

# Crystal-field-excitation-phonon coupling in $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$

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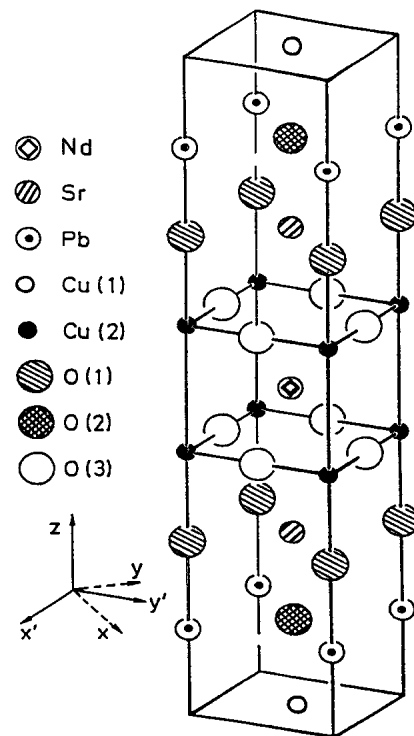
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We have observed a double-peak structure around  $300\text{ cm}^{-1}$  in the Raman spectrum of  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  single crystals. Polarization-dependent measurements show clearly the  $B_{1g}$  symmetry character of both peaks. Their dependence on temperature, isotopic substitution, and polarization can be interpreted by postulating a coupling between a crystal-field (CF) excitation of the  $\text{Nd}^{3+}$   $4f$  electrons and the  $B_{1g}$  phonon mode. We have fitted the spectra obtained at different temperatures in  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  single crystals, and also earlier observations in  $\text{NdBa}_2\text{Cu}_3\text{O}_7$ , with a theoretical model taking the occupation of CF excitations and phonons into account. From these fits we derive the CF-excitation-phonon coupling constant  $V$  for the two materials, the unperturbed energies of the phonon  $\omega_{\text{Ph}}$  and the CF excitation  $\omega_{\text{CF}}$ , and a parameter  $\kappa$ , which accounts for the temperature dependence of  $V$ . For  $\text{NdBa}_2\text{Cu}_3\text{O}_7$  the data reveal a self-energy anomaly of the  $B_{1g}$  mode near  $T_c$ . We have also estimated the coupling constant  $V$  for  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_8$  using experimental CF parameters from  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  and structural information of  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_8$ . We find  $|V| = 21.7\text{ cm}^{-1}$ , in good agreement with the experimental value of  $(23 \pm 3)\text{ cm}^{-1}$  at 10 K.

## I. INTRODUCTION

Raman scattering has been used in the high- $T_c$  materials to study phonons, the electronic continuum, and, more recently, crystal-field (CF) excitations. Heyen *et al.*<sup>1</sup> reported measurements on  $\text{NdBa}_2\text{Cu}_3\text{O}_7$  samples, where they observed an additional peak of  $B_{1g}$  symmetry around  $300\text{ cm}^{-1}$ . A similar feature near  $290\text{ cm}^{-1}$  was observed before by Yoshida *et al.*<sup>2</sup> in the same material. They attributed this feature to the O(2)-O(3)  $A_g$  in-phase motion. Heyen *et al.*,<sup>1</sup> however, attributed conclusively the double-peak structure to the coupling of the  $B_{1g}$  O(2)-O(3) out-of-phase phonon with a nearby CF excitation of the  $\text{Nd}^{3+}$  ions via electron-phonon interaction. Direct Raman scattering by excitations between crystal-field levels (i.e., without coupling to phonons) has recently been found in  $\text{Nd}_2\text{CuO}_4$ .<sup>3</sup> A coupling of CF excitations to phonons is expected to be observable in other high- $T_c$  compounds and related materials when CF excitations of the rare-earth ions lie close in energy to phonons of the same symmetry. Here we report our measurements on insulating  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  single crystals, a material with a crystal structure (Fig. 1) rather similar to that of  $\text{NdBa}_2\text{Cu}_3\text{O}_7$ , showing a peak of  $B_{1g}$  symmetry around  $335\text{ cm}^{-1}$ , which does not have pure phonon character. This paper is structured as follows. In Sec. II we show the spectra of a  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  single crystal for different polarization geometries, oxygen isotopes, and temperatures. In Sec. III we present theoretical considerations on the CF splitting of the elec-



Unit cell of  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_8$

FIG. 1. Unit cell of  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  (Ref. 6). Note that the  $x, y$  orthorhombic axes are rotated around  $z$  by  $45^\circ$  with respect to the orthorhombic axes of the homologous  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure.

tronic ground state of the  $4f$  electrons. Section IV contains a short description of the theoretical model used to interpret the data and the discussion of our results. Conclusions are drawn in Sec. V.

## II. EXPERIMENTAL RESULTS

Single crystals of  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  were grown with the  $\text{PbO-NaCl}$  flux method described previously.<sup>4</sup> Surface-polished small crystals, about  $1 \times 1 \times 0.25$  mm<sup>3</sup> large, were measured with a Raman setup using the 514.5 nm line of an  $\text{Ar}^+$  ion laser. The scattered light was dispersed with a DILOR XY spectrometer and recorded with a liquid-nitrogen cooled charge-coupled-device (CCD) detector. For isotopic replacement of  $^{16}\text{O}$  by  $^{18}\text{O}$  a powder of as-grown tiny crystals was first heated up to 530 °C in vacuum and then kept for 100 h in 48 mbar of  $^{18}\text{O}$  at the same temperature. The oxygen substitution treatment replaced 35%  $^{16}\text{O}$  by  $^{18}\text{O}$  in the  $\text{CuO}_2$  planes.

Figure 2 shows 10 K spectra for different polarization geometries given in Porto's notation  $i(jk)l$ , where  $i$ ,  $l$  denote the direction of the incident and scattered photons and  $j$ ,  $k$  their polarization, respectively. The upper spectrum corresponds to the orthorhombic  $B_{1g}$  symmetry and shows three distinct peaks at 228, 275, and 335  $\text{cm}^{-1}$ . The pure phonon of  $B_{1g}$  symmetry in this compound is expected at around 280  $\text{cm}^{-1}$  as known from a systematic study of its frequency for various rare-earth atoms in place of Nd.<sup>5</sup>

Due to the coupling between the CF excitations of the  $\text{Nd}^{3+}$  ions and the  $B_{1g}$  out-of-phase oxygen vibration in

the  $\text{CuO}_2$  planes, there is a second  $B_{1g}$  symmetry peak at 335  $\text{cm}^{-1}$ , similar to the case of  $\text{NdBa}_2\text{Cu}_3\text{O}_7$ .<sup>1</sup> The other  $A_g$  phonons at 90, 146, 252, 428, 482, and 577  $\text{cm}^{-1}$  have been assigned previously<sup>6</sup> to the  $\text{Pb-Sr-Cu(2)-O(1)}$ ,  $\text{Cu(2) in-phase}$ ,  $\text{Sr-O(3) in-phase}$ ,  $\text{O(3) in-phase}$ ,  $\text{O(1) in-phase}$ , and  $\text{O(2) in-phase}$  modes, respectively. The assignment which was made in Ref. 7 based on lattice dynamical calculations for the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  compound, since calculations for  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  were not yet available at that time, and therefore differs slightly from the assignment given here. The origin of the peaks at 184 and 200  $\text{cm}^{-1}$ , which become strongly resonant at laser energies around 2.6 eV Ref. 6 is unclear; they are not expected for the ideal structure.<sup>7</sup> In recent infrared measurements performed on the same sample two of the infrared active LO phonons ( $E_u$  symmetry) were found at 181 and 198.5  $\text{cm}^{-1}$  ( $T = 80$  K).<sup>8</sup> We conjecture that these modes might become observable in Raman scattering due to Fröhlich interaction.<sup>9</sup> We find that the relative intensities of the two peaks are also in agreement with the ratio of the oscillator strengths determined from the infrared spectra.<sup>8</sup> The peak of  $B_{1g}$  symmetry at 228  $\text{cm}^{-1}$ , which was observed previously,<sup>6</sup> cannot be assigned to phonons expected for the ideal structure. With increasing temperature the two dominant  $B_{1g}$  peaks move together and the intensity of the more CF-like peak at around 335  $\text{cm}^{-1}$  decreases (Fig. 3). It can be fitted as a separate peak only up to 80 K.

In the isotopically substituted sample the frequency of the  $B_{1g}$  phonon at  $T = 300$  K is lowered by  $6 \pm 1$   $\text{cm}^{-1}$ , i.e.,  $(2.08 \pm 0.35)\%$ . Assuming a dependence of this frequency like the inverse square root of the mass,  $\omega_{B_{1g}}(^{16}\text{O})/\omega_{B_{1g}}(^{18}\text{O}) = \sqrt{18/16}$ , the observed shift suggests

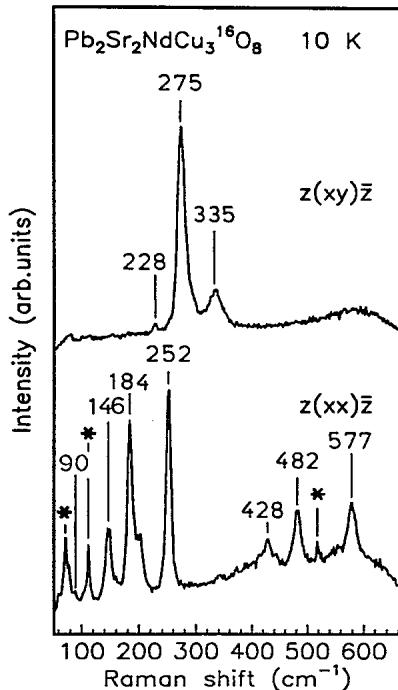


FIG. 2. Polarized Raman spectra at 10 K of a  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3^{16}\text{O}_{8+\delta}$  single crystal. The features marked by asterisks denote laser plasma lines.

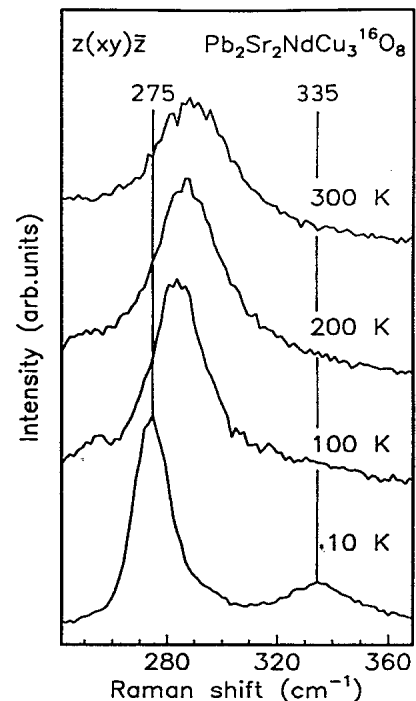


FIG. 3. Temperature dependence of the  $B_{1g}$  double-peak structure.

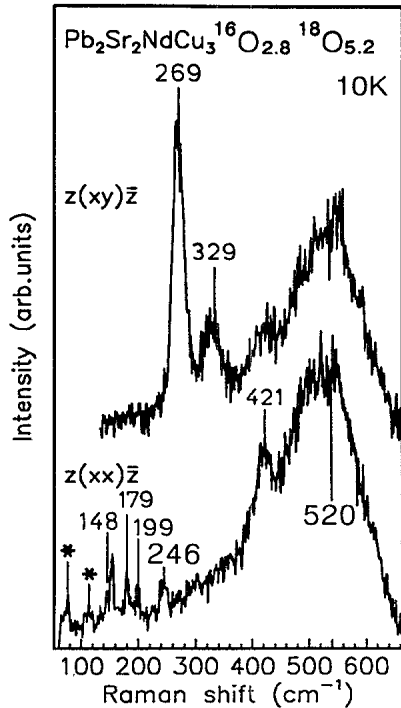


FIG. 4. Polarized Raman spectra at 10 K of a  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  single crystal. The features marked by asterisks denote laser plasma lines.

( $35 \pm 5$ )% replacement of  $^{16}\text{O}$  by  $^{18}\text{O}$  in the  $\text{CuO}_2$  planes. Figure 4 shows the  $A_g$  and  $B_{1g}$  spectra of the sample with partially replaced oxygen at 10 K. In the  $A_g$  spectrum the Sr-O(3) in-phase mode frequency is shifted considerably down in frequency, by about 2.8%, with respect to the  $^{16}\text{O}$  spectrum, which is an indication for a signif-

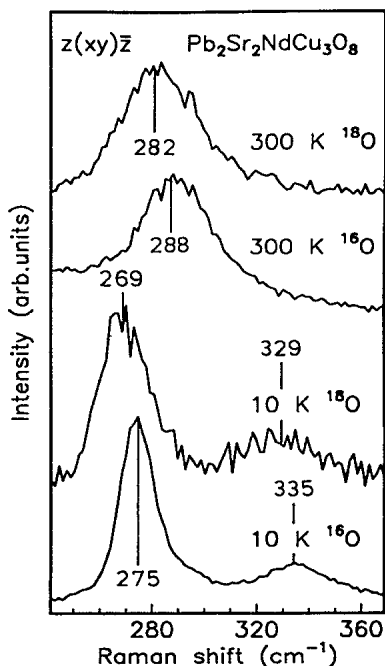


FIG. 5. Behavior of the  $B_{1g}$  double-peak structure under oxygen substitution at 10 and 300 K.

icant participation of oxygen atoms in this vibration, in contrast to the assignment of Ref. 7. Also the O(3) in-phase mode ( $421 \text{ cm}^{-1}$ ) shows an isotopic shift of about 1.6%. The unassigned peak around  $153 \text{ cm}^{-1}$  might be disorder induced. We attribute the broad hump around  $520 \text{ cm}^{-1}$  to disorder-induced scattering by the density of vibrational states of oxygen. Both components of the  $B_{1g}$  doublet are shifted towards lower frequencies also by about  $6 \text{ cm}^{-1}$  as compared to the  $^{16}\text{O}$  case (Fig. 5).

In order to determine accurately the temperature dependence of the coupling constant in  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  and  $\text{NdBa}_2\text{Cu}_3\text{O}_7$ , we carried out measurements on single crystals with 3 mW laser power in a point focus of  $30 \mu\text{m}$  diameter on the sample. We verified that under these conditions laser heating of the sample does not play a role.

### III. CRYSTAL-FIELD SPLITTING OF THE $\text{Nd}^{3+}$ ELECTRONIC GROUND STATE IN $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$

The electronic states of rare-earth atoms are described by Russell-Saunders terms  $^{2S+1}L_J$ , where  $L$ ,  $S$ , and  $J$  are the quantum numbers of the total orbital angular momentum  $\mathbf{L} = \sum_i \mathbf{l}_i$ , spin  $\mathbf{S} = \sum_i \mathbf{s}_i$ , and the resulting total angular momentum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$  of the  $4f$  electrons. Each term is  $(2J + 1)$ -fold degenerate. According to Hund's rules the ground state of the  $\text{Nd}^{3+}$  ion, which contains three electrons in its  $4f$  shell, is  $^4I_{9/2}$ . In crystal fields of different symmetries this state splits up according to Fig. 6 (taken from Ref. 1). In cubic ( $O_h$ ) symmetry there are two  $\Gamma_8^-$  quartets and a  $\Gamma_6^-$  Kramers doublet.<sup>10</sup> Further reduction of the symmetry splits the quartets into Kramers doublets of two different symmetries  $M_6^-$ ,  $M_7^-$  in tetragonal  $D_{4h}$  and only one symmetry  $M_6^-$  in the orthorhombic  $D_{2h}$  point group symmetry. Depending on the oxygen content, the  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  compounds have tetragonal or orthorhombic crystal structure<sup>11</sup> as is the case for  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  and  $\text{NdBa}_2\text{Cu}_3\text{O}_7$ , respectively. Hence the CF excitations should have the same symmetry properties in both compounds. As it was

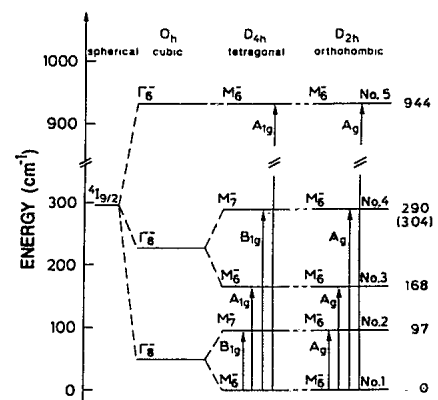


FIG. 6. Energy levels of  $\text{Nd}^{3+}$  in crystal fields of different symmetries. The energies on the right side of the levels are from neutron-scattering data (Ref. 20).

shown by Heyen *et al.*<sup>1</sup> the group-theoretical analysis of the CF excitations yields for  $D_{4h}$  the following single group symmetries:

$$M_6^- \times M_6^- = M_7^- \times M_7^- = A_{1g} + A_{2g} + E_g, \quad (1a)$$

$$M_6^- \times M_7^- = M_7^- \times M_6^- = B_{1g} + B_{2g} + E_g,$$

and for  $D_{2h}$ :

$$M_6^- \times M_6^- = A_g + B_{1g} + B_{2g} + B_{3g}. \quad (1b)$$

There have been no neutron-scattering investigations of the energies of CF excitations for  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  compounds. However, they should not differ too much from those in  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds, because the strongest contribution to the CF at the  $\text{Nd}^{3+}$  site is due to the nearest-neighbor oxygen atoms of the  $\text{CuO}_2$  planes and their positions are quite similar in both compounds.

#### IV. DISCUSSION

Two elementary excitations having the same symmetry and nearly the same energy can couple, leading to a renormalization of their energies and linewidths. This is the case for the  $B_{1g}$  phonon and CF excitation with the corresponding symmetry between the levels 1 and 4 in Fig. 6. The Hamiltonian for the coupled system in second-quantized notation may be written as

$$H = H_0 + H_1,$$

$$H_0 = \hbar\omega_{\text{Ph}}(a^\dagger + \frac{1}{2}) + \sum_{l=1,4;m} \hbar\omega_{\text{CF}}(l)c_{lm}c_{lm}^\dagger, \quad (2)$$

$$H_1 = V \sum_{m'n} (a + a^\dagger)(c_{1,m}c_{4,m'}^\dagger + c_{1,m}^\dagger c_{4,m'}),$$

where  $\hbar\omega_{\text{Ph}}$ ,  $\hbar\omega_{\text{CF}}$  are the phonon- and CF-excitation energies,  $l, m$  are the indices of the CF levels and their Kramers degeneracy, and  $V$  is the coupling constant between the phonon and the CF excitation.<sup>1</sup> At low temperatures the above equations decouple into a  $2 \times 2$  problem with the eigenenergies<sup>12</sup>

$$E_{1,2} = \frac{\hbar(\omega_{\text{Ph}} + \omega_{\text{CF}})}{2} \pm \sqrt{\left(\frac{\hbar(\omega_{\text{Ph}} - \omega_{\text{CF}})}{2}\right)^2 + V^2}. \quad (3)$$

Using the renormalized energies and the intensity ratio of the two peaks we derive from the  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  spectra at  $T = 10$  K the following values for the unrenormalized frequencies of the  $B_{1g}$  phonon  $\omega_{\text{Ph}}$ , the CF excitation  $\omega_{\text{CF}}$ , and the coupling constant  $V$  for the  $^{16}\text{O}$  case:

$$\begin{aligned} \omega_{\text{Ph}}(^{16}\text{O}) &= 287 \pm 3 \text{ cm}^{-1}, \\ \omega_{\text{CF}} &= 329 \pm 3 \text{ cm}^{-1}, \\ V &= 23 \pm 3 \text{ cm}^{-1}. \end{aligned} \quad (4a)$$

For the  $^{18}\text{O}$  case we obtain

$$\begin{aligned} \omega_{\text{Ph}}(^{18}\text{O}) &= 282 \pm 3 \text{ cm}^{-1}, \\ \omega_{\text{CF}} &= 315 \pm 3 \text{ cm}^{-1}, \\ V &= 25 \pm 3 \text{ cm}^{-1}. \end{aligned} \quad (4b)$$

The values in the  $^{16}\text{O}$  case are already published in Ref. 13.

In the  $^{18}\text{O}$  case the theoretical model describes the experimental data with an isotopic shift of 1.7% in the phonon energy, which agrees, within error, with that found at  $T = 300$  K  $[(2.08 \pm 0.35)\%]$ . The difference in  $\omega_{\text{CF}}$  for the oxygen substituted sample might be due to sample inhomogeneities, which can be caused by the heat treatment during the substitution. Note that there is also a small difference in  $\omega_{\text{CF}}$  between ceramic samples and single crystals in the  $\text{NdBa}_2\text{Cu}_3\text{O}_7$  compound.<sup>1</sup>

For higher temperatures it is not sufficient to take only the coupling of the CF transitions to transitions from the ground vibrational state into account, as implied by Eq. (3). Coupling to transitions from the  $n$ th occupied vibrational state to  $n+1$  and  $n-1$  leads to the Hamiltonian<sup>1</sup>

$$H^n = H_0^n + H_1^n, \quad (5)$$

where

$$\begin{aligned} H_1^n &= V \begin{pmatrix} \sqrt{(n+1)p_4} & \sqrt{(n+1)p_4} & \\ & \sqrt{np_1} & \sqrt{np_1} \\ & & \sqrt{np_1} \end{pmatrix}, \\ H_0^n &= V \begin{pmatrix} (n+1)\omega_{\text{Ph}} - \omega_{\text{CF}} & & \\ & n\omega_{\text{Ph}} & \\ & & (n-1)\omega_{\text{Ph}} + \omega_{\text{CF}} \end{pmatrix}. \end{aligned}$$

From this Hamiltonian the following spectral function was obtained:

$$\begin{aligned} R(\omega) &= \sum_{n=0}^{\infty} \sum_{i,j=1}^3 P_n \left[ \sum_{m=1}^3 \sqrt{m+n-1} \alpha_{im}^{n+1} \alpha_{jm}^n \right]^2 \\ &\quad \times L(E_i^{n+1} - E_j^n, \Gamma_{ij}), \end{aligned} \quad (6)$$

where  $L(E_i^{n+1} - E_j^n, \Gamma_{ij})$  is a Lorentzian line shape centered at the energy  $E_i^{n+1} - E_j^n$  with a half width at half maximum  $\Gamma_{ij}$ . The  $\alpha_{im}^n$  are admixing coefficients of the coupled wave functions. At 10 K we fitted the two peaks with two different linewidths accounting for their predominantly CF excitation or phonon character. Near zero temperature,  $p_4 = 0$ , and only the lowest CF levels are populated. It follows from the Hamiltonian of Eq. (5), that the two lowest possible excitations correspond to a transition from the ground state  $n=0$  by creation of one phonon (state with energy  $n\omega_{\text{Ph}}$ ,  $n=1$ ), which gives rise to the phononlike peak in the 10 K spectrum, and a transition from the ground state by creation of two phonons, one of which is annihilated by a CF excitation [state with energy  $(n-1)\omega_{\text{Ph}} + \omega_{\text{CF}}$ ,  $n=1$ ]. The second transition gives rise to the CF-like peak in the 10 K spectrum. At higher temperatures the average of the linewidths of both peaks was used for the fits, because transitions between higher excited states ( $n > 1$ ) have to be taken into account. The spectral function [Eq. (6)] differs from the one given in Sec. V of Ref. 1 insofar as all compo-

nents of the admixed wave functions are considered with their respective contributions to the Raman efficiency. To explain this in more detail let us follow the notation given earlier.<sup>1</sup> As a basis for the Hamiltonian [Eq. (5)] we have the unrenormalized states  $|n+1, \beta=0\rangle$ ,  $|n, 0\rangle$  and  $|n-1, \alpha=0\rangle$  corresponding to the energies  $(n+1)\omega_{\text{Ph}} - \omega_{\text{CF}}$ ,  $n\omega_{\text{Ph}}$  and  $(n-1)\omega_{\text{Ph}} + \omega_{\text{CF}}$ . For a particular transition between the renormalized states  $|j^n\rangle = \alpha_{j1}^n |n+1, \beta=0\rangle + \alpha_{j2}^n |n, 0\rangle + \alpha_{j3}^n |n-1, \alpha=0\rangle$  and  $|i^{n+1}\rangle = \alpha_{i1}^{n+1} |n+2, \beta=0\rangle + \alpha_{i2}^{n+1} |n+1, 0\rangle + \alpha_{i3}^{n+1} |n, \alpha=0\rangle$ , not only the "phonon contents"  $\alpha_{i2}^{n+1}$  and  $\alpha_{j2}^n$ , but also  $\alpha_{im}^{n+1}$  and  $\alpha_{jm}^n$  ( $m=1, 3$ ) contribute, since they account for phonon creation from the unrenormalized state  $|j^n = m\rangle'$  ( $|n+1, \beta=0\rangle$  for  $m=1$  and  $|n-1, \alpha=0\rangle$  for  $m=3$ ) to the state  $|i^{n+1} = m\rangle'$ , which does not change the CF states. Contributions from the additional couplings influence the theoretical spectra at temperatures  $T > 100$  K. Theoretical spectra were fitted to the data in Figs. 7 and 8 by a least-squares algorithm in the way just described. The value of the unrenormalized phonon and CF excitation energies as well as the coupling constants obtained from this procedure are shown in Figs. 9 and 10. For the  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  single crystal we obtain a temperature-dependent coupling constant  $V = V_0(1 - \kappa T)$ , with  $\kappa = 2.8 \times 10^{-3} \text{ K}^{-1}$  and  $V_0 = 23 \text{ cm}^{-1}$  (despite the improved data analysis). For the  $\text{NdBa}_2\text{Cu}_3\text{O}_7$  single crystal we obtain  $V_0 = 29 \text{ cm}^{-1}$  and  $\kappa = 5.2 \times 10^{-4} \text{ K}^{-1}$ . This value of  $V_0$  is slightly different from the one obtained in Ref. 1 ( $V_0 = 24.7 \text{ cm}^{-1}$ ), which we attribute to the improved fitting procedure. The temperature dependence of  $V_0$  is significantly reduced as compared to that reported in Ref. 1. Within the simple electron-phonon coupling<sup>14</sup> the tem-

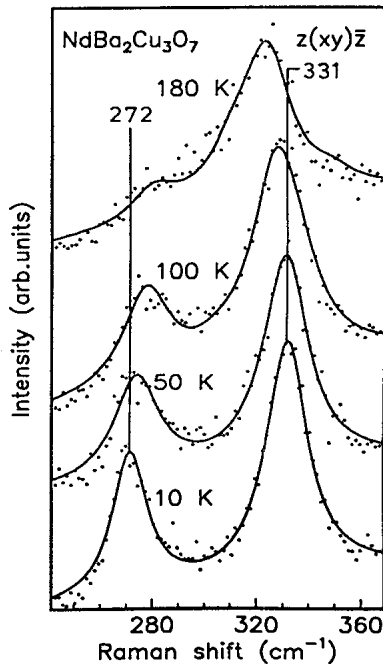


FIG. 7. Least-squares fits of the temperature dependence of the  $B_{1g}$  double peak in  $\text{NdBa}_2\text{Cu}_3\text{O}_7$ .

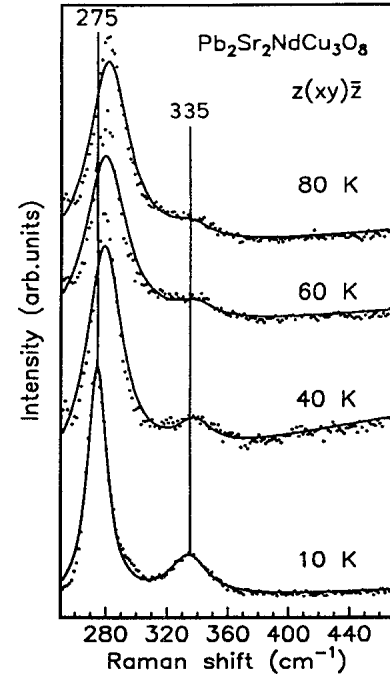


FIG. 8. Least-squares fits of the temperature dependence of the  $B_{1g}$  double peak in  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3^{16}\text{O}_{8+\delta}$ .

perature dependence of the spectra should be solely determined by the population factors for phonons and CF excitations,  $V$  being temperature independent, as it has been observed in other rare-earth compounds.<sup>15</sup> It was first assumed that anharmonic effects might be responsible for the remaining temperature dependence of  $V$ , which was reported in Ref. 1 to decrease quadratically with temperature. The data analysis performed here re-

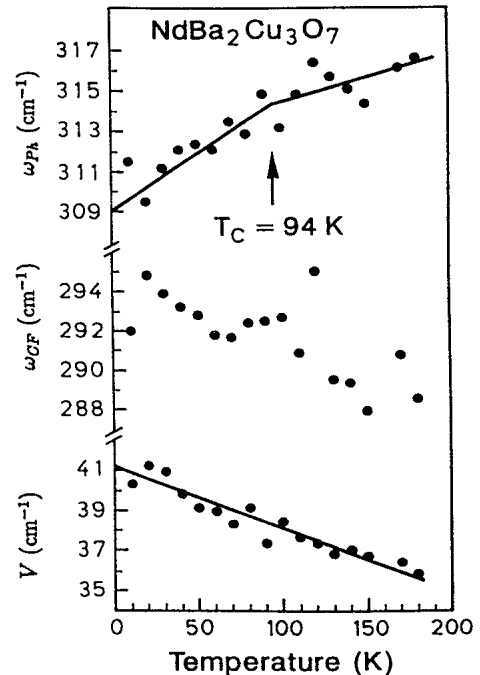


FIG. 9. Temperature dependence of  $V$ ,  $\omega_{\text{CF}}$ , and  $\omega_{\text{Ph}}$  in  $\text{NdBa}_2\text{Cu}_3\text{O}_7$ .

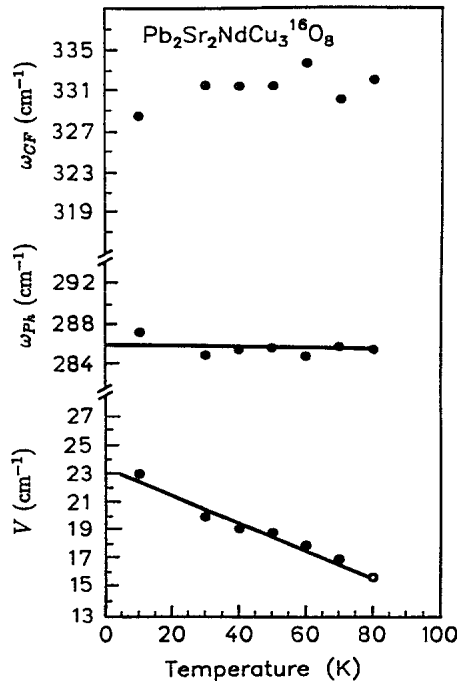


FIG. 10. Temperature dependence of  $V$ ,  $\omega_{CF}$ , and  $\omega_{Ph}$  in  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$ .

duces the strong decrease of  $V$  with  $T$  to a weaker linear one. We conjecture that the remaining temperature dependence may originate in the phonon dispersion, which has so far been neglected in the theory used in Ref. 1. At higher temperatures, the arguments given for neglecting the dispersion<sup>16</sup> may break down. A more elaborate treatment is required to properly take them into account. The parameter  $\kappa$  used here to represent these, and other possible residual effects, is to be regarded as purely phenomenological.

In the superconducting  $\text{NdBa}_2\text{Cu}_3\text{O}_7$  compound the phonon frequency  $\omega_{Ph}$  shows a softening by about  $6 \text{ cm}^{-1}$  between  $T_c$  and 10 K ( $T_c = 94 \text{ K}$  as determined by zero field cooled susceptibility measurements), with a kink at  $T_c$  as indicated by the solid line in Fig. 9. We derive  $\frac{\omega_{10\text{K}} - \omega_{90\text{K}}}{\omega_{90\text{K}}} = (-1.6 \pm 0.4)\%$  for the softening of the phonon frequency, which agrees well with the calculated change in the real part of the phonon self-energy of  $\text{NdBa}_2\text{Cu}_3\text{O}_7$ .<sup>17,18</sup> An analysis of the linewidths yields a broadening by  $2 \text{ cm}^{-1}$  between 90 K and 10 K, in good agreement with calculations.<sup>19</sup> Resistivity measurements on  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  reveal an insulating behavior.<sup>20</sup> In agreement with this there is no anomaly in  $\omega_{Ph}$ .

The CF energy  $\omega_{CF}$  in  $\text{NdBa}_2\text{Cu}_3\text{O}_7$  shifts by about  $6 \text{ cm}^{-1}$ , e.g., 2%, to lower values when increasing the temperature to 180 K. This can be attributed partly to the thermal expansion of the lattice. We calculated the CF energy  $\omega_{CF}$  for lattice parameters at 10 and 295 K (Ref. 21) and found it to shift by  $2 \text{ cm}^{-1}$  to lower values with increasing temperature. In  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  the data can be fitted only up to 80 K, hence no significant shift in  $\omega_{CF}$  is observed, in agreement with the behavior of  $\omega_{CF}$  in  $\text{NdBa}_2\text{Cu}_3\text{O}_7$  within the same temperature range.<sup>22</sup>

The constant for the coupling of the CF excitation to

the  $B_{1g}$ -phonon discussed above has been calculated recently for  $\text{NdBa}_2\text{Cu}_3\text{O}_7$  using the point-charge approximation and CF parameters determined from neutron-scattering experiments.<sup>22,23</sup> In order to obtain an estimate of the coupling constant for  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_8$  and in view of the fact that CF parameters for that material are presently not available, we decided to scale those of  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  (Ref. 24) with the geometrical coordination factors obtained from a recent structure determination of  $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_8$ .<sup>25</sup> Within a manifold  $|J, m_J\rangle$  the CF Hamiltonian is<sup>26</sup>

$$H_{CF} = \sum_{n,m} B_n^m O_n^m,$$

where  $O_n^m$  are Stevens' operator equivalents. In the point-charge approximation the CF parameters are given by<sup>26</sup>

$$B_n^m = -|e|q\langle r^n \rangle \Theta_n \gamma_n^m.$$

In this expression  $q$  is the ligand charge,  $\langle r^n \rangle$  represents a radial coordinate matrix element between one electron rare-earth ion wave functions, and  $\Theta_n$  is a reduced matrix element. The geometrical positions of the ligands surrounding the rare-earth ion enter via the coordination factors  $\gamma_n^m$ . In neutron-scattering experiments the intensities and spectral positions of CF excitations are analyzed to determine the parameters  $B_n^m$ . The CF excitation to phonon coupling constant  $V_{ij}$  is given by the modulation of the  $B_n^m$  by the phonon coordinate  $Q$  and the matrix element of the corresponding Stevens operator  $O_n^m$  between the CF level wave functions:

$$V_{ij} = \sum_{n,m} \frac{\partial B_n^m}{\partial Q} \langle \psi_i | O_n^m | \psi_j \rangle.$$

Using experimental CF parameters and structural information, the change in the  $B_n^m$  can be obtained from

$$\Delta B_n^m = \frac{\Delta \gamma_n^m}{\gamma_n^0} B_n^0.$$

For  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  (Ref. 24) this leads to  $|V_{14}| = 20.1 \text{ cm}^{-1}$ . The dominant coupling arises from the modulation of  $B_2^2$ . The CF parameters  $B_6^2$  and  $B_6^6$  yield smaller contributions which, luckily, partially compensate each other. To estimate the coupling constant for the  $B_{1g}$  mode in  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_8$  we use structural information from Ref. 25 for the Y-substituted compound, assuming that the positions of the Cu(2) and O(3) ions are not substantially changed by the replacement of the rare-earth ion. The environment of the  $\text{Nd}^{3+}$  ( $\text{Y}^{3+}$ ) ion is tetragonal, in close similarity to that in  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  (see Fig. 1). We therefore scale the experimental  $B_n^m$  obtained for  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  (Ref. 24) to account for geometrical changes in the  $\gamma_n^m$ . The diagonalization of the CF Hamiltonian with these scaled parameters gives new wave functions which, however, cause only negligible changes in the matrix elements of the  $O_n^m$ . Evaluating the  $\Delta \gamma_n^m$  from the static displacement of the O(3) ligands according to the phonon coordinate  $Q$  yields a coupling constant  $|V| = 21.7 \text{ cm}^{-1}$ . Again the domi-

nant contribution comes from  $\Delta B_2^2$ ;  $\Delta B_6^2$  and  $\Delta B_6^6$  give smaller and partially compensating values. The value of the coupling constant obtained this way is close to that for  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  and in good agreement with the experimental observations.

## V. CONCLUSIONS

We have reported polarization and temperature-dependent Raman measurements on  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  single crystals, which reveal the coupling between CF excitations of the rare-earth ion and the O(2)-O(3) out-of-phase  $B_{1g}$  phonon. Partial replacement (35%) of  $^{16}\text{O}$  by the  $^{18}\text{O}$  isotope allowed us to study this effect with modified phonon energies. With the aid of this model we derived from our 10 K data the unperturbed frequencies  $\omega_{\text{Ph}}$ ,  $\omega_{\text{CF}}$  and the coupling constant  $V$ . In addition we carried out measurements on a  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  sin-

gle crystal with low laser power in order to investigate the temperature dependence of  $V$  accurately. We found that  $V$  decreases linearly with temperature, by a smaller amount than in Ref. 1. From the fitted data we could also deduce a superconductivity induced softening of the unrenormalized phonon frequency by about  $6\text{ cm}^{-1}$ , which is absent in the  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_{8+\delta}$  compound due to the insulating properties of that sample. The CF excitation phonon coupling constant for  $\text{Pb}_2\text{Sr}_2\text{NdCu}_3\text{O}_8$  is well approximated using scaled CF parameters of  $\text{NdBa}_2\text{Cu}_3\text{O}_6$ .

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