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High-energy spin and charge excitations in La_2CuO_4

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Inelastic light scattering studies of La_2CuO_4, both pure and doped with lead, over the energy range 0–1 eV have revealed the presence of high-frequency A_{1g} scattering components, in the spectral region 3500–6000 cm^{-1}, while also providing the complete line shape for the previously reported spin-pair mode of B_{1g} symmetry. Two main bands, broad and overlapping, are observed in this region with maxima near 3500 and 5200 cm^{-1}. The various spectral features show different resonance behavior. We suggest that a model based upon coupled spin and charge excitations will be required to describe these spectra.

Light-scattering studies of the high-T_c oxides have thus far concentrated on three areas: the phonons,[1–4] the gap excitations,[5–8] and the magnetic fluctuations.[9–12] The most recent work[12] revealed a new set of excitations of exceedingly high energy (>0.5 eV) with a scattering cross section which exhibits a substantial and anomalous decrease upon cooling below T_c. In the present work, we report new Raman studies capable of probing excitation energies as high as 1 eV (8000 cm^{-1}) in the insulating parent of the superconducting copper oxides, La_2CuO_4. These spectra reveal the complete line shape for the previously observed spin-pair excitation[9] of B_{1g} symmetry. They also provide the first observation of two new excitations of A_{1g} symmetry. All three components exhibit strong resonant enhancement to their scattering cross sections as the incident laser wavelength is tuned from the red to the violet. The detailed shapes of the resonance profiles differ for the various spectra components. The line shapes and symmetries of these new features, as well as their comparison with the B_{1g} spin fluctuation mode, suggest the involvement of coupled charge and spin excitations.

The samples for this study were single crystals of nominally pure, stoichiometric La_2CuO_4, although from other work[13] we believe that they deviate somewhat from exact stoichiometry. Results from two samples are presented below. One is a crystal grown in PbO-CuO flux, thus containing some Pb as a substitutional impurity, with basal plane dimensions 8×10 mm^2. Scattering spectra were obtained from the as-grown (001) crystal face. The other crystal, grown (at higher temperature) from pure CuO flux and thus containing no major impurities, was cleaved to expose an (001) surface free of flux, with dimensions 1.5×3 mm^2. This crystal has a measured antiferromagnetic transition temperature of 265 K. Neither crystal has been subjected to post-growth annealing procedures.

Although Cu_2O has been observed[14] as a contaminant in insulating ceramic samples of $Ba_2RCu_3O_6$ (R=Sm, Ho), none of the Raman lines associated with Cu_2O were seen in the La_2CuO_4 spectra at room temperature or even at 10 K, where the Cu_2O lines are enhanced. While for the lead-doped sample exposure to air may cause the formation of a thin contaminant layer containing Cu_2O, for the higher-purity sample the crystal was cleaved just prior to obtaining the spectra, precluding the possibility of any surface contamination.

The Raman spectra were excited by an argon ion laser, operated in one of the available blue-green lines, with a power of 20 mW, focused by a cylindrical lens to a line about 0.1×1.5 mm^2 in size. Spectra were obtained in a few cases using 6328-Å light from a HeNe laser. The samples were stored and studied in air. The angle of incidence for the laser was $\sim65°$. The scattered light was collected at right angles to the incident beam, with $f/4$ optics, and imaged with $2\times$ magnification onto the input slit of a Spex Triplemate spectrometer interfaced to a Photometrics CCD (charge-coupled device) camera containing a liquid-nitrogen–cooled Thomson CCD array. The CCD is an array of 576×384 pixels, oriented with the larger number of pixels horizontal. The pixels are binned to create an effectively smaller array for a faster read cycle. The vertical dimension provides information used in discriminating against large noise spikes and for detecting the presence of surface contaminants. Exposure times for the spectra shown here are 10 min. Further details of the implementation of the CCD detector will be discussed elsewhere.[15] All spectral intensities reported and shown here are corrected for the gain of the CCD amplifier (20 photoelectrons per CCD unit). The Triplemate was modified with 150 lines per mm gratings throughout, in order to cover the wide range necessary for this experiment. Even with this modification the spectra shown have been generated by concatenating four spectra overlapping in frequency.[15] The response of the spectrometer and detection apparatus was accurately calibrated with a standard lamp on every individual run, so that all spectra are displayed here as actual scattered intensities, measured in cps in a spectral bandwidth constant in wavelength, typically 15 Å. Thus, all intensities shown may be directly compared, both within a given spectrum and among spectra taken with different incident energies. We note, though, that, due to absence of the requisite data, we have

not corrected the spectra for the wavelength dependence of the penetration depth, which may be considerable and which could differ between the two samples.

Scattering geometries in the following are specified according to the basal-plane directions of the incident and scattered light polarization vectors, with x and y denoting the directions along the Cu—O bonds and x' and y' rotated by 45°. For definiteness, we define y and y' to lie in the scattering plane.

The excellent sensitivity of the Triplemate-CCD combination, extending well into the red, enables us to study the spectra out to energy shifts of 8000 cm^{-1} (1 eV). In what follows, we denote symmetries in the D_{4h}^{14} space group appropriate to the tetragonal La_2CuO_4 structure. The B_{1g} spectra over this range, shown in Fig. 1 for four incident laser wavelengths, are essentially unchanged from those previously reported[9] except that far higher signal-to-noise was achieved, and thus the complete spectral shape is clearly apparent. In all four cases, the B_{1g} intensity (defined as the yx spectrum subtracted from the $y'x'$ spectrum) falls quite accurately to zero on the high-energy side.

In the A_{1g} symmetry, however, as shown in Fig. 2, spectra over this wide energy range reveal an unexpected high-energy feature, with a broad peak in the vicinity of 3300–5000 cm^{-1}, as well as a weaker structure which changes somewhat with laser frequency. This scattering is present in previously reported spectra,[9,12] but over the limited spectral range covered in that earlier work these features appear as a nearly flat background. The present spectra, in contrast, reveal their spectral shape. Such features are not expected from the spin-pair mechanism, at least according to conventional theory.[16] While a flat A_{1g} intensity is predicted for three-dimensional antiferromagnets,[17] in the case of a two-dimensional square lattice with a pure Heisenberg Hamiltonian, this component is identically equal to zero. Evidence that these features in fact represent Raman scattering and not fluorescence derives from the comparison of the spectra obtained with different incident energies (varying by 2400 cm^{-1} or half the energy shift of the peak) and also from the observed selection rules, which show clear A_{1g} symmetry at high energy.

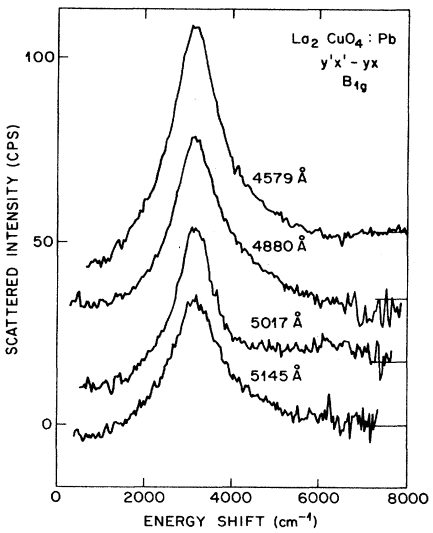

FIG. 1. Raman spectra of La_2CuO_4:Pb in B_{1g} symmetry for several incident laser wavelengths, as indicated. The yx component has been subtracted from the $y'x'$. The base lines are indicated at the right for the three upper spectra, which are shifted upward for clarity.

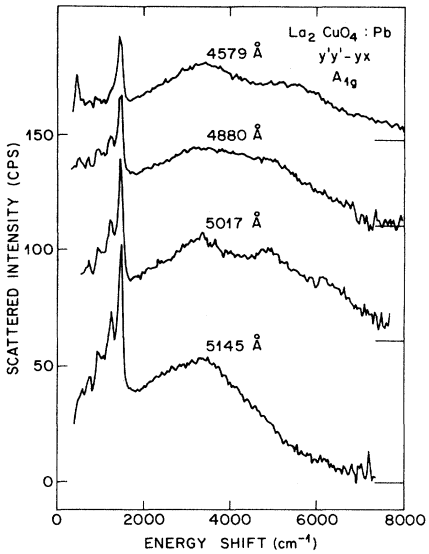

FIG. 2. Raman spectra of La_2CuO_4:Pb in A_{1g} symmetry for several incident laser wavelengths, as indicated. The yx component has been subtracted. The base lines are indicated as in Fig. 1.

The A_{1g} spectra may be described as a superposition of two broad bands, one situated at 3500 cm^{-1}, only slightly higher than the B_{1g} spin-fluctuation feature, and one situated at an energy around 5200 cm^{-1}. The relative intensity of the two features changes with incident laser wavelength, indicating some difference in the details of their resonant enhancement. The upper portion of the line shape clearly changes as laser frequency is varied, suggesting that it may be composed of numerous components with a range of resonance behavior correlated to the Raman shift. The resonance behavior of the various features is summarized in Table I. Intensities are given there as ratios to the intensity of the 1470-cm^{-1} mode, which was obtained independently for each laser frequency from the $y'y'$ spectrum by subtraction of the background extrapolated from higher-energy shift. The other measured intensities are total intensities at the specified spectral positions. Although a detailed study of the resonance behavior requires a broader range of laser frequencies than are available in the present work; such resonance curves may contain important information both on the coupling among the various excitations and on the higher interband transitions in the 1.8–2.5-eV range. We note that quantitative comparisons of spectral intensities over a wide range of incident energies require careful attention to such details as chromatic abberation in the lensing system as well as the spectral response of the apparatus. Over the range reported here, we estimate the uncertainty due to

TABLE I. Relative intensity of spectral features in La_2CuO_4. The intensities of both B_{1g} and A_{1g} features are given as a ratio to the intensity I_0 of the 1470 cm^{-1} two-phonon line.

Incident energy		PbO-CuO flux			CuO flux		
		B_{1g}	A_{1g}		B_{1g}	A_{1g}	
(Å)	(eV)	3100 cm^{-1}	3500 cm^{-1}	5200 cm^{-1}	3100 cm^{-1}	3500 cm^{-1}	5200 cm^{-1}
6328	1.98	$\lesssim$0.05	$\lesssim$0.3				
5145	2.42	0.5	0.8	0.25	0.4	0.6	0.4
5017	2.49	0.8	1.0	0.8			
4880	2.56	1.2	0.9	0.75	1.0	0.75	0.45
4579	2.73	2.00	1.2	0.90	3.1	0.9	0.80

such factors to be about 10%.

A less complete set of data has been obtained from the cleaved lead-free La_2CuO_4 sample. The use of a line focus, which reduces the power density at the sample surface, made it more difficult to obtain high-quality spectra from this smaller sample, since fluorescence from the sample edges can introduce spurious structure in the spectra. Nevertheless, as shown by the spectra in Fig. 3, the results are in fact quite similar to those in Fig. 2. The major difference lies in the apparent position of the highest frequency feature, which appears shifted slightly downward in this case, although we note that this apparent shift may be due to the different relative intensities of the two features. The resonance behavior of the spectral intensity is similar to that found for the lead-doped sample. There are small differences in the ratios (Table I) which may be experimentally significant, despite the quantitative difficulties noted above. Such subtle changes could indicate a dependence on the exact oxygen stoichiometry of the sample, or on defects, since our two sets of samples may well differ in this regard. We are currently exploring the spectral variations with different oxygen annealing treatments.

The excitations reported here lie in an energy range (0.1–1.0 eV) of clear potential importance for high-temperature superconductivity. The B_{1g} feature, from both energetic and symmetry considerations, is clearly magnetic in origin. Its interpretation[9] as a spin-pair excitation leads directly to a value for J, the Cu-Cu exchange, of $\sim$0.116 eV, in good agreement with subsequent neutron[18,19] and magnetic susceptibility[18] studies. Nevertheless, the line shape of this feature has been recognized as anomalous from the beginning, at least within the context of conventional spin-wave theory.[16] The spectra reported here, which provide a complete line shape for the B_{1g} feature for the first time, make it clear that the intensity above 4000 cm^{-1} is not due to a rising background, as might have previously been assumed, but is in fact real Raman scattering possibly associated with the B_{1g} feature itself. Possible explanations for the broad linewidth, and also for the extension of spectral weight beyond the $4J$=0.55 eV cutoff, may lie in the quantum fluctuations for the $S=\frac{1}{2}$ two-dimensional system, or may involve coupling between the spin excitations and some other degrees of freedom, such as charge transfer excitations.

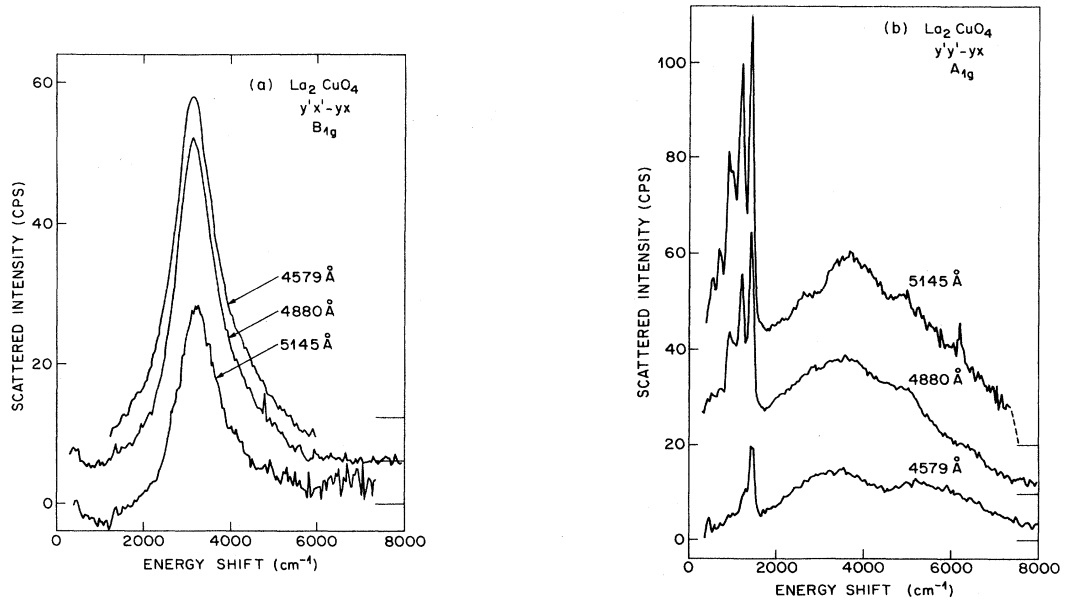

FIG. 3. Raman spectra similar to those in Fig. 1 [part (a)] and Fig. 2 [part (b)], obtained from an La_2CuO_4 crystal grown in pure CuO flux. Note that for (b) the order of the spectra has been reversed for clarity.

Similarly, the new A_{1g} excitations reported here may well involve contributions from both spin and charge degrees of freedom. Within the framework of standard spin-wave theory[16,17] the A_{1g} symmetry component in the spin-pair spectrum of a pure Heisenberg system vanishes for the two-dimensional square lattice. However, the influence of a strong resonant enhancement evident in Figs. 1 and 3(a) could conceivably relax the selection rules, as could defects. Such a breakdown of selection rules may be partially responsible for the A_{1g} spectral weight in the 3000–3500-cm^{-1} region, although in this case we would expect the resonance profile for the A_{1g} to be more strongly peaked than that for the B_{1g}, rather than the observed (reverse) behavior. We note that the selection rule against[10] zone boundary two-magnon scattering in the A_{1g} geometry is particularly sensitive to any perturbation which disturbs the centrosymmetry of the Cu site, due to the large phase space available near the zone boundary. Moreover, the feature near 5200 cm^{-1} lies near the expected value ($\lesssim 6J = 6500$ cm^{-1}) for a higher-order (four-spin) spin fluctuation. The lowest-energy four-spin excited state in this case would have A_{1g} symmetry in the Néel ordered lattice, consistent with the observed symmetry. However, under this simple interpretation the strong intensity observed for such a high-order process is difficult to understand.

The above discussion assumes purely magnetic origins for the observed features. On the other hand, a recent theoretical treatment[20] of the charge and spin excitations in the two-band Hubbard model[21] suggests that for some parameter values there exists a charge transfer excitation with an energy below 1 eV, which has A_{1g} symmetry. Thus, this idea provides an alternate explanation of the 5200-cm^{-1} mode. The difference in the A_{1g} line shape for our two samples lends some support to this interpretation, since the energy of this mode depends sensitively on carrier concentration. However, we note that the theory has not been carried out for the insulator, but only for the metal. Thus, this comparison is qualitative at best. An attractive feature of this approach, though, is its equivalent treatment of spin and charge transfer excitations. An extension of this model to include coupling of the two might provide a more accurate picture of the excitations in the cuprates than has heretofore been possible. It might also provide a better basis for explanation of our spectra than models based on spin or charge alone.

It is not yet possible to assess what role, if any, the excitations reported here might play in high-T_c superconductivity. However, we note that the recently reported continuum feature[12] observed (out to 4000 cm^{-1} or 0.5 eV) in $Ba_2YCu_3O_{6.7}$ exhibits an anomalous decrease in intensity upon cooling through $T_c \cong 60$. This feature may well be related to those examined here in insulating La_2CuO_4. Further experiments, including the detailed temperature dependence of these new modes, their dependence on doping, and the higher-frequency spectrum of the continuum, are in progress to explore this relationship.

In summary, we have reported here a new set of high-frequency excitations, of A_{1g} symmetry, observed by Raman scattering in insulating La_2CuO_4 single crystals. We tentatively ascribe these modes to some combination of spin and charge degrees of freedom in the CuO_2 planes. We suggest that they may be related to the Raman intensity anomaly recently reported[12] for high frequencies near T_c in $Ba_2YCu_3O_{6.7}$ and $Bi_2Sr_2CaCu_2O_8$. Although a definitive link cannot yet be made to the mechanism for superconductivity, these high-frequency modes clearly represent additional experimental information which must eventually be understood in the context of a full theory of the cuprate superconductors.

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