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Raman study of crystal-field excitations in $Nd_{1.85}Ce_{0.15}CuO_4$

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Eighteen Raman active crystal-field (CF) excitations were detected in $Nd_{1.85}Ce_{0.15}CuO_4$. They correspond to transitions within the $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ multiplets associated with the inequivalent sites of the Nd^{3+} ion. Three sets of CF parameters which describe the observed energy spectra were derived. One of the three Nd^{3+} sets describes levels which are very similar to those observed in Nd_2CuO_4 while the two others correspond to sites affected by the cerium doping. Kramers doublet splitting is also present indicating that antiferromagnetism persists in the CuO_2 planes even with 7.5% cerium doping.

INTRODUCTION

In spite of the widespread belief that optical techniques are not appropriate to study rare-earth electronic f-f transitions in opaque materials,[1,2] we have recently observed, by Raman scattering, the crystal-field excitations of the Nd^{3+} ion in as-grown and reduced Nd_2CuO_4 single crystals.[3–5] This provided a clear indication of the fact that Raman spectroscopy can be used as a probe of crystal-field (CF) excitations while monitoring the evolution of magnetic and electric properties in high-T_c superconductors. We have studied in detail the ground state Kramers doublet of Nd_2CuO_4 (Ref. 4) and have succeeded in measuring thirteen CF levels after reduction of the sample,[5] thus complementing previous neutron scattering studies.[6–11]

Boothroyd *et al.*[12] studied the CF excitations in $Nd_{1.85}Ce_{0.15}CuO_4$ pellets and found that the ground state transitions, located at 12.2, 20.3, 26.5, and 93.2 meV, looked broader than the corresponding ones in Nd_2CuO_4. Furrer *et al.*[13] interpreted those measurements as encompassing two sets of CF excitations (12, 20, 26, and 96 meV) and (15, 21, 27, and 93 meV) related, respectively, to Nd^{3+} ions perturbed and unperturbed by Ce doping. Even though x-ray absorption measurements,[14] x-ray induced photoemission studies,[15] and electron-energy-loss spectroscopy[16] indicated that the additional cerium electron goes into the Cu sites, Furrer *et al.*[13] concluded, on the basis of their CF parameters, that the charge enhancement occurs at the oxygen sites in the superconducting CuO_2 plane. Boothroyd *et al.*[6] claimed that the two sets of parameters given by Furrer *et al.* do not describe adequately the observed spectra. First, they invoked the fact that the energies of some of the transitions in $Nd_{1.85}Ce_{0.15}CuO_4$ are too low to justify retaining the Nd_2CuO_4 parameters to describe the undisturbed Nd^{3+} sites. Second, they noted that the parameters which describe the disturbed sites cause a reduction in the ratio of the intensities of the 26.5 and 20 meV peaks, contrary to what is observed experimentally.

A set of CF parameters, based on a fit to the anisotropic magnetic susceptibility, has been proposed for $Nd_{1.85}Ce_{0.15}CuO_4$ by Balakrishnan *et al.*[17] These parameters describe well the susceptibility but, according to Boothroyd *et al.*,[6] fail to reproduce the intensity ratio of the measured transitions.

Jones *et al.*[18] studied CF transitions in $Nd_{1.85}Ce_{0.15}CuO_4$ and its parent compound Nd_2CuO_4. They reported transmission spectra in films and reflectivity measurements in pellets measured with a sensitive optical spectrograph system in the visible. While they observed inhomogeneous broadening and dichroism due to the two-dimensional character of the material, they did not detect any change in the CF transition frequency when Nd_2CuO_4 is doped with cerium. A recent study of Stadlober *et al.*[19] reported the observation of three ground state CF excitations in $Nd_{1.84}Ce_{0.16}CuO_4$ at 100, 167, and 206 cm^{-1}. Comparing their measurements with the transitions detected in Nd_2CuO_4 by Jandl *et al.*,[3] they concluded that doping does not generate inequivalent sites but induces a shift to 100 cm^{-1} of the 119 cm^{-1} lowest ground state transition while keeping unchanged the two other transitions at 167 and 206 cm^{-1} of the parent compound.

In contrast to Stadlober *et al.*,[19] Sanjurjo *et al.*[20] studied Raman active CF excitations in $Pr_{1.85}Ce_{0.15}CuO_4$ and attributed the multiple peak structure observed between 100 and 175 cm^{-1} to the excitation between the Pr^{3+} ion ground state

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Γ_4 and the first excited Γ_5 state. Their analysis indicated the presence of two additional environments for the Pr^{3+} ions, which make them sensitive to doping and charge transfer due to Ce^{4+} and to local distortions.

On the other hand, the low temperature specific heat peak in Nd_2CuO_4 and in $Nd_{1.85}Ce_{0.15}CuO_4$, has been attributed by Boothroyd *et al.*[6] and Adelmann *et al.*[21] to a Schottky anomaly associated with the ground state Kramers doublet splitting instead of being due to a magnetic transition as reported by Markert *et al.*[22] and Lynn *et al.*[23] or to a Kondo effect as reported in diluted metallic samples.[24] The transitions around 0.3 and 0.6 meV observed in inelastic neutron scattering experiments at $T=15$ K on polycrystalline samples of Nd_2CuO_4,[25] have been attributed to the Nd^{3+} ground state doublet splitting.[6] Brugger *et al.*[26] studied the specific heat of $Nd_{2-x}Ce_xCuO_4$ for $0<x<0.2$. They observed that the Schottky anomaly, which is due to exchange interactions between Nd and Cu moments, shifts upon cerium doping to lower temperatures while coupling between Nd moments and conduction electrons gives rise to a heavy fermion system.

Recently, a CF Kramers doublet of the next higher ($J=11/2$) manifold around 2000 cm^{-1} (1993–1999 cm^{-1}) has been studied in Nd_2CuO_4 as a function of temperature up to 120 K.[4] The doublet splitting was observed to be slightly temperature dependent and of the order of 6 cm^{-1}. Discontinuities in the amplitude ratio of its two components at the 35 and 75 K magnetic phase transitions were associated with the simultaneous direction reversal of both the Nd magnetic moment and the copper exchange field. From the temperature evolution of the amplitude ratio, the CF ground state splitting due to the CuO_2 antiferromagnetic order was estimated to be 3 ± 1 cm^{-1}, in agreement with neutron and specific heat measurements.[6,21]

In this paper we present a Raman study of $Nd_{1.85}Ce_{0.15}CuO_4$. The purpose of this work is (i) to investigate the cerium doping effect on the Nd^{3+} ion CF levels and to determine whether there is more than one average site in the material, (ii) to analyze these levels and to calculate their corresponding CF parameters so as to obtain some insight about the site characteristics, and (iii) to detect whether a Kramers doublet splitting persists as a result of long range magnetic order. The latter represents an effort to resolve the controversy between Skanthakumar *et al.*,[27] whose neutron study implies the absence of antiferromagnetic order following 7.5% cerium doping, and Luke *et al.*[28] whose muon spin relaxation measurements suggest the appearance of static moments around 100 K for the same cerium composition. Answering these questions is relevant to the understanding of the superconductivity mechanism in the high-T_c cuprates with electron carriers since the observation of more than one type of site is an indication for the presence of important inhomogeneities on one hand, while on the other hand, the persistence of antiferromagnetism in the CuO_2 planes could be crucial to the mechanism.

EXPERIMENT

$Nd_{1.85}Ce_{0.15}CuO_4$ single crystals grown, from a CuO flux by spontaneous nucleation,[29] in two different laboratories by Chen and by Piñol were used in this study without previous reduction. Their typical thickness along the Z axis varied between 300 and 1000 μm. The 5145 Å and 4880 Å Ar^+ ion laser lines were used in Raman backscattering measurements performed in a closed cycle refrigerator at 18 K, with a multichannel spectrometer equipped with a CCD camera. The laser power was 10 mW focused to a 50 μm spot on the sample, and the incident light polarization was parallel to Z or to X while the outgoing polarization was in the XZ plane. Three main regions around 500, 2000, and 4000 cm^{-1} were studied in order to determine the effect of cerium doping on various CF levels of the Nd^{3+} ion $^4I_{9/2}$ ground multiplet and the $^4I_{11/2}$ and $^4I_{13/2}$ excited multiplets.

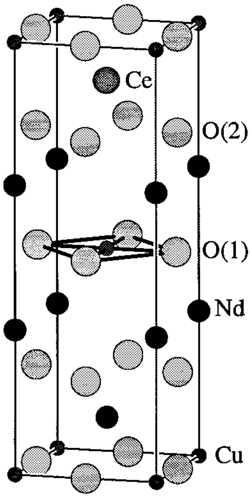

FIG. 1. Unit cell of Nd_2CuO_4 with one cerium ion substituting for one of the four neodymium ions.

RESULTS AND DISCUSSION

Like in Nd_2CuO_4, the Nd^{3+} ion site symmetry in $Nd_{1.85}Ce_{0.15}CuO_4$ is considered to be C_{4v} if no particularly low symmetry domains develop. Its ground state multiplet splits into three Γ_6 and two Γ_7 Kramers doublets while the first excited multiplet splits into three Γ_6 and three Γ_7 doublets and the second excited multiplet splits into three Γ_6 and four Γ_7 doublets. As discussed in the case of Nd_2CuO_4,[3] the Γ_6 to Γ_6 and Γ_6 to Γ_7 transitions are observed, respectively, in the (ZZ,XZ) and (XZ) polarization configurations. For 7.5% substitution of neodymium atoms by cerium atoms in Nd_2CuO_4, the probability of having 0 Ce atom, 1 Ce atom, 2 Ce atoms, and 3 Ce atoms in an ensemble of 10 Nd atoms is 0.46, 0.36, 0.14, and 0.03, respectively.[13] Thus the main observed CF excitations would be due either to unperturbed Nd^{3+} ions or to perturbed Nd^{3+} ions in the Nd_2CuO_4 tetragonal unit cell shown in Fig. 1 with one Nd^{3+} ion replaced by a Ce^{4+} ion. There are two types of perturbed Nd^{3+} ions, those at the distance $d=3.31$ Å of the Ce^{4+} ion in the same unit cell and those at the distance $a=3.94$ Å in the four first neighbor cells. The intensity ratio of scattering from unperturbed and perturbed Nd^{3+} ions would be almost equal to 2, assuming that the Raman polarizabilities are not affected by substitution. This simplified picture does not account for any phase separation, as reported by Lightfoot *et al.*,[30] or for the short-range atomic structure of $Nd_{2-x}Ce_xCuO_4$, as recently determined by real-space refinement of neutron powder-

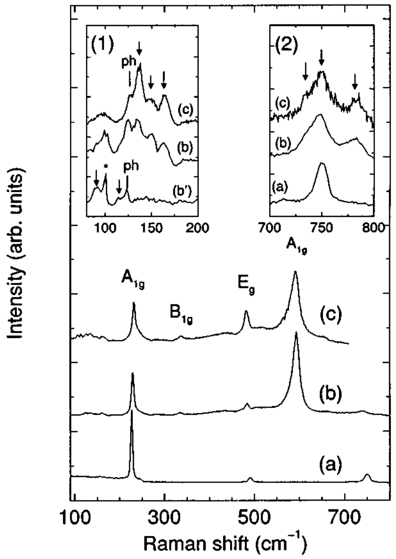

FIG. 2. Raman ground state CF excitations and phonons at 18 K in Nd_2CuO_4 (a) and in $Nd_{1.85}Ce_{0.15}CuO_4$ (b), (b′), and (c). In (a), (b), and (c) incident light polarization is parallel to Z while in (b′) it is parallel to X. Scattered light polarization is in the XZ plane. (a), (b), and (b′) are excited with the 4880 Å laser line while (c) is excited with the 5145 Å laser line. The insets illustrate with arrows the ground-state CF excitations of three inequivalent sites. ph and $*$ indicate the 120 cm^{-1} phonon and the 103 cm^{-1} plasma line, respectively.

diffraction data with the main result consisting in a structure formed by two types of local regions, one heavily distorted and one relatively undistorted. The structure within the distorted regions is reported to be ordered with a distinct symmetry that is nevertheless lower than the one of Nd_2CuO_4.[31]

In Fig. 2, Raman active phonons and CF excitations of $Nd_{1.85}Ce_{0.15}CuO_4$ at 18 K are presented and compared to the ones of Nd_2CuO_4. The insets (1) and (2) show expanded regions, around 150 and 750 cm^{-1}, where the CF excitations are located. Spectra were obtained using the 5145 and 4880 Å laser lines with the incident light polarization parallel to X or Z and the scattered light polarization in the XZ plane. The A_{1g} and E_g phonons are located as expected at 231 and 484 cm^{-1}, respectively, along with the 340 cm^{-1} B_{1g} phonon which is forbidden in this configuration but appears weakly because of polarization leakage. The strong oxygen local mode of Nd_2CuO_4 that is activated by cerium doping is detected at 590 cm^{-1}.[32,33] Comparing $Nd_{1.85}Ce_{0.15}CuO_4$ and Nd_2CuO_4 spectra, additional CF excitations below 200 cm^{-1} and three CF excitations around 735, 750, and 784 cm^{-1} are observed (inset 2 of Fig. 2). Considering the Γ_6 ground state symmetry and the experimental configurations (inset 1 of Fig. 2) the CF ground state excitations correspond to three Γ_6 states (located at 132 and 162 cm^{-1} with a possible weak excitation around 187 cm^{-1}) and three Γ_7 states (located at 95, 114, and 147 cm^{-1}). All these CF levels, which occur in triplets around the 752, 168, and 120 cm^{-1} CF excitations of Nd_2CuO_4, suggest the presence of three inequivalent sites associated with one unperturbed and two perturbed Nd^{3+} ion sites as a result of cerium doping.

The CF excitations are weak at 50 K and only the low energy 122 cm^{-1} E_g phonon that involves the vibration of the Nd^{3+} ions perpendicular to the c axis has been observed (Fig. 3). This phonon, initially reported only at room temperature in Nd_2CuO_4,[34] was studied later as a function of temperature.[3] Its interaction with the first excited Γ_7 ground state CF level in Nd_2CuO_4 results in a weakening of its intensity below 100 K. The observation of this phonon at low temperatures in $Nd_{1.85}Ce_{0.15}CuO_4$ is probably due to the slight energy shift of the CF level from 119 cm to 114 cm^{-1} that results in a reduction of the resonance with the phonon.

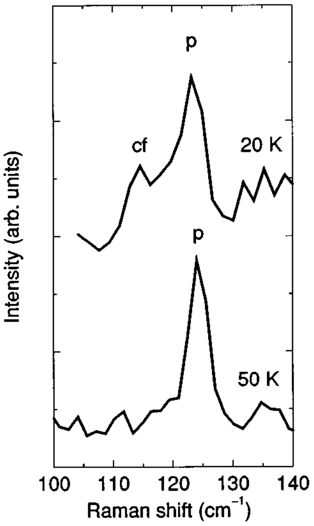

FIG. 3. E_g Raman phonon (p) and CF excitation (cf) in $Nd_{1.85}Ce_{0.15}CuO_4$ at different temperatures.

In Fig. 4, Raman spectra of the first excited multiplet CF levels of $Nd_{1.85}Ce_{0.15}CuO_4$ (b) and Nd_2CuO_4 (a) are shown. The three peaks observed around 1978, 1985, and 2000 cm^{-1} in $Nd_{1.85}Ce_{0.15}CuO_4$ correspond to the strongest CF excitation of the Nd^{3+} ion, around 1996 cm^{-1}, in Nd_2CuO_4. They provide additional evidence for the existence of three inequivalent sites for the Nd^{3+} ions in $Nd_{1.85}Ce_{0.15}CuO_4$.

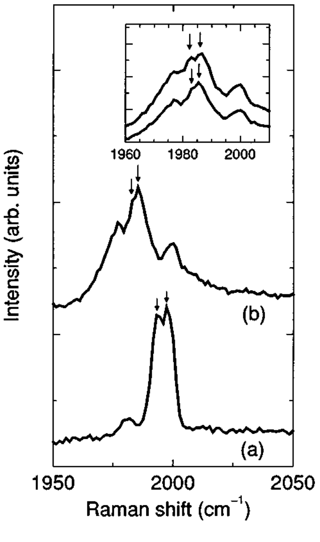

FIG. 4. Raman spectra of the CF transitions around 2000 cm^{-1} in Nd_2CuO_4 (a) and in $Nd_{1.85}Ce_{0.15}CuO_4$ (b). Splittings of the Kramers doublets, observed in $Nd_{1.85}Ce_{0.15}CuO_4$ (figure and inset) and in Nd_2CuO_4 spectra, are indicated with arrows.

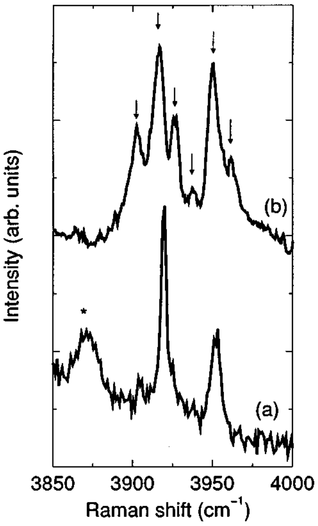

FIG. 5. Raman spectra of the CF transitions around 3900 cm^{-1} in Nd_2CuO_4 (a) and in $Nd_{1.85}Ce_{0.15}CuO_4$ (b). Triplet peaks due to different Nd^{3+} environments in $Nd_{1.85}Ce_{0.15}CuO_4$ are labeled with arrows; the asterisk $*$ denotes a luminescence band.

TABLE I. The CF parameters $B_{k,q}$ (in cm^{-1}) for different local environments in $Nd_{1.85}Ce_{0.15}CuO_4$ as compared with recent results for Nd_2CuO_4 (Ref. 5). Site II corresponds to unperturbed Nd^{3+} ions while sites I and III are influenced by cerium doping.

k,q	Site I	Site II	Site III	Nd_2CuO_4
2,0	556	−175	−420	−372
4,0	−2390	−2374	−2497	−2264
4,4	1673	1661	1889	1649
6,0	421	251	128	215
6,4	1387	1472		1477

The same considerations apply to the CF levels of the second excited multiplet shown in Fig. 5 where the 3922 and 3952 cm^{-1} peaks in Nd_2CuO_4 appear in triplicate in $Nd_{1.85}Ce_{0.15}CuO_4$ around (3901, 3916, 3926 cm^{-1}) and (3937, 3950, 3962 cm^{-1}), respectively. The presence of three inequivalent sites of the Nd^{3+} ions is thus documented for both the ground and excited states, in contrast to the neutron studies.[6,13] We emphasize the similarity of our measurements with Raman and neutron CF studies of $Pr_{1.85}Ce_{0.15}CuO_4$ where three inequivalent sites have also been reported for the Pr^{3+} ions.[20,35]

The persistence of antiferromagnetic order in $Nd_{1.85}Ce_{0.15}CuO_4$, as reported in the specific heat studies,[22,36] is confirmed by the measurement of CF excitations. A splitting of the ground state and first excited state Kramers doublets, is observed around 2000 cm^{-1} which is also the strongest CF excitation (see doublet 1983 and 1986 cm^{-1} in the inset of Fig. 4) and corresponds to the unperturbed site. This provides direct evidence for a molecular magnetic field related to the short range antiferromagnetic interaction in the CuO_2 plane.[4] While such a splitting of the order of 6 cm^{-1} in Nd_2CuO_4 (Ref. 4) implies, as reported, a ground state splitting of the order of 4 cm^{-1}, the splitting in $Nd_{1.85}Ce_{0.15}CuO_4$ is reduced to approximately 3 cm^{-1} with a corresponding ground state splitting of approximately 2 cm^{-1} if one assumes that the ground-state symmetry and eigenvector at the unperturbed site are, to a first approximation, not affected by cerium. As a consequence of doping, the exchange field acting on the Nd^{3+} ions is reduced. This conclusion is consistent with Luke *et al.*[28] who report a reduction of the Néel temperature from 250 K in Nd_2CuO_4 to 100 K in $Nd_{1.845}Ce_{0.155}CuO_4$. Our measurements also agree with the Schottky anomaly analysis in both Nd_2CuO_4 and $Nd_{1.85}Ce_{0.15}CuO_4$ which results in a reduction of the ground state splitting by almost a factor of 2, namely from ~4 to 2.3 cm^{-1}.[6]

In the following analysis, the crystalline electric field is treated as a perturbation on the intermediate-coupling $4f^3$ free ion energy levels. The CF Hamiltonian is written in terms of one-electron irreducible tensor operators as $H_{\mathrm{cf}}=\Sigma_{k,q}B_{kq}C_{kq}$ with five nonzero CF parameters $(B_{20},B_{40},B_{60},B_{44},B_{64})$ reflecting the C_{4v} symmetry of the Nd^{3+} ion crystal site position.[37] The CF spectrum corresponding to the central peaks in the Raman spectra of $Nd_{1.85}Ce_{0.15}CuO_4$ is very similar to that derived from the Nd_2CuO_4 CF levels.[5] We thus ascribe it to sites left unperturbed by the cerium doping. Even though it is not obvious how to group the satellite transitions (ground and excited levels), we have assumed that the low energy satellites correspond to one type of perturbed Nd^{3+} sites and the high energy satellites to the other type. Such grouping scheme stems from garnets where the CF interaction is rather similar to that in the cuprates.[38] For each of the three Nd^{3+} sites we have detected two Γ_6-Γ_6 and one Γ_7-Γ_7 transitions within the ground state multiplet $J=9/2$, one Γ_6-Γ_6 transition from the lowest ground state multiplet to the first excited one $J=11/2$, and two Γ_6-Γ_6 transitions from the lowest ground state multiplet to the second excited one $J=13/2$. The values of the CF parameters were determined by fitting the eigenvalues of the CF Hamiltonian to the energies of the detected Raman transitions (except for transitions to the $J=11/2$ multiplet since our analysis did not allow us to determine to which of the two close-lying Γ_6 levels around 2000 cm^{-1} they correspond) and also by taking into account the symmetry of the observed levels. The free ion energies of the ^4I_J multiplets were fixed to the best fit values obtained previously for Nd_2CuO_4 (Ref. 5) and the diagonalization procedure considered J mixing within the entire set of multiplets.

In Table I, the CF parameters for the three different sites are given and compared with the recently calculated Nd_2CuO_4 CF parameters.[5] In Table II, the energies of the measured CF excitations are compared with the results of the fit and the calculated CF parameters of Nd_2CuO_4.[5] The similarity between site II and Nd_2CuO_4 CF energy levels implies that site II corresponds to the unperturbed Nd^{3+}. The levels at 216, 1981, and 2409 cm^{-1} calculated for site II are in very good agreement with the inelastic neutron scattering measurements of corresponding transitions at 214±2.4, 1992±16 cm^{-1}, and 2402±16 cm^{-1}.[6] Also, the calculated site contribution to the susceptibility anisotropy, which is mainly governed by the sign and magnitude of the CF parameter B_{20},[11] is close to the experimental data.[17] The best-fit CF parameters of Table I for site III also lead to the correct susceptibility anisotropy. Both calculated ground state Γ_7 transitions, 216 cm^{-1} (site II) and 226 cm^{-1} (site III), com-

TABLE II. Calculated and observed CF levels for different local Nd^{3+} environments in $Nd_{1.85}Ce_{0.15}CuO_4$ as compared with the corresponding data for Nd_2CuO_4.

J	Site I Calc/Expt.		Site II Calc/Expt.		Site III Calc/Expt.		Nd_2CuO_4 Calc/Expt.	
	Energy	Γ_n	Energy	Γ_n	Energy	Γ_n	Energy	Γ_n
9/2	0/0	6/6	0/0	6/6	0/0	6/6	0/0	6/6
	100/95	7/7	114/114	7/7	145/147	7/7	119/120	7/7
	134/132	6/6	163/162	6/6	188/187	6/6	169/168	6/6
	224/-	7/-	216/-	7/-	226/-	7/-	213/206	7/7
	736/735	6/6	752/750	6/6	785/784	6/6	747/752	6/6
11/2	1956/1978	6/6	1981/1985	6/6	1986/2000	6/6	1986/1981	6/-
	1972/1978	6/6	1992/1985	6/6	2006/-	7/-	1999/1997	6/-
	2005/-	7/-	2004/-	7/-	2010/2000	6/6	2003/2011	7/-
	2066/-	7/-	2080/-	7/-	2106/-	7/-	2078/-	7/-
	2364/-	7/-	2392/-	6/-	2414/	6/-	2381/-	6/-
	2410/	6/-	2409/-	7/-	2450/-	7/-	2410/-	7/-
13/2	3897/3901	6/6	3913/3916	6/6	3920/3926	6/6	3919/3922	6/6
	3900/-	7/-	3919/-	7/-	3929/-	7/-	3923/-	7/-
	3941/3937	6/6	3950/3950	6/6	3962/3962	6/6	3953/3952	6/6
	3956/-	7/-	3969/	7/-	3988/-	7/-	3969/-	7/-
	4322/-	7/-	4348/-	7/-	4370/-	7/-	4338/4336	6/-
	4359/-	7/-	4352/-	6/-	4370/-	6/-	4341/-	7/-
	4387/-	6/-	4409/-	7/-	4461/-	7/-	4416/-	7/-
15/2	5775/-	7/-	5763/-	7/-	5780/-	7/-	5763/-	7/-
	5820/	7/-	5827/-	7/-	5823/-	7/-	5831/-	7/-
	5829/-	6/-	5865/-	6/-	5892/-	6/-	5872/-	6/-
	5889/-	6/-	5910/-	6/-	5926/-	6/-	5917/5920	6/-
	6464/-	6/-	6422/-	6/-	6429/-	7/-	6401/6400	6/-
	6478/-	6/-	6472/-	7/-	6493/-	7/-	6464/-	7/-
	6479/-	7/-	6572/	7/-	6580/-	7/-	6571/	7/-
	6550/-	7/-	6578/-	6/-	6642/-	6/-	6590/6588	6/-

ply with the uniform scaling conjecture.[39] In contrast to these two sites, best-fit CF parameters for site I are consistent with the observed susceptibility anisotropy only at low temperatures. The corresponding anisotropy remains strong but is reversed above ~40 K. Furthermore, the Γ_7 transition calculated at 224 cm^{-1} is not consistent with uniform scaling. These discrepancies could be indicative of a lower symmetry domain for site I, in agreement with the neutron diffraction measurements.[30]

While Stadlober *et al.* report only one series (100, 167, 206 cm^{-1}) for the ground state CF levels in their Raman study of $Nd_{1.84}Ce_{0.16}CuO_4$,[19] we detect unambiguously three inequivalent sites in samples of different thicknesses grown in two different laboratories. The presence of inhomogeneities may thus be responsible for differences between the various results of the different groups. It should be accounted for in the interpretation of $Nd_{1.85}Ce_{0.15}CuO_4$ data.

CONCLUSION

Our CF study of single crystal $Nd_{1.85}Ce_{0.15}CuO_4$ extends previous CF measurements of Nd_2CuO_4 and emphasizes the power of the Raman technique. Three different Nd^{3+} ion sites are observed in $Nd_{1.85}Ce_{0.15}CuO_4$. For each site six different levels have been detected and the CF parameters that describe the observed spectra have been derived. One of the sites (II) corresponds to the almost unperturbed Nd^{3+} ions while the other two sites (I and III) are influenced by the cerium doping. The presence of low symmetry regions (site I) is detected and the relative narrowness of the corresponding CF excitations suggests that these regions are ordered. The strongest CF excitation in the unperturbed site around 1985 cm^{-1} corresponds to a Kramers doublet that splits (1983–1986 cm^{-1}) under the action of the CuO_2 molecular magnetic field. This strongly suggests that there are regions in $Nd_{1.85}Ce_{0.15}CuO_4$ where ferromagnetic order persists.

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