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Optical properties of $La_2Cu_{1-x}Li_xO_4$ in the midinfrared

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The reflectivity and optical conductivity of single crystal $La_2Cu_{1-x}Li_xO_4$ are presented over a temperature range 15–365 K and comparisons are made to its superconducting counterpart $La_{2-x}Sr_xCuO_4$. Much like all superconducting cuprates $La_2Cu_{1-x}Li_xO_4$ transfers spectral weight from the charge-transfer band to the midinfrared (MIR) with increasing doping concentrations. However, unlike $La_{2-x}Sr_xCuO_4$, $La_2Cu_{1-x}Li_xO_4$ is nonmetallic up to Li concentrations as high as $x=0.50$. Furthermore, the charge-transfer (CT) band of $La_2Cu_{1-x}Li_xO_4$ is robust compared to the CT band of the prototypical superconducting cuprates while the MIR band grows at a comparable rate. This and the absence of a Drude tail in $La_2Cu_{1-x}Li_xO_4$ suggest that the spectral weight of the MIR band takes in part from excitations above the charge-transfer gap. Despite intensive theoretical and experimental effort to understand the origin of the MIR band there is no universal agreement to date on its mechanism. A few models are mentioned in the summary and will be addressed more thoroughly elsewhere.

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I. INTRODUCTION

One of the optical features common to all of the high-T_C cuprates is the growth of an optical band in the midinfrared concurrent with a loss of spectral weight in the charge-transfer band.[1,2] This behavior is also observed in structurally identical perovskites such as $La_{2-x}Sr_xNiO_4$.[3] The structural and magnetic properties of this class of cuprates are well documented. Undoped, these materials have tetragonal symmetry[4] with a slight orthorhombic distortion and possess three-dimensional (3D) spin-$\frac{1}{2}$ antiferromagnetic (AF) order[5–7] on the partially filled Cu $3d_{x^2-y^2}$ orbitals in the CuO_2 plane. Atomic substitution in the layers buffering the CuO_2 planes introduces charge into the CuO_2 lattice that quickly destroys the 3D spin order and suppresses the orthorhombic distortion. Band-structure and cluster calculations suggest that the doped charge has predominately O $2p_\sigma$ character.[8,9] Charge substitution has a dramatic and immediate effect on the transport properties. The cuprates undergo an insulator-to-metal transition in the lightly doped regime ($x\sim 0.02-0.03$) while in the moderately doped regime ($x\sim 0.08-0.23$) a superconducting phase manifests with phase-coherent transport occurring predominately in and parallel to the CuO_2 planes. In the heavily doped regime ($x\geqslant 0.25$) superconductivity is lost and the systems become metallic. Heretofore, the bulk of research, both optical and otherwise, has focused on this class of cuprates with out-of-plane charge doping and on some of their isostructural derivatives such as $La_{2-x}Sr_xNiO_4$. $La_2Cu_{1-x}Li_xO_4$, however, differs from the superconducting cuprates in two important respects: (i) hole carriers are doped by in-plane substitution of monovalant Li for divalent Cu and (ii) it has no superconducting phase.[10] Li^{+1} incorporates into the lattice with a closed-shell ($S=0$) configuration and substitutes for an in-plane Cu^{+2} site thereby introducing a hole into the CuO_2 plane. Hence, Li^{+1} introduces both a charge *and* a magnetic impurity into the 2D spin-$\frac{1}{2}$ AF CuO_2 planes. Resistivity measurements performed on $La_2Cu_{1-x}Li_xO_4$ (Refs. 10 and 13) show that it is nonmetallic up to Li concentrations as high as $x=0.50$, suggesting that the holes are tightly bound to their Li^{+1} host. This precludes a metallic, much less a superconducting, phase. Yet Li doping, much like Sr doping, destroys 3D AF order at low doping levels ($x\sim 0.02-0.03$). This differs markedly from $La_2Cu_{1-x}Zn_xO_4$ where Zn^{+2} introduces a spin-0 impurity but no excess charge into the CuO_2 plane. In this case 3D AF order is not destroyed until well into the heavily doped regime ($x\sim 0.3$).[14] Despite these key differences in chemical composition and conductivity, $La_2Cu_{1-x}Li_xO_4$ shares some of the optical properties of its superconducting cousins.

We present reflection and optical conductivity data for single crystals of $La_2Cu_{1-x}Li_xO_4$ in the light-to-moderately doped regime ($x\leqslant 0.10$) for light incident parallel to the CuO_2 plane ($\mathbf{E}\perp c$ axis). It is found that $La_2Cu_{1-x}Li_xO_4$ undergoes a similar transfer of spectral weight from the charge-transfer band to the midinfrared. For comparison purposes we will also present existing optical data for $La_{2-x}Sr_xCuO_4$,[1] since it is chemically similar and structurally identical to $La_2Cu_{1-x}Li_xO_4$ and has a superconducting phase. However, unlike the optical behavior observed in the superconducting cuprates, the charge-transfer band in $La_2Cu_{1-x}Li_xO_4$ remains comparatively intact up to $x=0.10$ with only a modest loss of spectral weight. This is concurrent with the growth of a midinfrared band at a rate nearly identical to that observed in $La_{2-x}Sr_xCuO_4$. As anticipated, no Drude tail is observed in insulating $La_2Cu_{1-x}Li_xO_4$. The far-infrared properties and phonon structure of $La_2Cu_{1-x}Li_xO_4$ will be presented elsewhere.[11]

II. EXPERIMENTAL RESULTS

The reflectivity of $La_2Cu_{1-x}Li_xO_4$ was performed with a Bruker 113v fast scan Fourier interferometer for measure-

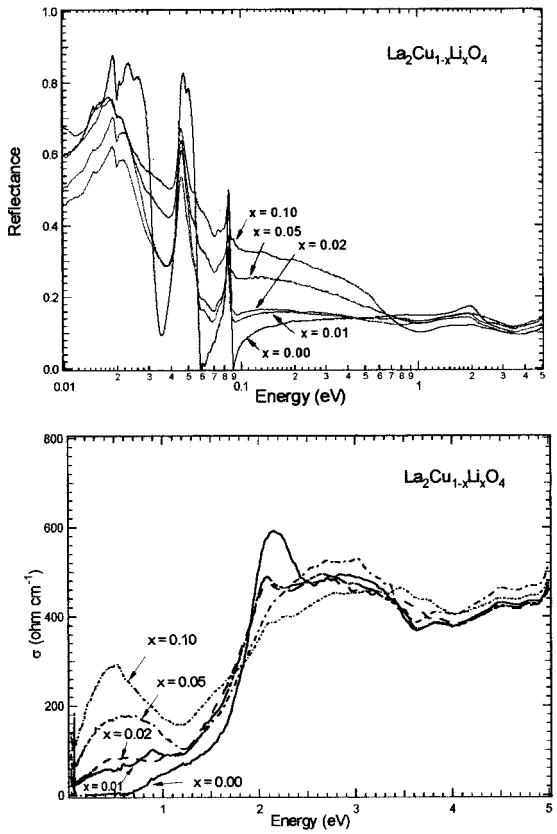

FIG. 1. (top) Reflectivity of $La_2Cu_{1-x}Li_xO_4$ at $T=300$ K and (bottom) corresponding optical conductivity for $x=0.00$, 0.01, 0.02, 0.05, and 0.10.

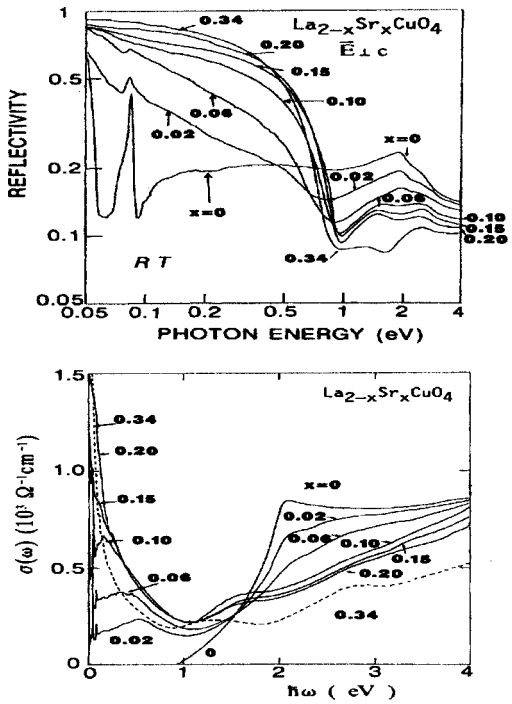

FIG. 2. (top) Reflectivity of $La_{2-x}Sr_xCuO_4$ at $T=300$ K and (bottom) corresponding optical conductivity (Ref. 1) for $x=0.00$, 0.02, 0.06, 0.10, 0.15, 0.20, and 0.34.

ments in the far- to midinfrared ($\leqslant 3000$ cm^{-1} or 0.372 eV) and a Perkin-Elmer monochrometer for energies above 0.125 and up to ≈ 5 eV. Both spectrometers were equipped with a He-flow cryostat for measurements down to 15 K. The reflectivity of the two spectrometers was then spliced below 0.372 eV (3000 cm^{-1}). To extract the optical conductivity and sum rule, a Kramers-Kronig transform was performed on the reflectivity of the full optical spectrum. This was accomplished by splicing existing reflection data for La_2CuO_4 above 4.5 and up to 45 eV and modeling the reflectivity to a free-electron response above 125 eV. All measurements were performed on single crystals of $La_2Cu_{1-x}Li_xO_4$ with light incident parallel to the CuO_2 plane (perpendicular to the c axis). X-ray powder-diffraction measurements on polycrystalline $La_2Cu_{1-x}Li_xO_4$ show that the Li^{+1} sites are homogeneously distributed in the CuO_2 lattice up to $x=0.10$.[13]

The reflectivity and optical conductivities of $La_2Cu_{1-x}Li_xO_4$ at $T=300$ K are shown for $x=0.00$, 0.01, 0.02, 0.05, and 0.10 in Fig. 1 (top) and Fig. 1 (bottom), respectively. The corresponding data for $La_{2-x}Sr_xCuO_4$ are given in Fig. 2 for Sr concentrations up to $x=0.34$.[1] The substitution of Li^{+1} for Cu^{+2} erodes the charge-transfer edge and spurs the growth of a midinfrared band between 0.125 and 0.87 eV (1000 and 7000 cm^{-1}). This behavior is more discernable in the optical conductivity where there is a redistribution of spectral weight in the charge-transfer band centered at 2.2 eV—representing the excitation of an electron from an O $2p_\sigma$ orbital to a neighboring Cu $3d_{x^2-y^2}$ orbital—accompanied by the growth of a band near 0.5 eV. The erosion and redistribution of the spectral weight in the charge-transfer band with increasing Li concentrations are illustrated in finer detail in Fig. 3. As seen in Fig. 1 (bottom), the midinfrared band is centered just below 0.5 eV and extends well into the near infrared up to the charge-transfer edge. A comparison of Figs. 1 (bottom) and 2 (bottom) underscores the similarities and key differences in the optical conductivities of $La_{2-x}Sr_xCuO_4$ and $La_2Cu_{1-x}Li_xO_4$. The charge-transfer band in $La_2Cu_{1-x}Li_xO_4$ remains comparatively robust up to $x=0.10$. This differs markedly from $La_{2-x}Sr_xCuO_4$ where the charge-transfer band erodes rapidly

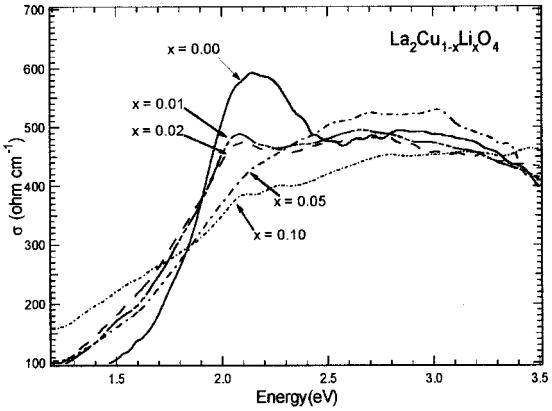

FIG. 3. In-plane optical conductivity of $La_2Cu_{1-x}Li_xO_4$ in the charge-transfer region for $x=0.00$, 0.01, 0.02, 0.05, and 0.10. $T=300$ K.

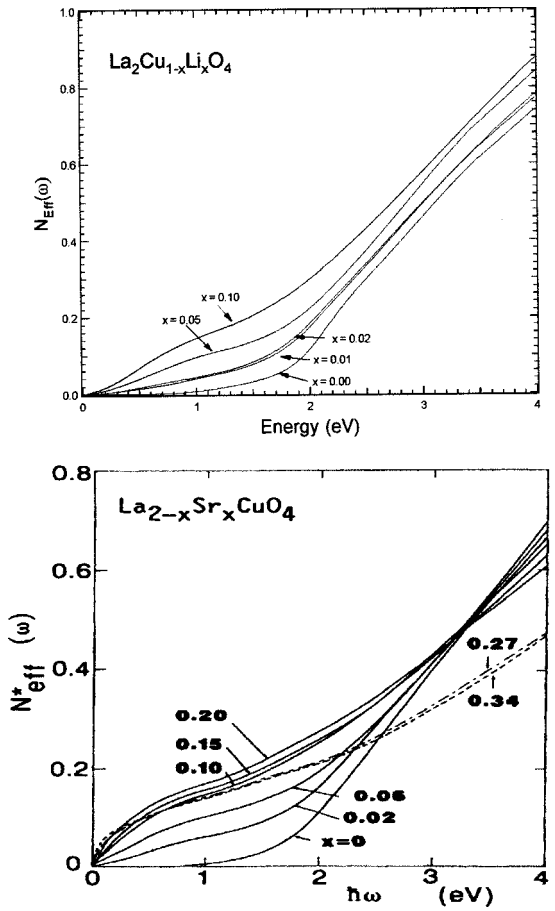

FIG. 4. In-plane sum rule for $La_2Cu_{1-x}Li_xO_4$ (top) and $La_{2-x}Sr_xCuO_4$. $T=300$ K.

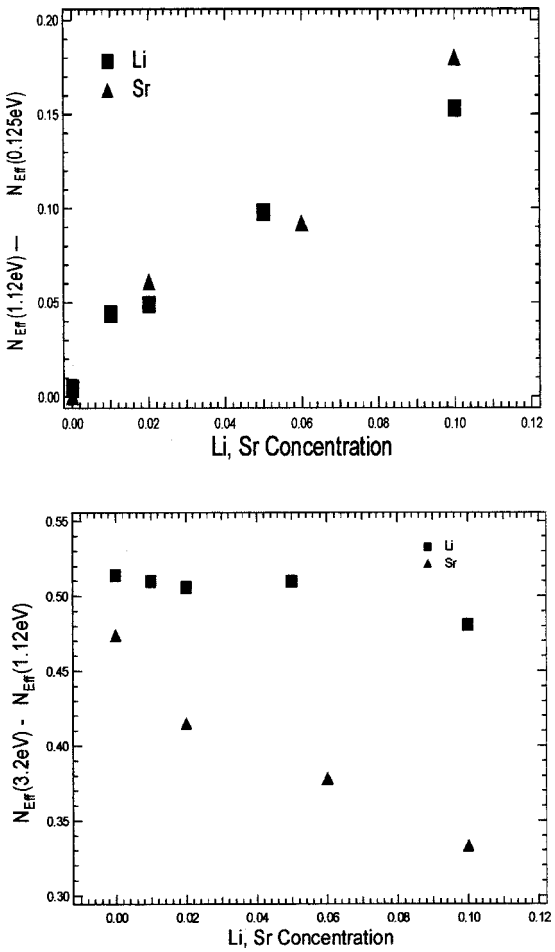

FIG. 5. (top) Sum rule of $La_2Cu_{1-x}Li_xO_4$ and $La_{2-x}Sr_xCuO_4$ evaluated at 1.1 eV (phonon and Drude tail contributions subtracted). (bottom) Integrated spectral weight in the charge-transfer region (3.2-1.12 eV). $T=300$ K.

with increasing x to a broad continuum for $x \geqslant 0.10$. Also lacking in $La_2Cu_{1-x}Li_xO_4$, as expected, is the presence of a Drude tail. Despite this marked difference in the optical spectra above 1 eV, the midinfrared bands of $La_2Cu_{1-x}Li_xO_4$ and $La_{2-x}Sr_xCuO_4$ appear to grow at similar rates in the light-to-moderately doped regime. Figure 4 plots the sum rules of $La_{2-x}Sr_xCuO_4$ and $La_2Cu_{1-x}Li_xO_4$ for Li and Sr concentrations up to $x=0.10$. Below 2 eV the sum rules grow at similar rates. However, above 2 eV the sum rule for $La_{2-x}Sr_xCuO_4$ merges at 3.2 eV for all reported Sr concentrations. By contrast, the sum rule for $La_2Cu_{1-x}Li_xO_4$ rises steadily with increasing x above 3 eV. This suggests that much of the spectral weight transferred to the midinfrared (MIR) in $La_2Cu_{1-x}Li_xO_4$ borrows from higher-lying excitations. Figure 5 (top) shows the sum rule evaluated below the charge-transfer edge (1.12 eV) as a function of Li and Sr concentrations and verifies that the MIR bands of $La_2Cu_{1-x}Li_xO_4$ and $La_{2-x}Sr_xCuO_4$ do indeed grow at nearly identical rates. Here, the spectral weight below 0.125 eV is subtracted to eliminate contributions from the phonons and Drude tail (in $La_{2-x}Sr_xCuO_4$).

The midinfrared band observed in $La_2Cu_{1-x}Li_xO_4$, much like the doping-induced MIR band observed in the prototypical high-T_C cuprates, exhibits little temperature dependence. In Fig. 6 the MIR optical conductivity of $La_2Cu_{90}Li_{10}O_4$ is shown for $T=365$, 300, 200, 90, and 15 K. The weak temperature dependence on the MIR band is readily apparent. This behavior is typical of all the Li^+ concentrations investigated here.

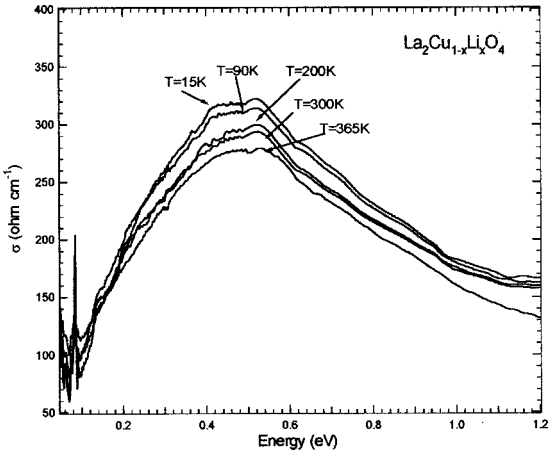

FIG. 6. Optical conductivity of $La_2Cu_{0.9}Li_{0.10}O_4$ in the MIR region for $T=365$, 300, 200, 90, and 15 K.

III. DISCUSSION AND SUMMARY

We can draw two immediate conclusions from the data concerning the MIR band in $La_2Cu_{1-x}Li_xO_4$. The first concerns the mobility of the charge carriers. Since mobile Sr holes and bound Li holes produce nearly identical MIR bands in the moderately doped regime ($x \geqslant 0.02$), it follows that the MIR band is independent of the carrier mobility. The second is that the MIR band is insensitive to the presence of charge and magnetic impurities in the CuO_2 plane. That is, the MIR band does not depend on the location of the doping site or on its effect on the spin lattice. Furthermore, the MIR band is due solely to the presence of charge carriers and is insensitive to the magnetic (spin-zero) nature of the Li^{+1} sites.[15] It is also noteworthy that the MIR band borrows very little from the charge-transfer band as the Li concentration is increased. This is apparent in Fig. 5 (bottom) where the integrated spectral weight of the charge-transfer region (3.2-1.12 eV) is plotted as a function of Li and Sr concentration. The spectral weight of the charge-transfer band changes little with Li doping up to $x=0.05$ and does not demonstrate appreciable loss until $x=0.10$, lending support to the theory that the MIR band acquires the bulk of its spectral weight from excitations above 5 eV. By contrast, the spectral weight of the charge-transfer band deteriorates rapidly with increasing Sr concentrations below $x=0.10$, indicating that a large portion of its weight is transferred to the MIR band.

The origin of the MIR band in the doped cuprates, now including $La_2Cu_{1-x}Li_xO_4$, is not understood at this time. Theorists and experimentalists alike have addressed this phenomenon, but to date there is no universally accepted mechanism for the MIR band. The fact that the midinfrared band is centered near 0.50 eV or roughly $3J$ suggests that the excitations may be magnetic. Others contend that the MIR band is the result of charge carriers coupling to the crystal lattice (small polaron hopping).[3] However, the temperature dependence of the small polaron[3] model is not consistent with the temperature dependence of the MIR band observed in $La_2Cu_{1-x}Li_xO_4$. Specifically, the model used by Eklund *et al.*[3] predicts that the MIR band will redshift and broaden with decreasing temperatures, but we see no evidence of this in Fig. 6. Others still propose that novel charge structures in the CuO_2 plane such as domain walls (stripes) drive the bound excitations in the midinfrared.[12] These are relevant, worthwhile explanations that will be addressed in future papers.

[1] S. Uchida, T. Ido, H. Takagi, T. Arima, Y. Tokura, and S. Tajima, Phys. Rev. B **43**, 7942 (1991).

[2] G. A. Thomas, in *Proceedings of the Thirty-Ninth Scottish Universities Summer School in Physics of High-Temperature Superconductivity*, edited by D. P. Tunstall and W. Barford (Hilger, Bristol, 1991).

[3] P. C. Eklund, A. M. Rao, G. W. Lehman, G. L. Doll, M. S. Dresselhaus, P. J. Picone, D. R. Gabbe, H. P. Jenssen, and G. Dresselhaus, J. Opt. Soc. Am. B **6**, 389 (1989).

[4] E. I. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys., Part 2 **36**, L123 (1987).

[5] S. Sugai, S. Shamoto, and M. Sato, Phys. Rev. B **38**, 6436 (1988).

[6] Y. Endo, K. Yamada, R. J. Birgineau, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. R. Thurston, J. M. Tranquada, B. Shirane, Y. Hidaka, M. Oda, Y. Enomoto, M. Suzuki, and T. Murakami, Phys. Rev. B **37**, 7443 (1988).

[7] R. J. Birgineau, D. R. Gabbe, H. P. Jennsen, M. A. Kastner, P. J. Picone, T. R. Thurston, G. Shirane, Y. Endo, M. Sato, K. Yamada, Y. Hidaka, M. Oda, Y. Enomoto, M. Suzuki, and T. Murakami, Phys. Rev. B **38**, 6614 (1988).

[8] F. Mila, Phys. Rev. B **38**, 11 358 (1988).

[9] P. W. Anderson, Science **235**, 1196 (1987).

[10] J. L. Sarrao *et al.*, Phys. Rev. B **44**, 9370 (1991).

[11] S. W. Moore *et al.* (unpublished).

[12] P. C. Hammel, B. J. Suh, and J. L. Sarrao, Phys. Rev. B **53**, 806 (1998).

[13] J. L. Sarrao, D. P. Young, Z. Fisk, E. G. Moshopoulou, J. D. Thompson, B. C. Chakoumakos, and S. E. Nagler, Phys. Rev. B **54**, 12 014 (1996).

[14] G. Xia *et al.*, Phys. Rev. B **42**, 8752 (1990).

[15] Optical studies performed by our group on $Sr_2Cu_{1-x}Co_xO_2Cl_2$ where divalent Co replaces Cu^{+2} and introduces a spin-$\frac{3}{2}$ impurity into the spin-$\frac{1}{2}$ AF CuO_2 planes indicate no MIR band.