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Infrared study of crystal-field excitations in $Nd_{2-x}Ce_xCuO_4$

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Infrared active crystal-field excitations were detected in $Nd_{2-x}Ce_xCuO_4$ single crystals for various x. They correspond to the ${}^4I_{9/2}\rightarrow{}^4I_{11/2}$, ${}^4I_{9/2}\rightarrow{}^4I_{13/2}$, and ${}^4I_{9/2}\rightarrow{}^4I_{15/2}$ intermultiplet transitions associated with the Nd^{3+} ion inequivalent sites. Two sets of crystal-field parameters which describe the observed energy spectra were derived. In addition to unperturbed sites, similar to those observed in Nd_2CuO_4, perturbed sites affected by cerium doping and compatible with available local structure deformation data are detected. We infer from our data that the Kramers doublets of Nd^{3+} are split and consequently that the antiferromagnetism in the CuO_2 planes persists in regions where the unperturbed sites are located, even with 7.5% cerium doping.

INTRODUCTION

Electron-type superconductivity appears for $0.14\leqslant x\leqslant 0.18$ in the $Nd_{2-x}Ce_xCuO_4$ compounds after oxygen reduction.[1] These materials have a simple tetragonal structure that renders them attractive for the study of fundamental properties associated with high-T_c superconductivity. Recently, Raman scattering and infrared spectroscopy have been successfully used to study the crystal-field (CF) excitations of the Nd^{3+} ion $4f^3$ electrons in Nd_2CuO_4 influenced by the local electric and magnetic properties.[2–6]

Boothroyd *et al.*[7] studied by neutron scattering $Nd_{1.85}Ce_{0.15}CuO_4$ pellets and identified broad transitions associated with the Nd^{3+} CF ground state at 98, 164, 214, and 752 cm^{-1}. While Furrer *et al.*[8] interpreted those measurements as encompassing two sets of CF excitations related to perturbed and unperturbed Nd^{3+} ions by Ce doping, Boothroyd *et al.*[9] claimed that the two sets of parameters given by Furrer *et al.*[8] do not describe adequately the observed spectra. Jones *et al.*[10] studied CF transitions in superconducting $Nd_{1.85}Ce_{0.15}CuO_4$ and its parent compound Nd_2CuO_4. They reported transmission spectra in films and reflectivity measurements in pellets. 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 when Nd_2CuO_4 was doped with cerium. We have recently observed Raman active intermultiplet CF excitations in $Nd_{1.85}Ce_{0.15}CuO_4$ and associated them with perturbed and unperturbed sites[11,12] in contrast to Stadlober *et al.*, who reported only one series for the ground-state CF excitations in their Raman study of $Nd_{1.84}Ce_{0.16}CuO_4$.[13] A good description of the Raman observations has been obtained using local structure information from neutron diffraction.[14]

In this paper we present an infrared transmission study of $Nd_{2-x}Ce_xCuO_4$ as a function of x for samples grown by two different techniques and with different electrical characters. The purpose of this work, which complements previous Raman studies,[11,12] is (i) to investigate the cerium doping effect on the Nd^{3+} ion CF levels, (ii) to analyze these levels and to calculate their corresponding CF parameters so as to obtain some insight about the sites characteristics, and (iii) to search for a Kramers doublet splitting due to persisting antiferromagnetic order in the unperturbed sites. The latter represents an effort to resolve the controversy between Skanthakumar *et al.*,[15] whose neutron study implies the absence of antiferromagnetic order as a result of 7.5% cerium doping, and Luke *et al.*,[16] 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. The presence of more than one site is an indication of spatial inhomogeneities on the one hand, while on the other hand, persistence of antiferromagnetism in the CuO_2 planes could be crucial to the mechanism as suggested recently by Emery and Kivelson[17] and exemplified by the stripe ordering in $La_{2-x}Sr_xNiO_4$-type materials.[18]

EXPERIMENT

Infrared absorption of $Nd_{2-x}Ce_xCuO_4$ single crystals was studied as a function of cerium doping (x) and temperature. Single crystals were grown, on the one hand, by the top-seeded solution method[19] with $x=0,0.005,0.01,0.1,0.2$ in platinum crucibles and with $x=0.05$ in an aluminum crucible, and on the other hand, by the traveling solvent floating zone technique[20] with $x=0.15$. The latter single crystal was not reduced and was not superconducting. In order to further characterize the $Nd_{2-x}Ce_xCuO_4$ single crystals, microwave conductivity at 16.5 GHz was measured, in the 4–300 K temperature range, using the standard cavity perturbation technique as described by Buranov and Schegolev.[21] An interest in this technique resides in its simplicity and in its electrical contactless setup.

The samples (typically $5\times0.7\times0.07\,\text{mm}^3$) were mounted in a continuous-flow temperature regulated helium cryostat with the XZ plane perpendicular to the incident beam. $0.5\ \text{cm}^{-1}$ resolution infrared transmission spectra in the $1800–8000\ \text{cm}^{-1}$ range were obtained using a Fourier-transform interferometer (BOMEM DA3.002) equipped with quartz and globar sources, InSb detector, and CaF_2 beam splitter.

RESULTS AND DISCUSSION

As in Nd_2CuO_4, the Nd^{3+} ion unperturbed site symmetry in $Nd_{2-x}Ce_xCuO_4$ is considered to be C_{4v}. The CF at this site splits the lowest energy multiplet 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.[22] The symmetry of excitations between these $4f$ states, which involves the direct product of their irreducible representations, corresponds to either

$$\Gamma_6 X\Gamma_6=\Gamma_7 X\Gamma_7=\Gamma_1+\Gamma_2+\Gamma_5$$

or

$$\Gamma_6 X\Gamma_7=\Gamma_7 X\Gamma_6=\Gamma_3+\Gamma_4+\Gamma_5.$$

The excitations of $\Gamma_1(z)$ and $\Gamma_5(x,y)$ symmetries are infrared active and our experimental configuration allows the detection of both $\Gamma_6\rightarrow\Gamma_6$ and $\Gamma_6\rightarrow\Gamma_7$ excitations.

Infrared transmission spectra, at $T=4.2\,\text{K}$ of $Nd_{2-x}Ce_xCuO_4$ as a function of x, are shown in Fig. 1(a) in the range $1900–2500\ \text{cm}^{-1}$. They correspond to CF excitations from the Γ_6 symmetry ground state of the multiplet $^4I_{9/2}$ to the first excited multiplet $^4I_{11/2}$. Individual components of the absorption bands corresponding to CF excitations of Nd^{3+} ions in different environments are determined by fitting the transmission spectra with mixed Lorentzian and Gaussian bands [Fig. 1(b)]. There is a set of the $\Gamma_6\rightarrow\Gamma_6$ and $\Gamma_6\rightarrow\Gamma_7$ CF transitions with frequencies only slightly shifted with respect to those observed in Nd_2CuO_4.[6,23] These transitions are thus associated with a site which is not perturbed by the Ce doping (assigned as site I in the following). Also, new absorption bands (1975, 1999, 2069, and $2364\ \text{cm}^{-1}$) are observed and their intensity is found to increase with doping. They are thus associated with the doping perturbed site II. Influence of the aluminum crucible compared to the platinum crucible manifests itself in the appearance of an additional type of site, with the CF excitations at 1962 and $2161\ \text{cm}^{-1}$.

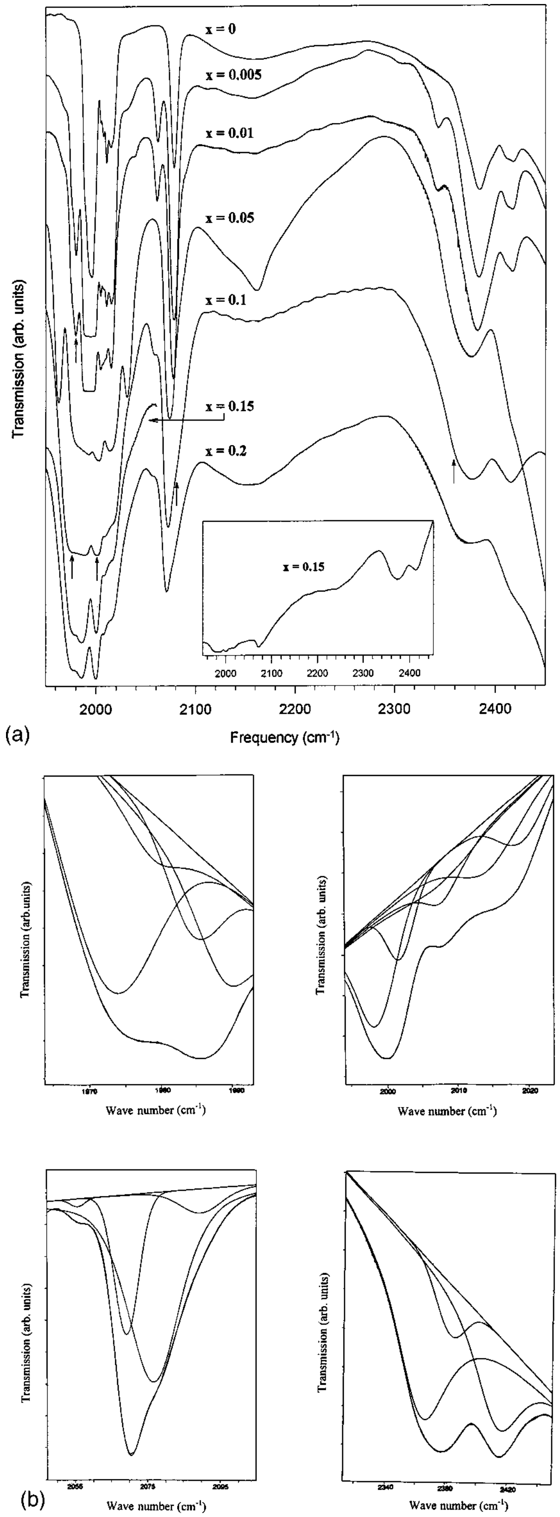

FIG. 1. CF absorption bands of the Nd^{3+} $4f$ electrons first excited multiplet ($^4I_{11/2}$) in $Nd_{2-x}Ce_xCuO_4$ as a function of cerium doping at $T=20\,\text{K}$; arrows indicate the new excitations resulting from doping (a). Fitting of the absorption bands (b).

Absorption bands, in the 3880–4440 and $5740–6640\ \text{cm}^{-1}$ ranges, that involve the second excited multiplet ($^4I_{9/2}\rightarrow{}^4I_{13/2}$) and third excited multiplet ($^4I_{9/2}\rightarrow{}^4I_{15/2}$) are shown as a function of doping in Figs. 2(a) and 3(a), respectively, with their associated band fitting [Figs. 2(b) and 3(b)]. They confirm the presence of the unperturbed site as indicated in Figs. 2(a) and 3(a) and the appearance of new bands (3897, 3912, 3933, 4302, and $4371\ \text{cm}^{-1}$) in the $3880–4440\text{-cm}^{-1}$ range and (5752, 5817, 5848, 5914, 6380, 6435, and $6549\ \text{cm}^{-1}$) in the $5740–6640\text{-cm}^{-1}$ range. Similarly, the perturbation due to the aluminum crucible is confirmed by bands around 3883, 4084, and $6007\ \text{cm}^{-1}$. Since

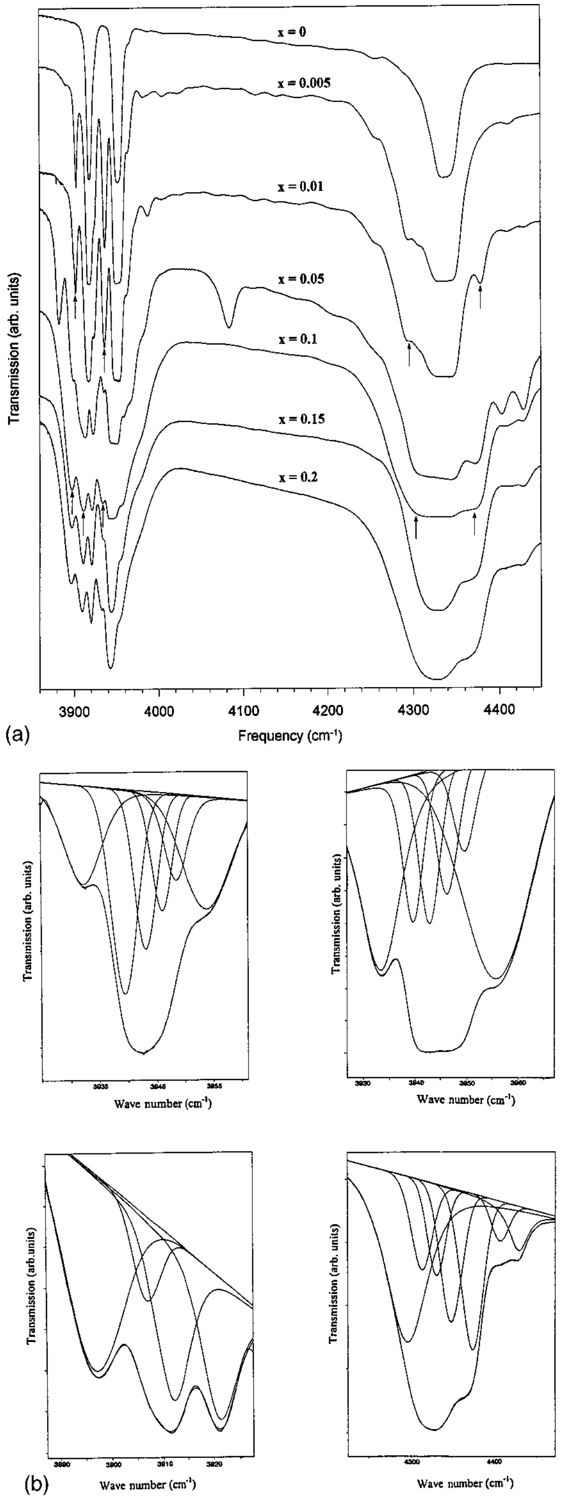

FIG. 2. CF absorption bands of the Nd^{3+} $4f$ electrons second excited multiplet ($^4I_{13/2}$) in $Nd_{2-x}Ce_xCuO_4$ as a function of cerium doping at $T=20$ K; arrows indicate the new excitations resulting from doping (a). Fitting of the absorption bands (b).

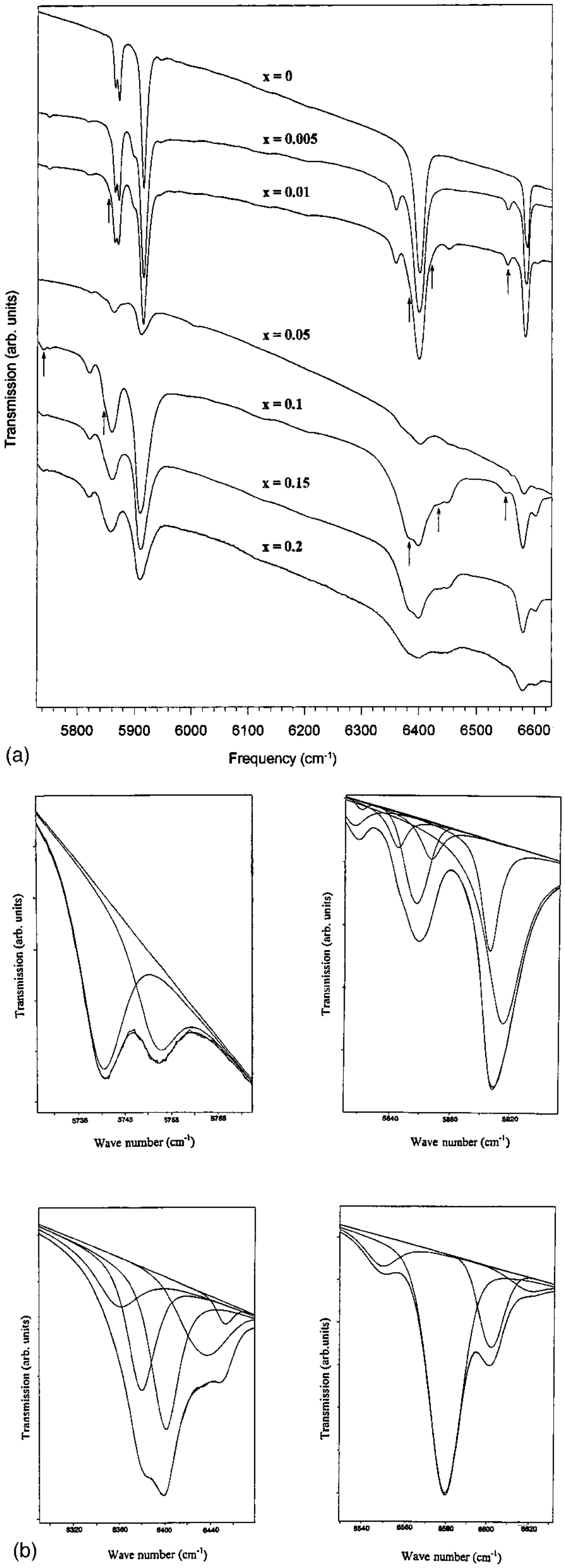

FIG. 3. CF absorption bands of the Nd^{3+} $4f$ electrons third excited multiplet ($^4I_{15/2}$) in $Nd_{2-x}Ce_xCuO_4$ as a function of cerium doping at $T=20$ K; arrows indicate the new excitations resulting from doping (a). Fitting of the absorption bands (b).

the energies of the CF excitations do not depend significantly on x, only the $x=0.15$ data are shown in our tables and considered in our analysis. Interestingly, we detect no difference between the spectra of the crystals grown by the traveling solvent floating zone technique and crystals grown in platinum crucibles. We also observe that the electrical character, resulting from cerium doping (semiconducting for $x \leqslant 0.01$ and metallic for $x \geqslant 0.05$), has no influence on the CF excitations of sites I and II.

The five CF parameters B_{kq} in the unperturbed site I, given in the second column in Table I have been deter-

TABLE I. The CF parameters B_{kq} (in cm^{-1}) for different local environments of the Nd^{3+} ion in $Nd_{1.85}Ce_{0.15}CuO_4$. The site I corresponds to the unperturbed regions while the site II is influenced by the cerium doping (see the text for details).

kq	Site I	Site II	Nd_2CuO_4 (Ref. 6)
2 0	−226 (18)	−226	−335 (22)
4 0	−2323 (35)	−2188	−2219 (33)
4 4	1567 (31)	1537	1634 (22)
6 0	218 (7)	245	224 (12)
6 4	1525 (6)	1472	1494 (9)

mined by a fit to the corresponding experimental bands (Table II) using a least-squares procedure.[24] Similarly, as in earlier studies of $Nd_{1.835}Ce_{0.165}CuO_4$ (Ref. 14) and $Pr_{2-x}Ce_xCuO_4$,[25] we tentatively attribute the appearance of an additional Nd^{3+} site in $Nd_{2-x}Ce_xCuO_4$ to a local disorder involving oxygen in the CuO_2 planes. This disorder, whose prominent feature is the vertical displacement of the in-plane oxygens of about 0.1 Å induced by doping, have been studied in $Nd_{1.835}Ce_{0.165}CuO_4$ using the pair distribution function analysis of neutron-diffraction data.[26,27] Within this scheme, 40% of the Nd^{3+} ions are in undistorted domains, and the remaining 60% of the Nd^{3+} ions are divided among three inequivalent sites of C_1 and C_s symmetry in distorted domains.

Using the superposition model, proven to be very efficient in the modeling of the fourth- and sixth-order CF parameters in cuprates,[14,28] we have estimated the impact of the local deformations described in Ref. 27 on the CF excitations. An important feature of this model is that it neglects ions outside the coordination polyhedron of the Nd^{3+} ion, which allows us to describe the CF interaction in the above-mentioned C_1 and C_s symmetry sites by the tetragonal symmetry Hamiltonian. A comparison with the experimental data given in the third column in Table II indicates that site II is the C_1 symmetry site of Ref. 27. The CF parameters for this site in $Nd_{1.85}Ce_{0.15}CuO_4$ are given in Table I, where the recently calculated Nd_2CuO_4 CF parameters[6] are shown for compari-

TABLE II. Calculated and observed infrared active 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. Experimental uncertainty is ±2 cm^{-1} and uncertainty due to B_{20} is given in brackets (see the text for details). * indicates Raman active CF excitations (Refs. 11 and 12) and ** denotes neutron measurements (Ref. 9).

	Site I Calc./Expt.		Site II Calc./Expt.		Nd_2CuO_4 Calc./Expt.	
J	Energy (cm^{-1})	Symmetry $i(\Gamma_i)$	Energy (cm^{-1})	Symmetry $i(\Gamma_i)$	Energy (cm^{-1})	Symmetry $i(\Gamma_i)$
$\frac{11}{2}$	1984/1987	6	1980(3)/1975		1993/1995	6
	1985*		1978*		2004/2006	6
	1993/2006	6	1990(2)/-		2008/2013	7
	1992±16**		2000(11)/1999		2080/2077	7
	2008/2015	7	2000*		2384/2383	6
	2072/2077	7	2064(6)/2069		2414/2414	7
	2384/2383	6	2363(13)/2364			
	2408/2414	7	2385(13)/-			
	2402±16**					
$\frac{13}{2}$	3910/3907	6	3707(1)/3897		3918/3918	6
	3912/3924	7	3901*		3921/3924	7
	3926*		3910(2)/3912		3951/3950	6
	3946/3948	6	3916*		3965/3964	7
	3950*		3941(7)/3993		4333/4329	6
	3960/3959	7	3937*		4338/-	7
	3962*		3953(6)/-		4412/4410	7
	4334/4319	6	4315(17)/4302			
	4336/4342	7	4317(7)/-			
	4406/4410	7	4380(20)/4371			
$\frac{15}{2}$	5742/5740	7	5747(3)/5752		5756/5754	7
	5820/5822	7	5822(1)/-		5828/5824	7
	5858/5865	6	5851(1)/5848		5865/5868	6
	5908/5906	6	5904(7)/5914		5914/5914	6
	6399/6401	6	6380(20)/6380		6395/6400	6
	6456/6453	7	6437(8)/6435		6460/-	7
	6575/-	7	6548(5)/6549		6571/6570	7
	6582/6580	6	6550(24)/6549		6585/6585	6

son. Note that we have set arbitrarily the site I value, $B_{20} = -226\,\mathrm{cm}^{-1}$, also in the C_1 symmetry site as the superposition model does not apply to the second-order CF parameters.

In Table II, the energies of the measured CF excitations are compared with the results of the fit for the undistorted domains, with the superposition model prediction for the C_1 symmetry site in the distorted domains in $\mathrm{Nd_{1.85}Ce_{0.15}CuO_4}$, and with the $\mathrm{Nd_2CuO_4}$ calculated and measured CF excitations.[6] For each superposition model calculated level given in Table II, an uncertainty is associated, obtained presuming that the value of the B_{20} parameter falls within 500 and 0 cm^{-1}. This uncertainty does not concern the data for site I. The similarity between site I and $\mathrm{Nd_2CuO_4}$ CF energy levels, measured and calculated, confirms that this site corresponds to the $\mathrm{Nd^{3+}}$ ions in unperturbed domains. Furthermore, it is seen that the observed levels in this site are in agreement with the excitations at 1985 and 3950 cm^{-1} that were associated with the unperturbed sites in earlier $\mathrm{Nd_{1.85}Ce_{0.15}CuO_4}$ Raman studies[11,12] as well as with the inelastic neutron-scattering data for this compound, 1992 ± 16 and $2402 \pm 16\,\mathrm{cm}^{-1}$.[9] We also assign the 3926 and 3962 cm^{-1} Raman active excitations, which were previously associated with a perturbed site,[11] to the $\Gamma_6 \rightarrow \Gamma_7$ intermultiplet excitations in site I. Site II excitations are in agreement with the Raman active excitations assigned to perturbed sites (1978, 2000, 3901, and 3937 cm^{-1}),[11,12] and with the prediction for the C_1 symmetry sites in distorted domains. Summarizing this part we conclude that, similar to the Raman study of the neighboring compound $\mathrm{Pr_{2-x}Ce_xCuO_4}$,[25] only the CF excitations associated with C_1 symmetry sites have been observed. There is no evidence for the presence of the C_s symmetry sites in distorted domains as described by the neutron-diffraction data.[26,27]

Kramers doublet splittings have been obtained by the fitting of the intermultiplet excitations associated with the unperturbed site I as indicated in Figs. 1(b), 2(b), and 3(b). In Table III, the $\mathrm{Nd^{3+}}$ Kramers doublet splittings in $\mathrm{Nd_{1.85}Ce_{0.15}CuO_4}$ are compared to the ones in $\mathrm{Nd_2CuO_4}$. Even though broadness of the bands prevents us from considering our fittings as nonequivocal, there is a strong indication of the persisting antiferromagnetic order in $\mathrm{Nd_{1.85}Ce_{0.15}CuO_4}$ as previously reported in the specific-heat studies[29,30] and the Raman measurements.[11]

CONCLUSION

The present infrared CF study of $\mathrm{Nd_{2-x}Ce_xCuO_4}$ for various cerium compositions extends a previous infrared CF study of $\mathrm{Nd_2CuO_4}$. Two different $\mathrm{Nd^{3+}}$ ion sites are observed in these compounds. For each site the intermultiplet CF excitations for $J = \frac{11}{2}$, $\frac{3}{2}$, and $\frac{15}{2}$ have been detected and the CF parameters that describe the observed spectra have been derived. One of the sites corresponds to the almost unperturbed $\mathrm{Nd^{3+}}$ ions while the other site is perturbed by the cerium doping. The CF excitations at the perturbed sites are compatible with the C_1 symmetry local structural changes determined by the real-space refinement of the neutron-diffraction data. The observed splitting of the Kramers doublets, ascribed to the exchange interaction Nd-Cu, suggests that the antiferromagnetic order in the $\mathrm{CuO_2}$ planes in the Ce-doped $\mathrm{Nd_2CuO_4}$ compounds persists in regions where the unperturbed sites are located.

TABLE III. $\mathrm{Nd^{3+}}$ Kramers doublets splitting (d.s.) in $\mathrm{Nd_{1.85}Ce_{0.15}CuO_4}$ compared to $\mathrm{Nd_2CuO_4}$ (Ref. 22). * corresponds to transitions involving the 5-cm^{-1} ground-state level.

J	Symmetry	$\mathrm{Nd_{1.85}}$ d.s. (± 1 cm^{-1})	$\mathrm{Ce_{0.15}CuO_4}$ d.s. (± 1 cm^{-1})	$\mathrm{Nd_2CuO_4}$ d.s. (± 1 cm^{-1})
$\frac{9}{2}$	Γ_6		5	5.5
$\frac{11}{2}$	Γ_6	1979* 1985 1989	4	3.5
	Γ_7	2002* 2008	3	3.5
	Γ_6	2014 2017	3	4
$\frac{13}{2}$	Γ_6	3940* 3943* 3946 3949	3	2.5
$\frac{15}{2}$	Γ_6	5859* 5867	2	2

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