

## Infrared study of crystal-field excitations in $\text{NdBa}_2\text{Cu}_3\text{O}_6$

A. A. Martin, T. Ruf, and M. Cardona

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

S. Jandl and D. Barba

*Département de Physique, Centre de Recherche en Physique du Solide, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1*

V. Nekvasil

*Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, 16200, Praha 6, Czech Republic*

M. Diviš

*Department of Metal Physics, Charles University, Ke Karlovu 2, 121 16 Praha 2, Czech Republic*

T. Wolf

*Forschungszentrum Karlsruhe, Institut für Technische Physik, D-76021 Karlsruhe, Germany*

(Received 2 July 1998; revised manuscript received 26 October 1998)

We have observed absorption bands corresponding to  $\text{Nd}^{3+}$  crystal-field (CF) excitations in  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  by infrared spectroscopy. The observed absorption peaks are assigned to different transitions between CF levels of the  $^4I_{9/2}$  ground state to the excited multiplets  $^4I_{11/2}$ ,  $^4I_{13/2}$ , and  $^4I_{15/2}$  of  $\text{Nd}^{3+}$  ions on the regular rare-earth sites. From fits to these levels, we have calculated a more precise set of CF parameters compared to previous results obtained on the basis of the ground state multiplet only. Crystal-field transitions from  $\text{Nd}^{3+}$  ions on the Ba site have also been observed. [S0163-1829(99)07009-5]

### I. INTRODUCTION

A precise measurement of the crystal-field (CF) excitations in rare-earth ( $R$ ) based high- $T_c$  superconductors (HTSC) is essential for providing detailed information on the electronic structure of the  $R$  ion. This information is important in order to understand, for example, the observed coexistence between superconductivity and long-range magnetic ordering of the  $R$  ion sublattice at low temperatures.<sup>1</sup> Furthermore, the CF excitations of  $f$  electrons in  $R$  elements can be used to study structural properties of high- $T_c$  superconductors since they are sensitive on a very local scale to crystalline electric fields as well as magnetic fields generated by neighboring magnetic ions. The  $R$  ions in HTSC are usually sandwiched between two  $\text{CuO}_2$  planes, where the superconducting carriers are located, and thus the crystal-field interaction at the  $R$  ion site has been used to probe the charge distribution and structural changes induced by doping and superconductivity.<sup>2-5</sup>

CF excitations in HTSC and related compounds have so far been mainly studied by inelastic neutron scattering (INS).<sup>6-8</sup> However, such measurements have only in a few cases been extended beyond the ground-state multiplet,<sup>9-11</sup> and intermultiplet transitions have hardly been reported for  $(R)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ .<sup>9,11</sup> Usually, the observation of CF levels in the ground-state manifold is not sufficient for a precise determination of CF parameters since it provides rather limited information (there are only a few transitions compared to the number of parameters).<sup>12</sup> These parameters appear in the CF Hamiltonian as prefactors of either Stevens operator equivalents or spherical tensor operators.<sup>13-15</sup> Therefore, it is important to detect as many transitions as possible.

Recently, electronic Raman spectroscopy and infrared absorption have been successfully used to study intermultiplet CF excitations in  $(R)_{2-x}\text{Ce}_x\text{CuO}_4$  ( $R = \text{Nd, Sm, Pr}$ ;  $x = 0.00$  and  $0.15$ ).<sup>16-21</sup> Sharp  $f$ - $f$  transitions in the visible ( $R = \text{Nd}$ ) have been observed in reflectivity and transmission measurements.<sup>22</sup> However, for  $(R)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ , reports on the direct measurement of CF excitations by optical techniques are scarce,<sup>23</sup> although indirect observations have been made in  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Nd123) by Raman scattering from coupled phonon-crystal field excitations.<sup>24</sup> In Nd123 a double-peak structure appears in the Raman spectra at low temperature. It is due to the hybridization of the  $B_{1g}$  O(2)-O(3) out-of-phase phonon with a nearby CF excitation. Via this coupling, the Raman efficiency of the CF excitation is borrowed from that of the phonon.

In this paper we report a systematic study of CF transitions from the ground state to all higher energy  $J$  multiplets of the  $^4I$  term in  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  by infrared absorption. We show that infrared measurements can be used as a valuable tool for CF studies. This optical technique complements inelastic neutron scattering experiments in a remarkable way, since it can be applied with high resolution to investigate small single crystals and is not limited to low energies.

### II. EXPERIMENT

Single crystals of  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  were grown by the self-flux method described elsewhere.<sup>25</sup> In order to reduce the oxygen content, they were annealed in an argon flow at  $750^\circ\text{C}$  for four days. The composition of the single crystals

was determined by energy-dispersive x-ray (EDX) measurements and by neutron diffraction. A deviation from stoichiometry was found for Nd which has an excess content of about 1%. The oxygen content was derived from the weight change of the samples. For the samples investigated here, we found  $\delta > 0.9$ . Note that this specimen was already used in the Raman study of Ref. 2. In the following we assume that it has a nominal composition of  $\text{NdBa}_2\text{Cu}_3\text{O}_6$ . The infrared (IR) measurements were carried out using a Fourier-transform interferometer (BOMEM), equipped with a quartz halogen lamp, an InSb detector, and a  $\text{CaF}_2$  beam splitter. The resolution was  $2 \text{ cm}^{-1}$  in the  $1800\text{--}8000 \text{ cm}^{-1}$  range. The single crystals, with approximate dimensions of  $1.5 \times 0.5 \times 0.07 \text{ mm}^3$  were mounted on the cold finger of a helium-cooled flow-through cryostat and studied in two configurations with the  $ab$  and  $ac$  planes perpendicular to the direction of the unpolarized incident beam ( $\vec{k} \parallel \vec{c}$  and  $\vec{k} \perp \vec{c}$ ), respectively. The spectra were measured over the temperature range from 4.2 to 300 K.

### III. RESULTS

Figure 1 shows IR transmittance measurements across  $ab$  and  $ac$  platelets of  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  obtained at 4.2 K in the regions where  ${}^4I_{9/2} \rightarrow {}^4I_{11/2}$  transitions occur. In Fig. 1(a), the  $ab$ -platelet spectrum shows five strong CF absorption bands (filled circles). The existence of the  $2092 \text{ cm}^{-1}$  peak is inferred from the much larger width of the  $2099 \text{ cm}^{-1}$  feature as compared to, e.g., that at  $1995 \text{ cm}^{-1}$ . In addition, two weaker CF absorption bands (asterisk) are also observed. The spectrum of the  $ac$  platelet in Fig. 1(a) is very similar to that of the  $ab$  platelet, except that the lines at  $2046$ ,  $2063$ , and  $2092 \text{ cm}^{-1}$  are better resolved. In Fig. 1(b), three prominent CF absorption bands (filled circles) show up much stronger in the  $ac$ -plane than in the  $ab$ -plane spectrum. Four weaker absorption bands (asterisks) are also observed.

In Fig. 2 we present IR spectra in the range of the  ${}^4I_{9/2} \rightarrow {}^4I_{13/2}$  transitions. The spectra of  $ab$  and  $ac$  platelets in  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  exhibit several common strong absorption bands (filled circles). Several weaker features are also observed (asterisks), some of them being more prominent in the  $ac$ -platelet than in the  $ab$ -platelet spectrum.

IR spectra in the range of transitions from the ground-state manifold to the highest excited multiplet,  ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ , are shown in Fig. 3. In the  $ac$  spectrum we detect eight prominent CF absorption bands (filled circles). Three weaker bands (asterisks) are also observed. In this region we did not find any absorption bands in the  $ab$  spectrum due to the very weak transmittance.

### IV. DISCUSSION

The ground state manifold of the  $4f^3$  configuration in  $\text{Nd}^{3+}$  is  ${}^4I_{9/2}$ ; it is thus tenfold degenerate. The energies of the next higher multiplets for the free ion are about 2000, 4000, and  $6000 \text{ cm}^{-1}$  for  ${}^4I_{11/2}$ ,  ${}^4I_{13/2}$ , and  ${}^4I_{15/2}$ , respectively.<sup>26</sup> When the  $\text{Nd}^{3+}$  ion is placed in a  $D_{4h}$  site symmetry, as in  $\text{NdBa}_2\text{Cu}_3\text{O}_6$ , the ground-state manifold splits into five Kramers degenerate doublets, while the higher multiplets split into 6, 7, and 8 Kramers doublets, respectively.

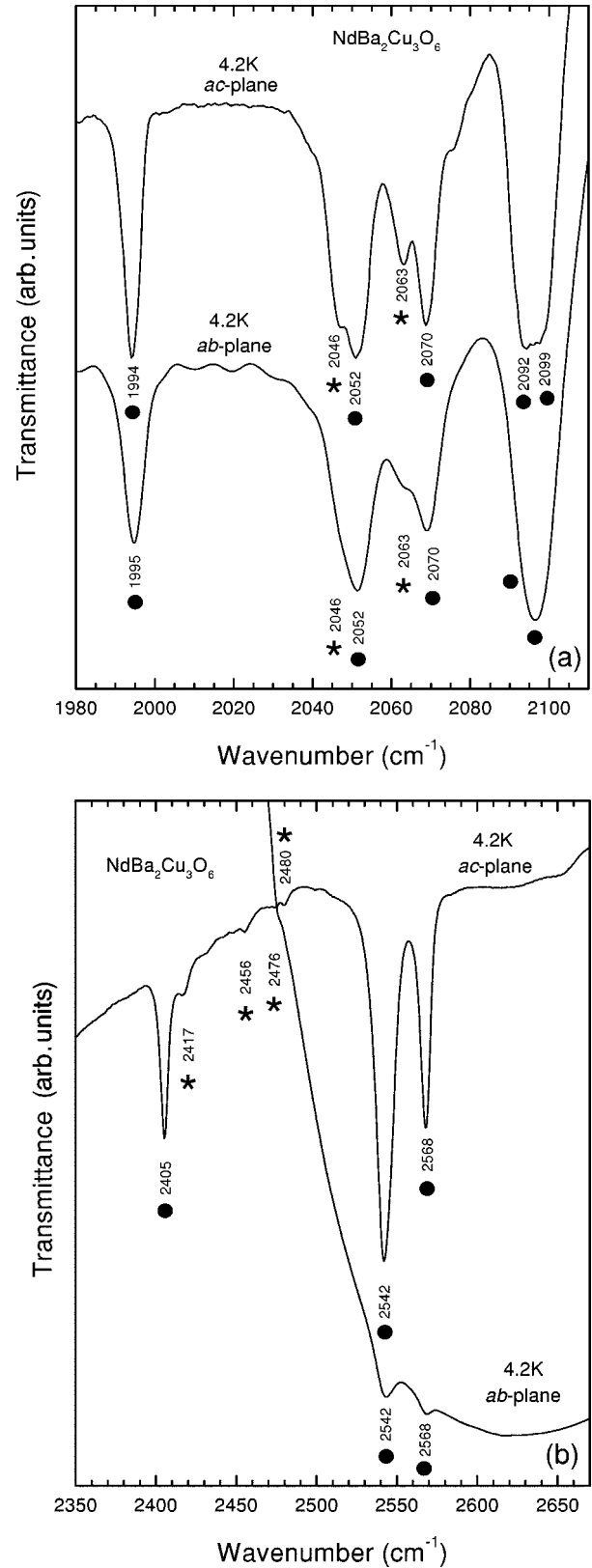


FIG. 1. IR transmittance spectra across  $ab$ - and  $ac$ -oriented platelets of  $\text{NdBa}_2\text{Cu}_3\text{O}_6$ . (a) and (b) show different energy intervals of the spectra. The peaks are CF transitions from the ground state manifold,  ${}^4I_{9/2}$ , to levels in the first excited multiplet,  ${}^4I_{11/2}$ . Filled circles and asterisks indicate strong and weak absorption bands, respectively. See text for details.

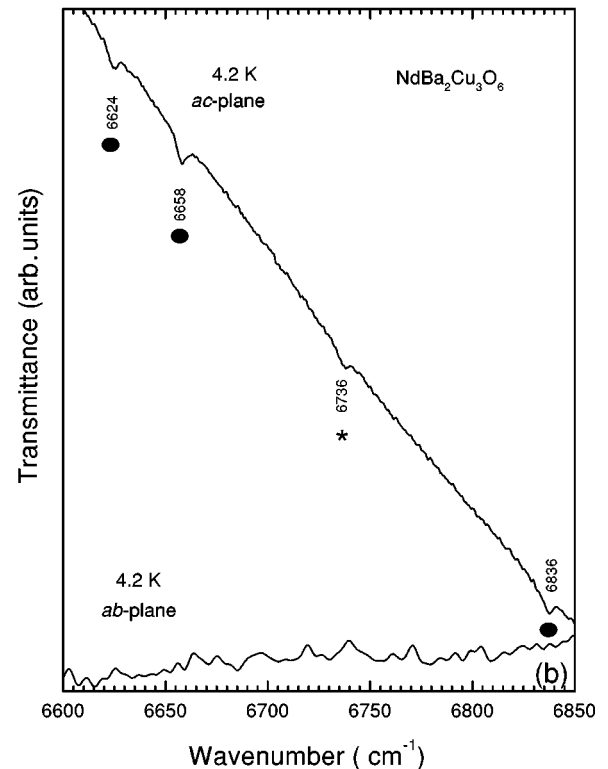
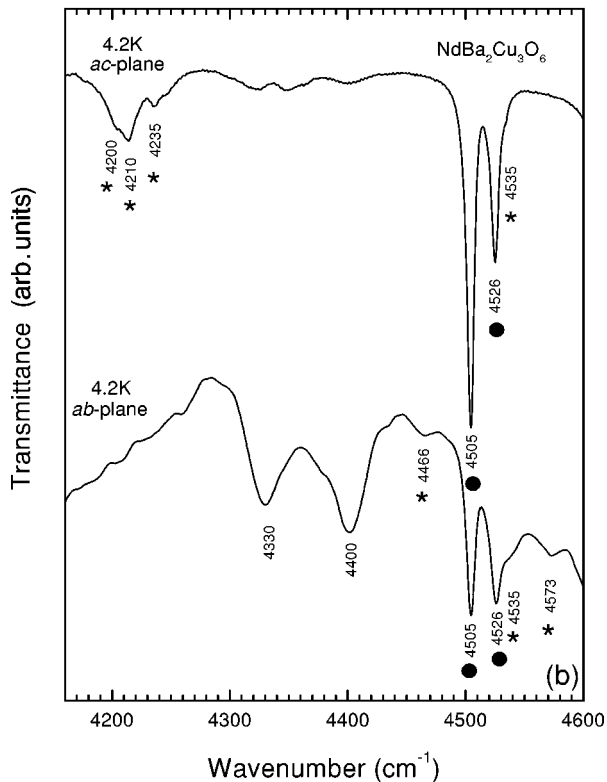
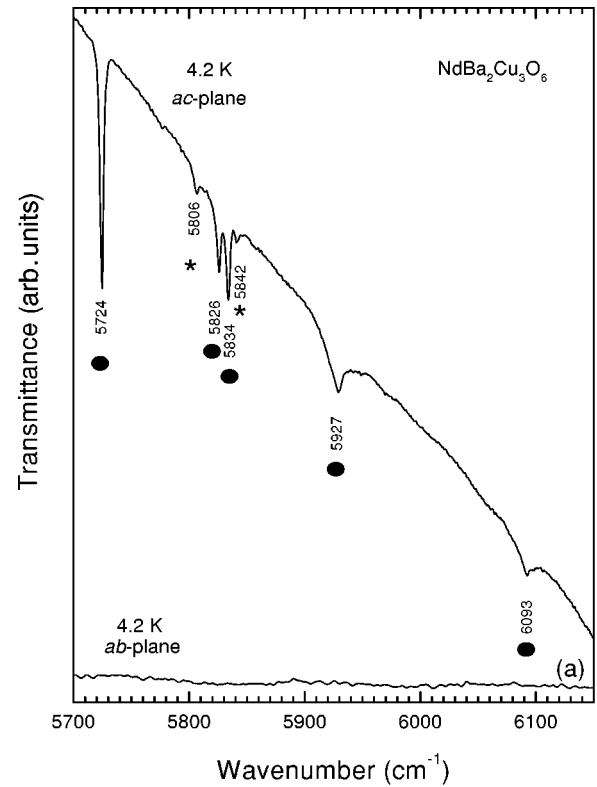
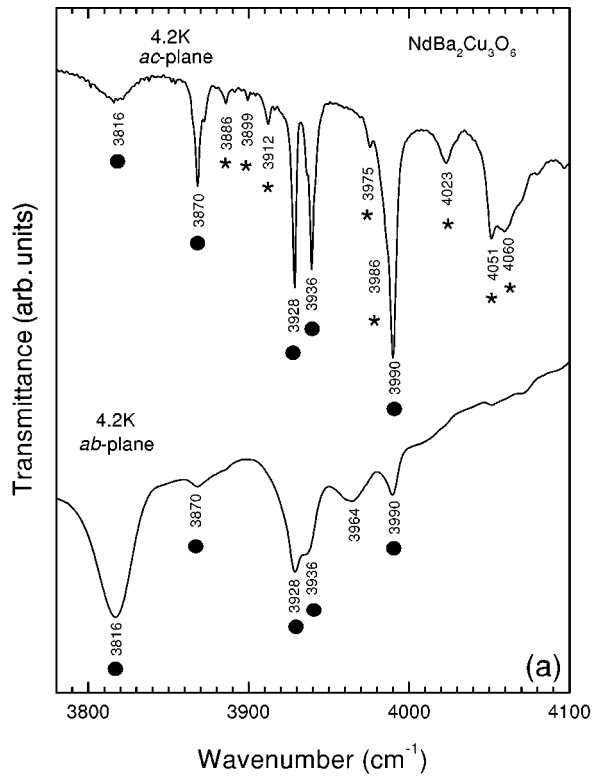


FIG. 2. IR spectra of CF transitions in  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  from the ground state manifold,  $4I_{9/2}$ , to the second excited multiplet,  $4I_{13/2}$  (*ab* and *ac* platelets at 4.2 K). (a) and (b) correspond to different energy intervals of the spectra. Filled circles and asterisks indicate strong and weak absorption bands, respectively. See text for details.

FIG. 3. IR spectra of CF transitions in  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  from the ground state manifold,  $4I_{9/2}$ , to the highest excited multiplet,  $4I_{15/2}$  (*ab* and *ac* platelets at 4.2 K). (a) and (b) correspond to different energy intervals of the spectra. Filled circles and asterisks indicate strong and weak absorption bands, respectively. See text for details.

In the following we analyze our IR spectra in terms of the CF interaction, the strongest perturbation of free-ion  $4f$  electron states of trivalent  $R$  ions in cuprates. The CF Hamiltonian is written in terms of one-electron irreducible tensor

operators  $C_{kq}$ , where the number of nonzero CF parameters depends on the site symmetry. Intermediate coupling<sup>27</sup> and  $J$  mixing within the entire  $4I$  term is taken into account.

The large number of peaks observed in our experimental

TABLE I. CF parameters (in  $\text{cm}^{-1}$ ) obtained from a fit to our IR measurements for CF transitions of  $\text{Nd}^{3+}$  ions on the regular ( $D_{4h}$ ) site and calculations with the superposition model for  $\text{Nd}^{3+}$  on Ba sites ( $C_{4v}$ ) (see Table II). A set of CF parameters determined previously from INS experiments (Ref. 8) is also shown. The uncertainty of each value is indicated in the brackets.

Parameter	$D_{4h}$ site (this work, fit)	$D_{4h}$ (Ref. 8)	$C_{4v}$ site (this work, calc.)
$B_{20}$	380(28)	565	0
$B_{40}$	-2956(34)	-2981	14
$B_{44}$	1664(25)	1678	-364
$B_{60}$	526(15)	556	-468
$B_{64}$	2021(10)	1965	700

IR spectra indicates that there exists more than one type of Nd site. Therefore we analyze the data in comparison with theoretical predictions for the  $^4I$  spectra of  $\text{Nd}^{3+}$  ions at regular  $D_{4h}$  symmetry sites as well as  $C_{4v}$  symmetry Ba sites. For this purpose we use a semiphenomenological superposition model, based on the assumption that contributions from oxygen ligands dominate.<sup>12</sup> This model was found earlier to provide satisfactory predictions for the 4th and 6th order CF parameters of  $R$  ions on regular sites in cuprates.<sup>12,28,29</sup> However, estimates for the 2nd order CF parameters by this model are unreliable due to their strong sensitivity to far-reaching CF interactions.<sup>30</sup> Note that *ab initio* calculations based on the full potential LAPW band structure in the framework of the local density approximation have recently provided good predictions for the 2nd order parameters,<sup>31</sup> and efforts for their use in the present context are in progress.

In a first step, we calculate the  $^4I$  CF spectrum for  $\text{Nd}^{3+}$  at  $D_{4h}$  sites with the CF parameters obtained by a best-fit treatment of inelastic neutron scattering data from the lowest energy  $J=9/2$  multiplet only.<sup>8</sup> The resulting  $^4I$  CF spectrum is compared to the prominent peaks of the IR data (filled circles in Figs. 1–3). A rough assignment of intermultiplet transitions is done for the well-isolated experimental absorption bands within  $20 \text{ cm}^{-1}$  of predicted CF levels. Together with the  $J=9/2$  levels from INS (0, 90, 155, 286, 933  $\text{cm}^{-1}$ )<sup>8</sup> this yields a set of  $J=9/2, 11/2, 13/2$ , and  $15/2$  CF levels which are used for a fit of CF parameters in a next step of refinement.

In a second fit we include in the input data also less well-isolated experimental lines, if they are close to calculated levels of the first fit within a few  $\text{cm}^{-1}$ . The best-fit CF parameters obtained by this procedure are given in Table I. The free-ion energies of the  $^4I_J$  multiplets, varied along with the CF parameters in fitting the data, are 0, 1856, 3821 and 5844  $\text{cm}^{-1}$ . Some lines, ascribed in the following to excitations at regular  $D_{4h}$  sites, were not included in the fit due to their close proximity to other lines (see Table II). To estimate the CF spectrum for  $\text{Nd}^{3+}$  ions at Ba sites from these ( $D_{4h}$  site) CF parameters we used the superposition model<sup>12</sup> and ligand positions determined for  $\text{NdBa}_2\text{Cu}_3\text{O}_{6.12}$ .<sup>32</sup> Due to the inapplicability of this model to 2nd order parameters  $B_{20}$  was set to zero. Note that the application of the above mentioned *ab initio* method for these sites would require considerable efforts going beyond the scope of this paper.

The experimental and the calculated CF levels are presented in Table II together with their respective symmetries. The observed absorption bands can be divided into three groups. The first group contains transitions that are assigned to CF levels of  $\text{Nd}^{3+}$  ions on regular  $D_{4h}$  sites. The fit is excellent for all the absorption bands in this group. The second group contains transitions which we ascribe to  $\text{Nd}^{3+}$  ions on the Ba site ( $C_{4v}$ ). Their experimental energies, given in Table II, are very close to the results of the superposition model calculation. The remaining absorption bands fall into a third group which we tentatively associate with  $\text{Nd}^{3+}$  ions on Ba sites surrounded by one or two chain oxygen ligands (named *defect* in Table II). Such defects may be present due to an incomplete reduction of the samples (see Sec. II). A superposition model calculation indicates that such extra oxygen ions increase the CF level splitting of Nd on Ba sites considerably. However, a quantitative description was not possible, and this assumption remains to be confirmed by further investigations, e.g., for Nd123 with varying oxygen or excess Nd content.

In Table I we compare our fitted ( $D_{4h}$  site) CF parameters with the set obtained from INS measurements.<sup>8</sup> The agreement between these data is rather good. However, it is interesting to note that the observation of infrared-active CF bands corresponding to  $d-d$  transitions within  $\text{Nd}^{3+}$  ions placed at the inversion center (the regular  $R$  site) is *electric dipole forbidden*. We conjecture that these bands become observable due to slight lattice imperfections related to a small amount of  $\text{Nd}^{3+}$  ions on the Ba sites, as detected in our experiment. The uncertainty associated with the mechanism which makes the observation of these IR transitions possible prevents us from using transition *intensities* in the data analysis beyond the *ad hoc* assignment of most of the strong peaks to transitions from the prevailing  $\text{Nd}^{3+}$  ions on  $D_{4h}$  sites. Note that due to the presence of a large amount of free carriers no transmission measurements can be performed in fully oxygenated samples (i.e.,  $\delta \approx 0$ ) of sufficient thickness to reveal dipole forbidden transitions. The quality of the crystal-field excitation *wave functions* associated with the fitted CF Hamiltonian could be checked, e.g., by calculating neutron scattering intensities or by comparing theory and data of the Zeeman effect in a similar way as has been done in one of our previous Raman studies.<sup>33</sup> Experiments on samples with varying oxygen or Ba content, analogous to the Raman study of Ref. 2, are in progress.

## V. CONCLUSIONS

We have observed electric dipole forbidden CF excitations of  $\text{Nd}^{3+}$  in the infrared transmission spectra of  $\text{NdBa}_2\text{Cu}_3\text{O}_6$ . The CF level energies correspond to transitions from the ground state manifold,  $^4I_{9/2}$ , to the three higher multiplets  $^4I_{11/2}$ ,  $^4I_{13/2}$ , and  $^4I_{15/2}$ . Most of the CF excitations can be assigned to  $\text{Nd}^{3+}$  ions on the regular  $R$  site of the compound. Some of the observed CF transitions are assigned to  $\text{Nd}^{3+}$  ions on Ba sites. From a fit to the infrared measurements we obtain CF parameters which are more precise than those determined by inelastic neutron scattering.

TABLE II.  $\text{Nd}^{3+}$  CF levels in  $\text{NdBa}_2\text{Cu}_3\text{O}_6$  as observed experimentally in the infrared transmission spectra of *ab*- and *ac*-oriented platelets and the corresponding energies obtained from the fit of a CF Hamiltonian to the data (see Table I). The CF levels given for  $D_{4h}$  and  $C_{4v}$  sites are for the  $\text{Nd}^{3+}$  ion on the regular site and on the Ba site, respectively. The  $C_{4v}$  levels were calculated from the CF parameters for the  $D_{4h}$  site levels using the superposition model. Levels in the column labeled *defect* might be associated with  $\text{Nd}^{3+}$  ions on Ba sites surrounded by one or two chain oxygen ligands. The experimental uncertainty is  $\pm 2 \text{ cm}^{-1}$ . Experimental data for the  $J=9/2$  manifold from INS are also included (Ref. 8).

Multiplet	Experiment			Theory		
	$D_{4h}$ site ( $\text{cm}^{-1}$ )	$C_{4v}$ site ( $\text{cm}^{-1}$ )	<i>defect</i> ( $\text{cm}^{-1}$ )	$D_{4h}$ site ( $\text{cm}^{-1}$ )	Symmetry $i (\Gamma_i)$	$C_{4v}$ site ( $\text{cm}^{-1}$ )
$^4I_{15/2}$	6836			6833	6	6193
	6736			6736	7	6192
	6658		6093	6655	7	6044
	6624			6623	6	5998
	5927			5935	6	5989
	5842 <sup>a</sup>		5826	5846	6	5896
	5834 <sup>a</sup>		5806	5831	7	5864
	5724			5723	7	5776
$^4I_{13/2}$	4535	4060	4573	4530	7	4063
	4526	4051	4466	4523	6	4014
	4505	4023	4400	4513	7	3981
	3990	3975	4330	3991	7	3962
	3986	3964	4235	3984	6	3928
	3936	3912	4210	3936	6	3916
	3928	3870	4200	3930	7	3877
			4051			
			3899			
			3886			
		3816				
$^4I_{11/2}$	2568	2052	2480	2568	6	2050
	2542		2476	2545	6	2024
	2092/2099 <sup>b</sup>		2456	2099	7	2005
	2063 <sup>b</sup>		2417	2061	7	1975
	2046 <sup>b</sup>		2405	2046	6	1954
	1994/1995		2070	1992	6	1939
$^4I_{9/2}$	933 <sup>a</sup>			938	6	273
	286 <sup>a</sup>			283	7	214
	155 <sup>a</sup>			156	6	64
	90 <sup>a</sup>			87	7	54
	0 <sup>a</sup>			0	6	0

<sup>a</sup>From INS. (Ref. 8).

<sup>b</sup>Energy levels not included in the fitting procedure due to their proximity to other lines.

#### ACKNOWLEDGMENTS

We thank H. Hirt, M. Siemers, J. Rousseau, and A. Breitschwerdt for technical assistance and J. Humlíček for a critical reading of the manuscript. A.A.M. acknowledges support from FAPESP-Brazil, Grant No. 96/06992-8. S.J. ac-

knowledges support from National Science and Engineering Research Council of Canada (NSERC) and le Fonds de Formation de Chercheurs et l'Aide à la Recherche du Gouvernement du Québec (FCAR), and V.N. and M.D. acknowledge support from the Grant Agency of the Czech Republic, Grant No. 202/96/0861.

- <sup>1</sup>I. W. Sumarlin, J. W. Lynn, T. Chattopadhyay, S. N. Barilo, and D. I. Zhigunov, *Physica C* **219**, 195 (1994).
- <sup>2</sup>A. A. Martin, T. Ruf, T. Strach, M. Cardona, and T. Wolf, *Phys. Rev. B* **58**, 14 349 (1998).
- <sup>3</sup>T. Strach, T. Ruf, A. M. Niraimathi, A. A. Martin, and M. Cardona, *Physica C* **301**, 9 (1998).
- <sup>4</sup>J. Mesot, P. Allenspach, U. Staub, A. Furrer, H. Mutka, R. Osborn, and A. Taylor, *Phys. Rev. B* **47**, 6027 (1993).
- <sup>5</sup>U. Staub, J. Mesot, M. Guillaume, P. Allenspach, A. Furrer, H. Mutka, Z. Bowden, and A. Taylor, *Phys. Rev. B* **50**, 4068 (1994).
- <sup>6</sup>L. Soderholm, C. K. Loong, G. L. Goodman, and B. D. Dabrowski, *Phys. Rev. B* **43**, 7923 (1991).
- <sup>7</sup>C. K. Loong, G. L. Goodman, L. Soderholm, B. Dabrowski, and D. G. Hinks, *J. Appl. Phys.* **67**, 4536 (1990).
- <sup>8</sup>P. Allenspach, J. Mesot, U. Staub, M. Guillaume, A. Furrer, S.-I. Yoo, M. J. Kramer, R. W. McCallum, H. Maletta, H. Blank, H. Mutka, R. Osborn, M. Arai, Z. Bowden, and A. D. Taylor, *Z. Phys. B* **95**, 301 (1994).
- <sup>9</sup>M. Guillaume, W. Henggeler, A. Furrer, R. S. Eccleston, and V. Trounov, *Phys. Rev. Lett.* **74**, 3423 (1995).
- <sup>10</sup>A. T. Boothroyd, S. M. Doyle, D. McK. Paul, and R. Osborn, *Phys. Rev. B* **45**, 10 075 (1992).
- <sup>11</sup>U. Staub, L. Soderholm, R. Osborn, M. Guillaume, A. Furrer, and V. Trounov, *J. Alloys Compd.* **225**, 591 (1995).
- <sup>12</sup>V. Nekvasil, M. Diviš, G. Hilscher, and E. Holland-Moritz, *J. Alloys Compd.* **225**, 578 (1995).
- <sup>13</sup>K. W. H. Stevens, *Proc. Phys. Soc. London, Sect. A* **65**, 209 (1952).
- <sup>14</sup>M. T. Hutchings, *Solid State Phys.* **16**, 227 (1964).
- <sup>15</sup>B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Wiley, New York, 1965).
- <sup>16</sup>S. Jandl, M. Iliev, C. Thomsen, T. Ruf, M. Cardona, B. M. Wanklyn, and C. Chen, *Solid State Commun.* **87**, 609 (1993).
- <sup>17</sup>J. A. Sanjurjo, G. B. Martins, P. G. Pagliuso, E. Granado, I. Torriani, C. Rettori, S. Oseroff, and Z. Fisk, *Phys. Rev. B* **51**, 1185 (1995).
- <sup>18</sup>M. L. Sanjuan and M. A. Laguna, *Phys. Rev. B* **52**, 13 000 (1995).
- <sup>19</sup>J. D. Perkins, J. M. Graybeal, M. A. Kastner, R. J. Birgeneau, J. P. Falck, and M. Greven, *Phys. Rev. Lett.* **71**, 1621 (1993).
- <sup>20</sup>S. Jandl, P. Richard, V. Nekvasil, D. I. Zhigunov, S. N. Barilo, and S. V. Shiryaev, *J. Lumin.* **78**, 197 (1998).
- <sup>21</sup>S. Jandl, P. Dufour, T. Strach, T. Ruf, M. Cardona, V. Nekvasil, C. Chen, B. M. Wanklyn, and S. Pinol, *Phys. Rev. B* **53**, 8632 (1996).
- <sup>22</sup>M. L. Jones, D. W. Shortt, B. W. Sterling, A. L. Schawlow, and R. M. Macfarlane, *Phys. Rev. B* **46**, 611 (1992).
- <sup>23</sup>A. Zibold, H. L. Liu, D. B. Tanner, J. Y. Wang, M. Grüninger, H. P. Geserich, T. Kopp, T. Wolf, W. Widder, and H. F. Braun, *Phys. Rev. B* **55**, 11 096 (1997).
- <sup>24</sup>E. T. Heyen, R. Wegerer, and M. Cardona, *Phys. Rev. Lett.* **67**, 144 (1991).
- <sup>25</sup>Th. Wolf, *J. Cryst. Growth* **9**, 1010 (1989).
- <sup>26</sup>C. A. Morrison and R. P. Leavitt, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1982), Vol. 5.
- <sup>27</sup>K. Rajnak, *J. Chem. Phys.* **43**, 847 (1965).
- <sup>28</sup>L. Soderholm, C.-K. Loong, U. Staub, S. Skanthakumar, J. Simon Xue, J. P. Hammonds, J. E. Greedan, and M. Maric, *Physica C* **246**, 11 (1995).
- <sup>29</sup>V. Nekvasil, *Physica C* **170**, 469 (1990).
- <sup>30</sup>V. Nekvasil, *Solid State Commun.* **65**, 1103 (1988).
- <sup>31</sup>M. Diviš, V. Nekvasil, and J. Kuriplach, *Physica C* **301**, 23 (1998).
- <sup>32</sup>M. Guillaume, P. Allenspach, W. Henggeler, J. Mesot, B. Roessli, U. Staub, P. Fisher, A. Furrer, and V. Trounov, *J. Phys.: Condens. Matter* **6**, 7963 (1994).
- <sup>33</sup>T. Strach, T. Ruf, M. Cardona, S. Jandl, V. Nekvasil, C. Chen, and B. M. Wanklyn, *Phys. Rev. B* **56**, 5578 (1997).