RAMAN STUDY OF La2-xBaxCuO4 (x= 0, 0.016) SINGLE CRYSTALS

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RAMAN STUDY OF $La_{2-x}Ba_xCuO_4$ (x= 0, 0.016) SINGLE CRYSTALS

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Abstract. – Raman scattering of $La_{2-x}Ba_xCuO_4$ ($x = 0, 0.016$) single crystals has been measured at various temperatures in the frequency range between 100 and 5000 cm^{-1}. Besides an A_{1g} phonon line at 430 cm^{-1}, the disorder-induced phonon lines and the phonon overtone and combination lines are observed. A two-magnon band observed at $\sim$ 3000 cm^{-1} is also discussed.

Introduction

Recently, neutron scattering studies have revealed that nonsuperconducting La_2CuO_4 is a system with strongly correlated spin fluctuations of a two-dimensional (2D) nature [1]. Lyons *et al.* have reported on the two-magnon Raman scattering in La_2CuO_4 [2] and $YBa_2Cu_3O_x$ [3], and the exchange constants J being $\sim$ 1100 cm^{-1} and $\sim$ 950 cm^{-1}, respectively. The study on the spin fluctuation in the 2D antiferromagnetic CuO_2 planes has become crucial in making clear the mechanism of the superconductivity in high-T_c oxides.

In this paper, we report on a study of the Raman spectra in the frequency range 100 $\sim$ 5000 cm^{-1} for antiferromagnetic $La_{2-x}Ba_xCuO_4$ ($x = 0, 0.016$) and $LaSrFeO_4$.

Experimental

Single crystals of La_2CuO_4 were grown by the top-seeded solution growth method [4], that of $La_{1.984}Ba_{0.016}CuO_4$ by the flux method and that of $LaSrFeO_4$ by the floating zone method. The content of Ba in $(LaBa)_2CuO_4$ crystals was determined by X-ray fluorescence analysis. It is reported that the crystals of La_2CuO_4 have the orthorhombic Pccn structure at room temperature [5] and those of $LaSrFeO_4$ have the K_2NiF_4 type tetragonal I4/mmm structure [6]. The real crystal structure of the above $(LaBa)_2CuO_4$ compounds is orthorhombic, but it can be considered to be pseudo-tetragonal because of its small deviation from the K_2NiF_4 structure. In our pseudo-tetragonal notation, x is parallel to one of the Cu-O-Cu directions, and z is perpendicular to the CuO_2 plane. The La_2CuO_4 sample was an alumina polished (010) platelet and $(LaBa)_2CuO_4$ and $LaSrFeO_4$ samples were (001) platelets with the size of about $4 \times 4 \times 1$ mm^3. The $(LaBa)_2CuO_4$ sample was annealed at 800 °C for 24 hours in O_2 atmosphere.

Raman scattering was measured with excitation wavelengths of 488.0 and 514.5 nm of Ar^+ laser in the back-scattering configuration. A triplemonochromator (Jasco R-750) with a conventional photon counting system (photomultiplier RCA C31034A) was used for the analysis and detection of the scattered light. The Raman spectra in the temperature range 15 $\sim$ 300 K were measured in a closed cycle cryogenic refrigerator (Displex CS-202).

Results and discussion

Figure 1 shows Raman spectra of La_2CuO_4 single crystal at 65 K together with that of antiferromagnetic $LaSrFeO_4$ with Néel emperature T_N=380 K [6]. The frequencies of these peaks in La_2CuO_4 are 480, 725, 940, 1000, 1125, 1190, 1240 and 1440 cm^{-1}, and those in $LaSrFeO_4$ are 230, 320, 475, 620, 710, 970, 1200 and 1500 cm^{-1}.

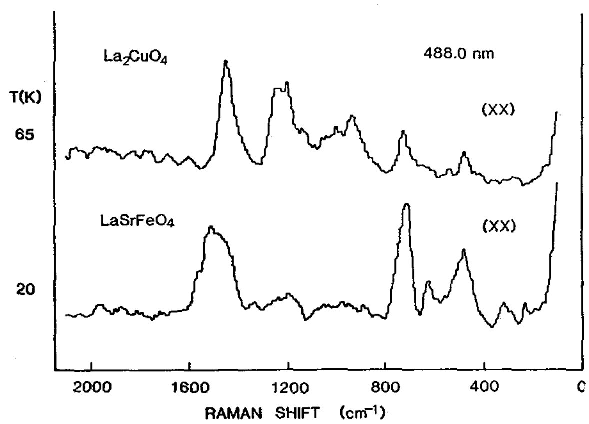

Fig. 1. – Raman spectra of La_2CuO_4 and $LaSrFeO_4$ single crystals at low temperatures in (XX) polarization.

The Raman peaks at 480 and 725 cm^{-1} are generally observed in transition-metal oxides containing heavy atoms such as La, Pb and Bi, and these peaks seem to be due to the excitation of phonons over all the Brillouin zone. In general, Raman active phonon modes are $k \simeq 0$ because of the momentum conservation rule. But it can be ruled out by the breakdown of the translational symmetry in the irregular lattice with imperfections such as oxygen vacancies, dislocations, and impurities. The rather strong 940 and 1440 cm^{-1} peaks are ascribed to the phonon overtone modes of the fundamental 480 and 725 cm^{-1} modes, respectively, and the peaks around 1200 cm^{-1} may be due to the combination mode.

Figure 2 shows Raman spectra of La_2CuO_4 at various temperatures. As seen here, the intensity of all the Raman peaks decreases with increasing temperature. This result contradicts the general tendency that the integrated intensity of Raman lines increases with increasing temperature. It may be due to a resonance Raman effect or an unknown thermal broadening effect which are associated with the lattice modes in the vicinity of crystalline surfaces.

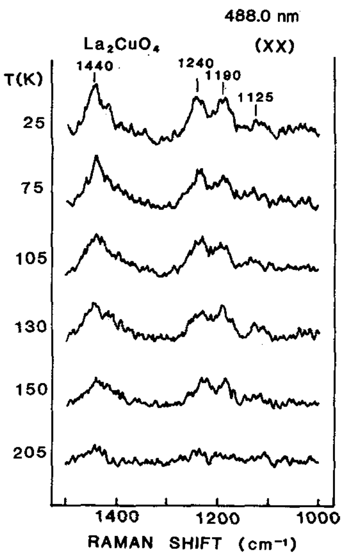

Fig. 2. – Raman spectra of a La_2CuO_4 single crystal at various temperatures in (XX) polarization.

Figure 3 shows Raman spectra of as-grown and O_2−annealed $La_{1.984}Ba_{0.016}CuO_4$ crystals in the frequency range 100 ~ 5000 cm^{-1}. In addition to phonon overtone lines up to 1500 cm^{-1}, there is a broad band at ~ 3000 cm^{-1} in both samples. This band is ascribed to two-magnon excitation in antiferromagnetic spin systems, as reported by Lyons *et al.* [2].

The susceptibility peak which corresponds to the Néel temperature was observed at 130 K for the as-grown $La_{1.984}Ba_{0.016}CuO_4$ sample and was not observed down to 5 K for the O_2−annealed sample in the SQUID magnetization measurements. This means that the three-dimensional (3D) magnetic ordering disappeared by annealing. In figure 3, the annealing effect on the phonon overtone lines is large, however, change in the two-magnon spectrum seems to be not so large. This will be due to the fact that the 2-magnon Raman spectrum reflects predominantly the exchange coupling in the 2D antiferromagnetic spin system of CuO_2 plane, while, T_N is from the 3D magnetic ordering.

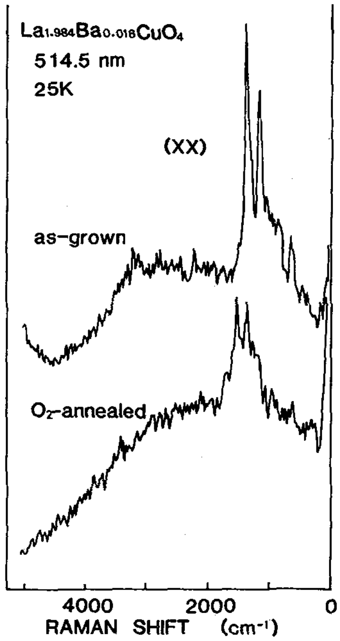

Fig. 3. – Raman spectra of as-grown and O_2−annealed $La_{1.984}Ba_{0.016}CuO_4$ single crystals in (XX) polarization.

In relation to the mechanisms of high-T_c superconductivity in copper oxides, it is pointed out that the fluctuation of spin singlet states in $s = 1/2$ 2D Heisenberg system plays an important role [1]. Further studies on the dynamical properties of magnetism in the 2D Heisenberg systems may be necessary to clarify the role of the exchange coupling in the formation of superconducting Cooper pairs.

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