

Coupled magnon-phonon excitations in $\text{Sr}_2\text{CuCl}_2\text{O}_2$ at high pressure

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High-pressure optical experiments have been performed on midinfrared excitations unique to the layered cuprates, yet whose physical origin has been unresolved. Measurements of high-pressure midinfrared spectra of $\text{Sr}_2\text{CuCl}_2\text{O}_2$ unambiguously identify the $\sim 2800\text{-cm}^{-1}$ absorption as an unusual quasibound two-magnon + phonon excitation. We further show that the broad peak centered near $\sim 4000\text{ cm}^{-1}$ is a four-magnon + phonon excitation, with spectral weight $\sim 10^2$ times larger than predicted by theory. These excitations reveal unusual latent interactions coupling charge, spin, and lattice degrees of freedom in the CuO_2 planes.

Optical studies of the lamellar cuprates (e.g., $R_2\text{CuO}_4$ and $R\text{Ba}_2\text{CuO}_6$, where R is a rare-earth element) have provided important insights into the unusual properties of cuprate superconductors. However, fundamental questions persist regarding the optical excitations of lamellar cuprates even in their *insulating* phases. Recently, three different midinfrared (MIR) optical absorption bands were discovered in the insulating single-layer spin-1/2 cuprates ($R_2\text{CuO}_4$ and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$) by Perkins *et al.*¹ These MIR bands consist of one sharp peak near $\sim 2800\text{ cm}^{-1}$ ($\sim 0.35\text{ eV}$) with two broad higher-energy sidebands. The first sideband, centered near $\sim 4000\text{ cm}^{-1}$ (0.5 eV), dominates their spectral weight. These bands were shown to be intrinsic excitations of the CuO_2 layers, and have since been observed in bilayer cuprates.² To our knowledge, only cuprates are known to display this full set of excitations. Hence these unusual MIR excitations are unique to the layered cuprates, yet their physical origin remains controversial and unresolved. Further insight into their origin is important for understanding the unusual properties of the cuprates, as these fundamental MIR excitations reflect the latent interactions coupling charge, spin, and lattice degrees of freedom.

The MIR excitations were originally attributed to a $d_{3z^2-r^2}$ exciton with one- and two-magnon sidebands.¹ However, cluster calculations do not predict an exciton in this energy range.³ An alternate explanation for their origin was later provided by Lorenzana and Sawatzky (LS).⁴ They proposed that the sharp $\sim 0.4\text{-eV}$ peak corresponds to the absorption of one optic phonon plus a different quasiparticle excitation of the Heisenberg Hamiltonian consisting of a long-lived quasibound state of two magnons ("bimagnon"). Their calculated line shape closely fits the measured peak. While composite two-magnon + phonon excitation has previously been observed in NiO, it is not a virtual bound state and hence is much broader in energy.^{5,6} Apparently, an analogous two-spinon + phonon excitation was recently ob-

served in one-dimensional (1D) Sr_2CuO_3 .⁷ However, the sidebands are absent in both NiO and Sr_2CuO_3 .

LS further speculated that the two higher-energy sidebands were four-magnon + phonon (4MP) excitations (with magnons arranged either in a plaquette or a row), an excitation which appears to have not been observed in any noncuprate material. LS note that these sidebands are a consequence of quantum fluctuations in the spin-1/2 cuprates, although ordinarily their optical absorption strength would be so weak as to be barely observable. Indeed, numerical calculations⁸ predict 4MP sidebands to be very weak for the cuprates, with spectral weight just $\sim 3\%$ of the bimagnon (i.e., an absorption length of $\sim 1\text{ cm}$). However, the experimental data are in stark contrast with this expectation, with the sidebands being $\sim 10^2$ times larger than calculated. The first sideband has \sim three times the spectral weight of the putative bimagnon, and $\sim 75\text{--}80\%$ of the total spectral weight in the MIR.

Measurements on the isostructural spin-1 La_2NiO_4 have added to the controversy.⁹ A MIR absorption was observed whose line shape was consistent with the predicted bimagnon,¹⁰ strikingly, however, no sidebands were observed. Within the 4MP model, scaling arguments based on staggered magnetization suggest that La_2NiO_4 should have significant sidebands with $\sim 1/2$ the spectral weight found in La_2CuO_4 .¹¹

At present, there are two competing possibilities for the higher-energy sidebands. (i) They have an entirely different origin than the putative $\sim 2800\text{-cm}^{-1}$ bimagnon (e.g., exciton phonon or exciton magnon¹¹). This would readily explain the difference between the MIR absorptions in La_2CuO_4 vs La_2NiO_4 , as the Cu and Ni excitons need not be degenerate. However, the presence of such a low-energy exciton in the cuprates would be surprising. (ii) The sidebands are an observation of the putative 4MP excitation. This requires that some unanticipated mechanism *unique to the cuprates*

strongly enhances their spectral weight by \sim two orders of magnitude. Based upon the origin of 4MP excitation as well as their absence in La_2NiO_4 , this suggests quantum fluctuations are important.

Here we show that measurements of optical absorption and Raman spectra as a function of hydrostatic pressure can be used to unambiguously identify the MIR excitations in insulating $\text{Sr}_2\text{CuCl}_2\text{O}_2$. Two-magnon Raman scattering in the insulating antiferromagnetic CuO_2 layers has been proven to be an important probe of the spin excitations, allowing direct measurement of the superexchange constant J .^{12,13} Application of pressure is known to appreciably modify J (by $\sim 1\%$ /GPa).^{14,15} Our measurements show that the pressure dependencies of the two-magnon Raman and the MIR absorption features are identical within experimental error, consistent with the behavior expected for the two- and four-magnon (“multimagnon”) excitations of Lorenzana and Sawatzky.

$\text{Sr}_2\text{CuCl}_2\text{O}_2$ (SCOC) has the La_2CuO_4 (LCO) structure with La replaced by Sr and one apical O replaced by Cl. Unlike LCO, it retains a tetragonal structure to low temperatures and has important advantages for optical studies of the insulating cuprates. Micaceous single crystals¹⁶ were carefully selected and loaded into the diamond cells with various pressure media (i.e., NaCl and Ne). MIR absorption spectra were measured at room temperature in the range from 2200 to 9000 cm^{-1} (~ 0.27 – 1.1 eV) with a conventional light source using a Nicolet 750 Fourier transform infrared (FTIR) spectrometer equipped with CaF_2 beamsplitter and MCT detector. Sample thickness was about 50–70 μm , and the high-pressure chamber was about 120–150 μm in thickness and 180–200 μm in diameter at the start of the pressure run. We used type *Ia* diamonds with 400- μm flat culets, and rhenium gaskets. Reference transmission spectra were taken near the sample through the pressure medium. Room-temperature two-magnon Raman spectra were excited by the 514.5-nm line of an Ar-ion laser and recorded by a single ISA HR-460 spectrometer (with notch filters) and Dilor-XY spectrometer, both equipped with charge-coupled device (CCD) detectors. Additional low-temperature Raman measurements were performed in a continuous flow cryostat with quartz infrasil windows. We measured the pressure using R_1 fluorescence from small ruby chips inside the sample chamber.¹⁷

Figure 1 shows MIR absorption and two-magnon Raman spectra at several pressures. We clearly resolve two features in the MIR absorption spectra (denoted by arrows): a relatively sharp peak (the putative bimagnon) and the first sideband. At low pressure, their energies are ~ 2800 and ~ 4000 cm^{-1} , respectively. Both peaks increase in energy with increasing pressure. The second broad higher-energy sideband centered near ~ 6000 cm^{-1} appears as a weak “shoulder” on the broad ~ 4000 - cm^{-1} absorption. Due to its weakness and overlap with the first sideband, its position could not be determined with sufficient precision to accurately obtain its pressure coefficient, although its energy clearly increases with pressure. The two-magnon Raman spectra were corrected by subtracting the background signal from the diamond anvils. The spectra clearly display the two-magnon Raman peak (denoted by arrow). Raman spectra taken at 295 and 80 K (not shown) were very similar, the

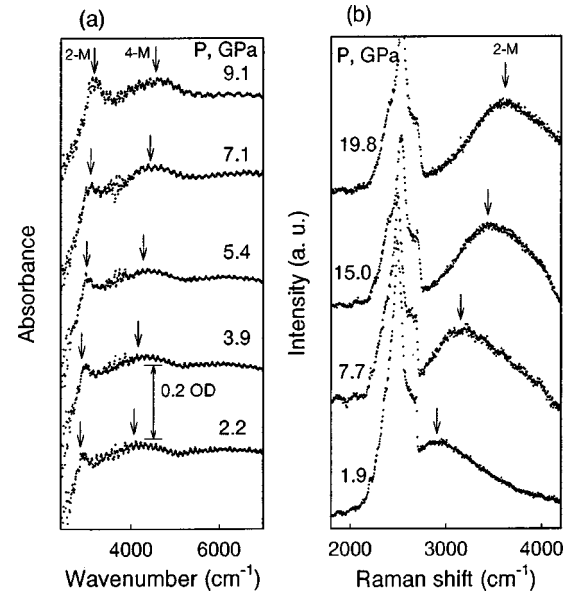


FIG. 1. Room-temperature MIR absorption (a) and two-magnon Raman scattering (b) spectra in SCOC at several pressures (NaCl medium). The spectra are vertically offset for clarity. Optical density (OD) values at 4M peak position in (a) are about 0.35(3) for all pressures shown which corresponds to the absorption coefficient about 115–160 cm^{-1} (sample thickness was about 50–70 μm). Arrows denote peaks discussed in the text. Incomplete cancellation of the strong Raman signal from the diamond yields the ~ 2500 - cm^{-1} structure in (b), which is therefore not associated with the sample. Raman spectra were not corrected for the spectrometer (HR460) and CCD response, which is featureless and almost flat in the spectral range of Raman measurements.

only difference being a slight 3–5% softening of the two-magnon energy at room temperature [similar to observations in LCO (Ref. 13)].

Attempts to fit the two-magnon Raman and narrow ~ 2800 - cm^{-1} absorption peaks were difficult due to their asymmetric, non-Lorentzian line shapes. It was found that the error involved in such fitting procedures was comparable to that of simply assigning the peak position based on the maximum in the spectrum. In either case, the estimated error was 50–100 cm^{-1} , depending on the data quality. Somewhat larger errors (~ 200 cm^{-1}) were encountered in determining the position of the 4000- cm^{-1} sideband absorption (fitted as a Voigt profile, which is a convolution of Gaussian and Lorentzian profiles).

Figure 2 displays the measured two-magnon Raman peak (80 and 295 K), and the two absorption peaks (295 K) as a function of pressure. The two-magnon Raman peak provides a quantitative measure of the pressure-dependent superexchange coupling, i.e., $J(P) = E_{2M}(P)/2.76$, ignoring Oguchi corrections.¹⁸ If the MIR absorption peaks have multimagnon origin, the ratio of their energies divided by $J(P)$ should give a constant reflecting the number of magnons involved. This is shown in the inset. For the ~ 2800 - cm^{-1} absorption, we find $E(P)/J(P) \sim 2.7$, close to the Ising bond-counting value of 3, which corresponds to a pair of interacting magnons. For the ~ 4000 - cm^{-1} absorption, we find $E(P)/J(P) \sim 3.7$, close to the Ising bond-counting result of 4 for two

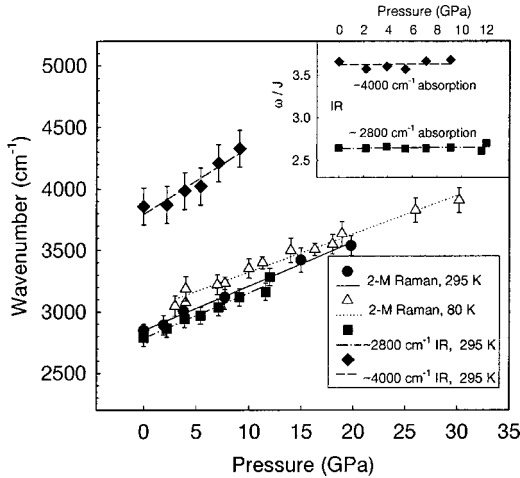


FIG. 2. Pressure dependence of the two-magnon Raman, and ~ 2800 - and ~ 4000 - cm^{-1} absorption peaks at 295 K. Raman data at 80 K are also shown. Inset shows the ratio of the ~ 2800 - and ~ 4000 - cm^{-1} MIR absorption peak energies to the measured super-exchange coupling J versus pressure. Their constant ratios indicate a multimagnon origin.

pairs of interacting magnons arrayed on a plaquette. Note that within experimental error, both ratios are independent of pressure.

We compare the relative pressure dependencies of these excitations in Fig. 3. The measured pressure coefficients for two-magnon Raman and the ~ 2800 - cm^{-1} MIR absorption peak are identical [$1.26(15)\%$ GPa^{-1} and $1.30(20)\%$ GPa^{-1} , respectively] at 295 K. The pressure coefficient of the first sideband absorption near ~ 4000 cm^{-1} is $1.16(25)\%$ GPa^{-1} (295 K), again very close to that of the two-magnon Raman peak. Thus the pressure dependences of both the ~ 2800 - and ~ 4000 - cm^{-1} absorptions are closely proportional to J , consistent with their being predominantly composed of magnons. This is fully consistent with the LS model, with the ~ 2800 - cm^{-1} peak thus identified as the ‘bimagnon’ and the ~ 2800 - cm^{-1} peak identified as the 4MP excitation. The pressure dependence of the two-

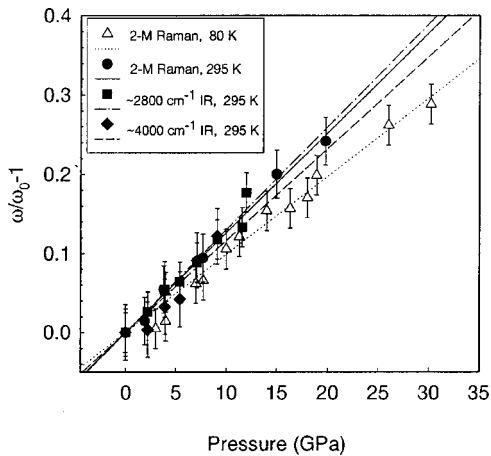


FIG. 3. Relative pressure dependence of two-magnon Raman, and ~ 2800 - and ~ 4000 - cm^{-1} absorption peaks. Room-temperature data for the Raman and both MIR absorption peaks are in very good agreement. The different slope for the 80-K Raman data is discussed in the text.

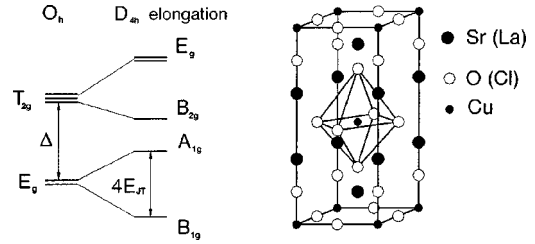


FIG. 4. Energy-level diagram of d transitions in $\text{Sr}_2\text{CuCl}_2\text{O}_2$ (La_2CuO_4). The lowest transition [$d(x^2-y^2)-d(3z^2-y^2)$] is directly related to Jahn-Teller distortion in the isostructural La_2CuO_4 . It is shown in the text that Jahn-Teller distortion is most likely to be suppressed by the increasing pressure, thus producing *negative* pressure shift of this lowest-energy ($4E_{JT}$) exciton.

magnon Raman scattering at 80 K is slightly reduced relative to the 295 K result, being about 1.01 (10%) GPa^{-1} . This is easily understood by the reduced temperature softening¹⁹ of the two-magnon feature at higher pressures due to the increased exchange interaction (kT/J decreases with increasing pressure).

Regarding the possible origin of ~ 4000 - cm^{-1} absorption we may ask the following question: is it possible that $d_{3z^2-r^2}$ exciton^{1,11} has the pressure dependence similar to two-magnon feature? We show below by simple arguments that this is unlikely, and, in fact, we expect that the $d_{3z^2-r^2}$ exciton energy has *negative* pressure coefficient. The exciton has never been measured in cuprate bearing materials, however, it was observed in several Cu^{2+} compounds²⁰ and its pressure dependence was estimated recently from measurements of pressure dependence of the charge-transfer band in CuCl_6 systems.²¹ In Fig. 4 we show splitting of d levels in tetragonal symmetry of La_2CuO_4 , isostructural to $\text{Sr}_2\text{CuCl}_2\text{O}_2$. Cubic field (O) produces crystal-field splitting Δ , and tetragonal field (D_{4h}) further splits T_{2g} and E_g levels. It can be shown²⁰ that the splitting of the lowest E_g level is described by Jahn-Teller theorem, and the lowest exciton energy is equal to

$$\Delta_e = 4E_{JT} = \frac{2V^2}{M\omega^2}, \quad (1)$$

where V is electron-phonon coupling parameter, M is the mass of one of the six ligands in cubic symmetry, and ω is the vibrational frequency for radial vibrations of ligands. Very simple consideration gives coupling of electronic E_g states to vibrational E_g modes. It is well established fact that vibrational modes of oxygen atoms in cuprates have positive pressure shifts.²² We also measured positive pressure shifts for all phonon modes in this experiment.²³ Assuming that electron-phonon coupling V is not strongly pressure-dependent,²¹ we conclude that E_{JT} decreases with increasing pressure [Eq. (1)]. This conclusion about suppression of Jahn-Teller distortion by pressure is also supported by recent pressure work on CuCl_6 systems.²¹

A further argument against the $d_{3z^2-r^2}$ exciton explanation of ~ 4000 - cm^{-1} absorption is the fact that this feature correlates with two-magnon ~ 2800 - cm^{-1} absorption in different cuprates.¹¹ The ratio of the ~ 4000 - cm^{-1} feature to the two-magnon ~ 2800 - cm^{-1} feature is equal to $1.38(2)$ in La_2CuO_4 , $1.37(2)$ in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, and to $1.37(2)$ in

Nd_2CuO_4 , while two-magnon IR feature is found at 3330 cm^{-1} in La_2CuO_4 , at 2880 cm^{-1} in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, and at 2730 cm^{-1} in Nd_2CuO_4 (all frequencies given at 10 K).¹¹ It is highly unlikely that $d_{3z^2-r^2}$ exciton correlates with two-magnon feature in La_2CuO_4 having Cu atoms surrounded by octahedrally coordinated oxygen atoms, in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ having apical Cl ions, and in Nd_2CuO_4 which has square planar oxygen atoms with no apical ions. This would actually be possible if the strong Cu-O in-plane bonding dominates the exciton energies. However, it is then very difficult to reconcile the low value of Jahn-Teller splitting $\Delta_e = 4E_{JT} \sim 4000\text{ cm}^{-1}$, with this extreme case of Jahn-Teller distortion when apical ions are completely “removed” from the octahedral ligand complex surrounding Cu^{2+} ion.^{20,21}

In the LS model, the symmetry-breaking phonon is crucial to the appearance of multimagnon excitations, as the crystal structure has inversion symmetry. Without the phonon, magnon pairs are electric dipole forbidden. The specific phonon involved is the Cu-O stretch (breathing mode), which modulates the Cu-O bond length and hence the superexchange coupling J . Consequently, this phonon strongly interacts with magnons. Surprisingly, the energy of the $\sim 2800\text{ cm}^{-1}$ bimagnon absorption is almost degenerate with the two-magnon Raman peak, while the phonon energy is $\sim 580\text{ cm}^{-1}$. This results from a near cancellation of the magnon-magnon interaction with the phonon energy.¹⁰ The two-magnon Raman peak corresponds to magnon pairs with momentum $\mathbf{k}=0$, whereas the bimagnon is dominated by pairs at $\mathbf{k}=(\pi,0)$ where the magnon-magnon interaction is larger. The presence of the phonon should, at some level, alter the precise proportionality of the peak energy to $J(P)$. However, there are two factors that apparently suppress this correction. First, the bulk of the MIR excitation energies arise from the magnons. Second, our Raman data yield a value for the relative pressure dependence of the Cu-O phonon modes of $\sim 0.9\text{--}1.25\%$ GPa^{-1} , i.e., very close to that of J .

We believe that the remarkable enhancement of the 4MP spectral weight points to different physics. More detailed calculations including effects such as ring exchange have not explained the discrepancy.²⁵ We suggest that interactions beyond nearest neighbor are likely important. Exchange interactions beyond nearest neighbors are known to be non-negligible in SCOC,²⁶ and likely affect the high-frequency spin dynamics.²⁷ Hence this 4MP excitation may provide a sensitive test for calculations using a more extended spin Hamiltonian. In view of the importance of quantum fluctuations to multimagnon creation as well as the absence of 4MP excitations in La_2NiO_4 , the enhanced 4MP excitation may also point towards an important role for quantum fluctuations. Magnons may be more heavily “dressed” in the cu-

prates than previously thought. For example, a local “spin liquid” region of RVB-like correlated singlet states may surround the plaquette of flipped spins.²⁵

Finally, there are reasons to believe that the coupling of the Cu-O stretch phonon (P) to the four-magnon (4M) may be anomalous in the cuprates. In this regard the spin-1/2 cuprates are special, as quantum fluctuations are maximal and the exchange coupling is unusually strong. Hence four-magnon creation is quantum enhanced and the magnon-phonon coupling energy is unusually large. For these reasons, composite 4MP excitation may have an effective charge much larger than perturbation theory would predict. It is insightful to examine the 4MP bond textures (in real space) that result from different 4M and P wave vectors. From this simple approach, it is clear (via examination of the affected bonds) that the 4MP interaction is attractive. To couple to a $\mathbf{q}=0$ photon the 4M (P) must have wave vector $+\mathbf{Q}$ ($-\mathbf{Q}$), with maximal density of states when \mathbf{Q} is on the zone boundary. For $\mathbf{Q}=(\pi/a, \pi/a)$, the plaquette of 4 flipped spins favors the same bond variations as the “breathing mode” phonon with $-\mathbf{Q}$. Similar attraction occurs at $\mathbf{Q}=(0, \pm\pi/a)$ or $(\pm\pi/a, 0)$ where the 4MP resembles dimerized rows, possibly signaling latent tendencies within the undoped insulator that contribute to stripe formation once doped holes are introduced.

In conclusion, high-pressure midinfrared (MIR) absorption and two-magnon Raman spectra of the insulating antiferromagnet SCOC clearly identifies the narrow $\sim 2800\text{ cm}^{-1}$ absorption as a quasibound bimagnon (two-magnon + optic phonon), as its pressure coefficient is identical to the two-magnon Raman excitation. The measured pressure coefficient of the broad absorption peak centered near $\sim 4000\text{ cm}^{-1}$ is closely similar. Both its energy and pressure dependence are consistent with an unusual four-magnon + phonon (4MP) excitation. This excitation is generic to all layered cuprates, yet its spectral weight is unexpectedly $\sim 10^2$ times larger than predicted by theory. The absence of 4MP excitations in isostructural spin-1 La_2NiO_4 strongly argues that more extended spin couplings, quantum fluctuations, and/or magnon-phonon coupling are playing an unanticipated yet crucial role in the cuprates. The interactions responsible for these unusual absorption features give important insight into the latent interactions coupling charge, spin, and lattice degrees of freedom in the cuprates. As such, they may also be relevant to the behavior of the doped compounds.

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