

## Raman effect in $\text{Nd}_2\text{CuO}_{4-x}$ single crystals

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The Raman spectra of  $\text{Nd}_2\text{CuO}_{4-x}$  single crystals have been measured. The lines in the spectra are classified on the basis of a symmetry analysis of the phonon modes at the  $\Gamma$  point in the Brillouin zone, a comparison of the masses of the vibrating ions, and a comparison with the vibrations in high- $T_c$  superconductors which have been studied previously. A two-magnon scattering light is observed.

Crystals of  $\text{Nd}_2\text{CuO}_{4-x}$  are the starting point for the production of new electron superconductors  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  with  $T_c = 24$  K (Refs. 1 and 2). The phonon spectra of these crystals (for both the original phase and the superconducting phase) and the changes which occur in these spectra in the conversion from nonsuperconducting  $\text{Nd}_2\text{CuO}_4$  to superconducting  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  deserve study. This letter reports a study of the Raman effect in nonsuperconducting  $\text{Nd}_2\text{CuO}_{4-x}$ .

The  $\text{Nd}_2\text{CuO}_{4-x}$  crystals were grown by slow cooling in a platinum crucible in air. The crystals were platelets with dimensions up to  $4 \times 4 \times 1$  mm with a mirror-finish basal plane. The symmetry of the single crystals was monitored by  $x$ -ray diffraction:  $D_{4h}^{17}$  ( $I4/mmm$ ),  $a = 3.954 \text{ \AA}$ ,  $c = 12.143 \text{ \AA}$ .

Raman spectra were recorded for various faces of the crystals in a backscattering geometry on a triple spectrometer with a microscope attachment (Microdil-28) at room temperature. The beam from an  $\text{Ar}^+$  laser ( $\lambda = 4880 \text{ \AA}$ ,  $5140 \text{ \AA}$ ) was focused on the sample in a spot  $< 3 \mu\text{m}$  in size. The power of the laser beam at the sample was kept below a fraction of a milliwatt to avoid a heating of the illuminated region.

The  $\text{Nd}_2\text{CuO}_4$  crystal has a body-centered tetragonal structure with two formula units per unit cell<sup>1,2</sup> (Fig. 1). The primitive cell in these crystals is half as large and contains a single formula unit. The number of phonon branches is set by the number of atoms in the primitive cell, so for  $\text{Nd}_2\text{CuO}_4$  it is 21:  $A_{1g} + B_{1g} + 2E_g + 4A_{2u} + B_{2u} + 5E_u$ , where  $g$  and  $u$  are respectively even and odd vibrations. Since the  $\text{Nd}_2\text{CuO}_4$  structure is centrally symmetric, only even vibrations are active in the Raman scattering, and only odd ones in the IR scattering, according to the alternate prohibition rule. The Nd ions with a positional symmetry  $C_{4v}$  (Fig. 1) are responsible for the vibrations  $A_{1g} + E_g + A_{2u} + E_u$ , while the O2 ions, in positions of  $D_{2d}$  symmetry, are responsible for the vibrations  $B_{1g} + E_g + A_{2u} + E_u$ . The  $A_{1g}$  and  $E_g$  vibrations of Nd ions and the  $B_{1g}$  and  $E_g$  vibrations of O2 ions are active in the Raman spectrum. The vibrations of the other ions are odd and are not active in the Raman scattering for a high-quality crystal. Consequently, a single vibration ( $A_{1g}$ ) is allowed in the  $zz$  polarized spectrum, while two ( $A_{1g}$  and  $B_{1g}$ ) are allowed in the  $xx$  and  $yy$  polarized spectra. Two  $E_g$  vibrations should be manifested in the  $zx$ ,  $zy$ ,  $xz$ , and  $yz$  depolarized spectra.

Figures 2 and 3 show experimental Raman spectra of  $\text{Nd}_2\text{CuO}_{4-x}$  single crystals.

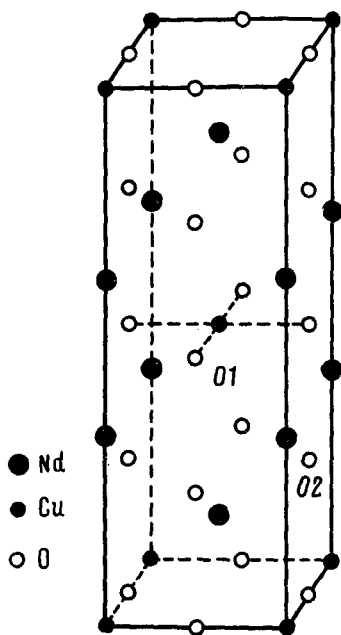


FIG. 1. Unit cell of  $\text{Nd}_2\text{CuO}_4$ .

There are four obvious lines at 220, 336, 485, and  $625\text{ cm}^{-1}$ ; in addition, there is a broad feature with a maximum near  $3000\text{ cm}^{-1}$  (Fig. 3). The integral intensity of the lines in the  $zz$  polarization is about four times that in the  $xx$  polarization. When the laser beam is scanned over the surface of the sample, we observe a difference of 3–4  $\text{cm}^{-1}$  in the frequencies of the Raman lines.

It can be seen from a comparison of the polarized and depolarized spectra that there is only a single  $A_{1g}$  line here ( $220\text{ cm}^{-1}$ ). Since only vibrations of Nd ions are active in this polarization, the sole line in the  $zz$  polarization, with a frequency of  $220\text{ cm}^{-1}$ , should be classified as an  $A_{1g}$  vibration of Nd.

In the  $xx$  polarization, the line at  $220\text{ cm}^{-1}$  is accompanied by another, at  $336\text{ cm}^{-1}$ . This line persists in the spectrum of  $x'y'$  polarization (the  $x'$  and  $y'$  axes are rotated  $45^\circ$  from the  $x$  and  $y$  axes) [Fig. 2(b)]. This line thus has  $B_{1g}$  symmetry and should be attributed to  $B_{1g}$  vibrations of O2 oxygen ions. In the  $zx(z\gamma)$  depolarized spectrum we see a single line, at  $485\text{ cm}^{-1}$ . In this polarization,  $E_g$  vibrations of Nd and O2 ions are allowed. Since the vibrations with respect to the heavier Nd ions should be expected in the region  $< 300\text{ cm}^{-1}$ , the line at  $485\text{ cm}^{-1}$  should be attributed to  $E_g$  vibrations of O2 oxygen ions. This assignment agrees with the vibration frequencies of oxygen in other high- $T_c$  superconductors.<sup>3-7</sup> We have not been able to detect  $E_g$  vibrations of Nd ions in the  $zx$  spectrum in the low-frequency region.

A characteristic difference between the Raman spectra of the  $\text{Nd}_2\text{CuO}_{4-x}$  crystals and those of the high- $T_c$  superconductors based on rare-earth, bismuth, and thallium cuprates<sup>3-7</sup> is the presence of an intense Raman line corresponding to  $E_g$  vibrations. This result may be a consequence of a pronounced warping of the Nd-O2 layer.

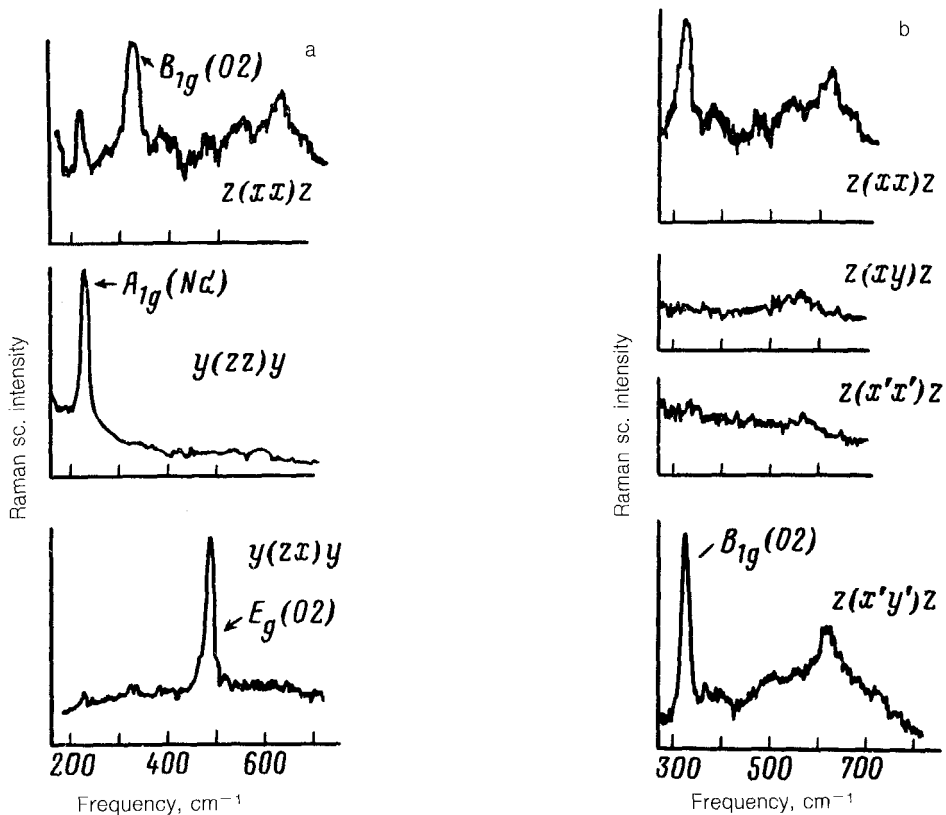


FIG. 2. a—Polarized and depolarized Raman spectra of an  $\text{Nd}_2\text{CuO}_{4-x}$  single crystal; b—polarized and depolarized Raman spectra of an  $\text{Nd}_2\text{CuO}_{4-x}$  single crystal when the coordinate system is rotated  $45^\circ$ .

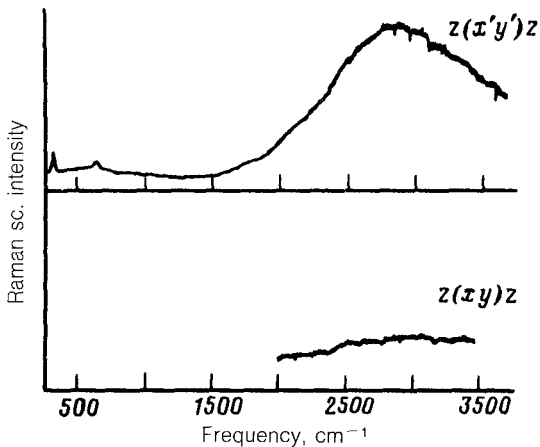


FIG. 3. Raman spectrum of  $\text{Nd}_2\text{CuO}_{4-x}$  in the high-frequency region.

The reasons for the Raman activity of off-diagonal phonon modes were analyzed in detail in Ref. 7.

In the  $xx$  and  $x'y'$  polarized spectra we see a weak line at  $625\text{ cm}^{-1}$  [Fig. 2(b)]. This line is probably due to defects, but we do not rule out the possibility that it appears in the spectra as a result of two-phonon scattering. A study of the temperature dependence of the intensity of this line would resolve the question.

Also noteworthy is the broad feature observed in the high-frequency region. It has a high intensity in the  $x'y'$  polarization and a considerably lower intensity in the  $x'x'$  polarization (Fig. 3). A similar effect has been seen previously in insulating crystals ( $\text{La}_2\text{CuO}_4$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_6$ ,  $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ ).<sup>8-10</sup> In our case the excitation in the high-energy part of the spectrum has the symmetry and energy of a two-magnon excitation in the  $\text{CuO}_2$  plane. The value estimated for the exchange integral  $J$  from the relation  $\omega_{2m} = 2.7J$  for  $\text{Nd}_2\text{CuO}_{4-x}$  is  $\approx 1100\text{ cm}^{-1}$ .

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<sup>6</sup>K. F. McCarty *et al.*, *Phys. C* **157**, 135 (1989).

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<sup>8</sup>K. B. Lyons *et al.*, *Phys. Rev. B* **37**, 2353 (1988).

<sup>9</sup>K. B. Lyons *et al.*, *Phys. Rev. B* **39**, 9693 (1989).

<sup>10</sup>K. F. McCarty *et al.*, *Phys. C* **157**, 135 (1989).

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