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4f-levels in rare earth cuprates: Crystal field and exchange interaction

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Abstract

Measurements of the infrared transmission spectra up to ~10 000 cm^{-1}, ab-initio calculations based on the density functional theory and the use of an anisotropic exchange Hamiltonian to describe the magnetic coupling of rare earth (RE)–Cu are new instruments shown in this paper to provide an additional insight into the nature of the 4f splitting in rare earth (RE) cuprates. (i) Sets of the parameters of the crystal field Hamiltonian for trivalent Nd and Sm in regular as well as in Ba-sites in $\text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{6+y}$ are determined; (ii) Nd_2CuO_4 is found to be an exceptionally suitable system to study the anisotropy of the exchange interaction: Kramers doublet splittings due to the superexchange Cu–Nd interaction, deduced from the intermultiplet transitions spectra, are interpreted in terms of an effective Hamiltonian for the Nd^{3+} ion expressed in terms of single electron spherical tensor operators up to the sixth order; (iii) it is shown that the defects in Nd_2CuO_4, $\text{Nd}_{2-x}\text{Gd}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, that give rise to satellites in the spectra of 4f excitations, are universal and related to a local lattice deformation associated with a charge inhomogeneity. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In spite of the widespread belief that optical techniques are not appropriate to study the 4f excitations in opaque materials, crystal field (CF) excitations of rare earth (RE) ions in RE_2CuO_4 have been observed by Raman scattering (see e.g. Ref. [1] and references therein). Next, following the early reflection and transmission measurements in the visible region [2], sharp f–f transitions have been observed in Nd_2CuO_4 by IR absorption spectroscopy [3]. Surveyed in this report are results of several recent studies of RE cuprates based on this experimental technique.

The report is organized as follows: In the next Section we will show how the IR transmission measurements combined with model calculations have been used to study the CF interaction for the RE^{3+} (Re=Nd, Sm) ions in the regular D_{4h}-symmetry sites and in the substituted C_{4v}-symmetry Ba-sites in $\text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{6+y}$ (y~0). In Section 3 we will analyze the splitting of the Kramers doublets of Nd^{3+} in Nd_2CuO_4 in terms of the anisotropic Nd–Cu coupling. The nature of satellites in the CF spectra in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ is discussed in Section 4.

2. Crystal field in $\text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{6+y}$ (RE=Nd,Sm)

The IR spectra of single crystalline $\text{NdBa}_2\text{Cu}_3\text{O}_{6+y}$ (y~0) and $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{6+y}$ ($x\leq 0.01$, $x=0.05$, 0.11 and 0.03, y~0) have been measured using a Fourier-transform interferometer in the temperature range from 4.2 to 300 K. The IR-active transitions involving Kramers doublets within the ^{4}I term and the ^{6}H terms in the Nd- and Sm-compounds, respectively, were determined. Several transitions are shown in Figs. 1 and 2 as an example. These transitions are electric-dipole forbidden for the RE^{3+}ions placed at the regular D_{4h} symmetry sites in ideal $\text{REBa}_2\text{Cu}_3\text{O}_6$. We conjecture that they become observable due to lattice imperfections. A detailed CF analysis of the IR spectra, including also the inelastic neutron scattering data for the lowest J multiplet in $\text{NdBa}_2\text{Cu}_3\text{O}_6$ [4], allowed us to unambiguously identify and fit a nearly

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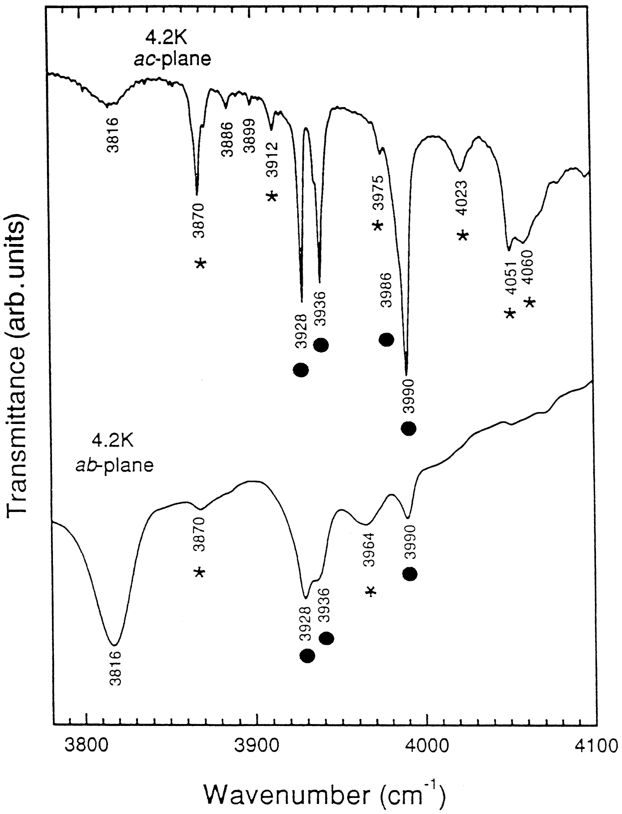

Fig. 1. IR transmission spectra of CF transitions ($^4I_{9/2} \rightarrow ^4I_{13/2}$) at $T=8$ K in $NdBa_2Cu_3O_6$ in the 3800–4100 cm^{-1} range (accross *ab*- and *ac*-oriented platelets at 4.2 K). Filled circles and asterisks indicate the regular (D_{4h}) and Nd/Ba (C_{4v}) sites, respectively. Remaining peaks are associated with defects [4].

complete CF spectra of the lowest-energy Russel–Saunders terms of Nd and Sm at regular sites [5,6].

Detailed CF calculations for $Sm_{1+x}Ba_{2-x}Cu_3O_{6+y}$ indicate that additional bands observed in the IR spectra correspond to the Sm^{3+} ions in the C_{4v} symmetry Ba sites. The fourth and sixth order CF parameters in these sites have been predicted using the superposition model, proven to be very efficient in CF modeling in cuprates [7]. The parameter B_{20}, for which this model does not apply, was calculated using an ab-initio method based on the density functional theory (DFT) [8,9]). Within the DFT, the parameter B_{20} of the CF Hamiltonian, originating from the effective potential, *V*, inside the crystal, is written as

$$B_{20} = a_0^2 \int_0^\infty |R_{4f}(r)| V_0^2(r) r^2 \, dr \qquad (1)$$

where the non-spherical component V_0^2 (r) reflects besides the nuclear potentials and Hartree part of the inter-electronic interaction also the exchange correlation term which accounts for many particle effects. The radial wave function R_{4f} describes the radial shape of the localized 4f charge density of Sm^{3+} ion in the studied compounds. This method was first tested in calculation of B_{20} for regular sites in $SmBa_2Cu_3O_6$ and $NdBa_2Cu_3O_6$. The resulting values of 320 and 412 cm^{-1} compare favorably with the respective phenomenological values. All the above mentioned CF parameters are summarized in Table 1.

3. Anisotropy of the Nd–Cu exchange interaction in Nd_2CuO_4

The IR transmission study of the ^4I_J, $J=9/2$, 11/2, 13/2 and 15/2 multiplets of Nd^{3+} in the antiferromagnetic Nd_2CuO_4 single crystals yielded a splitting of the Kramers doublets of the order of a few cm^{-1} due to the exchange interaction between Nd and Cu [10]. In an earlier study this interaction has been interpreted using a mean field model within which an isotropic part of the exchange term vanishes for symmetry reasons and the anisotropic interaction arising from the orbital degeneracy of the Nd^{3+} ions is represented by a pseudo-dipolar term [11]. An analysis of the doublet splittings revealed, in a qualitative agreement with Ref. [11], that the dominant contribution to the Nd–Cu coupling is provided by anisotropic terms in the exchange Hamiltonian [10]. In the following we present an analysis of the doublet splittings based on the complete Hamiltonian within the molecular field approximation [12–14] describing the exchange interaction of the 4f electrons of a Nd ion with the magnetically polarized Cu sublattice.

The single-ion perturbation Hamiltonian under consideration, *H*, includes besides the standard CF term also the exchange term H_{exch} [12]:

$$H_{\text{exch}} = -2\sum_{k,q} \alpha_{kq} \sum_i T_q^{[k]}(i) s(i) \cdot \boldsymbol{n} \qquad (2)$$

where α_{kq} are the exchange parameters, $T_q^{[k]}$ are the unit irreducible tensor operators which act on the orbital part of the Nd wave function; $\mathbf{s}(i)$ is the spin operator of the *i*th Nd electron and $\boldsymbol{n}$ is the unit vector directed along the crystallographic *a*-axis in our case. The Nd site symmetry C_{4v} implies that there are six independent parameters in H_{exch}.

A least squares procedure has been used to fit the splitting of the eight observed Kramers doublet splittings using the above mentioned perturbation Hamiltonian. Attempts to fit these splittings with an isotropic exchange parameter α_{00} entirely failed. The inclusion of α_{20} leads to only a partial improvement of the fit; which indicates that the higher order terms in Eq. (2), neglected in Ref. [1], are important. The results of the final fit considering all six parameters α_{kq} as unknowns are summarized in Table 2; the corresponding best-fit values of α_{kq} are given in Table 3.

4. CF spectra in Ce–doped Nd_2CuO_4

An interpretation of the impact of doping on the CF spectra in RE cuprates is still a matter of debate. For

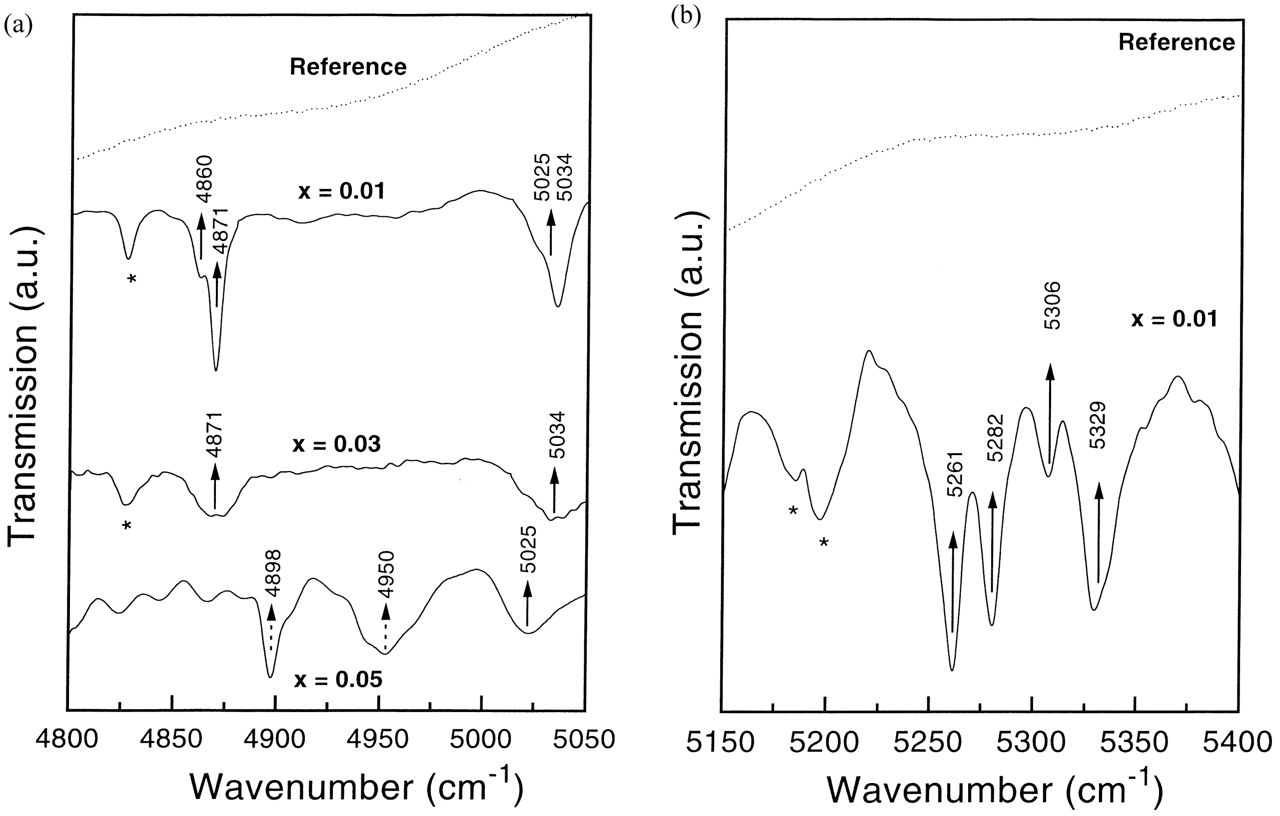

Fig. 2. IR spectra of CF transitions ($^6H_{5/2} \rightarrow {}^6H_{13/2}$) in $Sm_{1+x}Ba_{2-x}Cu_3O_6$ at $T = 8$ K in the 4800–5050 cm^{-1} range (a) and in the 5150–5400 cm^{-1} range (b). Arrows and dashed arrows indicate the regular (D_{4h}) and Sm/Ba (C_{4v}) sites, respectively.

example, the most prominent and widely discussed Ce-doping induced feature observed in early Raman [15] and neutron [16] studies of $Pr_{2-x}Ce_xCuO_4$ at ~125 cm^{-1} was recently found to be a low frequency E_g phonon rather than an assumed CF transition [17]. The Ce-doping induced broadening of the 4f excitations in the inelastic neutron scattering spectra of $Nd_{2-x}Ce_xCuO_4$ [18] have been interpreted in terms of two different Nd^{3+} environments [19]. However, the two sets of the CF parameters given in Ref. [18] do not describe adequately the neutron spectra [20].

The IR spectroscopy enables us to study the above mentioned phenomena in $Nd_{2-x}Ce_xCuO_4$ in more detail [21]. The IR active CF excitations detected in non-super-

Table 1
CF parameters (in cm^{-1}) in $Sm_{1+x}Ba_{2-x}Cu_3O_6$ [6] and $Nd_{1+x}Ba_{2-x}Cu_3O_6$ [5] obtained by an analysis of the IR spectra (see text)

B_{kq}		D_{4h} site		C_{4v} site Sm
k	q	Sm	Nd	
2	0	282(5)	380(28)	−227
4	0	−2481(12)	−2956(34)	24
4	4	1307(10)	1664(25)	−331
6	0	321(12)	526(15)	−427
6	4	1931(6)	2021(10)	624

Table 2
Splitting of the Nd^{3+} Kramers doublets in Nd_2CuO_4 as measured by infrared transmission [9] and calculated using Eq. (1) [13] (all energies in cm^{-1})

J multiplet	CF level [3]	Splitting	
		Observed	Calculated
9/2	g.s.	5.5	5.7
	1995	3.5	3.7
	2006	3.5	3.5
11/2	2013	4.0	3.7
	2077	2.0	2.1
	2414	3.0	2.9
13/2	3950	2.5	2.7
15/2	5868	2.0	1.3

Table 3
The best-fit values of the exchange parameters (in cm^{-1})

Exchange parameter (α_{kq})	
α_{00}	−7(4)
α_{20}	−491(130)
α_{40}	−177(33)
α_{44}	−257(12)
α_{60}	15(16)
α_{64}	47(13)

conducting single crystals grown by various techniques were found to correspond to intermultiplet transitions associated with the Nd^{3+} ion inequivalent sites. Examples of the IR spectra are given in Fig. 3. Two sets of the CF transitions have been identified. There is a set of transitions with frequencies only slightly shifted with respect to those observed in Nd_2CuO_4 [3] associated with a Nd site which is not perturbed by the Ce-doping (site I).

Intriguing are new absorption bands, associated with the doping perturbed site II. An appearance of this site is attributed in this study to a local structure deformation in the CuO_2 planes associated with Ce-doping induced charge transfer [22]. A prominent feature of this disorder, studied in $Nd_{1.835}Ce_{0.165}CuO_4$ using the pair distribution function analysis of neutron diffraction data, is the vertical displacement of the in-plane oxygens of about 0.1 Å induced by doping. 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 [22,23].

The superposition model was used [23] to estimate the impact of the above mentioned local deformations on the CF excitations. A comparison of the model prediction with the experimental data indicates that site II is the C_1 symmetry site in Ref. [21]. Similarly as in the Raman study of the neighboring compound $Pr_{2-x}Ce_xCuO_4$ [17], there is no evidence for the presence of the C_s symmetry sites.

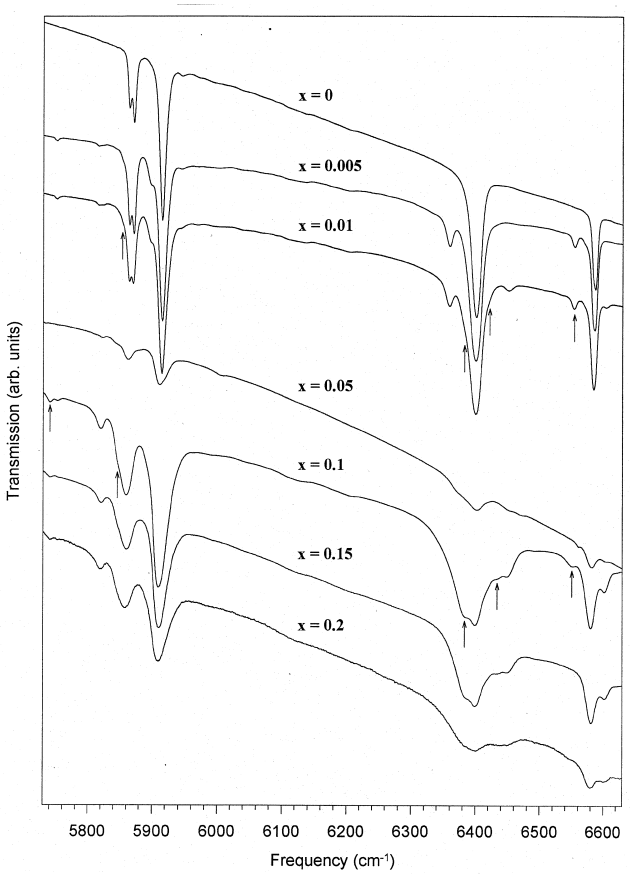

Fig. 3. CF absorption bands ($^4I_{9/2} \rightarrow {}^4I_{13/2}$) in $Nd_{2-x}Ce_xCuO_4$ as a function of cerium-doping at $T=20$ K. Arrows indicate the new excitations resulting from doping. Remaining peaks correspond to excitations in the regular sites [21].

Detailed analysis of the IR spectra revealed the splitting of Kramers doublets associated with the unperturbed site I [21], ascribed to the exchange interaction Nd–Cu of similar strengths as in the parent compound [10]. Even though the broadness of the bands does not allow us to consider fittings as non-equivocal, there is a strong indication of the persisting antiferromagnetic order in Ce-doped Nd_2CuO_4 as previously reported in the specific heat studies [24,25] and the Raman measurements [13].

The above described site II excitations exist in Nd_2CuO_4 [10] and Gd-doped Nd_2CuO_4 [26]. Their intensity does not increase with Gd-doping in the latter compound in contrast to $Nd_{2-x}Ce_xCuO_4$ where the intensity of these excitations increases with Ce-doping [18] and its subsequent electron injection into the CuO_2 planes. These findings indicate that there is a universal tendency in the Nd_2CuO_4 type compounds to the local structure deformation associated with a charge inhomogeneity. This situation provides a hint for the electronically driven phase separation as a possible scenario for the Ce-doping induced metallization of the insulating parent compound.

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