

The 1430 cm⁻¹ Raman line in single crystals of La₂CuO_{4-y}

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The Raman line at 1430 cm⁻¹ (M-line) in single crystal La₂CuO_{4-y} was studied as a function of doping, temperature, magnetic field, and excitation wavelength. Upon Li doping the line becomes broader, and it vanishes rapidly with Sr-doping. The line also broadens with increasing temperature and increasing applied magnetic field. Resonance enhancement was found for decreasing laser excitation energies but was not as pronounced as the enhancement of several alleged two-phonon lines. Many of these features are correlated with the 2D antiferromagnetic ordering measured in this system by neutron scattering. The possible identification of this line as a one-spin excitation is favored by the data though a two-phonon excitation is also considered.

I. INTRODUCTION

Light scattering provides information on different types of elementary excitations in solids such as lattice, magnetic, and electronic excitations. La₂CuO_{4-y} shows a very strong magnetic interaction,¹ unusual electronic properties, and a strong electron-lattice interaction. Therefore, any peaks in the Raman spectra of La₂CuO_{4-y} must be examined carefully in order to identify the origin of the excitation. In this paper, we focus only on the 1430 cm⁻¹ line (M-line) which is the strongest feature in the Raman spectrum of La₂CuO_{4-y} in the range of $\omega < 2000$ cm⁻¹ taken with the (xx) polarization configuration.²⁻⁴ (See Fig. 1.) We report here several properties of this line: the dependence of the line on Li and Sr doping; the dependence on temperature; a small effect of a magnetic field on the lineshape of the line; and we also compare the resonance enhancement, as the laser excitation energy is varied, to that of other lines. The possible identification of this line as either a one-spin magnetic excitation or a two-phonon excitation is discussed.

II. EXPERIMENTAL DETAILS

The measurements presented here were performed on single crystals which were grown from flux by the top seeded solution technique described elsewhere.⁵ All the crystals were characterized using x-ray diffraction and Laue diffraction patterns. Although the Laue patterns show clear Bragg spots, twinning and oxygen vacancies were

also likely present. The crystals were further characterized by magnetic susceptibility measurements. A small cusp associated with the 3D magnetic ordering was observed in the undoped crystal at 237 K. However, the magnetic susceptibility measurement on the Li-doped sample showed a strong suppression of this cusp, indicating that the 3D magnetic ordering is almost completely suppressed upon Li doping.⁶ The undoped and Li-doped single crystals show similar temperature-dependent resistivities and exhibit insulator-like behavior.^{4,7} The two single crystals, containing 1.5% and 3% Sr, were not superconducting; however, they are much more metallic than the undoped sample. The resistivity ρ of the 3% Sr-doped sample is almost temperature independent and at 10 K, the resistivity ρ is smaller by four orders of magnitude compared with typical resistivity values for the undoped crystals at the same temperature.

All the Raman spectra of the doped and undoped single crystals were taken in a backscattering configuration with the 4880 and the 5145 Å lines of an Ar⁺ ion laser. The high-quality undoped crystal was also studied with different laser excitation energies obtained from Ar⁺, Kr⁺, and dye lasers. The laser beam was focused with a lens of 10 cm focal length to a spot size smaller than 100 microns. The laser was kept at a power level below 35 mw to avoid local heating. The spectra were detected by a 0.85 m double monochromator, equipped with a single channel photon counting system.

III. RESULTS AND DISCUSSION

In Fig. 1 we present polarized Raman spectra of undoped, 4% Li-doped, and 3% Sr-doped La₂CuO_{4-y} samples,

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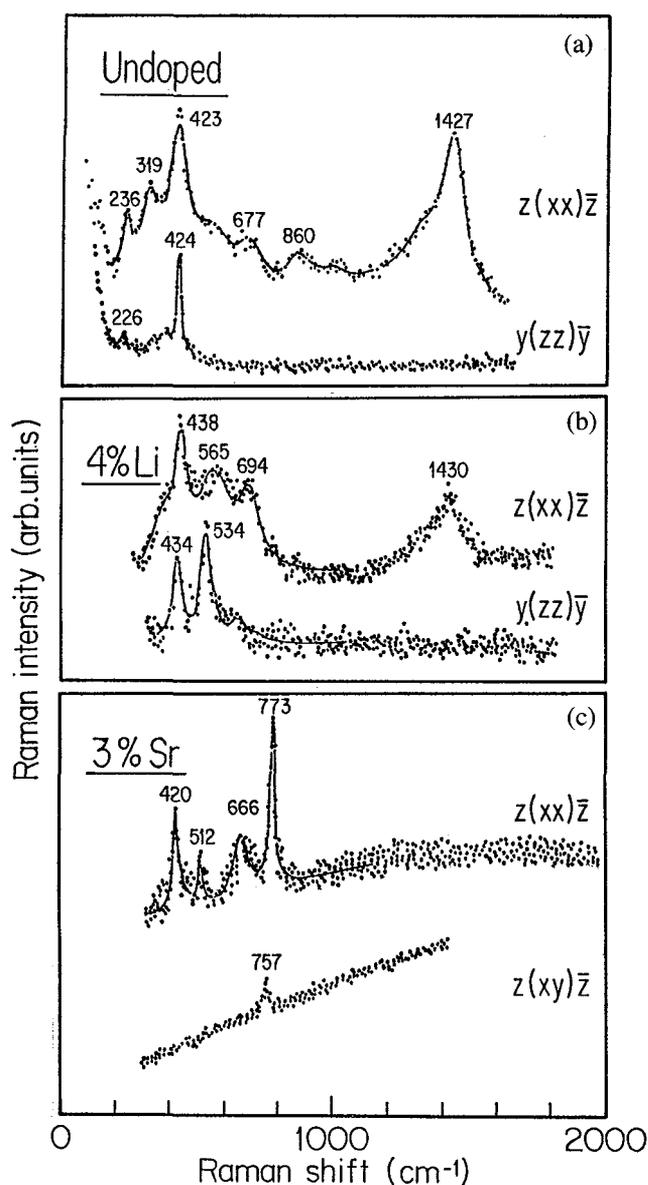


FIG. 1. Polarized Raman spectra of (a) undoped, (b) Li-doped, and (c) Sr-doped single crystals of $\text{La}_2\text{CuO}_{4-y}$. All the spectra were taken at room temperature with the 4880 Å line of an Ar^+ ion laser. Our main focus is the M-line at 1430 cm^{-1} .

where y denotes small deviations from oxygen stoichiometry and can be either positive or negative. The spectra presented in Fig. 1 were taken in the $z(xx)\bar{z}$ and $y(zz)\bar{y}$ configurations for the first two samples and in the $z(xx)\bar{z}$ and $z(xy)\bar{z}$ configurations for the Sr-doped crystal. The z direction is the tetragonal \hat{c} axis while x and y refer to the in-plane axes along the Cu–O bonds. The notation $z(xy)\bar{z}$, for example, describes the scattering configuration where the incident beam is along the z direction with the electric field vector \mathbf{E} along the x axis, and the scattered beam is along the \bar{z} direction with \mathbf{E} parallel to y . All the spectra in this figure were measured with a laser excitation wavelength of 4880 Å. The lines in the low-frequency region of the spec-

tra are associated with phonons and were discussed elsewhere.⁴ Here we focus our attention on the Raman line at 1430 cm^{-1} (the M-line). From these spectra and polarized measurements in the $(x'x')$ and $(x'y')$ configurations (where x', y' denote the axes rotated by 45° with respect to x, y) we conclude that the line must have A_1 symmetry.

The characteristics of the M-line depend strongly on doping. The line is broadened in the Li-doped samples and is not observed in either the 1.5% or the 3% Sr-doped samples. In Fig. 2 we see that the room temperature linewidth increases by a factor of three as the Li doping increases to about 6%. From Fig. 1 we also notice that the intensity of the M-line relative to the intensity of the first-order Raman-active phonon ($\sim 425 \text{ cm}^{-1}$) decreases upon Li doping. In a recent paper, it was shown that the M-line depends also on the oxygen content,⁸ with the line vanishing in a Li-doped sample ($\sim 3\%$) which was annealed in oxygen at 1000°C for 24 h.

We further measured the variation of the line position and width as a function of temperature. A large effect (see Fig. 3) was found in the sample containing about 6% Li.

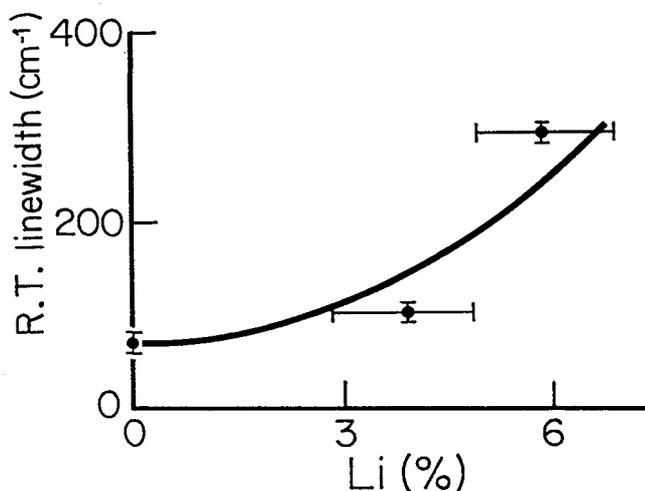


FIG. 2. The dependence of the room temperature linewidth (full-width at half-maximum intensity) of the Raman line at 1430 cm^{-1} upon Li doping.

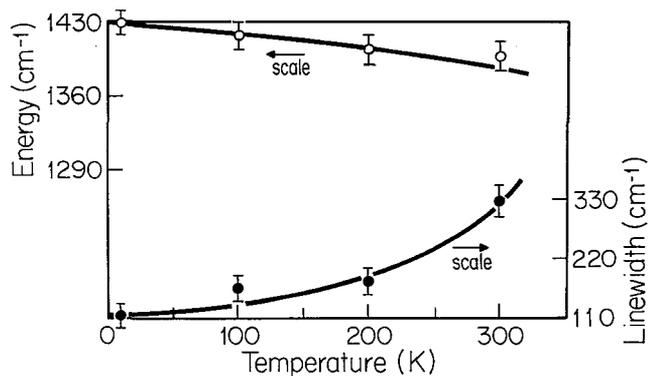


FIG. 3. The temperature variation of the energy (frequency) and the linewidth (full-width at half-maximum intensity) of the 1430 cm^{-1} line in the 6% Li-doped single crystal of $\text{La}_2\text{CuO}_{4-y}$.

Although the frequency of the line slightly decreases with increasing temperature, the linewidth dramatically increases, showing an increase by almost a factor of three when the temperature is varied from 10 K to 300 K. In contrast, the lineshape of the undoped sample exhibits only a small variation with temperature, namely a monotonic increase in the linewidth (from about 50 to 60 cm^{-1} full-width at half-maximum (FWHM) upon increasing the temperature from 4 K to room temperature.

Motivated by the observed magnetism in this material (e.g., Endoh *et al.*⁶ and references cited therein), we looked for magnetic effects on the lineshape of all the lines in the Raman spectra. Since we were limited to magnetic fields of 10 tesla, we might not expect a strong effect since the exchange interaction, J , is too high ($\sim 700\text{--}1000 \text{ cm}^{-1}$).^{2,9} We, however, observed a small change in the lineshape of the M-line in a magnetic field ($\mathbf{H} \perp \hat{c}$). No effect was found for the one-phonon line at $\sim 425 \text{ cm}^{-1}$, the two-phonon line at $\sim 1200 \text{ cm}^{-1}$, and for the configuration $\mathbf{H} \parallel \hat{c}$. In Fig. 4 we see that the intensity of the line decreases and the linewidth increases when the magnetic field increases from 6 tesla to 10 tesla; there is no detectable change in linewidth or intensity from $H = 0$ to $H = 6 \text{ T}$. The variation of the linewidth and the intensity of the M-line, calibrated with respect to the 1200 cm^{-1} line, for various magnetic fields is plotted in the inset of Fig. 4.

Remarkable differences are found between the Raman spectra, taken at different laser excitation energies ω_L , as shown by the two spectra in Fig. 5. The upper spectrum was taken with $\lambda_L = 5145 \text{ \AA}$ and the lower one with

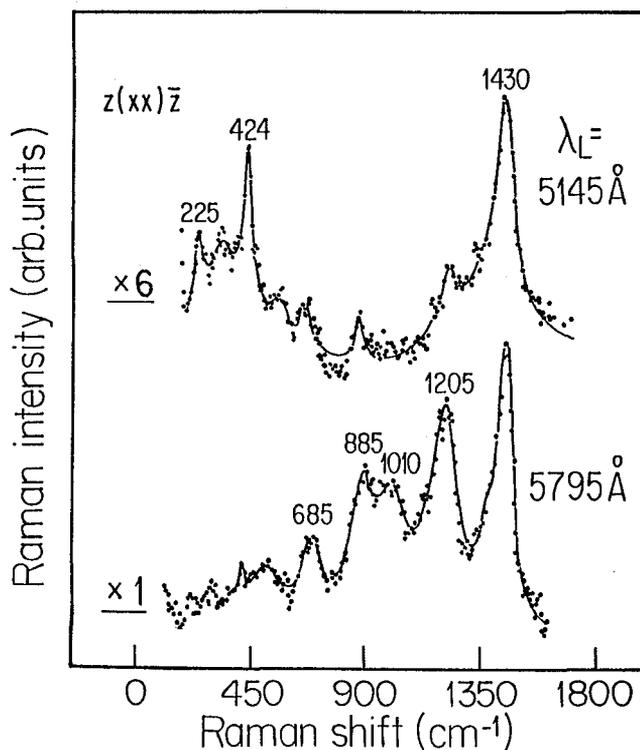


FIG. 5. Polarized room temperature Raman spectra of single crystal $\text{La}_2\text{CuO}_{4-y}$. The upper spectrum was taken with a 5145 \AA laser line and the lower with a 5795 \AA laser line. Note the increased scale factor of the upper spectrum.

$\lambda_L = 5795 \text{ \AA}$. All the lines that exhibit an intensity enhancement relative to the M-line are associated with a

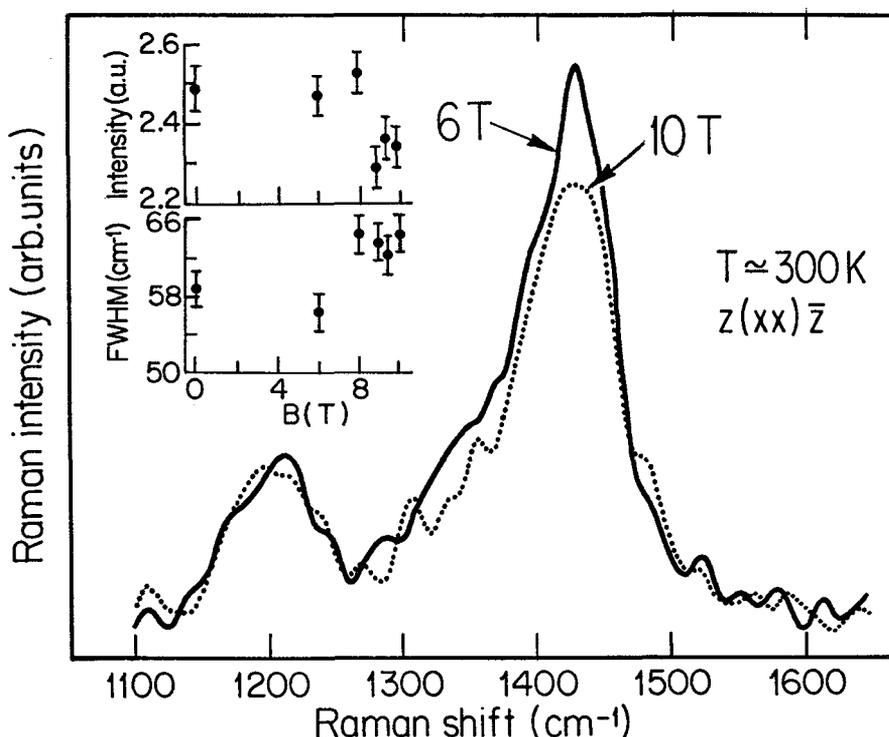


FIG. 4. The change in the lineshape of the 1430 cm^{-1} Raman line under an applied magnetic field ($\mathbf{H} \perp \hat{c}$). The spectra were taken at room temperature with the 4880 \AA Ar^+ ion laser line and with the $z(yy)\bar{z}$ scattering configuration. In the inset the variation of the intensity and linewidth is given as a function of magnetic field.

resonant effect due to an electronic gap at 2.1 eV.¹⁰ In the present study, we emphasize the difference in behavior between the M-line and the other high-frequency lines. Figure 6 shows the integrated intensities of the 883 and 1205 cm⁻¹ lines relative to that of the M-line.

The properties of the M-line can be summarized as follows:

- (1) A_1 symmetry;
- (2) Linewidth broadened upon Li doping;
- (3) Not observed for samples containing 1.5% and 3% Sr, and for sample heavily annealed in oxygen;
- (4) Broader linewidths for increasing temperature (especially pronounced for Li doping);
- (5) Small variation of the lineshape with application of a magnetic field;
- (6) Different dependence of the line intensity on laser excitation energy relative to other Raman lines.

On the basis of the above properties we suggest that the M-line has a magnetic origin. The identification of the line as a first-order phonon excitation seems unlikely because its energy is too high; its energy scale, however, is consistent with a possible multi-phonon excitation. We have two experimental arguments against the multi-phonon explanation: first, the M-line shows a magnetic field-dependent effect (though small). In principle, one can argue that the magnetic field effect on the lineshape of the M-line may originate from magnetostriction, namely a change in the lattice constant associated with a magnetic phase transi-

tion. However, it was recently reported that the magnetostriction effect in $\text{La}_2\text{CuO}_{4-y}$ is very small: $\Delta a/a$ is less than 10^{-7} .¹¹ Such changes in the lattice constants are too small, by at least three orders of magnitude, to be seen in the Raman spectra. The second argument against the multi-phonon explanation is related to the very different dependence of the M-line intensity on laser excitation energy compared with other Raman lines, as is shown in Fig. 6. However, since the electronic bands of this material are yet not known, there remains the possibility that different Raman lines can show different enhancements at other electronic gaps.

The suggestion of the magnetic origin of the M-line is based on the correlation between the properties of this line and the properties of the 2D magnetic correlation phenomena reported by the MIT/NTT/Brookhaven group,^{1,6,9} who found that the 2D magnetic correlation length strongly depends on doping. In the undoped material, they found the correlation length, ξ , to be ≈ 200 Å. Upon Li doping ξ decreases to about 50 Å, and in the Sr-doped crystal, they found ξ to be very small ($\xi \leq 20$ Å).

The properties of the M-line are consistent with the behavior of the 2D antiferromagnetic correlation for the following reasons: the line becomes broader upon Li doping, consistent with the shorter ξ , and completely disappears in the Sr-doped crystals which have yet shorter ξ . From symmetry considerations we can exclude the possibility that the line is a two-spin excitation, since such excitations are not expected on the basis of Parkinson's theory¹² to possess A_1 symmetry. The line may, however, be due to a magnetic defect-induced one-spin excitation. This is an excitation of a spin which is confined to a small area in real space by some defect in the magnetic ordering. For such a defect the excitation energy would be SJ times the number of interacting nearest neighbors, which is three since one of the nearest neighbors has a defect. We thus obtain for the energy E_M of the M-line $\sim 3SJ$, and by taking $S = \frac{1}{2}$ we get $J = 950$ cm⁻¹ for the nearest neighbor intraplanar antiferromagnetic interaction which is consistent with the various suggested values for J from the literature,^{2,9} $\sim 750 < J < 1100$ cm⁻¹.

In conclusion, various properties of the Raman line at 1430 cm⁻¹ have been examined in terms of two-phonon and magnetic origins. From the present results, we cannot completely eliminate the two-phonon mechanism; however, the current evidence favors the identification of the M-line as a defect-induced one-spin excitation.

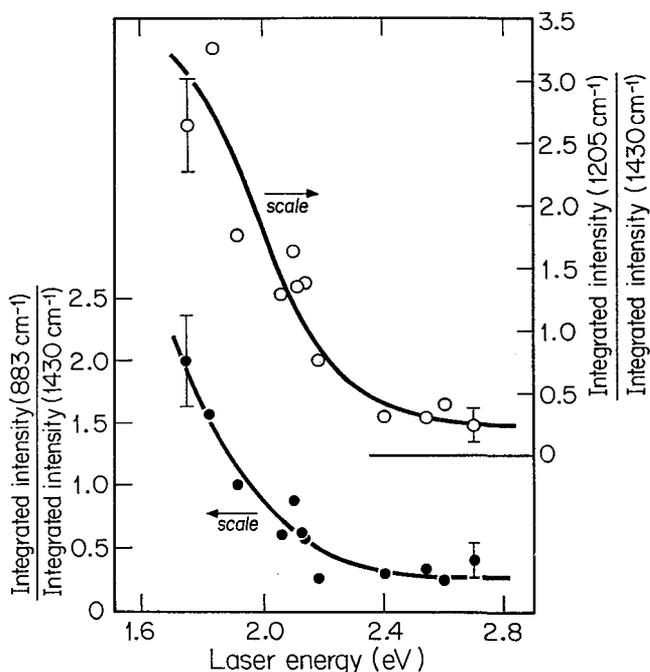


FIG. 6. Ratio of the integrated intensities of the (a) 883 cm⁻¹ and (b) 1205 cm⁻¹ Raman lines relative to the 1430 cm⁻¹ line as a function of laser excitation energy.

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