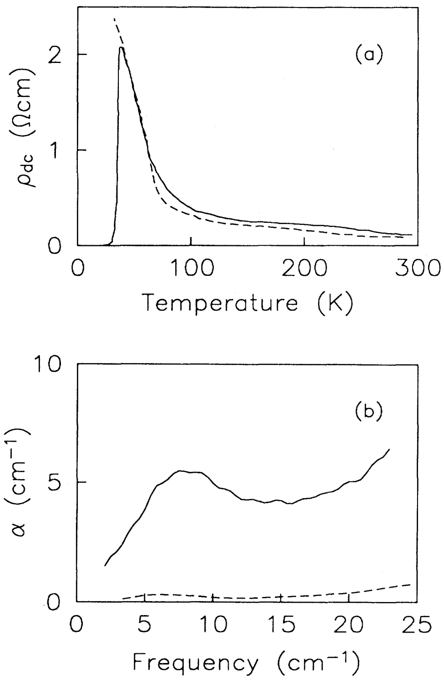

FIG. 2. (a) The dc resistivity of sintered pellets of polycrystalline La_2CuO_{4+y}. The solid line shows the superconducting behavior of the oxygen-annealed sample, and the dashed line, the semiconducting temperature dependence of the vacuum-annealed sample. (b) The absorption coefficient for 10% La_2CuO_{4+y} small particles in Teflon. Solid line: superconducting sample; dashed line: semiconducting sample.

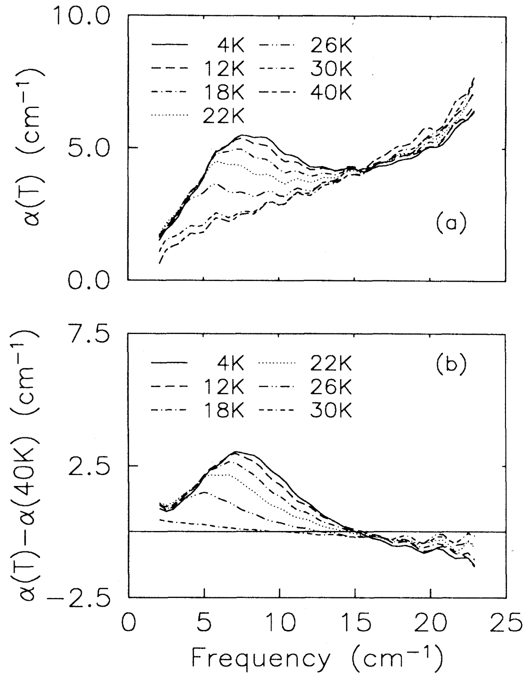

FIG. 3. (a) The temperature dependence of the absorption coefficient for 10% La_2CuO_{4+y} superconducting particles in Teflon. (b) The difference between the absorption coefficient at a given temperature and that at 40 K.

same. After the bulk properties were measured, the superconducting and semiconducting La_2CuO_{4+y} were made into pellets of isolated particles in Teflon following the procedure described earlier.[8]

The solid line in Fig. 2(b) shows the far-infrared absorption spectrum of 10% superconducting isolated particles of La_2CuO_{4+y} in Teflon. This sample has a broad absorption peak around 8 cm^{-1}. Even though the position of this absorption peak appears to coincide with that of the in-plane spin-wave mode assigned by neutron scattering,[7] it cannot be attributed to AFMR, because the integrated absorption strength is more than 3 orders of magnitude larger than the value expected from Eq. (1). The dashed line in Fig. 2(b) shows that the resonance feature is suppressed for the vacuum annealed semiconducting sample.

The temperature-dependent properties of the resonance which are displayed in Fig. 3 provide evidence that this resonance feature is related to superconductivity in undoped La_2CuO_{4+y}. Figure 3(a) shows the temperature dependence of the 10% oxygen annealed La_2CuO_{4+y} in Teflon. A strongly temperature-dependent resonant feature is seen below 30 K, but the spectrum remains almost temperature independent at higher temperatures. To clearly show the temperature dependence of the absorption peak, we plot the difference between $\alpha(T)$ and $\alpha(T=40\ \mathrm{K})$ in Fig. 3(b). The absorption peak, located around 7.5 cm^{-1} at 4 K, moves to lower frequency as the temperature approaches T_c and the line strength weakens. This behavior is quite similar to that of the sphere resonance[8] observed along the c axis in superconducting $La_{2-x}Sr_xCuO_{4+y}$ particles.

It is surprising that a sphere resonance can be seen in the oxygen-annealed La_2CuO_{4+y} particles, since the fraction of superconducting phase in this material is typically much less than 1%.[17] Our results demonstrate that even a small trace of superconducting La_2CuO_{4+y} phase can be identified by far-infrared transmission in the small particle geometry because of the giant dipole resonance. Both the strong resonance observed in our powder La_2CuO_{4+y} data, and the data of Collins *et al.*[6] are consistent with a sphere resonance of superconducting particles: the small particle geometry translates the bulk conductivity δ function of the superconducting condensate from zero to finite frequency.[8]

To summarize, we have measured the transmission of La_2CuO_{4+y} in both single-crystal and small particle forms at low temperature. Within our experimental uncertainty, the "in-plane" AFMR mode has not been identified in single crystal or in powder La_2CuO_{4+y} samples. However, small particles of superconducting La_2CuO_{4+y} do exhibit an electric-dipole-active sphere resonance in the 8-cm^{-1} frequency region.

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