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Correlation between superconductivity and optical excitations

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A series of reflectivity measurements on $La_{2-x}Sr_xCuO_4$ ceramics indicates a correlation between the concentration of positive carriers and both the spectral weight of optical excitations below 1 eV and the occurrence of superconductivity.

The variation of the optical spectrum with carrier concentration has provided insight into the nature of unusual superconductors as indicated by the study of $BaPb_{1-x}Bi_xO$, by Tajima *et al.*[1] Following the discovery of superconductivity at higher temperatures in the CuO ceramics,[2] we reported[3] reflectivity R spectra of $La_{2-x}Sr_xCuO_4$ for $x=0$ and 0.175, and of $Ba_2YCu_3O_{9-\delta}$ ($\delta\sim2.1$) and noted an unusual feature near $\frac{1}{2}$ eV in both materials. We cautioned, however, that the shape of the observed reflectivity could be distorted by the polycrystalline nature of the samples and their optical anisotropy.

We show here that, in a more extensive study of the $La_{2-x}Sr_xCuO_4$ ceramics, the oscillator strength below 1 eV grows with x and thus scales roughly with the concentration of holes up to $x\sim0.175$. Surprisingly, at larger x, the intensity below 1 eV decreases, but its behavior as a whole remains correlated with the occurrence of superconductivity: the oscillator strength peaks at the concentration x which appears to be optimum for superconductivity. We suggest that these correlations of the spectral weight and T_c with the hole density have implications for theoretical considerations of the superconducting mechanism in the oxide superconductors.

Previously we found that the integrated oscillator strength below 1 eV in $La_{1.825}Sr_{0.175}CuO_4$ corresponded to a carrier density $N_{\rm eff}m/m^*$ of 2.5×10^{21} cm^{-3}, where m and m^* are the bare mass and the effective mass determined by the band structure. This density approximately accounts for the concentration of positive carriers estimated assuming one hole per Sr atom (1.9×10^{21} cm^{-3}). Herr and co-workers[4,5] reached a similar conclusion using Kramers-Kronig (KK) analysis of R data from a $La_{2-x}Sr_xCuO_4$ sample with $x=0.15$.

Figure 1 shows our new R spectra as a function of $\log_{10}$ frequency ν for four $La_{2-x}Sr_xCuO_4$ samples with Sr concentrations x as labeled. The samples were prepared and polished as previously described,[6] but with slightly longer sintering times and other minor modifications to improve homogeneity. All samples in the set were sintered at the same time and were polished also as a set, and finally were reheated in oxygen overnight together. After the measurements of R, the samples were coated with Al films and were remeasured to allow the calculation of accurate absolute values of R. The variation of R with x is striking: For energies below about 8000 cm^{-1} (1 eV), R increases with Sr concentration until $x=0.175$ and then decreases in the sample with $x=0.225$. Above 8000 cm^{-1}, the trend is reversed indicating that oscillator strength is transferred from higher energies to the region below 1 eV and then back again with increasing x.

This trend is also illustrated in Fig. 2 which shows the effective optical conductivity σ obtained by KK analysis of the data in Fig. 1 as a function of photon energy E in eV. This σ is not the conductivity along any of the crystal axes because the analysis does not take into account the optical anisotropy of the crystallites (and does not constitute convincing evidence for a peak in σ near $\frac{1}{2}$ eV), but is an accurate description of the observed R. Also shown is the spectrum for a ceramic sample of La_2CuO_4. This $\sigma(\omega)$ is similar in shape to the previously recorded[7] results for a single crystal of La_2CuO_4 (with electric field in the a-b plane) but smaller by a factor ~2. The values of σ from the KK analysis were found to be insensitive to the form of the extrapolation of R to zero frequency, but sensitive to the high frequency extrapolation. The form used at large frequency, ω, for the data in Fig. 2 was $R=R_0+(R_u-R_0)\omega_u^4/\omega^4$, with $R_0=0.1$, $\omega_u=3.7$ eV (the upper limit of our experimental range), and R_u the corresponding value of R. Extrapolation with $R_0=0$ yielded a higher σ for $E>2$ eV by about a factor of 2 but

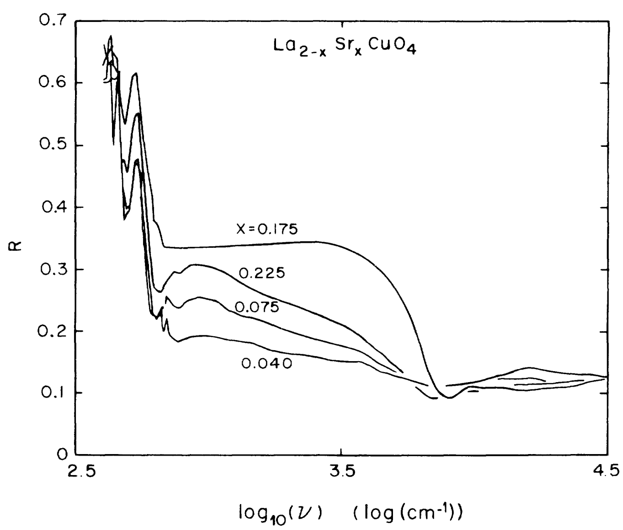

FIG. 1. Reflectivity as a function of $\log_{10}$ (wave number) in cm^{-1} for a series of polycrystalline pressed pellet samples of $La_{2-x}Sr_xCuO_4$, with the values of x as labeled.

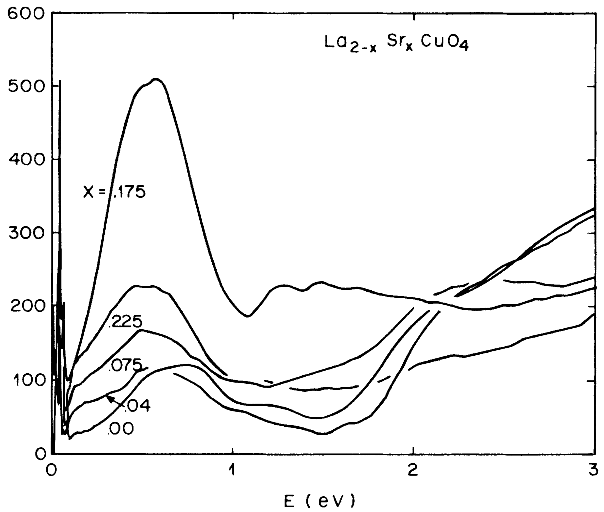

FIG. 2. Effective optical "conductivity" as a function of photon energy in eV for a series of polycrystalline pressed pellet samples of $La_{2-x}Sr_xCuO_4$ with different values of x as labeled. These data are obtained from reflectivity measurements, including those shown in Fig. 1, using a Kramers-Kronig transformation. This effective conductivity shown is not the value along any of the (anisotropic) crystallographic directions, but provides a reasonable estimate of the oscillator strength above and below 1 eV.

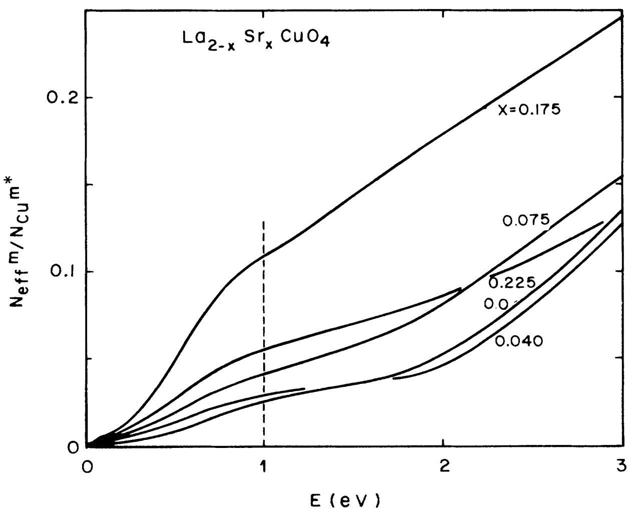

FIG. 3. Value of the oscillator strength below 1 eV obtained from an integration of the data in Fig. 2 up to that energy for our series of samples at the values of x as labeled.

had little effect at lower energy.

In addition to the spectral weight below 1 eV (in a peak at 0.60 eV for $x=0$), a second region of large σ is shown at $E>2$ eV. To evaluate the oscillator strengths[4] of these features we define the quantity $f(E)$ as

$$f(E)\equiv N_{\text{eff}}m/(N_{\text{Cu}}m^*)=2m/(\pi e^2 N_{\text{Cu}})\int_0^E \sigma d\omega \ .$$

The results for $f(E)$ for the five samples of Fig. 2 are shown in Fig. 3. The significance of this oscillator strength is that, if $m=m^*$, $f(E)$ is the fraction of electrons which contribute to σ below energy E, normalized to one electron per Cu atom ($N_{\text{Cu}}=1.1\times10^{22}$ cm^{-3}). For the $x=0$ sample, the numerical integration of $\sigma(E)$ gives $f(1\ \text{eV})=0.05$ and $f(3\ \text{eV})=0.25$.

We define the integrated oscillator strength below 1 eV by $f(1\ \text{eV})$ and plot this quantity versus x as the solid circles in Fig. 4. As indicated by the dashed line, which is a guide to the eye, this oscillator strength peaks near $x=0.175$, at about the Sr concentration previously identified[8] as that with the largest superconducting volume fraction. The measurement of Herr *et al.*[4] gives a value of $f(1\ \text{eV})$ in agreement with the dashed curve at $x=0.15$. Also shown in Fig. 4 are values of T_c, shown as open circles corresponding to the right axis, for the same set of samples and for a sample with a sharp transition at $x=0.15$ measured previously. Magnetization measurements show no signs of superconductivity in any of our new samples except that with $x=0.175$.

These T_c results are in agreement with those on some $La_{2-x}Sr_xCuO_4$ samples made previously[6,8] which showed, for samples with an average x near 0.15, a sharp transition with a T_c of 36 K. The new results disagree at higher and lower x, where a broad transition in the dc electrical conductivity and a small Meissner effect were seen. We believe that the difference arises because the sample set measured here is more nearly homogeneous in Sr concentration, and the older set contained some volume fraction with x near the optimum value. The main point of Fig. 4 is unaffected and clear; the oscillator strength below about 1 eV varies with the hole concentration and correlates with the superconductivity.

In summary, we have measured the reflectivity and superconducting transition temperatures of a series of

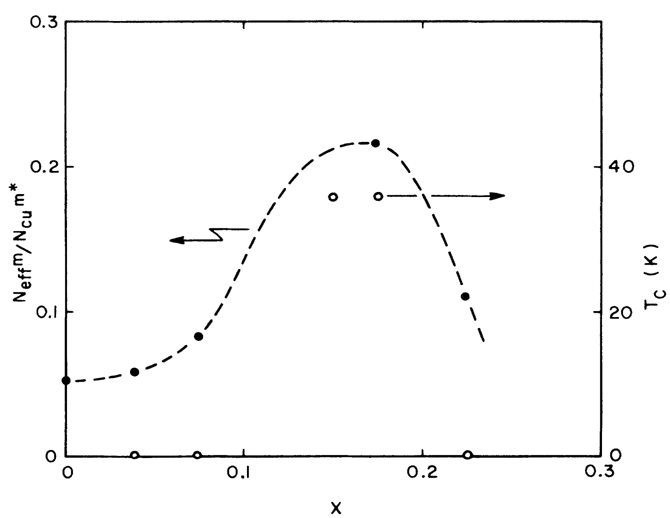

FIG. 4. Oscillator strength below 1 eV (left axis, open circles) as a function of the Sr concentration x. The curve is a guide to the eye. Also shown (right axis and solid points) are values of T_c for the same samples.

ceramic samples of $La_{2-x}Sr_xCuO_4$ for five values of x and have discussed a sixth value. Previously for $x=0$, in a crystalline sample, we found[7] an anisotropic (quasi-2D) semiconductor with an energy gap of 2 eV. In all samples we observe frequency dependent conductivity below 1 eV within this gap. This contribution grows initially with the concentration of holes until the optimum value for superconductivity is reached near $x=0.175$. At this point the oscillator strength below 1 eV accounts for essentially all the carriers introduced by the Sr doping. The strong correlation of the hole density with both the oscillator strength below 1 eV and T_c may provide a clue to the pairing mechanism in these compounds.

Note added. Since completing this work we have learned of measurements on $La_{2-x}Sr_xCuO_4$ single crystals[9] and have made measurements on $Ba_2YCu_3O_{9-\delta}$ single crystals[10] neither of which show significant deviation from Drude behavior in the a-b plane of energies below about 1 eV. We have also found theoretically[11] that a peak similar to that found here can be produced by an average of randomly aligned crystallites with substantial anisotropy.

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