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Magnons and phonons in Nd_2CuO_4

Shunji Sugai
Department of Physics, Faculty of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560, Japan

Tamaki Kobayashi and Jun Akimitsu
Department of Physics, Aoyama-Gakuin University, 6-16-1 Chitosedai, Setagaya, Tokyo 157, Japan
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Antiferromagnetic magnons in Nd_2CuO_4, which is the mother material of the electron superconductor $(Nd_{1-x}Ce_x)_2CuO_{4-y}$, are observed by Raman scattering. The effective exchange integral estimated from the two-magnon peak energy is 1070 cm^{-1}, which is unexpectedly large in spite of the large Cu-Cu atomic distance compared with those in other superconducting oxides. Lattice vibrations are also investigated. A large two-phonon peak due to the intralayer breathing mode is observed at 1178 cm^{-1}.

The common properties of high-temperature superconducting oxides have been that (1) the carriers for the superconductivity are holes, and (2) the basic structures are CuO_6 octahedra and CuO_5 pyramids. Very recently Tokura, Takagi, and Uchida[1] discovered a superconductor $(L_{1-x}Ce_x)_2CuO_{4-y}$ (L = Nd, Pr, and Sm) in which carriers are electrons.[2] This material has no structural component of octahedron or pyramid. In the case of holes, they enter oxygen sites on CuO_2 planes or at apexes of CuO_5 pyramids, and the spin interaction with Cu^{2+} d^9 electrons is considered as the origin of the superconductivity in many models. If carriers are electrons, they enter the 4s band or the upper-Hubbard band. The spin interaction between itinerant electrons and Cu d electrons is very different from the case of holes; therefore, most theories are subjected to crucial influence. This Raman scattering experiment was done to investigate the magnetic properties of Nd_2CuO_4 which is the mother material of electron-superconductor $(Nd_{1-x}Ce_x)_2CuO_{4-y}$. The lattice vibrations are also presented.

Samples used in this experiment are single crystals grown by a flux method at the surfaces of molten sources in crucibles. Raman scattering is made by a single-channel photon counting method equipped with a double-monochromator (Spex 1400) and an Ar-ion laser (Spectra Physics 164). The laser beam of $\approx$50–100 mW was focused on the area of 30×500 μm^2 of the sample surface using a cylindrical lens.

Figure 1 shows the Raman spectra measured with a 5145-Å laser beam at 30 and 273 K. The notation of the polarization configuration $(x, x+y)$ indicates that the incident light is polarized along the x axis but the scattered light is not analyzed. However, the instrumental efficiency of the x component is about four times larger than the y component for the polarization analysis of the scattered light in this experimental condition; therefore, the spectra show effectively the (x,x) polarization component. The 2890-cm^1 peak at 30 K is the two-magnon scattering peak. At 273 K the peak energy decreases to 2810 cm^{-1}, but the intensity is almost the same. This magnon is supposed to be a spin fluctuation of the local antiferromagnetic spin order on the two-dimensional CuO_2 layers as in the case of $(La_{1-x}Sr_x)_2CuO_4$, $YBa_2Cu_3O_{7-y}$, and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+y}$.[3–8] The scattering intensity of the two-magnon peak in Nd_2CuO_4 compared with phonon peaks is much larger than in the insulating phases of other superconducting materials. It suggests that the electron-magnon interaction in the Raman process of this material is larger than that in other materials.

The effective exchange interaction $J^* = 1070$ cm^{-1} at 30 K is compared with other superconducting materials: 1200 cm^{-1} in La_2CuO_4 (Cu-Cu distance is about 3.81 Å),[5–7,9] 1140 cm^{-1} in $Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{8+y}$ (3.84 Å),[10] and 1010 cm^{-1} in $YBa_2Cu_3O_{6.3}$ (3.86 Å).[4,6,8,9] The Cu-Cu distance in Nd_2CuO_4 is 3.95 Å.[11] If J^* depends only on the Cu-Cu distance, the expected J^* is smaller than in $YBa_2Cu_3O_{7-y}$ contrary to the experimental results. This may be related with the crystal structure of Nd_2CuO_4 which has no oxygen atoms above and below Cu atoms. This suggests that the exchange interaction is affected by the hybridization between Cu 3d electrons and O 2p electrons at the sites deviated from CuO_2 planes in the CuO_6 octahedron or CuO_5 pyramid structures.

The peaks at 1178 cm^{-1} in the 30-K spectra (1158 cm^{-1} at 273 K) is due to the two-phonon scattering of an intralayer breathing mode of oxygen atoms. Peaks below 700 cm^{-1} are mainly single-phonon peaks.

Figure 2 shows the incident wavelength dependence of the Raman spectra. With the excitation of 4579 Å the intensity of the two-phonon peak decreases, but the intensities of the two-magnon and single-phonon peaks are almost the same, which is different from the case of $(La_{1-x}Sr_x)_2CuO_4$ and $YBa_2Cu_3O_{7-y}$.[7,9] This indicates that the electronic levels of Nd_2CuO_4 related to the resonant scattering have different interactions with magnons from other materials.

The crystal structure of Nd_2CuO_4 is tetragonal $I4/mmm$ (D_{4h}^{17}) (Ref. 11) and includes one molecular unit per primitive cell as shown in Fig. 3. The translational vectors are $[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$, $[\frac{1}{2},-\frac{1}{2},\frac{1}{2}]$, and $[-\frac{1}{2},\frac{1}{2},\frac{1}{2}]$. The normal modes are $A_{1g}+E_g+A_{2u}+E_u$ from the vibration of two Nd atoms, $A_{2u}+E_u$ from a Cu atom, $A_{2u}+B_{2u}+2E_u$ from two O atoms on the CuO_2 layer,

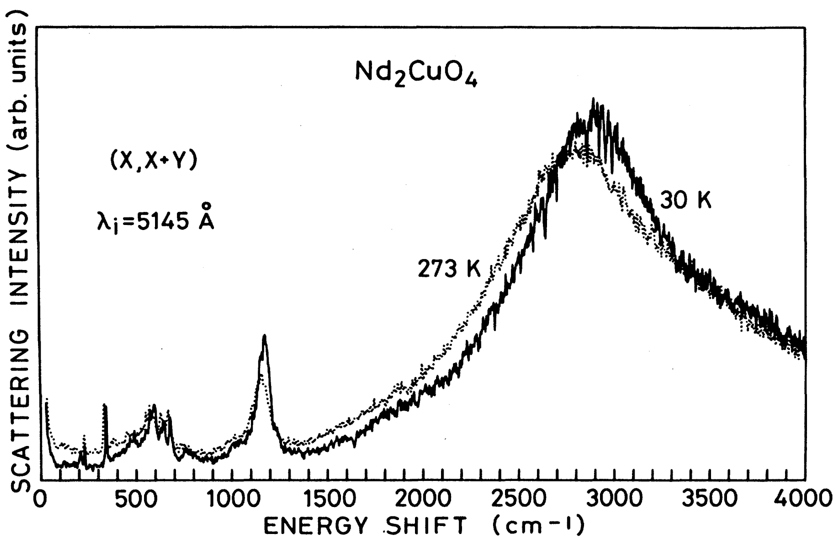

FIG. 1. (x,x) Raman spectra of Nd_2CuO_4 at 30 K (curve) and 273 K (dots) measured with the incident light of 5145 Å.

and $B_{1g}+E_g+A_{2u}+E_u$ from two O atoms at the outside of the layer. The A_{1g}, B_{1g}, and E_g modes are Raman active and the A_{2u} and E_u modes are infrared active. Figures 3(a)–3(d) show the atomic displacements of the Raman-active modes. Figure 3(e) shows the intralayer breathing mode which has strong electron-phonon interaction.

Figure 4 shows polarized Raman spectra of Nd_2CuO_4 at 30 K excited with a 5145-Å beam. The mode assignments were made by comparing with similar modes in other high-T_c superconducting oxides.[12–15] The 230-cm^{-1} mode observed in the (x,x) and (z,z) spectra is assigned to the A_{1g} mode of Nd(1,2) atoms [Fig. 3(a)]. The 344-cm^{-1} mode in the (x,x) spectra is assigned to the B_{1g} mode of O(3,4) atoms [Fig. 3(c)], which disappears in the (x',x') polarization configuration and is observed in (x',y') with strength nearly equal to that in (x,x), where x' and y' are [1,1,0] and [1,−1,0], respectively. The 494-cm^{-1} mode in the (x,z) spectra is assigned to the E_g mode of O(3,4) atoms [Fig. 3(d)]. The last E_g mode of Nd atoms is expected in the (x,z) spectra, but the 231-cm^{-1} mode observed in this polarization configuration is probably the A_{1g} mode which appeared by small misorientation of the sample. The 209-cm^{-1} peak observed in the (x,x) spectra at 30 K with B_{1g} symmetry becomes broad and merges into the background at 273 K.

The scattering observed at 400∼700 cm^{-1} in the (x,x) spectra and at about 589 cm^{-1} in the (x,y) spectra is mainly single-phonon scattering activated by the anharmonic oscillation due to the strong electron-phonon and

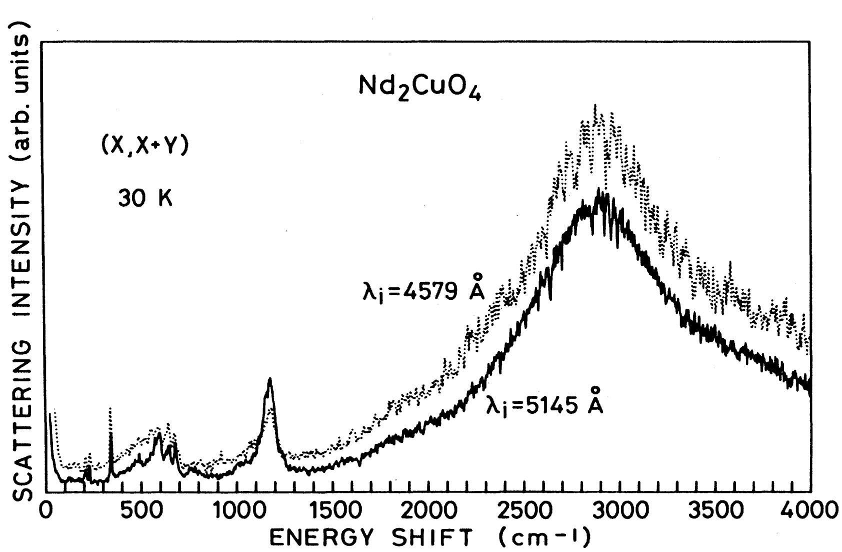

FIG. 2. (x,x) Raman spectra of Nd_2CuO_4 at 30 K with the excitations of 5145 Å (curve) and 4579 Å (dots).

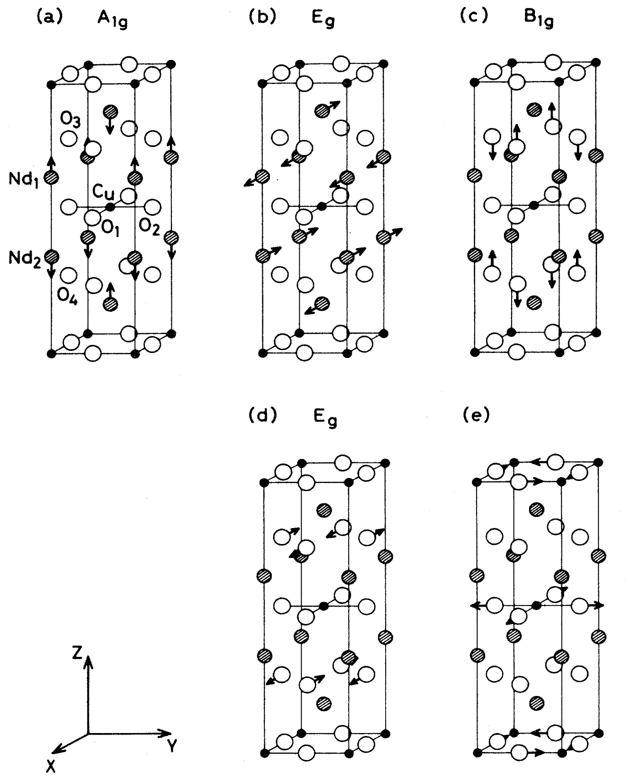

FIG. 3. Atomic displacements of the even-parity normal modes: (a) the A_{1g} mode of Nd(1,2) atoms, (b) E_g of Nd(1,2), (c) B_{1g} of O(3,4), (d) E_g of O(3,4), and (e) the intralayer breathing mode of O(1,2).

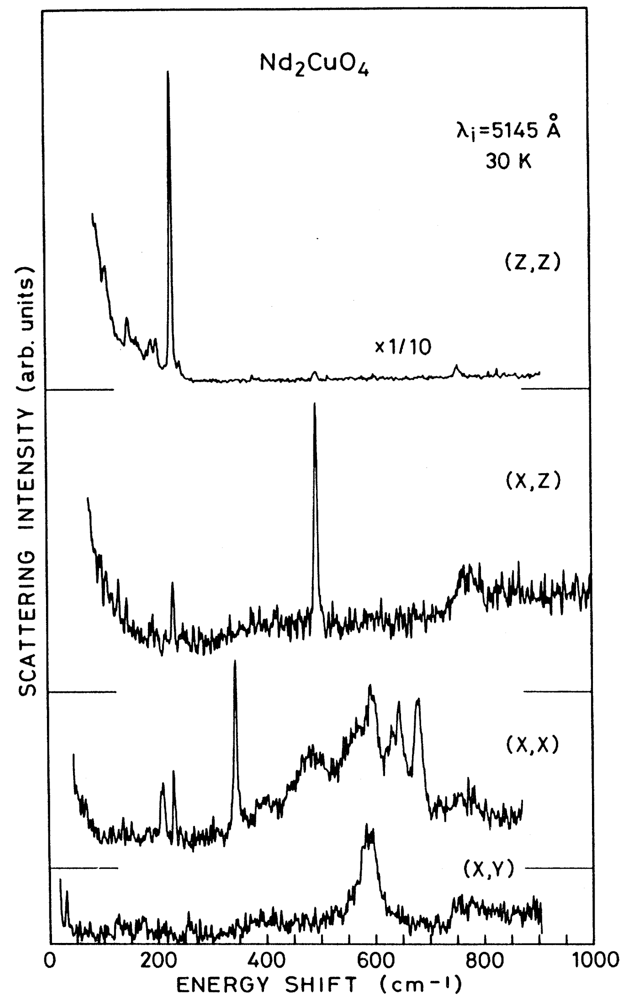

FIG. 4. Raman spectra of Nd_2CuO_4 at 30 K with the excitation of 5145-Å light. Allowed symmetries are A_{1g} and B_{1g} in the (x,x) spectra, B_{2g} in (x,y), A_{1g} in (z,z), and E_g in (z,x).

magnon-phonon interactions, or imperfection of the crystals. For this crystal structure the vibrations of O(1,2) atoms on the CuO_2 layers give only odd-parity modes which are Raman inactive. However, the strong electron-phonon interaction gives rise to the two-phonon scattering of the intralayer breathing mode [Fig. 3(e)] as observed at 1178 cm^{-1} at 30 K. The intralayer breathing-mode energy 589 cm^{-1} is comparable with the three-dimensional breathing-mode energy 560 cm^{-1} in $BaBiO_3$,[16] but smaller than the breathing-mode energies in other superconducting materials; 716 cm^{-1} in La_2CuO_4, 650 cm^{-1} in $YBa_2Cu_3O_{6.3}$, and 677 cm^{-1} in $Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{8+y}$.

In conclusion, the existence of antiferromagnetic magnons in Nd_2CuO_4 is confirmed by two-magnon Raman scattering. The strong scattering intensity and the different resonant Raman effect from other high-temperature superconductors suggest the difference of the electronic levels and the electron-magnon interaction in this material.

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