RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 42, NUMBER 1 1 JULY 1990

High-energy spin excitations in the insulating phases of high-T_c superconducting cuprates and La_2NiO_4

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(Received 21 March 1990)

High-energy spin excitations up to above 8000 cm^{-1} were measured by polarized Raman scattering in the insulating phases of $S=\frac{1}{2}$ copper oxides, La_2CuO_4, $YBa_2Cu_3O_{6.2}$, $Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{8+y}$, Nd_2CuO_4, and Pr_2CuO_4, and an $S=1$ nickel oxide La_2NiO_4. All the copper oxides commonly show anomalous spectra, especially the secondary scattering peaks near $4J$ (J is the two-spin superexchange energy). Those anomalies are caused by the large four-spin cyclic exchange interactions. The present experiments demonstrated that the four-spin exchanges show distinctive characteristics in cuprates as compared to other materials.

The high transition temperature (T_c) superconducting cuprates have characteristic spin states: the superexchange energies (J) are as high as 1000 cm^{-1},[1] the two-dimensional local antiferromagnetic orders continue even above the antiferromagnetic transition temperatures (T_N),[2] and the spin excitations are observed even in doped superconducting materials.[3] One of the authors (S.S.) has performed high-energy-shifted Raman-scattering experiments up to 10000 cm^{-1} in La_2CuO_4 and found a new spin excitation peak at 4550 cm^{-1} besides the two-magnon peak at 3230 cm^{-1}.[4] He assigned the new peak as a four-magnon peak caused by the four-spin cyclic exchange interaction.[5-7] This paper demonstrates that the second peaks are commonly observed in the insulating phases of all the high-T_c superconducting cuprates, but not in La_2NiO_4 which is isostructural with La_2CuO_4. The differences in the present analyses of the Raman spectra from those by Lyons *et al.*[8] and Singh *et al.*[9] are discussed.

The single crystals of superconducting cuprates were synthesized by a CuO flux method. The La_2NiO_4 single crystals were made by a floating-zone method heated by infrared radiation in the atmosphere of 1% O_2+99% N_2 at 1800 °C followed by reduction in pure He gas of 5.5 atm at 1000 °C for 15 h.[10] The resultant La_2NiO_4 crystals are insulating. The structure is orthorhombic at room temperature and shows a first-order structural phase transition at about 80 K. T_N is supposed to be above room temperature. The Raman signal was obtained in a backscattering configuration by a single-channel photon-counting apparatus equipped with a GaAs-photocathode photomultiplier ($R943-02$). The obtained data were corrected for the spectral sensitivity of the spectroscopic system.

Figures 1 and 2 show polarized Raman spectra at 30 K in the insulating phases of $S=\frac{1}{2}$ copper oxides: hole superconductors La_2CuO_4, $YBa_2Cu_3O_{6.2}$, and $Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{8+y}$, electron superconductors Nd_2CuO_4 and Pr_2CuO_4, and an $S=1$ nickel oxide, La_2NiO_4. The solid curves are the B_{1g} spectra measured at the (x',y') polarization configuration and the dotted curves are the $A_{1g}+B_{2g}$ spectra at (x',x'). The B_{2g} components are about 10% or less. Here (x',y') indicates that the polarization of the incident light is parallel to the $x'=[110]$ direction and the scattering light to the $y'=[1\bar{1}0]$, where x, y, and z are the axes of the CuO_2 quasisquare lattice. These two figures are shown to demonstrate that the different incident light wavelength (λ_i) can separate the Raman parts and the luminescence parts. In the cuprates the peaks above 7000 cm^{-1} for $\lambda_i=4579$ Å and the peaks at about 5500 cm^{-1} for $\lambda_i=5145$ Å are due to luminescence. The absolute energy extends from 11000 cm^{-1}, the lower limit of the detector, to 15000 cm^{-1} for $\lambda_i=4579$ Å. This luminescence has anomalous polarization dependence, in which the B_{1g} component is much larger than the A_{1g}. The existence of the perpendicular polarization to the incident light indicates that this luminescence does not originate from impurities, defects, or normal electronic states, but may be related to carrier-spin complexes. The peaks below 800 cm^{-1} are mainly from one-phonon scattering and the peaks between 800 and 1500 cm^{-1} are from two-phonon scattering. Very

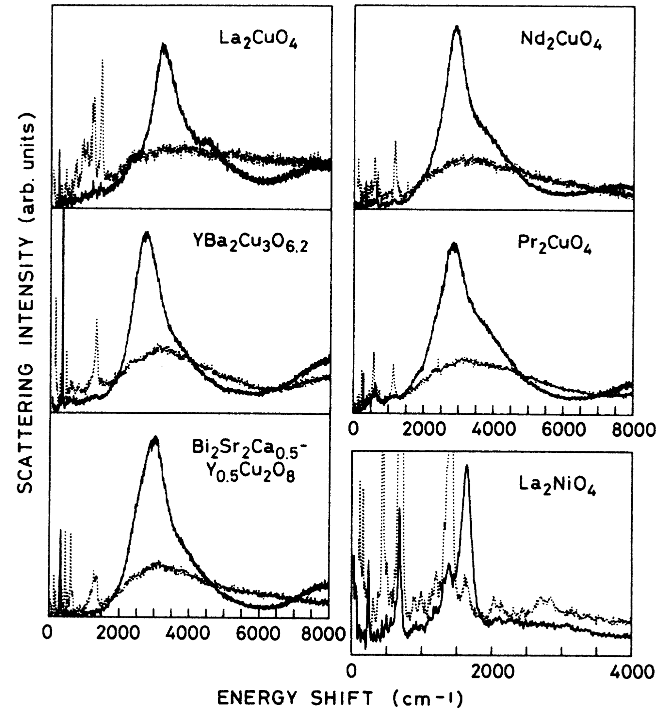

FIG. 1. Polarized Raman spectra at 30 K for $\lambda_i = 4579$ Å. The solid curves are the (x',y') spectra with B_{1g} symmetry, and the dotted curves are the (x',x') spectra with dominantly A_{1g} symmetry. The (x',x') and (x',y') spectra are plotted with the same scale for each compound.

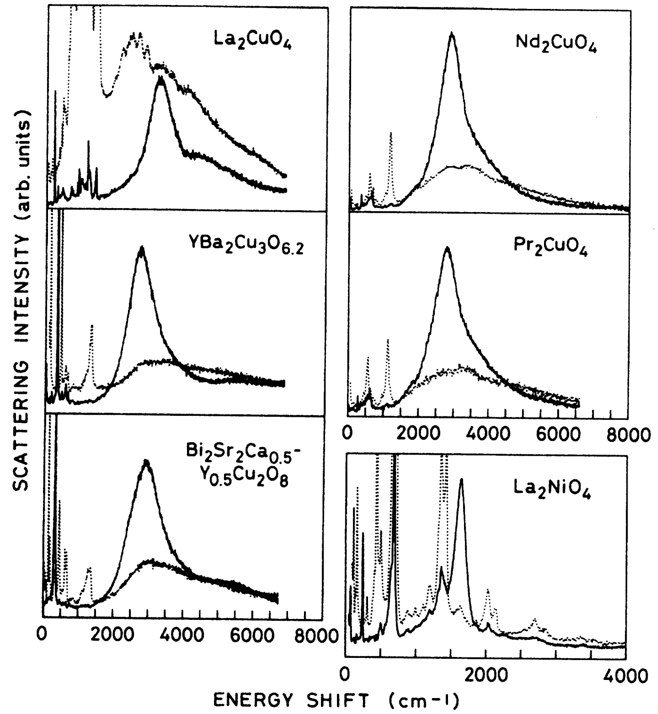

FIG. 2. Polarized Raman spectra at 30 K for $\lambda_i = 5145$ Å. The solid curves are the (x',y') spectra and the dotted curves are the (x',x') spectra.

strong even-order multiphonon resonant scattering is observed in the A_{1g} spectra of La_2CuO_4, when excited with $\lambda_i = 5145$ Å. The isostructural La_2NiO_4 shows multiphonon scattering of the 674- and 718-cm^{-1} modes.

The two-magnon scattering peaks are observed in the B_{1g} spectra at 3230 cm^{-1} in La_2CuO_4, 2730 cm^{-1} in $YBa_2Cu_3O_{6.2}$, 3080 cm^{-1} in $Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{8+y}$, 2890 cm^{-1} in Nd_2CuO_4, 2820 cm^{-1} in Pr_2CuO_4, and 1640 cm^{-1} in La_2NiO_4. The estimated J is 1200 cm^{-1} for La_2CuO_4, 1010 cm^{-1} for $YBa_2Cu_3O_{6.2}$, 1140 cm^{-1} for $Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{8+y}$, 1070 cm^{-1} for Nd_2CuO_4, 1040 cm^{-1} for Pr_2CuO_4, and 240 cm^{-1} for La_2NiO_4, on the assumption that the peak energy is $2.7J$ for the $S = \frac{1}{2}$ copper oxides and $6.7J$ for the $S = 1$ nickel oxide ignoring the four-spin cyclic exchange interactions. The temperature dependence of the scattering intensities in the cuprates is so slight that the rise in temperature from 30 to 273 K causes the peak intensities to decrease by only about 10%, in contrast to 50% in La_2NiO_4. This is related to the strong antiferromagnetic correlation on the two-dimensional CuO_2 layers,[2] although the origin of the abnormally large correlation length above T_N is not known.

In La_2NiO_4 the linewidth of the two-magnon peak is narrow and the shape is close to the theoretical curve. On the other hand the cuprates show theoretically unexpected characteristics not only in the very broad linewidths of the two-magnon peaks[6,9,11] and the high-energy tails up to $8J$,[4,8,9] but also in the following two facts. (i) The B_{1g} spectra have secondary scattering intensities near $4J$ (classical cutoff energy for the two-magnon scattering). These new $4J$ peaks are clearly observed only in La_2CuO_4. The reason is assumed to be that the La_2CuO_4 crystal has smaller carrier density than other compounds. The carrier density induced by nonstoichiometry is monitored by the two-phonon scattering intensity in the A_{1g} spectra. The present La_2CuO_4 crystal shows the large two-phonon peak with intensity eight times the broad scattering intensity at 3500 cm^{-1} for $\lambda_i = 5145$ Å. This intensity ratio decreases rapidly with the increase of the carrier density, simultaneously with broadening of the $4J$ peak. (ii) The A_{1g} spectra have a clearly different structure from the B_{1g} spectra and the scattering intensities are half as large as the B_{1g} spectra. The strong A_{1g} spectra are not explained by the known theory of two-magnon scattering, which predicts weak structureless flat spectra in the A_{1g} symmetry.[12]

Singh *et al.*[9] explained the large linewidth of the B_{1g} two-magnon peak in La_2CuO_4 by the $S = \frac{1}{2}$ quantum spin fluctuations and the A_{1g} and B_{2g} spectra by the diagonal-second-neighbor spin-pair excitations permitted by the quantum spin fluctuations. They did not, however, include the $4J$ peak, because their spectra did not show the clear peak, which may be due to a little larger carrier density and the higher measuring temperature than the present experiments. And it should be noted that the A_{1g} spectra in La_2CuO_4 contain lots of multiphonon components. The theoretically estimated second-neighbor exchange energy J_2 is 5–8%,[13,14] so that it is very difficult to explain the large scattering intensity up to $8J$. The high-energy continuum may exist above the magnon dispersion curve. The theoretical work in the two-dimensional $S = \frac{1}{2}$

system has not been done, so that it is difficult to estimate this effect.

If the new $4J$ peaks are assigned to the four-magnon peaks, the high-energy tails up to $8J$ are naturally explained. The energy of the interacting four magnons created on the neighboring four sites on a square is roughly $(4ZS-4)J$, where $Z=4$ is the number of neighboring spins and $S=\frac{1}{2}$. The energy $4J$ is close to the new peak energy. The four magnons created on other sites have larger energy than $5J$. In order to change neighboring four spins on the square, two mechanisms are considered; (a) a single process caused by the four-spin cyclic exchange and (b) multiple processes including twice the two-spin exchanges in the resonant Raman condition. In the case of (b) the scattering intensity is expected to depend strongly on the incident light wavelength. The change of the $4J$ peak intensity in La_2CuO_4 for $\lambda_i=4579$ as compared to 5145 Å is only 1.5 times, which is much less than the six-times ratio for the two-phonon intensity. Moreover the intensity ratio of the new peak to the two-magnon peak is almost constant for the above incident wavelengths. Therefore the mechanism (b) is discarded.

The four-spin cyclic exchange interactions in copper oxides are expected to be large, because the energy difference of the Cu d orbital and the O p orbital is small, ~ 2 eV.[6,7,14] The dominant matrix element of Raman scattering from this process is

$$M_{ijkl}=\sum_{\mu\nu}\frac{\langle\phi_{j\uparrow}\phi_{k\downarrow}\phi_{l\uparrow}\phi_{i\downarrow}|H'_{e\text{-}r}|\phi_{\nu\uparrow}\phi_{k\downarrow}\phi_{l\uparrow}\phi_{i\downarrow}\rangle\langle\phi_{\nu\uparrow}\phi_{k\downarrow}\phi_{l\uparrow}\phi_{i\downarrow}|H'_{4\,\text{spin}}|\phi_{\mu\uparrow}\phi_{j\downarrow}\phi_{k\uparrow}\phi_{l\downarrow}\rangle\langle\phi_{\mu\uparrow}\phi_{j\downarrow}\phi_{k\uparrow}\phi_{l\downarrow}|H'_{e\text{-}r}|\phi_{i\uparrow}\phi_{j\downarrow}\phi_{k\uparrow}\phi_{l\downarrow}\rangle}{(E_\nu+\hbar\omega-\hbar\omega_1)(E_\mu-\hbar\omega_1)}\ .$$

Here $H'_{e\text{-}r}$ is the electron-radiation interaction, $H'_{4\,\text{spin}}$ is the four-spin cyclic exchange interaction, $i\sim l$ are the neighboring Cu atomic sites on a square, ϕ_μ and ϕ_ν are any orbitals of sites i and j, and ω_1 is the incident radiation frequency. The scattering intensities of the four-magnon and the two-magnon peaks are roughly proportional to the square of the four-spin exchange interaction and of the two-spin superexchange interaction, respectively. The scattering intensities of the new $4J$ peaks are roughly 25–40% of the two-magnon peaks in the B_{1g} spectra of Fig. 1. Then the four-spin exchange interactions estimated from the present experiments are roughly 50–60% of J. Of course this estimation is too rough, because the mixing effects of the two- and four-spin exchange interactions and the quantum spin effects are not taken into account. But it is comparable to the recent calculation by Schmidt and Kuramoto that K is 25–67% of J and five to eight times J_2 according to the parameters and the boundary conditions.[14] Thus we conclude that the new peaks are the four-magnon peaks caused by the four-spin cyclic exchange interactions.

In the above discussion it is assumed that the four-spin exchange interactions work directly only in the formation of the four-magnon peaks, but do not essentially alter the magnon states. The four-spin exchange interactions, however, strongly modify the magnon dispersion curves and frustrate the antiferromagnetic orders as observed in the very large linewidths of the two-magnon peaks. The stability of the four-magnon scattering in the doped superconducting cuprates and the definite difference from La_2NiO_4 suggest the importance of the four-spin cyclic exchange interactions for the superconductivity.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture, Japan.

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