Infrared study of the crystal-field excitations in $NdMnO_3$ in high magnetic fields

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Nd^{3+} ion crystal field excitations in $NdMnO_3$ single crystals have been studied by infrared transmission as a function of temperature and under applied magnetic field. Lifting of the ground state Kramers doublet degeneracy ($\sim 14\ cm^{-1}$) due to the Mn^{3+}-Nd^{3+} interaction has been observed below the canted-antiferromagnetic phase transition ($T_N \sim 75$ K). Zeeman splittings of the Nd^{3+} ion excited crystal field levels have been analyzed and the crystal field Hamiltonian parameters have been calculated.

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I. INTRODUCTION

Intensive efforts have been devoted to the understanding of the rare-earth manganites $R_{1-x}A_xMnO_3$ (R=lanthanides and A=Ba, Sr, or Ca) magnetotransport properties. The substitution of the rare-earth ion R^{3+} by a divalent cation A^{2+} generates, due to charge compensation, Mn^{4+} that leads to double exchange interactions and simultaneous observation of metallic and ferromagnetic character.[1–3] A colossal negative magnetoresistance that reflects strong interconnections between the electrical and magnetic properties has been observed near the concomitant paramagnetic insulator-ferromagnetic metallic phase transition.[4] Nd-based compounds are interesting since the strength of the double exchange interactions is weaker than in the La-based compounds, due to larger lattice distortions provoked by the smaller Nd ions.[5] Consequently, a closer competition with new generic instabilities, such as antiferromagnetic superexchange, orbital and charge ordering, would exist between the electron–phonon, electron–electron and the double exchange interactions in a system like $Nd_{1-x}Ca_xMnO_3$ as compared to $La_{1-x}Ca_xMnO_3$.[6] The undoped $RMnO_3$ parents, that are characterized by an antiferromagnetic low-temperature ground state,[7] have been comparatively less studied particularly for other than R=La. These are insulators and develop static Jahn-Teller distortions. The study of the parent compound $NdMnO_3$ physical properties represents an interesting starting point to the understanding of the more complex interactions in the doped systems.

Neutron diffraction measurements performed on the orthorhombic $NdMnO_3$ perovskite (space group D_{2h}^{16}-*Pbnm*, with four formula units in the cell) suggest the coexistence of ferromagnetic and antiferromagnetic interactions resulting in canted antiferromagnetic layered structure for the Mn subsystem.[8,9] The structure may be viewed as a stacking of MnO_2-NdO layers along the c axis with tilts of the MnO_6 octahedra. The Jahn-Teller distortions are static and coherent in this structure where the three pairs of Mn^{3+}-O^{2-} bonds are of different lengths. The Mn^{3+} spins order at $T_N \sim 75$ K and their moments saturate at ~ 20 K.[8] While no evidence for the Nd^{3+} ordering, down to 1.8 K, was reported in Ref. 8; the Nd sublattice orders in a ferromagnetic arrangement with the moments parallel to the c direction below ~ 13 K according to Ref. 9. A recent study of Raman active phonons in $NdMnO_3$ (Ref. 10) has indicated that the phonon frequencies, intensities, and bandwidths are sensitive to the magnetic evolution of the Mn^{3+} sublattice as a function of temperature with no particular indication for Nd^{3+} sudden moment ordering. In particular, similarly to orthorhombic $LaMnO_3$, the $NdMnO_3$ structure is distorted by a static Jahn-Teller effect consistent with the *Pbnm* space group and the most intense Raman active B_{1g} phonon ($\sim 601\ cm^{-1}$) softens below $T_N \sim 75$ K following the paramagnetic to canted-antiferromagnetic phase transition.

A significant anisotropic contribution of the Nd^{3+} ions to the low-temperature magnetic and thermodynamic (specific heat) properties of $NdMnO_3$ single crystals, reflecting a noticeable crystal-field (CF) splitting of the Nd^{3+} electronic

states, was reported recently.[11,12] As a result of the Nd-Mn exchange interaction, the low-temperature $NdMnO_3$ magnetic behavior is basically determined by the Nd^{3+} ground state Kramers doublet (KD) splitting ($\sim$14 cm^{-1}) as determined by the far infrared transmittivity measurements.[12]

Infrared transmission technique has been used successfully for the study of rare-earth CF excitations in high-temperature superconducting cuprates and their parent compounds.[13–15] In these materials, and similarly to the manganites, the electrons are strongly correlated and magnetism plays a major role. For instance Nd^{3+} CF excitations study in $La_{2-x-y}Nd_xSr_yO_4$ revealed in addition to the C_{4v} symmetry regular sites, sites of lower symmetry related to the stripes formation.[16] In spite of the interesting informations, concerning the local inhomogeneities, electronic and magnetic properties, that provide the rare-earth ion CF excitation studies, these have been limited in the manganites to the measurement in the far infrared range.[12]

In this article we study the Nd^{3+} CF excitations in $NdMnO_3$ as a function of temperature and under applied magnetic field up to 13 T. The objectives are: (i) to report the Nd^{3+} CF excitations in $NdMnO_3$ single crystals as detected by infrared transmission spectroscopy, (ii) to examine the influence of the antiferromagnetic phase transition around $T_N \sim 75$ K and the persistent Jahn-Teller effect on the CF excitations, (iii) to determine the parameters of the CF Hamiltonian that describe the magnetic data including the Zeeman splittings of the Kramers doublets.

II. EXPERIMENTS

The $NdMnO_3$ studied single crystal was grown by the floating zone method as described in Ref. 17. For the infrared studies, the sample (1, 2 mm,200 μm) was mounted with the *a* axis (*Pbnm* setting) parallel to the incident radiation. 0.5 cm^{-1} resolution transmission spectra at 8 K and at 12 K in 1–7 T applied magnetic field, were obtained in the 1800–8000 cm^{-1} wave number range with a Fourier transform interferometer (BOMEM DA3.002 at the University of Sherbrooke) equipped with an InSb detector, quartz-halogen and globar sources and a CaF_2 beamsplitter. For measurements under higher magnetic fields up to 13 T (Grenoble High Magnetic Field Laboratory), the sample was placed in the bore of a superconducting magnet, in a helium bath cryostat at 1.8 K. A composite Si bolometer placed directly beneath the sample was used to measure the intensity of the transmitted light. A Bruker Instruments model 113 Fourier Transform Spectrometer, equipped with tungsten and globar light sources, was used to collect and analyze spectra with a resolution of 2 cm^{-1}. As data collected in the two laboratories in magnetic fields up to 7 T coincide within the experimental accuracy, only those from Grenoble are shown for the measurements under magnetic field. The paramagnetic to canted-antiferromagnetic phase transition of the sample was confirmed by prior Raman measurements with the observation of the 601 cm^{-1} B_{1g}. Raman active mode softening below 75 K; also width of the phonons (few cm^{-1} at 4.2 K) indicated absence of oxygen nonstoichiometry in the studied sample.[10]

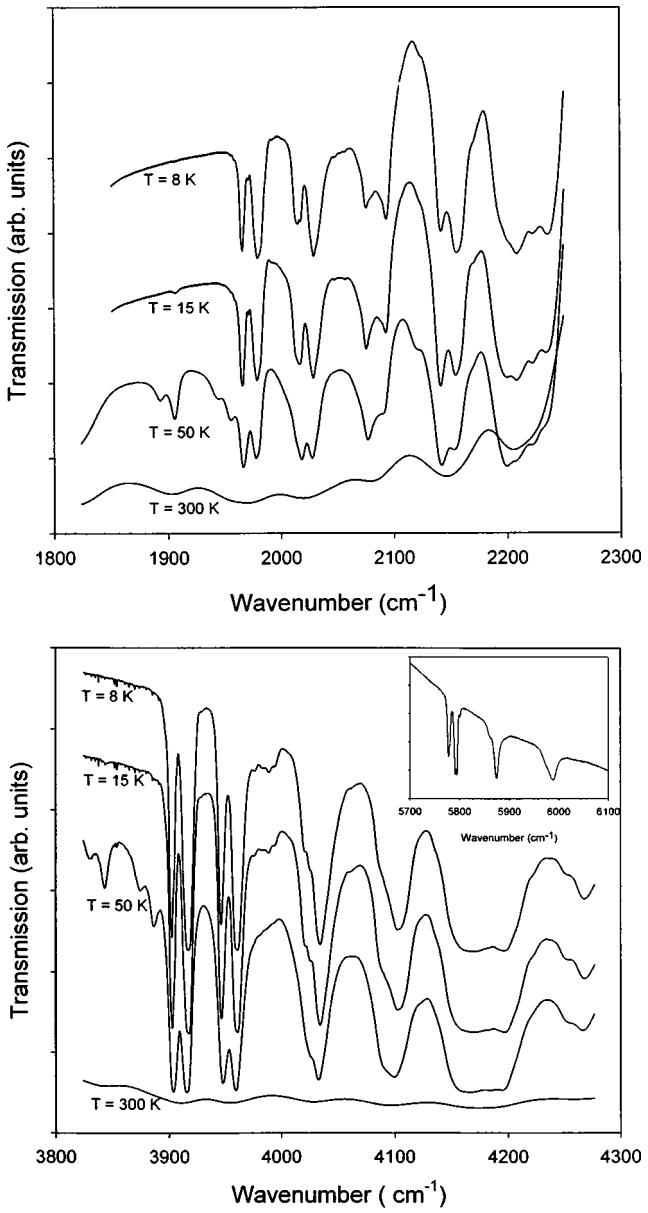

FIG. 1. (a) Temperature evolution of the $Nd^{3+}I_{9/2} \rightarrow I_{11/2}$ CF transitions in $NdMnO_3$ as determined by infrared transmission. (b) Temperature evolution of the $Nd^{3+}I_{9/2} \rightarrow I_{13/2}$ CF transitions in $NdMnO_3$ as determined by infrared transmission. Inset: $I_{9/2} \rightarrow I_{15/2}$ CF transitions at $T = 8$ K.

III. EXPERIMENTAL RESULTS

In Figs. 1(a) and 1(b), temperature evolution of the $I_{9/2} \rightarrow I_{11/2}$ and $I_{9/2} \rightarrow I_{13/2}$ CF transitions is presented. At low temperatures three $I_{9/2} \rightarrow I_{15/2}$ transitions are detected [Fig. 1(b) inset]. Above $T_N \sim 75$ K, the six ($I_{11/2}$) and seven ($I_{13/2}$) expected CF levels are observed in the 1950–2250 cm^{-1} ($\sim$1967,2021,2079,2147,2205,2227 cm^{-1}) and 3900–4300 cm^{-1} (3910,3954,4029,4096,4168,4196, 4260 cm^{-1}) ranges, respectively. Their widths are broad typically from 20–30 cm^{-1} at 300 K down to 80 K. At high temperatures, above 100 K, satellites associated with the ground state excited levels $\sim$68 and 181 cm^{-1} are observed.

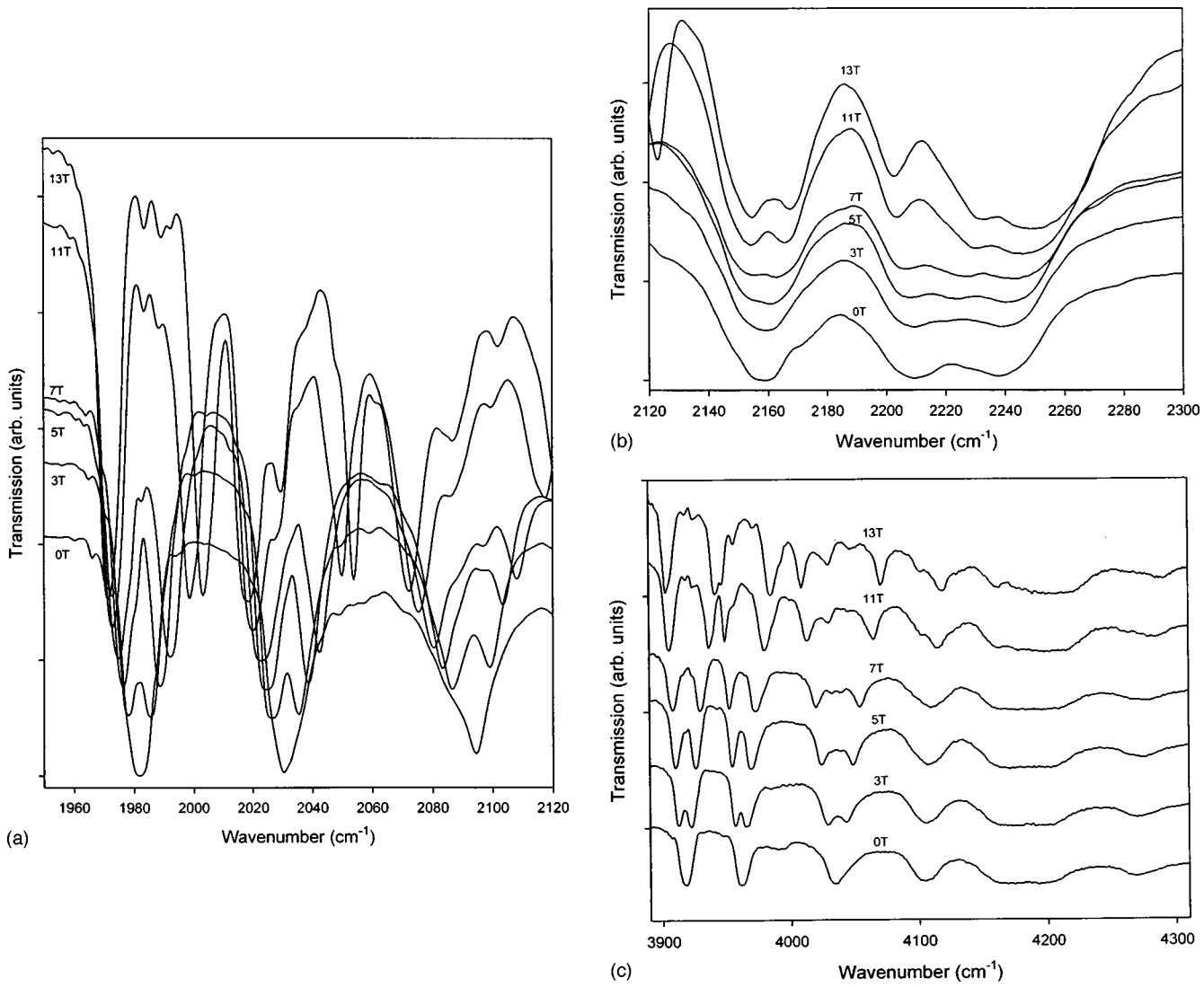

FIG. 2. (a) $Nd^{3+}I_{9/2}\rightarrow I_{11/2}$ three lowest CF transitions in $NdMnO_3$ as a function of applied magnetic field ($\mathbf{B}\|\mathbf{a}$) at $T=1.8$ K. (b) $Nd^{3+}I_{9/2}\rightarrow I_{11/2}$ three highest CF transitions in $NdMnO_3$ as a function of applied magnetic field ($\mathbf{B}\|\mathbf{a}$) at $T=1.8$ K. (c) $Nd^{3+}I_{9/2}\rightarrow I_{13/2}$ CF transitions in $NdMnO_3$ as a function of applied magnetic field ($\mathbf{B}\|\mathbf{a}$) at $T=1.8$ K.

Below 75 K, degeneracy of the KD ground state is lifted due to the Nd-Mn exchange interaction following the occurrence of the antiferromagnetic phase transition; typically at 8 K: (1966–1980,2015–2029,2076–2090,2142–2156,2194–2208, 2223–2237 cm^{-1}), (3903–3917,3936–3960,4020–4034,4088–4102,4167–4181,4195–4209,4253–4267 cm^{-1}), and (5779–5793,5860–5874,5974–5988 cm^{-1}) for the $I_{11/2}$, $I_{13/2}$, and $I_{15/2}$ multiplets, respectively. This lifting of degeneracy is not masked by absorption band broadenings due to distortions generated by the Jahn-Teller effect and the MnO_6 octahedra rotation in the orthorhombic structure of $NdMnO_3$. As temperature is lowered between 75 and 4.2 K the doublet splittings increase from $\sim$8 cm^{-1} reaching $\sim$14 cm^{-1} at 8 K for the ground-state KD. At $\sim$1.8 K the low energy excited multiplet KD components disappear following the depletion of the ground state excited level KD. The high energy excited multiplet KD components are slightly blue-shifted at 1.8 K as compared to 8 K; typically 1982, 2031, 2091, 2159, 2213, 2238 cm^{-1} for the $I_{11/2}$ state and 3918, 3962, 4035, 4105 cm^{-1} for the $I_{13/2}$ resolved bands.

Additional KD splittings due to the external magnetic field applied parallel to the *a*-axis are shown in Fig. 2. At 1.8 K the high energy KD component of the ground state is not thermally populated and does not contribute to the CF excitations. Hence the observed splittings are directly related to the excited multiplets KD. Additional Zeeman components with weaker splittings (Fig. 2) is indicative of twinning as previously reported in Ref. 12. Evolution of the KD splittings of the $I_{11/2}$ and $I_{13/2}$ multiplet levels as a function of magnetic field are presented in Figs. 3(a) and 3(b). At 13 T, KD splittings vary between $\sim$14 to 15 cm^{-1} for the $I_{11/2}$ levels and $\sim$17 to 63 cm^{-1} for the $I_{13/2}$ levels.

If the $NdMnO_3$ structure was ideal perovskite, the Nd^{3+} ions would have occupied centrosymmetrical sites preventing the CF excitations from being infrared active. The Jahn-Teller distortions lower the Nd^{3+} site point group symmetry rendering the CF excitations magnetic/electric dipole allowed. Also, the static and coherent character of the Jahn-Teller distortions counters excessive broadening of the CF transitions as confirmed by the Raman active

phonon widths.[10,18] Lifting of the Nd^{3+} KD degeneracies below 75 K confirms the antiferromagnetic Mn^{3+} moment ordering and the detected ground state splitting [$\sim$11 cm^{-1} (50 K), 13 cm^{-1} (15 K) and 14 cm^{-1} (8 K)] is in agreement with the submillimeter transmission measurements of Mukhin *et al.*[12] Compared to the parent of the electron-doped high T_c superconductors Nd_2CuO_4, whose ground state KD splitting is 5.5 cm^{-1},[13] the exchange molecular field should be at least as important in $NdMnO_3$. The exchange interactions and their corresponding KD splittings exhibit no particular anomaly that would confirm the Nd^{3+} sublattice ferromagnetic ordering around $\sim$13 K as inferred by Muñoz *et al.*[9] With no applied external magnetic field, the evolution of the energy levels is rather smooth with temperature as typically observed for the lowest $I_{11/2}$ level [1978 cm^{-1} (50 K), 1979 cm^{-1} (15 K), 1980 cm^{-1} (8 K), 1982 cm^{-1} (1.8 K)] indicating that the exchange interactions, involving Nd^{3+} moments, evolve with temperature.

IV. DISCUSSION

The CF interaction Hamiltonian can be written as[19]

$$H_{CF} = \sum_{k,q} B_{kq}[C_q^k + C_{-q}^k], \tag{1}$$

where the functions C_q^k transform as tensor operators under simultaneous rotation of the coordinates of all the f electrons, B_{kq} are the so-called CF parameters. The x, y, and z axes of the Hamiltonian are parallel to the crystallographic a, b, and c axes (*Pbnm* setting), respectively.

The splitting $2\Delta_i$ of the ith crystal field Kramers doublet in the external magnetic field $\mathbf{H}\|\mathbf{a}$ is determined by[11,12]

$$\Delta_i^2 = (\Delta^{ex}{}_i)^2 + (g_x{}^i \mu_B H_x/2)^2, \tag{2}$$

where $\Delta^{ex}{}_i$ is the Nd-Mn exchange splitting for canted antiferromagnetic Mn spin configuration, g_x being the x component of the g tensor.

In an elementary unit cell, the Nd^{3+} ions occupy the Wyckoff 4c positions with the point symmetry C_s that allows 15 parameters: B_{20}, Re B_{22}, $\pm$Im B_{22}, B_{40}, Re B_{42}, $\pm$Im B_{42}, Re B_{44}, $\pm$Im B_{44}, B_{60}, Re B_{62}, Im B_{62}, Re B_{64}, $\pm$Im B_{64}, Re B_{66}, $\pm$Im B_{66}, determined in this work from the experimental data. Given the number of these parameters, the success of the numerical search for reliable CF parameters strongly depends on the initial estimate. The task is complicated by the lack of CF data in similar structures, usually serving well for this purpose.

We have also considered the technique of descending symmetries.[19,20] Within this approach the observed C_s symmetry site spectra are extrapolated to the O_h symmetry spectra. The symmetry was then reduced by a series of perturbations consisting of distortions from the ideal perovskite structure.[20] However, in contrast to Ref. 20 where this method is applied to $YAlO_3$ the structure of $NdMnO_3$ (Ref. 21) appears to be less suitable for this method since the environments of Nd and Mn are much more distorted than those of Y and Al, respectively. In particular, the Nd-O coordination polyhedron can be divided into two coordination spheres composed of eight and four oxygens. The Nd-O distances in the first coordination sphere fall into the 2.36–2.62 Å interval while the Nd-O distances in the second coordination sphere correspond to the 3.166–3.581 Å interval.[21] The Hamiltonian orthorhombic parameters were thus predicted using the *ab initio* methods and the superposition model calculations[22] considering the available structural data for $NdMnO_3$.[21]

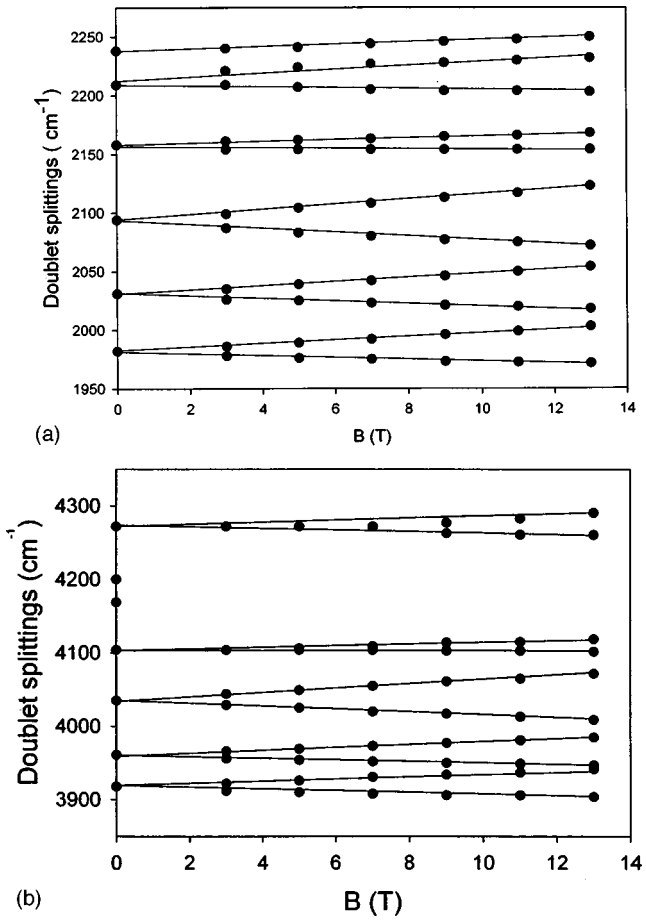

FIG. 3. (a) Evolution at $T=1.8$ K of the $I_{11/2}$ Kramers doublet Zeeman splittings as a function of applied magnetic field. Lines are a guide for the eye. (b) Evolution at $T=1.8$ K of the $I_{13/2}$ Kramers doublet Zeeman splittings as a function of applied magnetic field. Lines are a guide for the eye.

In our best-fit search for the CF parameters the free ion energies of the ^4I_J multiplets were also allowed to vary and the diagonalization procedure considered J mixing within the entire set of multiplets. In the first step we used as an input 19 CF levels (first column of Table I) deduced from the IR transmission spectra (Figs. 1 and 2). Energies of the Kramers doublet exchange splittings were approximated by their average value. No minimum in the sum of the squares of deviations was found. In the second step we extended the input with x components of the g tensors[23] deduced for 11 of these 19 levels by fitting the Zeeman splittings of excited doublets using Eq. (2) and by the available y and z components of the ground state g tensor.[16] In our calculations small contributions of the van Vleck shifts of the excited KD were taken

TABLE I. The experimental CF energy levels within the ^4I term and the absolute values of the Kramers doublet g tensors of Nd^{3+} in $NdMnO_3$ as compared to the calculated values based on the phenomenological CF parameters given in the fourth column of Table II.

CF level	E(Expt.) (cm^{-1})	E(Calc.) (cm^{-1})	$\|g_x\|$ (Expt.)	$\|g_x\|$ (Calc.)
$^4I_{9/2}$	0	−1	3.6/2.4/3.8[a]	2.7/2.3/2.9[a]
	68	57	—	0.5
	181	191	—	4.6
	—	415	—	4.6
	—	459	—	1.4
$^4I_{11/2}$	1973	1998	5.2	5.2
	2022	2029	5.8	4.8
	2084	2060	8.4	7.2
	2149	2164	2.0	2.7
	2201	2207	5.2	4.6
	2230	2208	2.4	3.1
$^4I_{13/2}$	3910	3945	6.4	6.1
	3948	3956	6.2	6.1
	4027	4014	10.2	10.6
	4095	4071	2.6	2.8
	4174	4166	—	8.0
	4202	4211	—	0.05
	4260	4266	—	8.1
$^4I_{15/2}$	5786	5787	—	8.9
	5867	5855	—	6.4
	5981	5991	—	13.4
	—	6031	—	6.0
	—	6144	—	4.5
	—	6324	—	7.8
	—	6439	—	1.5
		6528	—	13.7

[a]The experimental[11] and calculated values of $|g_x|/|g_y|/|g_z|$.

into account [third column in Table I; Figs. 3(a),3(b)].

The set of the CF parameters, which brought the sum of squares of deviations to a minimum, is given in Table II, the calculated CF levels and g_x values are given in the second and fourth columns of Table I, respectively. Note that the main features of the CF spectra including the Zeeman splittings are described by the orthorhombic terms in Hamiltonian: the imaginary terms associated with the C_s symmetry improved the overall fit relatively very little (compare second and third columns in Table II). We have tried in vain many "blind" fits using various initial estimates. This indicates that the resulting best-fit parameters of $NdMnO_3$ represent the global minimum rather than the local minimum.

TABLE II. Crystal field parameters determined for Nd^{3+} in $NdMnO_3$ (in cm^{-1}) by numerical treatment of the experimental data for the orthorhombic and C_s symmetry Hamiltonian (see text). The value in parentheses indicates the mean error associated with the parameter.

	Best-fit (*orthorhombic*)	Best-fit (C_s)
B_{20}	256 (79)	310 (61)
Re B_{22}	59 (54)	47 (44)
B_{40}	−1665(138)	−1664(67)
Re B_{42}	357 (85)	525 (63)
Re B_{44}	779 (92)	640 (54)
B_{60}	−255(107)	−337(61)
Re B_{62}	658 (59)	603 (47)
Re B_{64}	−1095(59)	−978(50)
Re B_{66}	502 (78)	401 (52)
Im B_{22}		−67(43)
Im B_{42}		−6(52)
Im B_{44}		−39(66)
Im B_{62}		57 (67)
Im B_{64}		−224(59)
Im B_{66}		90 (56)

V. CONCLUSIONS

We have reported a CF study of Nd^{3+} ion $4f^3$ electron excited states in $NdMnO_3$. In addition to the detection of the ground state Kramers doublet splitting at $T_N \sim 75$ K, analysis of the observed infrared active excitations $I_{9/2} \rightarrow I_{11/2}, I_{13/2}, I_{11/2}$ under applied magnetic field has allowed the determination of the CF Hamiltonian parameters. Extension of such a study to other rare-earth manganites, in different doping regimes characterized by highly correlated electrons and various magnetic ground states, should add to the understanding of these complex system microscopic properties.

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