Two-magnon Raman scattering in $(La_{1-x}Sr_x)_2CuO_4$

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The two-dimensional two-magnon peak in $(La_{1-x}Sr_x)_2CuO_4$ decreases rapidly from $x=0$ to $x=0.01$. For $x>0.03$ scattering is observed over a very wide energy region from low energy to over 4000 cm^{-1}. This indicates that the correlation length of the two-dimensional spin order decreases rapidly from $x=0$ to $x=0.01$. This decrease can be related to the rapid decrease of the three-dimensional antiferromagnetic transition temperature (T_N), while at $x>0.03$ the correlation still retains a short length and a short time. At $x<0.01$ the scattering is in a resonant state with narrow electronic levels of which transition energy is about 18 000 cm^{-1}. The narrowness of these energy levels, and the simultaneous extinction of resonance and the two-magnon scattering, suggest that these are localized levels relating to the Cu spins.

INTRODUCTION

Competition between superconductivity and antiferromagnetism observed in some superconductors arouses much interest. On increasing Sr concentration in $(La_{1-x}Sr_x)_2CuO_4$ or on increasing oxygen concentration in $YBa_2Cu_3O_{7-\delta}$, superconductivity appears at the end of the antiferromagnetic phase.[1-5] The examination of the spin dynamics in the antiferromagnetic phase is important for the investigation of the superconducting mechanism.

Recently Lyons *et al.*[6,7] reported two-magnon peaks at 3000 cm^{-1} in the Raman spectra of La_2CuO_4 and 2600 cm^{-1} in insulating $YBa_2Cu_3O_{7-\delta}$ with a large oxygen deficiency. These energies are much higher than the two-magnon peak energy in K_2NiF_4.[8] The magnon energy in La_2CuO_4 is consistent with the extrapolated energy from the small wave-vector region measured by neutron scattering.[9] Lyons *et al.*[6] mentioned that polishing of the sample surface reduced the two-magnon peak intensity drastically so they used mostly as-grown (001) faces with and without acid etching. In this experiment all the data were obtained on polished surfaces in order to remove the problem of surface contamination. This paper reports the polarization dependence of the two-magnon peak including the polarization configuration of the incident light electric field parallel to the z axis, its temperature dependence, Sr concentration dependence, and the resonant Raman effect.

EXPERIMENTAL RESULTS

Most of the samples used in this experiment are as-grown single crystals synthesized by a flux method using CuO. The Sr concentration was examined by electron-probe microanalysis (EPMA). Raman scattering data were collected in a backscattering configuration with equipment of a double monochromator (Spex 1400) and an Ar-ion laser (Spectra Physics 164). Most of the experiment was done with a 5145-Å beam. The obtained spectra were corrected by the spectral efficiency of the spectrometer and the photomultiplier.

Figure 1 shows the Raman spectra of La_2CuO_4 measured at the polarization configuration $(\hat{e}_i \| \hat{e}_s \| x)$, $(\hat{e}_i \| y, \hat{e}_s \| x)$, and $(\hat{e}_i \| \hat{e}_s \| z)$, where $\hat{e}_i$ and $\hat{e}_s$ denote the unit vectors of the polarization directions of the incident and scattered radiation. x, y, and z denote the crystallographic axes for the tetragonal phase. The peaks below 800 cm^{-1} are mainly due to single-phonon scattering and the peaks between 800 and 1500 cm^{-1} are two-phonon scattering. The results of phonon scattering are presented elsewhere. The broad peak at 3230 cm^{-1} in the $\hat{e}_i \| \hat{e}_s \| x$ spectra is assigned to the two-magnon scattering peak. In the $(\hat{e}_i \| y, \hat{e}_s \| x)$ and $(\hat{e}_i \| \hat{e}_s \| z)$ spectra no peak is observed near 3000 cm^{-1}. The peak energy is in good agreement with the energy reported by Lyones *et al.*,[6]

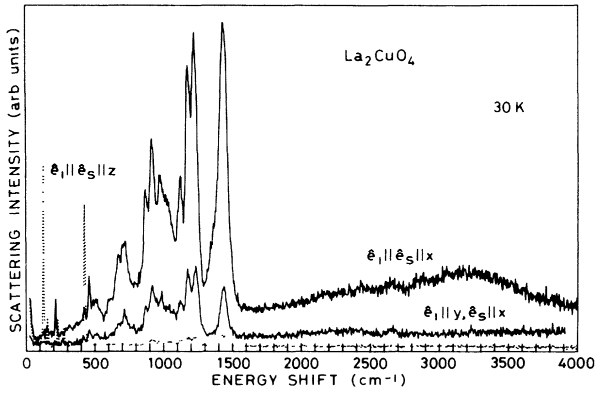

FIG. 1. Polarized Raman spectra in La_2CuO_4 at 30 K. The x, y, and z denote the crystallographic axes for the tetragonal phase.

but the intensity is much weaker than theirs. The two-magnon scattering is allowed, if $(\hat{e}_i \cdot \hat{\sigma}_{ij})(\hat{e}_s \cdot \hat{\sigma}_{ij})(\mathbf{S}_i \cdot \mathbf{S}_j)$ is nonzero,[10–12] where $\hat{\sigma}_{ij}$ is the unit vector connecting nearest-neighbor spin sites i and j. In La_2CuO_4 and $YBa_2Cu_3O_{7-\delta}$ spins of Cu atoms are arranged on the quasi-square lattice sheets, so that the allowed polarization directions are $\hat{e}_i \| \hat{e}_s \| x$ and $\hat{e}_i \| \hat{e}_s \| y$, where x and y are the axes of the two-dimensional square lattice. x and y are also the crystallographic axes in the tetragonal phase. If three-dimensional spin order is developed, two-magnon scattering is also allowed in the $\hat{e}_i \| \hat{e}_s \| z$ polarization configuration. However, no two-magnon peak is observed in the $\hat{e}_i \| \hat{e}_s \| z$ spectra. Neutron scattering experiments revealed that the two-dimensional antiferromagnetic spin order exists instantaneously with the correlation length up to 200 Å at 300 K on the two-dimensional Cu-O sheet as a fluctuation.[9] The experimentally observed two-magnon scattering in the Raman spectra is, therefore, attributed to the dynamics of two-dimensional antiferromagnetic spin order as suggested by Lyons *et al.*[6] The two-dimensionality of the observed magnon is also supported by the temperature dependence and the oxygen concentration dependence of the Raman peak.

Figure 2 shows the temperature dependence of the Raman spectra in $(La_{1-x}Sr_x)_2CuO_4$. The solid curves are the spectra at low temperatures and the dotted curves are at 273 K. The energies of the two-magnon peaks at $x = 0$ and $x = 0.005$ change little even at 273 K, which is higher than the three-dimensional antiferromagnetic transition temperature $T_N = 230$ K for $x = 0$ and about 130 K for $x = 0.005$.[5]

It is known that the three-dimensional T_N in La_2CuO_4 strongly depends on oxygen concentration.[13,14] The reduction of oxygen deficiency by annealing in an oxygen atmosphere at 400 °C for 3 d did not bring any noticeable change in the two-phonon and two-magnon scattering spectra. This is distinguished from the case of $YBa_2Cu_3O_{7-\delta}$ in which the decrease of oxygen concentration induces the antiferromagnetic phase and causes the increase of the two-magnon scattering peak above $\delta = 0.4$.

The peak energy of the two-magnon density of states is $2nSJ$, where $n = 4$ is the number of nearest-neighbor spins, $S = \frac{1}{2}$, and J is the exchange integral. Magnon-magnon interaction changes the peak to a triangular shape and reduces the peak energy to about 2.7 J.[7] The observed peak energies are 3230 cm^{-1} at 30 K and 3130 cm^{-1} at 273 K for $x = 0$ and $x = 0.005$, 3060 cm^{-1} at 30 K and 2920 cm^{-1} at 273 K for $x = 0.017$, and 2860 cm^{-1} at 100 K and 2840 cm^{-1} at 273 K for $x = 0.035$. The corresponding J's are 1200 cm^{-1} at 30 K and 1160 cm^{-1} at 273 K for $x = 0$ and $x = 0.005$, 1130 cm^{-1} at 30 K and 1080 cm^{-1} at 273 K for $x = 0.017$, and 1060 cm^{-1} at 100 K and 1050 cm^{-1} at 273 K for $x = 0.035$.

Below T_N two-magnon scattering is expected in the $\hat{e}_i \| \hat{e}_s \| z$ spectra, if the exchange interaction is strong enough. Figure 3 shows the Raman spectra in $\hat{e}_i \| z$ above and below $T_N = 230$ K. At low temperatures the 156 cm^{-1} peak and two-phonon peaks at 800–1500 cm^{-1} are

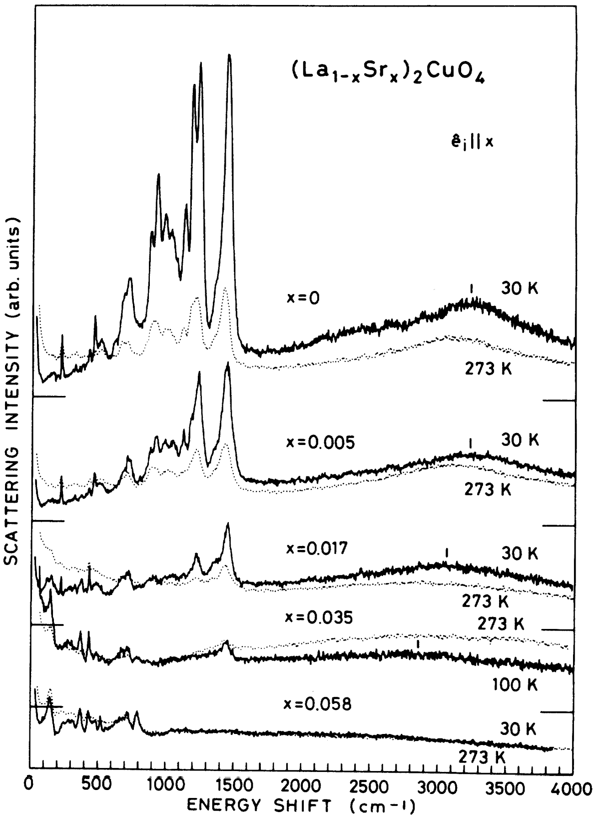

FIG. 2. Temperature dependence of the $(\hat{e}_i \| x)$ Raman spectra in $(La_{1-x}Sr_x)_2CuO_4$ with $x = 0$, 0.005±0.001, 0.017±0.004, 0.035±0.005, and 0.058±0.004.

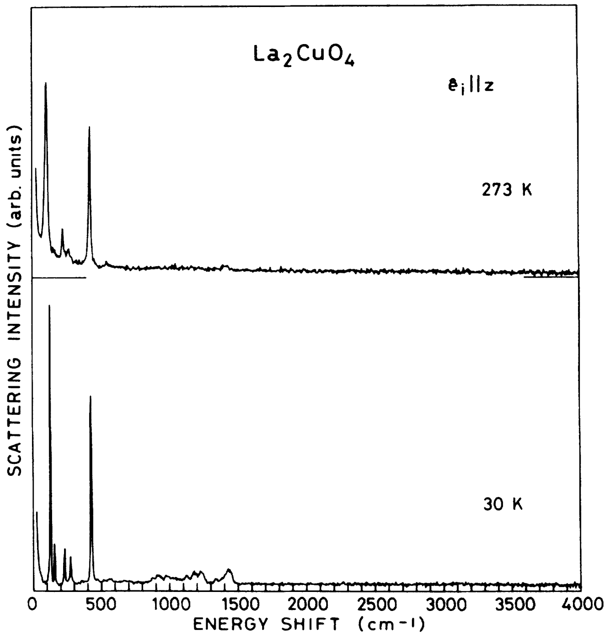

FIG. 3. $(\hat{e}_i \| z)$ Raman spectra of La_2CuO_4 at 273 and 30 K.

enhanced, but one can find no triangular peak which is characteristic of two-magnon scattering. This result indicates that the exchange integral along the z axis is very weak.

The peak intensity and the shape of two-magnon scattering are very sensitive to the Sr concentration. Figure 4 shows the Sr concentration dependence of the Raman spectra in the $\hat{e}_i \| x$ polarization configuration. On increasing x from 0 to 0.035, the two-magnon peak and the two-phonon peaks decrease. The simultaneous decrease of two-phonon and two-magnon scattering suggests that there exists a relation between these two scattering mechanisms. At $x = 0.035$ the low-energy scattering increases and a very broad peak with the maximum at 2500–3000 cm^{-1} appears. The quality of the $x = 0.035$ sample surface is a little worse than other samples. At $x = 0.058$ the peak near 3000 cm^{-1} is missing, but very broad scattering intensity ranging from low energy to over 4000 cm^{-1} is noticeable.

It is noteworthy that the samples with $x = 0.035$ and $x = 0.058$ have fairly large scattering intensity ranging from low energy to over 4000 cm^{-1}. The possible origins of the scattering in this high-energy region in the sample with large carrier density are overdamped magnons, collective and single-particle excitation of free carriers, and luminescence. The collective mode of free carriers, or plasmon, has carrier density dependence like $\omega_p^2 = 4\pi n e^2/\epsilon_\infty m^*$, where ω_p is the plasma frequency, n is the carrier density, e is the charge, ϵ_∞ is the dielectric constant at high frequency, and m^* is the effective mass. The observed peak energy has little dependence on carrier density. The scattering from single-particle excitation is limited to a small energy region from momentum conservation. Thus the observed scattering is not caused by the free carriers. Generally luminescence is very weak in an opaque energy region and especially in a sample with large carrier density. The observed temperature dependence of the scattering intensity which decreases on decreasing temperature from 273 to 100 K in the sample with $x = 0.035$ is opposite to the normal temperature dependence of luminescence. The scattering intensity in the $\hat{e}_i \| \hat{e}_s \| x$ polarization configuration is several times the intensity in $\hat{e}_i \| \hat{e}_s \| z$ as in the case of two-magnon scattering in La_2CuO_4. Thus the origin of the scattering ranging from low energy to over 4000 cm^{-1} in the samples with $x = 0.035$ and $x = 0.058$ is assigned to the overdamped magnon which has a correlation length of the order of the nearest-neighbor spin distance. The correlation length of the antiferromagnetic spin order is reduced by the interaction between localized spins and free carriers. The experimental result from Raman scattering suggests that the two-dimensional correlation length decreases rapidly from $x = 0$ to $x = 0.01$, which corresponds to the rapid decrease of the three-dimensional T_N from $x = 0$ to $x = 0.01$,[5] and at $x > 0.03$ the correlation length is reduced to the order of the nearest-neighbor spin distance; still the correlation of spins remains.

Figure 5 shows the incident photon energy dependence of the spectra in La_2CuO_4. The spectra were corrected by the spectral response of the spectrometer and the photomultiplier. The one-phonon scattering intensity is almost the same, but the two-phonon and two-magnon scattering shows strong dependence on incident light wavelength. The two-phonon peaks decrease and the two-magnon peak increases with the increase of the photon energy from 5145 Å (19436 cm^{-1}) and 4880 Å (20492 cm^{-1}) to 4579 Å (21839 cm^{-1}). The change of the scattering intensity with the incident light wavelength indicates that the scattering is resonant. The most dominant term of resonant scattering intensity is proportional to

$$\left[\frac{1}{\omega_i - \Delta} \frac{1}{\omega_1 - \Delta - \omega_0} \right]^2 ,$$

which shows double resonance at $\omega_i = \Delta$ and $\omega_i = \Delta + \omega_0$. Here ω_i is the incident photon energy, Δ is the intermediate electronic transition energy, and ω_0 is the elementary excitation. The observed enhancement of the higher energy mode for higher incident photon energy indicates that the system is in the outgoing resonant condition of $\omega_i = \Delta + \omega_0$. The transition energy Δ is estimated as

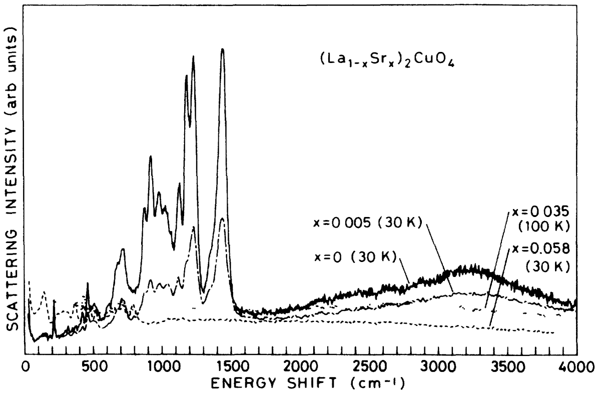

FIG. 4. Sr concentration dependence of the $(\hat{e}_i \| x)$ Raman spectra in $(La_{1-x}Sr_x)_2CuO_4$.

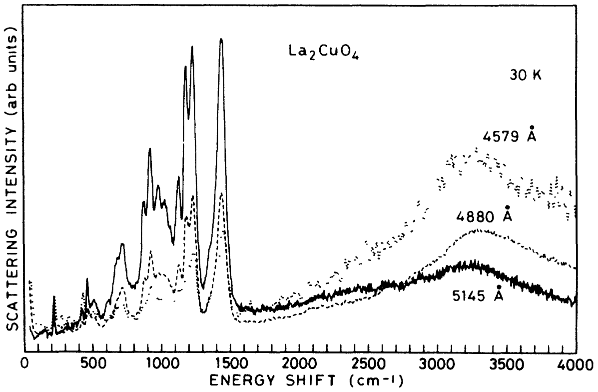

FIG. 5. Incident light wavelength dependence of the $(\hat{e}_i \| x)$ Raman spectra in La_2CuO_4.

18000 cm^{-1} (2.2 eV) from the change of the intensities of the two-phonon and the two-magnon scattering. The energy width is about 1000 cm^{-1} or less. This width is too narrow for the normal interband transition. It is hard to attribute the extinction of the resonance effect at $x=0.058$ to the small change of the Fermi level caused by the increase of the carrier density in the sample in which only 6% of La is substituted for Sr. Therefore the electronic levels for the 18000 cm^{-1} transition are assigned to the narrow levels made by the localized electrons relating to the Cu spins. The extinction of resonance at $x=0.058$ is probably due to the level broadening of the localized state which is related to the correlation length of the antiferromagnetic spin order.

In Fig. 2 the increase of the scattering intensity at low temperatures in $(La_{1-x}Sr_x)_2CuO_4$ with $x=0$ and $x=0.005$ is due to the closer approach to the resonance. On decreasing temperature the electronic transition energy Δ increases and the two-phonon scattering of 800–1500 cm^{-1} approaches the outgoing resonant condition much closer, so that the two-phonon scattering is more enhanced than the two-magnon scattering. At $x=0.035$ the larger intensity at 273 K than at 100 K above 1000 cm^{-1} may be due to the sample quality lower than other samples. At $x=0.058$ the spectra do not change in the energy region higher than 1000 cm^{-1}.

CONCLUSIONS

In conclusion, two-dimensional magnon scattering was observed as a triangular peak in $(La_{1-x}Sr_x)_2CuO_4$ with $x \leq 0.035$. For larger x the observed scattering ranging from low energy to over 4000 cm^{-1} was assigned to come from overdamped magnons made by the interaction between localized Cu spins and free carriers. Two-magnon scattering exists even in the superconducting region above $x=0.025$.[5] At $x<0.01$ the two-magnon and the two-phonon scattering shows resonant Raman enhancement. This resonant scattering revealed the existence of narrow electronic levels with the transition energy of about 18000 cm^{-1}. The narrowness of the width of these energy levels and the simultaneous extinction of the resonance and the two-magnon scattering suggests that these levels are the localized electronic levels relating to the Cu spins. The three-dimensional two-magnon peak was not observed in the $\hat{e}_i \| \hat{e}_s \| z$ polarization configuration.

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