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# Raman study of intermultiplet crystal-field excitations in $Nd_2CuO_4$

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We have observed Raman active $Nd^{3+}$ crystal-field (CF) excitations as a function of temperature in reduced single crystals of $Nd_2CuO_4$. The lines detected correspond to 13 different transitions involving crystal-field split levels of the ($J=\frac{9}{2}$) ground state as well as the higher excited multiplets with $J=\frac{11}{2}$, $\frac{13}{2}$, and $\frac{15}{2}$. Eight of these excitations have been measured out of resonance, thus allowing their symmetry to be determined. Using these levels, we have calculated an unequivocal set of CF parameters, thus solving an outstanding controversy between different neutron measurements. We conjecture that changes in the spectra measured on the reduced sample compared to the as-grown one result from the removal of apical oxygen.

## I. INTRODUCTION

It has been shown recently that Raman scattering allows one to study the rare-earth crystal-field (CF) excitations in $Nd_2CuO_4$ and $Pr_2CuO_4$.[1–4] This optical technique complements remarkably inelastic neutron scattering experiments since it can be applied with high resolution to small single crystals like those obtained for high-$T_c$ materials. In the case of $Nd_2CuO_4$, the $Nd^{3+}$ ion ground state splitting due to the $CuO_2$-plane molecular field has been clearly observed in Raman studies,[1,2] thus solving a controversy in inelastic neutron scattering measurements regarding these Kramers doublets.[5–8] A temperature-dependent Raman study of a CF excitation in $Pr_2CuO_4$ also gave evidence for an acoustic phonon relaxation process between CF ground state levels.[3]

CF excitation measurements are important for the understanding of thermodynamical properties, such as magnetic susceptibility or specific heat in high-$T_c$ superconductors containing rare-earth elements. These excitations can also be used to study the charge transfer to the $CuO_2$ planes following electron doping, as for instance in $Nd_{1.85}Ce_{0.15}CuO_4$,[9] or to monitor oxygen-vacancy-induced charge redistribution in the $CuO_2$ planes of nonstoichiometric $RBa_2Cu_3O_{7-x}$.[10] Furthermore, they allow the observation of two-dimensional percolative networks generating superconductivity[11] and of the opening of a gap in the spin excitations of the $CuO_2$ planes.[12]

A precise measurement of the CF excitations, which contribute strongly to inelastic neutron scattering, is also required in order to determine correctly the generalized phonon density of states. This is essential for comparing the Eliashberg coupling function measured this way to that obtained from tunneling experiments and for a subsequent deduction of the eventual role of phonons in the electron pairing mechanism responsible for high-$T_c$ superconductivity.[13]

The accurate detection of as many levels as possible is essential for the use of CF excitations as an efficient local probe of magnetic and electric fields. The observation of only a few levels is not sufficient for a precise determination of the CF parameters that describe, with the help of Stevens operator equivalents[14,15] within the ground state multiplet or spherical tensor operators[16] when intermediate coupling and $J$ mixing are considered (Wybourne notation), the CF Hamiltonian.[5,6] So far, neither neutron nor Raman experiments could detect more than a few CF excitations due to their weak response in both techniques. For instance, considering reported Raman results, only excitations within the lowest $J$ multiplet were observed in $Pr_2CuO_4$,[3] while in the more favorable case of $Nd_2CuO_4$, in addition to all the $^4I_{9/2}$ levels some of the first and second excited state levels ($^4I_{11/2}$, $^4I_{13/2}$) have been detected.[1,2]

In the case of $Nd_2CuO_4$, there is no disagreement in the neutron measurements of the $Nd^{3+}$ ion CF ground level splittings; nevertheless, the interpretation of the data results in different CF parameters. More than six sets of parameters that do not agree in absolute value, or sometimes even in sign, have been reported.[5,6] Also, since neutron studies use polycrystalline powders, the symmetry representation attributed to the levels must be based on the relative intensity of the peaks and is thus model dependent. This leads to assignments that do not always agree. Hence, while the 170 $cm^{-1}$ level is recognized to have $\Gamma_6$ symmetry by one group,[9,17] another group[18] assigned it recently to a $\Gamma_7$ representation. The major difficulty in determining an unequivocal set of CF parameters (and the corresponding level symmetries) by neutron diffraction experiments is certainly due to the limited number of detected levels. Only three out of four transitions associated with the $^4I_{9/2}$ multiplet are clearly observed in neutron measurements of $Nd_2CuO_4$ at low

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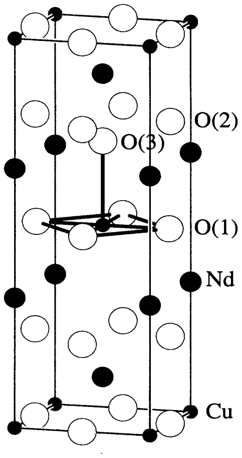

FIG. 1. $Nd_2CuO_4$ unit cell showing a possible oxygen defect O(3).

temperatures.[6] Adelmann *et al.*[19] succeeded in determining the sign of the CF parameter $B_{20}$ from the electric field gradient at the Gd nuclei in $(Nd_{1-x}Gd_x)_2CuO_4$, but the disagreement in the different parameter values remained unsettled. The removal of these uncertainties in the CF parameters is only possible by the detection of transitions to excited multiplet states.[20] In this paper we show that such levels and their symmetry can be obtained by means of Raman spectroscopy which thus gives the experimental input required for precise model calculations. Intermultiplet transitions between the $J=9/2$ and the higher manifolds with $J=11/2$, 13/2, and 15/2 are observed in reduced $Nd_2CuO_4$ as a function of temperature, and from the detected levels a set of CF parameters is determined.

We also show that the large number of lines found in Raman spectra may also help to solve the long-standing controversy concerning the oxygen stoichiometry of $Nd_2CuO_4$. An understanding of this issue is required in order to clarify the role of the reduction necessary to render $Nd_{1.85}Ce_{0.15}CuO_4$ superconducting. While some iodometric or thermogravimetric analyses suggest that there is an excess of oxygen above the nominal value of 4,[21,22] other authors claim that there is a lack of oxygen $O_{4-\delta}$ with $\delta < 0.045$.[23,24] These studies are particularly difficult, since the variations in oxygen stoichiometry as a result of reduction are very small (reported values vary between 0.01 and 0.04 oxygen atoms per formula unit). The same disagreement also exists in neutron investigations about the absence or presence of apical oxygen defects that could be the source of nonstoichiometry.[25,40] A comparison between the $Nd^{3+}$ ion CF levels of as-grown and reduced $Nd_2CuO_4$ crystals might thus lead to further insight into the problem: If the reduction process removes apical oxygen a [O(3) in the structure shown in Fig. 1], one would expect CF Raman features associated with these defects to become weaker after the reduction. However, if the reduction removes oxygen atoms from the O(1) or O(2) positions (see Fig. 1), the number of defects would be enhanced and associated CF Raman features should become more pronounced. The comparison between the Raman spectra of reduced and as-grown $Nd_2CuO_4$ may thus help to clarify microscopic details of the reduction process.

## II. EXPERIMENT

The $Nd_2CuO_4$ single crystal ($\approx 2\times2\times1$ mm$^3$) used in this study was grown from a CuO flux by spontaneous nucleation as described by Changkang *et al.*[26] and was reduced at $T=900$ °C for 18 h in a nitrogen stream. Raman backscattering measurements were performed in a closed-cycle refrigerator between 8 K and 300 K using a multichannel spectrometer equipped with a charge-coupled device (CCD) camera. The 4765 Å, 4880 Å, and 5145 Å $Ar^+$-laser lines were used for excitation. The laser power was 10 mW focused to a 50 $\mu$m spot on the sample. We chose incident as well as scattered light polarizations parallel to the $z$ axis.

Four main regions of CF Raman-active transitions around 500 cm$^{-1}$, 2000 cm$^{-1}$, 4000 cm$^{-1}$, and 6000 cm$^{-1}$ were studied in order to determine CF levels of the $Nd^{3+}$ ion $^4I_{9/2}$ ground state multiplet as well as the $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$ excited state multiplets and to determine the effects of reduction. Higher temperatures allowed us to investigate intermultiplet transitions also from some of the excited states of the $^4I_{9/2}$ manifold.

## III. RESULTS AND DISCUSSION

The $Nd^{3+}$ free ion $4f^3$ ground state multiplet $^4I_{9/2}$ is tenfold degenerate, while the first ($^4I_{11/2}$), second, ($^4I_{13/2}$), and third ($^4I_{15/2}$) excited multiplets are 12-, 14-, and 16-fold degenerate, respectively. Placed in a site of $C_{4v}$ symmetry in $Nd_2CuO_4$, the $Nd^{3+}$-ion ground state multiplet splits into $3\Gamma_6+2\Gamma_7$ while the first, second, and third excited multiplets split into $3\Gamma_6+3\Gamma_7$, $3\Gamma_6+4\Gamma_7$, and $4\Gamma_6+4\Gamma_7$ doublets, respectively; all of these multiplets are Kramers degenerate. The symmetry of excitations between these $4f$ states, which involves the direct product of their irreducible representations, corresponds to either

$$\Gamma_6\times\Gamma_6=\Gamma_7\times\Gamma_7=A_1+A_2+E$$

or

$$\Gamma_6\times\Gamma_7=\Gamma_7\times\Gamma_6=B_1+B_2+E.$$

The excitations of $A_1$, $B_1$, $B_2$, and $E$ symmetry are Raman active.[27] The strongest Raman scattering efficiency occurs for the $A_1$ ($z^2$) representation[1] and therefore our experimental configuration was set to detect the $\Gamma_6\rightarrow\Gamma_6$ and $\Gamma_7\rightarrow\Gamma_7$ excitations.

In Fig. 2, measurements at 9 K in the 500 cm$^{-1}$ region are shown with the purpose of clarifying the level symmetries of the CF ground state multiplet and the origin of the 716 cm$^{-1}$ peak observed in the as-grown sample.[1] Four Raman active excitations can be seen: The strong 229 cm$^{-1}$ $A_{1g}$ phonon and the very weak 490 cm$^{-1}$ $E_g$ phonon confirm that the experimental $ZZ$ configuration is realized with negligible leakage. Additionally, two CF excitations are observed at 168 cm$^{-1}$ and 752 cm$^{-1}$. Since the ground state multiplet splits in two $\Gamma_7$ and three $\Gamma_6$ levels, either two $\Gamma_6\rightarrow\Gamma_6$ or one $\Gamma_7\rightarrow\Gamma_7$ transition(s) should be expected, depending on whether the lowest state has $\Gamma_6$ or $\Gamma_7$ symmetry. The obser-

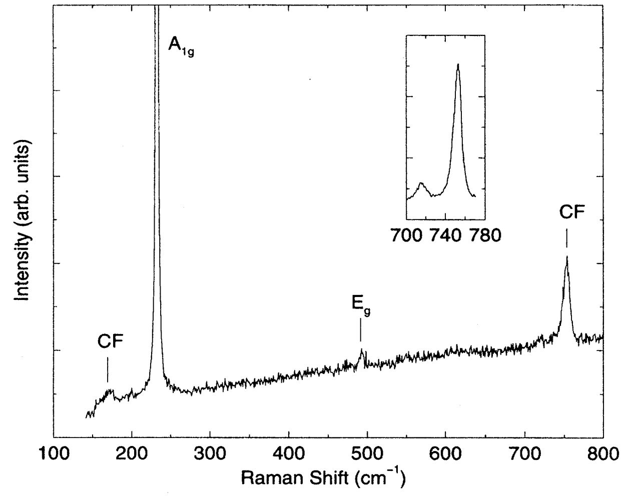

FIG. 2. CF excitations and phonons of reduced $Nd_2CuO_4$ observed at 9 K in $x(zz)\bar{x}$ scattering configuration. The inset shows the 752 $cm^{-1}$ CF excitation together with the 716 $cm^{-1}$ satellite in the as-grown $Nd_2CuO_4$ sample of Ref. 1.

vation of two CF transitions conclusively confirms their $\Gamma_6$ character in accordance with Refs. 1, 9, and 17 and in disagreement with Ref. 18. In Ref. 1 a satellite of the 752 $cm^{-1}$ line was detected at 716 $cm^{-1}$ (see inset of Fig. 2) and attributed to a CF excitation of perturbed $Nd^{3+}$ ions close to a defect. The spectrum of the reduced sample in Fig. 2 also shows this side peak. However, its relative intensity compared to the main line is lower, a fact which we tentatively attribute to the removal of defects after reduction.

We have studied in more detail than in Ref. 1 the temperature dependence of the 752 $cm^{-1}$ peak as shown in Fig. 3 and find that it has a large shift of about 15 $cm^{-1}$ between 10 K and 300 K. The observation of this excitation by Raman scattering is consistent with the expected selection rules for the highest CF $^4I_{9/2}$ multiplet level assuming that the ground state has $\Gamma_6$ symmetry. Orlov[28] pointed out that the energy of this excitation is unexpectedly large for a $^4I_{9/2}$ crystal-field level. He therefore attributed it to a paramagneto vibrational incoherent scattering process[29] instead, leading to the appearance of phonon peaks in neutron spectra under conditions where only CF scattering is expected. While Lynn *et al.*[30] reported in their phonon density of states measurements on $Nd_{1.85}Ce_{0.15}CuO_4$ that the peak at ≈ 95 meV (758 $cm^{-1}$) may be partly phononic in origin, Sumarlin *et al.*[13] showed later that the dependence of the intensity of this CF excitation on neutron momentum transfer agrees well with the square of the magnetic form factor which excludes any phonon contribution. However, even if this excitation is pure CF, it seems to be more sensitive to phonon coupling than to magnetic changes, since the important frequency shift takes place between 100 K and 300 K where coupling to phonons is usually strong, and not between 10 K and 80 K where two magnetic phase transitions occur.[2]

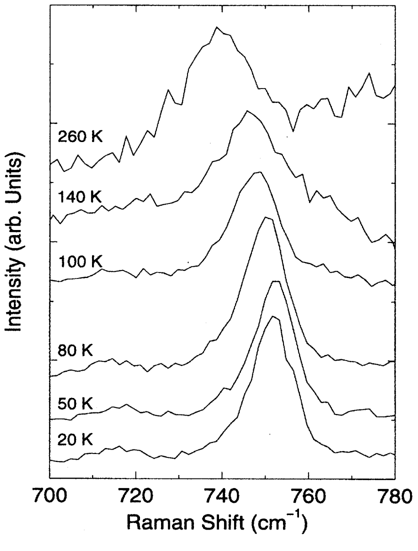

FIG. 3. Temperature evolution of the 752 $cm^{-1}$ CF excitation.

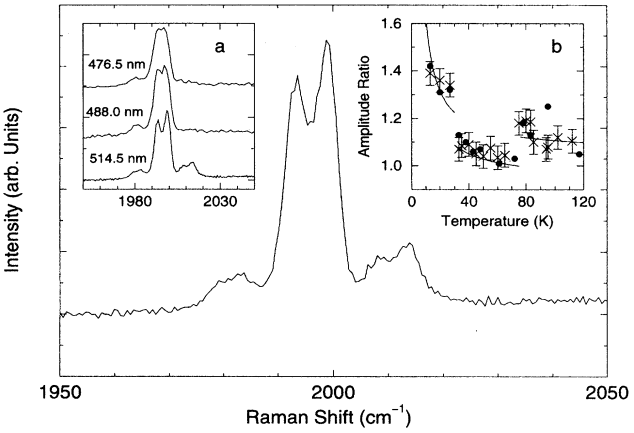

FIG. 4. CF excitations observed around 2000 $cm^{-1}$ at 8 K. Inset (a): Resonance behavior of the 2011 $cm^{-1}$ excitation. Inset (b): Amplitude ratio of the main doublet in reduced $Nd_2CuO_4$ (×) and in as-grown $Nd_2CuO_4$ (●, from Ref. 2 without error bars).

In Fig. 4, CF excitations around 2000 $cm^{-1}$ are presented for the reduced sample excited with the 5145 Å laser line. Compared to the as-grown sample of Ref. 1, where only one doublet level was reported in this energy range, this specimen allows one to observe three doublets at 1979/1983 $cm^{-1}$, 1995/1999 $cm^{-1}$, and 2008/2014 $cm^{-1}$ whose energies were determined by fitting Gaussian line shapes to the spectra. The excitation at 2008/2014 $cm^{-1}$ is resonantly enhanced at 5145 Å and almost undetectable with the 4765 Å and 4880 Å laser lines [inset of Fig. 4(a)]. The amplitude ratio of the main doublet (1995/1999 $cm^{-1}$), shown in the inset of Fig. 4(b), behaves as described in Ref. 2 for an as-grown sample: The magnetic phase transitions at 30 K and 75 K (Refs. 31–33) are clearly observable. The relative error in the amplitude ratio measured on the reduced sample is ±0.025. This represents an improvement of the experimental accuracy as compared to earlier measurements, particularly for higher temperatures.

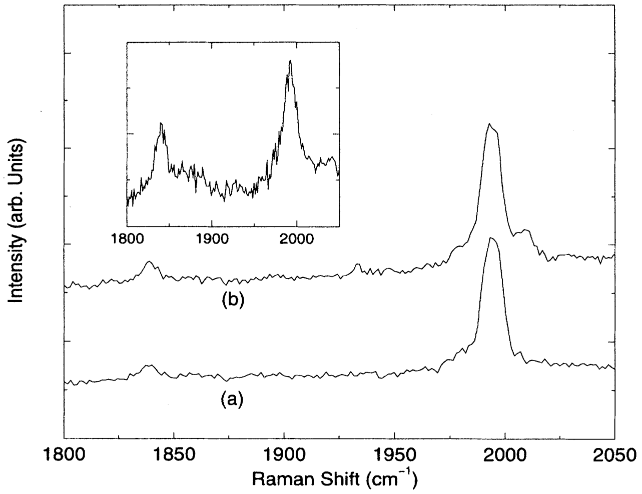

FIG. 5. CF excitations observed around 2000 cm$^{-1}$ at 100 K for 5145 Å laser excitation (a) and 4880 Å laser excitation (b). The inset is observed at 280 K.

Measurements were performed at high temperatures to detect transitions either from the lowest $^4I_{9/2}$ $\Gamma_7$ state (120 cm$^{-1}$) to higher $\Gamma_7$ levels or from the second $\Gamma_6$ state of the ground state multiplet (168 cm$^{-1}$) to higher $\Gamma_6$ levels. A CF excitation at 1837 cm$^{-1}$ is shown in Fig. 5 for both 4880 Å and 5145 Å laser wavelengths. This excitation could either correspond to a transition between the 120 cm$^{-1}$ $\Gamma_7$ state and a $\Gamma_7$ crystal-field level at 1957 cm$^{-1}$, or to a transition between the 168 cm$^{-1}$ $\Gamma_6$ state and another $\Gamma_6$ level, most likely the one at 1999 cm$^{-1}$ (energy difference 1831 cm$^{-1}$). It is interesting to note that the level detected at 1988 cm$^{-1}$ in Ref. 1 is not observed in this work, a fact which we also attribute to the reduction and the concomitant removal of defects. In the inset of Fig. 5 the same spectral region is shown at 280 K in the $ZZ+XZ$ configuration. In addition to the already mentioned feature at 1837 cm$^{-1}$ and the (1995/1999) cm$^{-1}$ doublet, a broader structure centered around 1875 cm$^{-1}$ appears which could also be due to a transition between a thermally populated level of the $^4I_{9/2}$ multiplet and a $^4I_{11/2}$ state.

In Fig. 6, CF levels in the 4000 cm$^{-1}$ region are presented for 4750 Å (a), 4880 Å (b), and 5145 Å (c) laser excitation. We observe transitions with doublet splittings at the wave numbers 3951/3953 cm$^{-1}$, 3919/3925 cm$^{-1}$, and 3904/3907 cm$^{-1}$, as determined by fitting Gaussian line shapes to the spectra. The two higher-frequency doublets could correspond to two of the three expected $\Gamma_6 \rightarrow \Gamma_6$ transitions. One should be cautious about the assignment of the 3904-3907 cm$^{-1}$ structure since it is just barely observed with the 5145 Å excitation line and is very weak when excited with the 4750 Å and 4880 Å lines. It could either correspond to a $\Gamma_7$ level excited in resonance, or, like the 716 cm$^{-1}$ peak discussed previously, be due to residual defects.

A spectrum of the 4000 cm$^{-1}$ region for $T = 120$ K is displayed in Fig. 7(a), showing the sharp CF excitations around 3920 cm$^{-1}$ and 3952 cm$^{-1}$ from Fig. 6 superimposed on several additional structures at 3840 cm$^{-1}$, 3875 cm$^{-1}$,

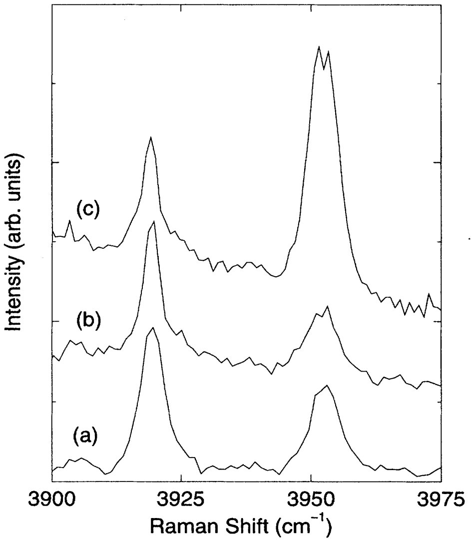

FIG. 6. CF excitations observed around 3900 cm$^{-1}$ at 20 K in reduced $Nd_2CuO_4$ observed with different laser excitations of 4765 Å (a), 4880 Å (b), 5145 Å (c).

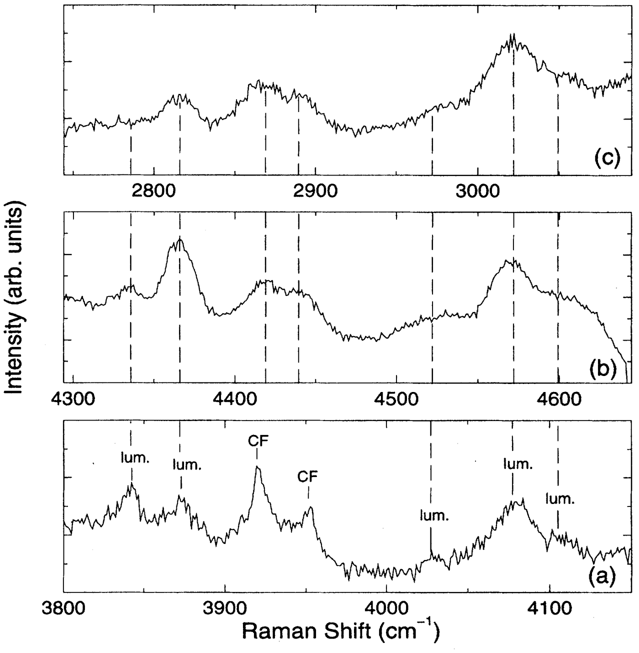

FIG. 7. CF levels (CF) and luminescence bands (lum.) of reduced $Nd_2CuO_4$ observed around 4000 cm$^{-1}$ at 120 K obtained with the 4880 Å laser line (a). Luminescence bands at 120 K obtained with the 4765 Å (b) and 5145 Å (c) laser line. The horizontal scales have been shifted by the difference in wave numbers so as to bring into coincidence luminescence features.

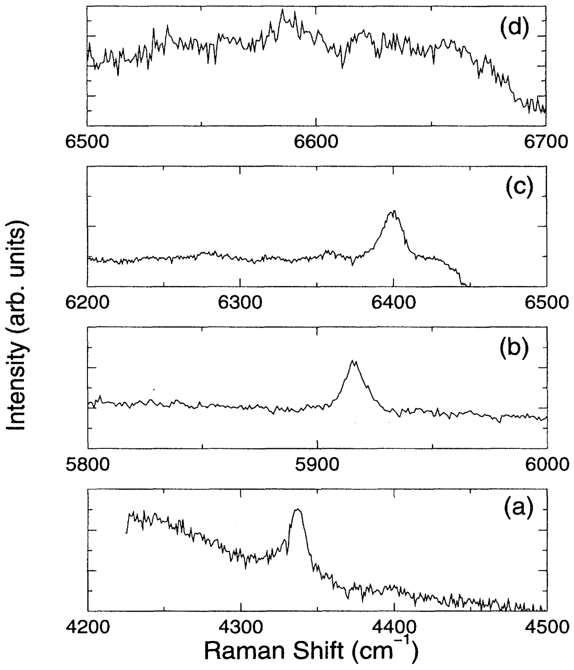

FIG. 8. CF excitations at 20 K obtained with two laser lines 5145 Å (a), 4765 Å (b),(c),(d) for which resonance effects appear.

TABLE I. $Nd^{3+}$ ion CF levels in $Nd_2CuO_4$ as observed experimentally and predicted by the CF parameters of Table II.

| | Experiment | | Theory | |
|---|---|---|---|---|
| Multiplet | Energy (cm$^{-1}$) | Symmetry $i$ ($\Gamma_i$) | Energy (cm$^{-1}$) | Symmetry $i$ ($\Gamma_i$) |
| | 6588 | | 6590 | 6 |
| | | | 6571 | 7 |
| | | | 6464 | 7 |
| | 6400 | | 6401 | 6 |
| $^4I_{15/2}$ | 5920 | | 5917 | 6 |
| | | | 5872 | 6 |
| | | | 5831 | 7 |
| | | | 5763 | 7 |
| | | | 4416 | 7 |
| | | | 4341 | 7 |
| | 4336 | | 4338 | 6 |
| $^4I_{13/2}$ | | | 3969 | 7 |
| | 3951/3953 | 6 | 3953 | 6 |
| | | | 3923 | 7 |
| | 3919/3925 | 6 | 3919 | 6 |
| | | | 2410 | 7 |
| | | | 2381 | 6 |
| | | | 2078 | 7 |
| $^4I_{11/2}$ | 2008/2014 | | 2003 | 7 |
| | 1995/1999 | 6 | 1999 | 6 |
| | 1979/1983 | 6 | 1986 | 6 |
| | 752 | 6 | 747 | 6 |
| | 206 | 7 | 213 | 7 |
| $^4I_{9/2}$ | 168 | 6 | 169 | 6 |
| | 120 | 7 | 119 | 7 |
| | 0 | 6 | 0 | 6 |

3925 cm$^{-1}$, 3945 cm$^{-1}$, 4030 cm$^{-1}$, 4080 cm$^{-1}$, and 4110 cm$^{-1}$. However, these features are not CF transitions between $^4I_J$ levels, but rather luminescence bands. This is confirmed by the shift or their position when measured with the 4765 Å and 5145 Å laser lines as shown in Figs. 7(b) and 7(c). They probably correspond to transitions from the $^4G_{5/2}$ and $^2G_{7/2}$ levels to the $^4I_{9/2}$ ground state multiplet.[34] We conjecture that the observation of these luminescence bands, which are absent in as-grown samples, is related to defect elimination following reduction. As shown by a recent infrared study on as-grown, reduced, and oxygen-annealed samples,[38] these defects are attributed to apical oxygens in agreement with Klamut[39] and Radaelli *et al.*[40]

Four additional CF lines that are detected under resonance in the 4000 cm$^{-1}$ and 6000 cm$^{-1}$ ranges are shown in Fig. 8. The 4336 cm$^{-1}$ excitation (a) is strong with the 5145 Å laser line and weak for 4765 Å excitation. The 6400 cm$^{-1}$ and 6588 cm$^{-1}$ excitations are observed with the 4765 Å laser line only, whereas the 5920 cm$^{-1}$ line can be detected with the 4765 Å as well as the 4880 Å excitation line. The two excitations at 6400 cm$^{-1}$ and 6588 cm$^{-1}$ are most likely CF excitations, since no luminescencelike behavior is detected at the corresponding frequencies with other laser lines. No symmetry representations have been assigned to these levels because they are observed under resonance conditions where selection rules are not necessarily fulfilled.

In the following analysis, the crystalline electric field is treated as a perturbation of the $4f^3$ free ion energy levels. The CF Hamiltonian is written in terms of one-electron irreducible tensor operators $C_{kq}$ as[14–16] $H_{CF}=\Sigma_{k,q}B_{kq}C_{kq}$ with five nonzero CF parameters ($B_{20}$, $B_{40}$, $B_{60}$, $B_{44}$, $B_{64}$) related to the $C_{4v}$ symmetry of the $Nd^{3+}$ ion crystal site position.[35] The values of these parameters are determined by fitting the eigenvalues of the CF Hamiltonian to the energies of the 13 detected Raman transitions, also taking into account the symmetries of the 8 levels observed out of resonance. The free ion energies of the $^4I_J$ multiplets are treated as unknown parameters and the diagonalization procedure considers $J$ mixing within the entire set of multiplets. The energies of split Kramers doublets are approximated by their average value. In Table I, the energies of the measured CF excitations are compared with the results of the fit. The agreement of calculated level positions and symmetries with the measured lines is excellent. Using the model we can identify the origin of the features located at 1837 cm$^{-1}$, 1875 cm$^{-1}$, and 3907 cm$^{-1}$: The first one corresponds to a transition between the 168 cm$^{-1}$ ($\Gamma_6$) and the 1999 cm$^{-1}$ ($\Gamma_6$) levels. The structure at 1875 cm$^{-1}$ observed at 280 K is due to a transition between the 120 cm$^{-1}$ ($\Gamma_7$) and 1999 cm$^{-1}$ ($\Gamma_6$) levels. The 3907 cm$^{-1}$ excitation, like the one at 716 cm$^{-1}$, probably has its origin in remaining apical oxygens[40] which locally change the crystal field for some of the $Nd^{3+}$ ions. In Table II we compare our calculated CF parameters, which also describe the observed susceptibility anisotropy well,[36] with the different reported sets of parameters obtained from neutron measurements. The good agreement between our parameters and those reported in Ref. 37 deserves to be emphasized.

TABLE II. $Nd^{3+}$ ion CF parameters obtained from our Raman measurements compared to different published sets of parameters.

| Parameter | This work ($cm^{-1}$) | Ref. 5 ($cm^{-1}$) | Ref. 6 ($cm^{-1}$) | Ref. 17 ($cm^{-1}$) | Ref. 35 ($cm^{-1}$) | Ref. 18 ($cm^{-1}$) | Ref. 37 ($cm^{-1}$) | Ref. 8 ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $B_{20}$ | -327(24) | -226 | -2291 | 500 | -516 | -690 | -327 | -514 |
| $B_{40}$ | -2264(45) | -2121 | -2775 | -1944 | -1936 | -1783 | -2199 | -1700 |
| $B_{60}$ | 215(17) | 274 | -710 | 540 | 597 | 474 | 215 | 593 |
| $B_{44}$ | 1649(24) | 1605 | 750 | 1726 | 2000 | 1895 | 1566 | 1600 |
| $B_{64}$ | 1477(21) | 1476 | 839 | 1379 | 1573 | 1437 | 1552 | 1572 |

## IV. CONCLUSIONS

We have determined a large number of intermultiplet CF excitations from the $J=9/2$, 11/2, 13/2, and 15/2 multiplets in reduced $Nd_2CuO_4$ using Raman spectroscopy. A very accurate set of CF parameters has been derived which predicts correctly all observed energy levels and their symmetries, thus permitting an unambiguous assignment of the $Nd^{3+}$ ion ground state and the excited multiplets. We have also detected the splitting of many Kramers doublets which can be attributed to the magnetic interaction between the rare-earth sublattice and the $CuO_2$ planes. Sample reduction allows us to observe intermultiplet CF level transitions and line splittings as well as luminescence bands associated with higher CF states. These transitions may also be involved in the strong resonances found for the Raman intensities of some of the CF excitations. We conjecture that these improvements result from the removal of apical oxygens in the reduction process.

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