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Simulation of optical and magnetic properties of neodymium ($4f^3$) in the solid state: extreme sensitivity to the wave vector's composition

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Abstract

The optical absorption spectra of neodymium at 4 K are reproduced with a very good agreement between calculation and experiment ($15<\mathrm{rms}<20$ cm^{-1}). The wavefunctions which are obtained as a result of the energy calculation can be used to compute other physical properties. Among them we consider the paramagnetic susceptibility and the electron paramagnetic resonance. We report the results of these calculations concerning six compounds (Nd_2O_2S, A-Nd_2O_3, NdOCl, NdOF, Nd^{3+}:$LaCl_3$ and NdF_3) for which the optical absorption spectra were thoroughly interpreted. We notice that these properties, depending on the point symmetry of the neodymium, are very sensitive to the values of the coefficients of the kets in the wavefunctions. These wavefunctions are extremely dependent on the crystal field parameters (cfps). A regard on the magnetic properties is very useful to determine if a set of crystal field parameters which fits the overall Stark levels is also convenient for the ground state ($^4I_{9/2}$). A comparison is also made between cfps determined from atomic positions in the structure (Simple Overlap Model) and phenomenological cfps. We also consider the effect of the spin-correlated crystal field (SCCF) through the action of its radial contribution represented by the c_k parameters ($k=2,4,6$).

Keywords: Optical properties; Magnetic properties; Neodymium; Wave vector composition

1. Introduction

The optical properties of the rare-earth compounds have been widely studied for 30 years. This is due to their huge application as laser and luminescent materials. The position of the discrete energy levels of the $4f^N$ configuration in solids is, in general, well simulated using an Hamiltonian which implies the adjustment of both free atom and crystal-field parameters (cfps). The neodymium compounds have been among the most studied because of the relative simplicity of the $4f^3$ configuration and of its important potential applications. It can be also considered as 'structural local probe' [1] by looking at the position of the well-isolated $^2P_{1/2}$ level with regard to the lowest component of the ground state $^4I_{9/2}$. The optical absorption spectra at 4 K allow to construct an energy level scheme with more than 100 energy levels. Usually a good agreement is found between calculation and experiment ($10<\mathrm{rms}<20$ cm^{-1}), when the simulation is done on the complete basis of 364 $|SLJM_J\rangle$ kets (182 Kramers' doublets).

The aim of this work is to compare the energy level schemes and magnetic properties calculated from (i) phenomenological crystal field parameters B^k_q and (ii) from semi-empirically calculated B^k_q [2]. Moreover, we shall underline the extreme sensitivity of the optical and magnetic properties to the choice of sets of parameters, i.e. to the composition of the wavefunctions.

For this purpose, six compounds (Nd_2O_2S, A-Nd_2O_3, NdOCl, NdOF, Nd^{3+}:$LaCl_3$ and NdF_3) have been selected, due to their well known energy level schemes [3–8] and crystallographic structures. They are also spread on the nephelauxetic scale [9], which indicates different degrees of covalency. The sensitivity to the spin correlated cfps [10], reduced to their radial part c_k [11], is also examined.

2. Methods of calculation

2.1. Crystal field theoretical background

Before diagonalization, the secular determinant of a $4f^N$ configuration is constructed on the $|SLJM_J\rangle$ basis comprising (i) the free-ion interactions with the coulombian repulsion H_{CR}, the spin–orbit coupling H_{SO} as well as the two- and three-body interactions and the higher order

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spin–spin and spin–other-orbit interactions and (ii) the crystal field interaction:

$$H_{\mathrm{CF}} = \sum_{k,q,i} B_q^k (C_q^k)_i$$

In order to take into account the interactions between two electrons we shall also consider the spin-correlated crystal field hamiltonian H_{SCCF}. The algorithm of that interaction has been fully developed and tested by Rukmuni et al. [12]. In the present case, because our purpose is to see mainly its effect on the position of the lowest energy levels, main contributors to the magnetic properties, it is more convenient to reduce this interaction to a 'radial' interaction, as defined by Judd [11]. This is equivalent to replacing the cf tensorial operator $(C_q^k)_i$ by $(C_q^k)_i + c_k(\vec{S}.\vec{s}_i)(C_q^k)_i$. In that expression $\vec{S}$ and $\vec{s}_i$ are the total and electron spins, respectively. Thus, the crystal field hamiltonian becomes:

$$H_{\mathrm{CF}} = \sum_{k,q,i} B_q^k (C_q^k)_i \left[1 + c_k(\vec{S}.\vec{s}_i)\right]$$

in which only three c_k parameters ($k=2$, 4, 6) are introduced.

After diagonalization of the secular determinant, the associated wavefunctions allow to calculate the paramagnetic susceptibility and its variation versus temperature, according to the van Vleck formula [13] as well as the effective magnetic splitting g factors.

It is also useful to define the crystal field strength parameters as:

$$S_k = \left[\frac{1}{2k+1} \sum_{q=-k}^{q=+k} \left|B_q^k\right|^2 \right]^{1/2}$$

and the total crystal field strength

$$S = \left[\frac{1}{3} \sum_{k=2,4,6} S_k^2 \right]^{1/2}$$

[14]. These parameters permit a fast comparison between different compounds.

2.2. The Simple Overlap Model

We have previously shown [2] that the Simple Overlap Model (SOM) allows to estimate the crystal field parameters from the crystallographic structure. The model supposes [15,16] that the crystal field effect can be assimilated to the potential produced by an effective charge distribution spread in a small region situated around the mid point of the metal–ligand distance. It calculates the B_q^k parameters according to the relation:

$$B_q^k = \rho \left(\frac{2}{1 \pm \rho} \right)^{k+1} A_q^k \, \langle r^k \rangle$$

in which ρ is the overlap between the 4f orbitals of the central ion and the 5s and 6p orbitals of the ligand and A_q^k

Table 1
Crystal field and strength parameters (in cm^{-1})

	Nd_2O_2S		A-Nd_2O_3		NDOCL		NdOF		Nd^{3+}:$LaCl_3$		NdF_3	
	CF [4]	SOM [3]	CF [5]	SOM [3]	CF [6]	SOM (This work)	CF [7]	SOM [3]	CF [8]	SOM (This work)	CF [9]	SOM [3]
B_0^2	171	−60	−836	−633	−920	−659	−163	−111	153	430	184	−103
B_2^2											−208	167
iB_2^2											113	−29
B_0^4	897	621	634	553	−333	−857	−1649	1484	−344	−438	276	446
B_2^4											482	550
iB_2^4											−16	−150
B_3^4	946	820	−1606	−1346			−1434	1425				
iB_3^4												
B_4^4					−819	−689					99	522
iB_4^4											−73	−168
B_0^6	544	783	752	1120	934	933	1121	1729	−724	−604	−1023	−1566
B_2^6											168	522
iB_2^6											346	395
B_3^6	−321	−617	237	−1030			784	1282				
iB_3^6												
B_4^6					−209	−1072					−892	−671
iB_4^6											54	230
B_6^6	286	812	672	1313			919	1491	474	−407	−602	−580
iB_6^6											271	839
S_2	86.8	26.8	373.9	283.3	411	249.9	19.7	50.5	68.4	192.1	170.8	117.2
S_4	531.3	438.6	786	660.9	401.7	432.7	968.4	834.3	114.7	145.7	375.6	402
S_6	209.8	455.4	348.7	725.1	271.7	493.7	536.5	908.2	273.7	231.5	569.3	701.6
S_{total}	333.6	365.4	541.3	589.6	367	405.5	693.3	712.6	175.8	193	405.9	471.7

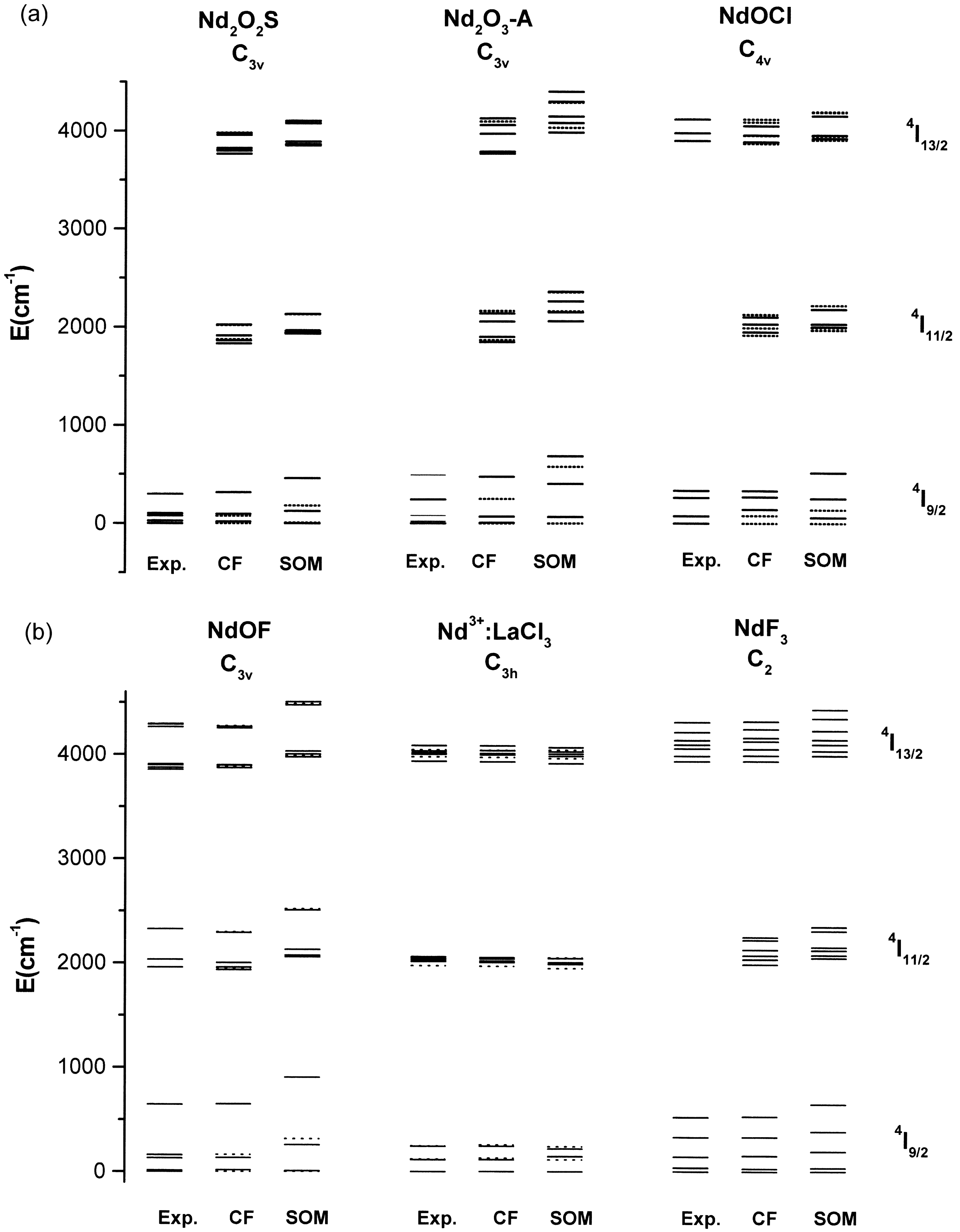

Fig. 1. $^4I_{9/2,\ 11/2,\ 13/2}$ Stark energy levels: comparison between experiment (A), CF (B) and SOM (C) calculations. Solid and dotted lines represent two different irreducible representations $\mu=1/2$ and $\mu=3/2$, respectively.

is the lattice sum over neighbours belonging to the first coordination sphere associated to the ligand charge factor g_i. They are empirically estimated to: $-1.2 \leq g_O \leq -0.8$, $-1 \leq g_{Cl} \leq -0.9$ and $-1 \leq g_F \leq -0.9$. $\langle r^k \rangle$ are the radial integrals: for the neodymium $\langle r^2 \rangle = 1.114$ (a.u.)^2, $\langle r^4 \rangle =$ 2.91 (a.u.)^4 and $\langle r^6 \rangle = 15.03$ (a.u.)^6 [17].

3. Application

For the six compounds previously mentioned, the crystal-field parameters (cfps) have been determined from optical and crystallographic data [2]. The results are summarised in Table 1. It is obvious that some discrepancies exist between the phenomenological and SOM calculated cfps. It is also known [4,8] that several different sets of parameters can yield similar behaviour of experimental values. In a first step, the $4f^3$ secular determinant is diagonalized with these different sets of cfps. The free ion parameters are those obtained by adjustment to the optical data (for Refs. see Table 1). Fig. 1a,b presents the energy sequence of the $^4I_{9/2,11/2,13/2}$ levels, which have a main importance for calculations of the magnetic properties.

3.1. Energy levels

The global phenomenological simulation of the rare-earth energy level schemes is usually very satisfactory. On the other hand the application of SOM, in which aspect of the chemical bonding is taken into account, is more tedious. If comparisons are made between the phenomenological and SOM calculated energy level schemes (Fig. 1a,b), the better agreement occurs for Nd^{3+} in $LaCl_3$ for the whole spectrum. For the other compounds the divergences appear as a function of the nature of the ligands (F^-, Cl^-, O^{2-} and S^{2-}). For A-Nd_2O_3 we observe a bad reproduction of the ground state splitting $^4I_{9/2}$. We have already shown [4] that the set which fits well the energy splitting of the ground state under the complete calculation is not always adequate for overall manifold of the Stark levels. So the bad reproduction of the ground state with SOM is not surprising. However, the crystal field strengths are globally consistent, even if some discrepancies are found between the individual S_k especially for S_2 and S_6 (Fig. 2). The splittings of the $^4F_{3/2}$ and $^2P_{3/2}$ levels, directly linked to the parameters of rank 2, can be represented as a function of S_2 and the variation is actually linear (Fig. 3).

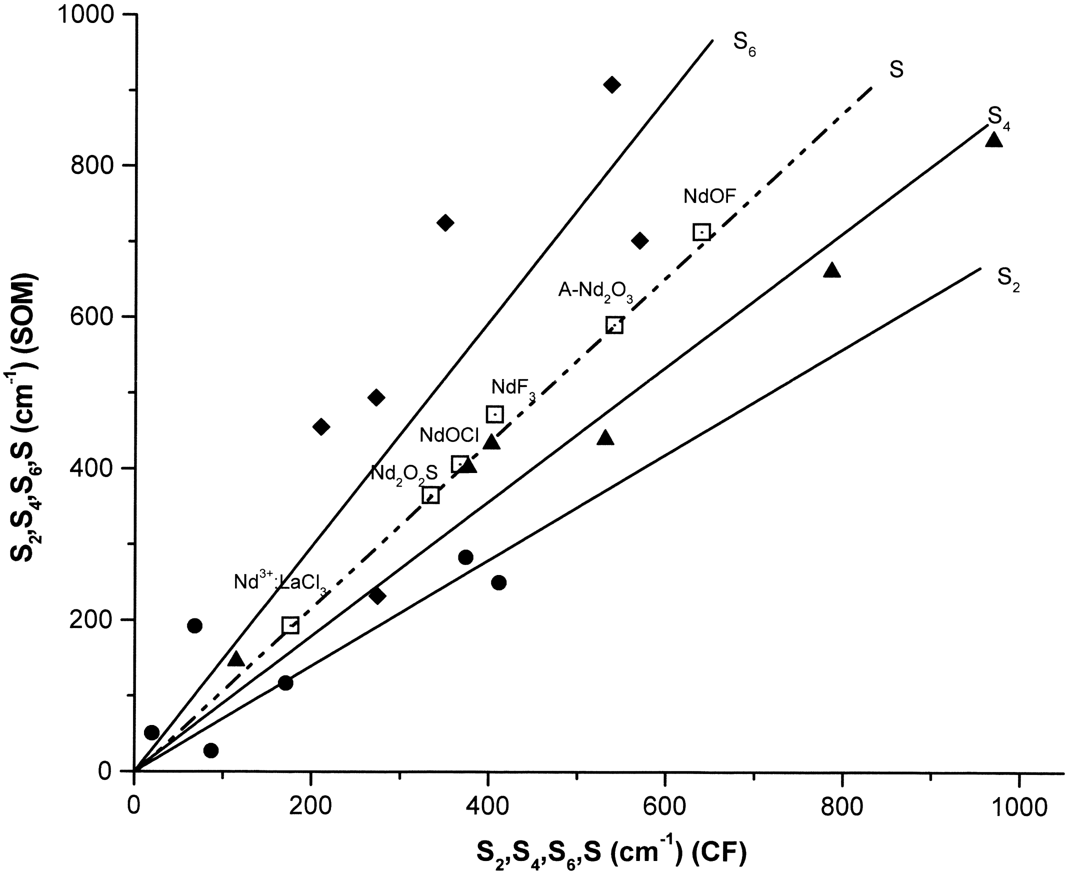

Fig. 2. Comparison between CF and SOM crystal field strengths: S_2 (solid circles), S_4 (solid up triangles), S_6 (solid diamonds) and S (open squares). The dotted line is the ideal comparison for S total strength. The agreement is good for all compounds. The full lines represent the best average representation for S_2, S_4 and S_6.

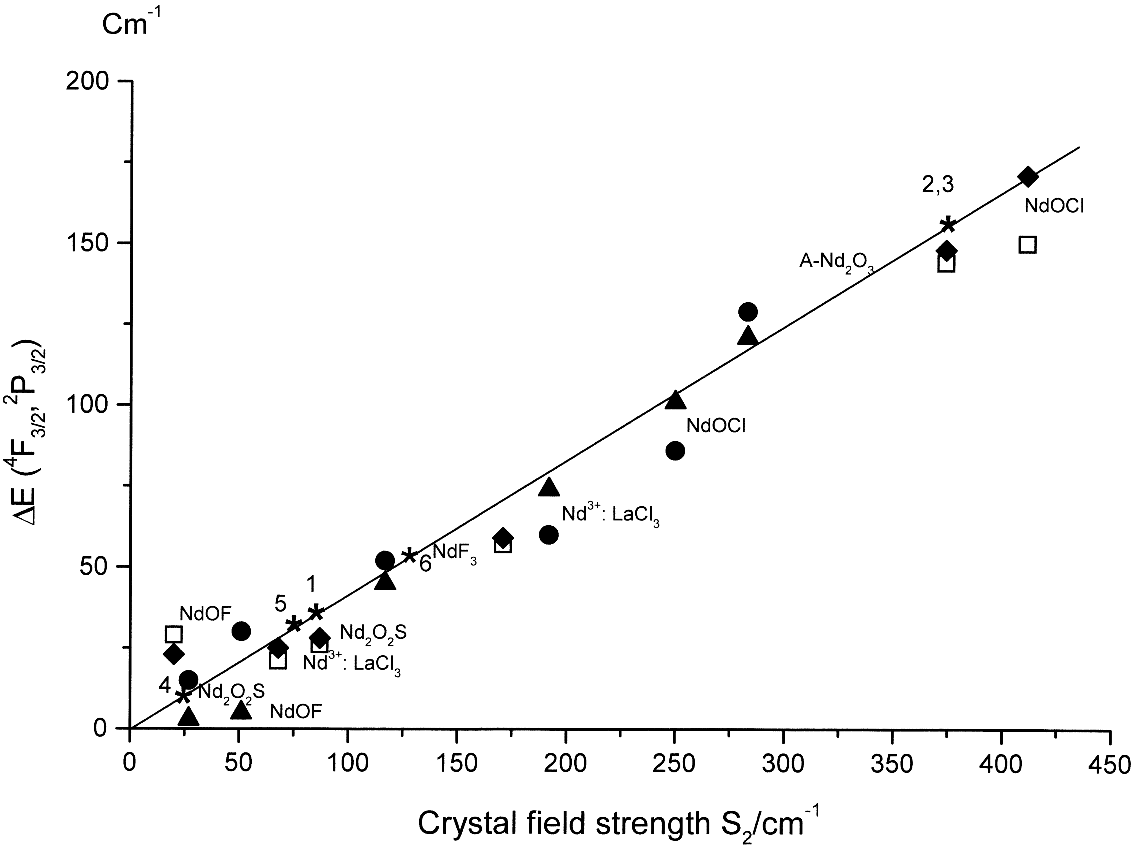

Fig. 3. Evolution of the splittings of $^4F_{3/2}$ and $^2P_{3/2}$ as a function of S_2: CF $^4F_{3/2}$ (open squares), SOM $^4F_{3/2}$ (solid circles), CF $^2P_{3/2}$ (solid diamonds) and SOM $^2P_{3/2}$ (solid up triangles). The stars indicate the experimental $^4F_{3/2}$ splitting of Nd_2O_2S (1), A-Nd_2O_3 (2), NdOCl (3), NdOF (4), Nd^{3+}:$LaCl_3$ (5) and NdF_3 (6).

3.2. Paramagnetic susceptibility

The variation of the paramagnetic susceptibility versus temperature (Fig. 4), is calculated with the van Vleck formula in which the input wavefunctions are derived from the calculations [18] (Table 1). For NdOCl, Nd^{3+}:$LaCl_3$ and NdF_3 a good reproduction of both anisotropies is found although the phenomenological and SOM cfps are rather different. The experimental results obtained from Nd_2O_2S are not very confident due to small sized crystals with hazardous orientation; a curve with an experimental 'spoon shape' is observed at low temperature for $1/\chi_\perp$. This particularity is nicely reproduced by CF calculation and not at all by SOM. For A-Nd_2O_3 the anisotropy is badly reproduced which probably correspond to a poor simulation of the positions of the lowest energy levels (see below). For NdOF only the average susceptibility is measured on polycrystalline powders, the agreement is good at low temperature in all cases and the experimental curve diverges at higher temperature from phenomenological simulation. On the contrary, the calculated curve with SOM parameters curiously reproduce well the variation versus temperature. The role of temperature variations of the crystallographic parameters and atomic positions can be suspected because the cfps values determined by SOM are those determined at room temperature, whereas the phenomenological cfps were determined from low-temperature spectroscopic measurements [6].

3.3. g Values

The g values, only depending of the lowest Stark level of the ground state $^4I_{9/2}$, are very sensitive to the wavefunction composition, i.e. to the cfps. It can be said that this kind of measurements constitutes one of the best proof for the quality of the simulation. Only Nd^{3+}:$LaCl_3$ and NdF_3 have been investigated. The results are satisfying for Nd^{3+}:$LaCl_3$ and only an important difference for SOM with regard to experimental values is found for NdF_3:

Nd^{3+}:$LaCl_3$	Exp [19]	CF	SOM
$g_\perp$	1.76	1.77	1.77
$g_\parallel$	3.99	4.07	4.13
NdF_3	Exp [20]	CF	SOM
g_x	1.72	1.72	2.40
g_y	3.02	3.02	2.09
g_z	1.03	1.03	2.62

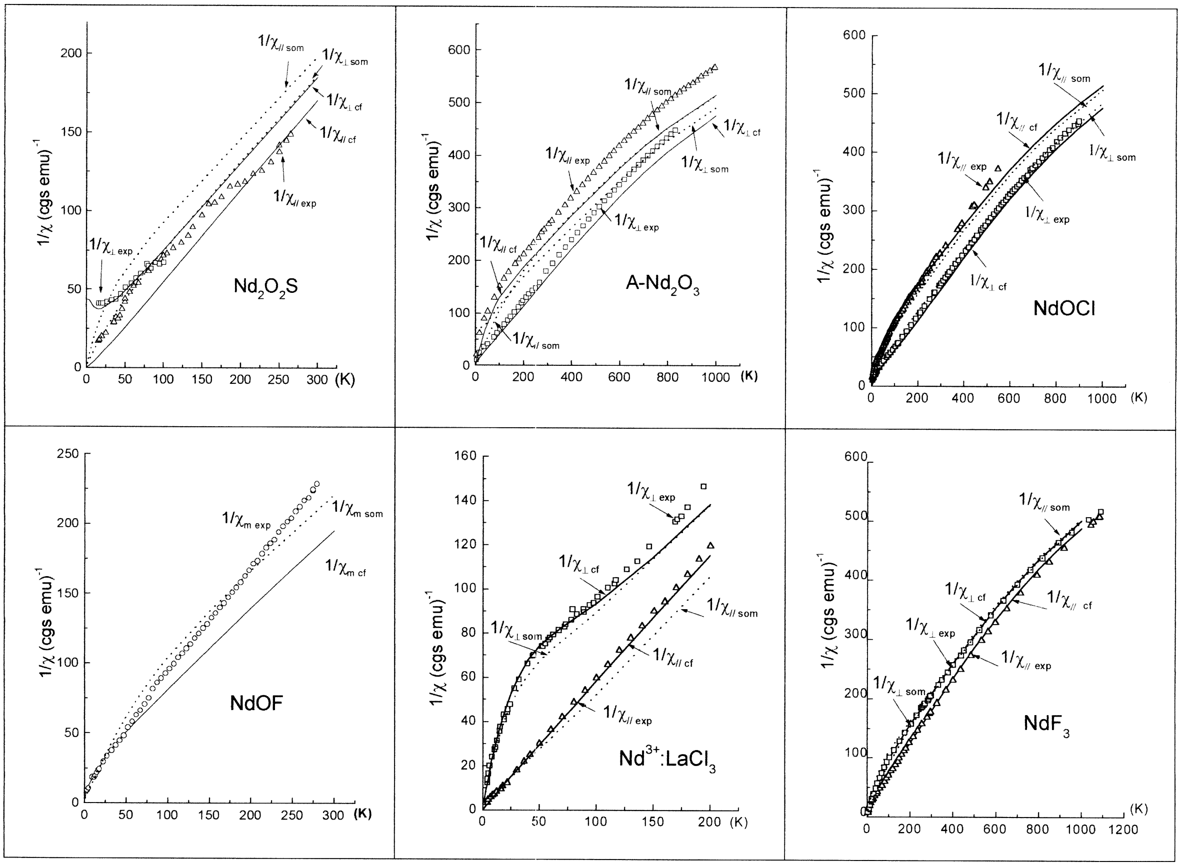

Fig. 4. Thermal variation of the inverse of the parallel (up triangles) and perpendicular (squares) or average (circles) paramagnetic susceptibilities, measured and computed (solid line, CF calculation; dotted lines, SOM calculation).

4. Discussion

They are several reasons for these deviations: (i) between CF and SOM calculations, the difference arises from the estimation of the effective charge of the ligand (as an example A-Nd$_2$O$_3$ for which the degree of covalence is difficult to evaluate), (ii) the wavefunction composition, (iii) the energy difference between the ground crystal field level and the first excited state, and/or the exchange of the irreducible representation of the ground state. We have characterized each state by the M_J value of the most important ket in the wavefunction composition, connected with the crystal quantum number μ ($M_J = \mu$ (mod.q)) convenient for the description of irreducible representations in isomorphic point groups.

As an example in Nd$_2$O$_2$S the percentage of multiplicity four (97%) and two (3%) is the same for CF and SOM calculations, but for the two lowest levels which are very close, the irreducible representations are reversed.

CF: $E = 0\ \mathrm{cm}^{-1}$ $\mu = 3/2$ principal component: 77.62% $|^4I_{9/2,\,9/2}\rangle$

$E = 17\ \mathrm{cm}^{-1}$ $\mu = 1/2$ principal component: 48.86% $|^4I_{9/2,\,-5/2}\rangle$

SOM: $E = 0\ \mathrm{cm}^{-1}$ $\mu = 1/2$ principal component: 76.38% $|^4I_{9/2,\,-5/2}\rangle$

$E = 7\ \mathrm{cm}^{-1}$ $\mu = 3/2$ principal component: 49.14% $|^4I_{9/2,\,3/2}\rangle$

We have shown [3] that, when the Stark ground state is involving only the kets with $M_J = \pm 3/2, \pm 9/2$, the perpendicular susceptibility is independent of temperature at low temperatures. The $1/\chi_\perp$ from CF calculation presents a constant value of about 40 (cgs emu)$^{-1}$ until 30 K. On the other hand for SOM calculation $1/\chi_\perp \rightarrow 0$ and the irreducible representation of the lowest Stark level is $\mu = 1/2$ (Fig. 1). Moreover we remark that the anisotropy is reversed.

The same particularity is observed for A-Nd$_2$O$_3$, for CF as well as for SOM calculations with $1/\chi_\perp \rightarrow 6$ and $1/\chi_\perp \rightarrow 71$ (cgs emu)$^{-1}$, respectively. This difference should be due to the splitting of the two lowest Stark levels (7 and 67 cm^{-1}).

To argue our observations concerning the 'hypersensitivity' to the wavefunction composition we consider the cases of Nd^{3+}:LaCl$_3$ and NdF$_3$. In the first case the percentage of the lowest state is similar (97% $|^4\mathrm{I}_{9/2}\rangle$) for two calculations and the agreement is perfect for both. In the second case a regard on the three principal components reveals identical M_J but with a value of 90.3% $|^4\mathrm{I}_{9/2,\mathrm{MJ}}\rangle$ for CF and 81.95% for SOM, i.e. a difference of about 8%. This small difference induces very important variation on g values (30–150% for SOM).

5. Influence of the c_k parameters

Even if the simulation of a given energy level scheme is globally satisfying, discrepancies remain between experimental and calculated levels. The larger differences are found for the $^2H_{11/2}$ level of Nd^{3+} [21]. A great part of the misfit is solved if mixing with levels of excited configurations, through the odd crystal field parameters and/or through multiconfiguration coulombian interactions, are introduced [22]. Except for $4f^2$ and $4f^3$ configurations, such interactions are difficult to handle in the simulation procedure. It is more convenient to introduce the two electron crystal field interactions. Bishton and Newman [23] have reported that 637 two-electron parameters can be constructed for a low symmetry site, whereas only 41 are necessary for octahedral symmetry. This great number of supplementary parameters makes a simulation not realistic. Then, it is simpler to reduce that interaction to the radial exchange force operating as a correction on the B_q^k, due to the contraction (or dilatation) of the radial function. This formalism has been defined by Judd [11] or in its orthogonal expression by Reid [24]. The c_k parameters have $|c_2| \leq 0.05$, $|c_4| \leq 0.1$ and $|c_6| \leq 0.3$ as approximate limits. According to Judd they should be in general negative, even if Newman suggested that in certain cases c_6 could be positive [10].

Keeping in mind the simulation of the ground levels for paramagnetic calculation as target, we examined the c_k value's action on the Stark splitting of the $^4I_{9/2}$ ground state. The case of A-Nd_2O_3 is of particular interest in reason of the relatively bad simulation of the $^4I_{9/2}$ Stark level sequence with phenomenological as well as with SOM calculated cfps and, consequently, of the anisotropic paramagnetic susceptibility curves (Fig. 4). The experimental sequence is 0, 21, 78, 244, 491 cm^{-1}, to be compared to 0, 7, 70, 250, 475 cm^{-1} (phenomenological simulation) and to 0, 66, 404, 576, 683 cm^{-1} (from SOM calculation). When the c_k values vary independently, it is seen that c_2 has almost no effect on the $^4I_{9/2}$ total splitting (less than 1%). This splitting can be estimated as unvarying in a large range: $-0.4 \leq c_2 \leq 0.3$. At that point we can note that this parameter is the only two-electron parameter that can improve the excited $^4F_{3/2}$ and $^2P_{3/2}$ levels, not affected by c_4 and c_6. On the contrary the individual action of c_4 and c_6 parameters is linear in the $^4I_{9/2}$ splitting, increasing from negative to positive values, the most important being for c_6, with a variation of ±30% for the total splitting. Finally, we found that the values suggested by Judd [11], all with negative signs: $c_2 = -0.05$, $c_4 = -0.1$ and $c_6 = -0.3$, giving the following sequence: 0, 72, 243, 406, 463 cm^{-1} (Fig. 5) are satisfying for the global $^4I_{9/2}$ splitting and improve the simulation of the para-

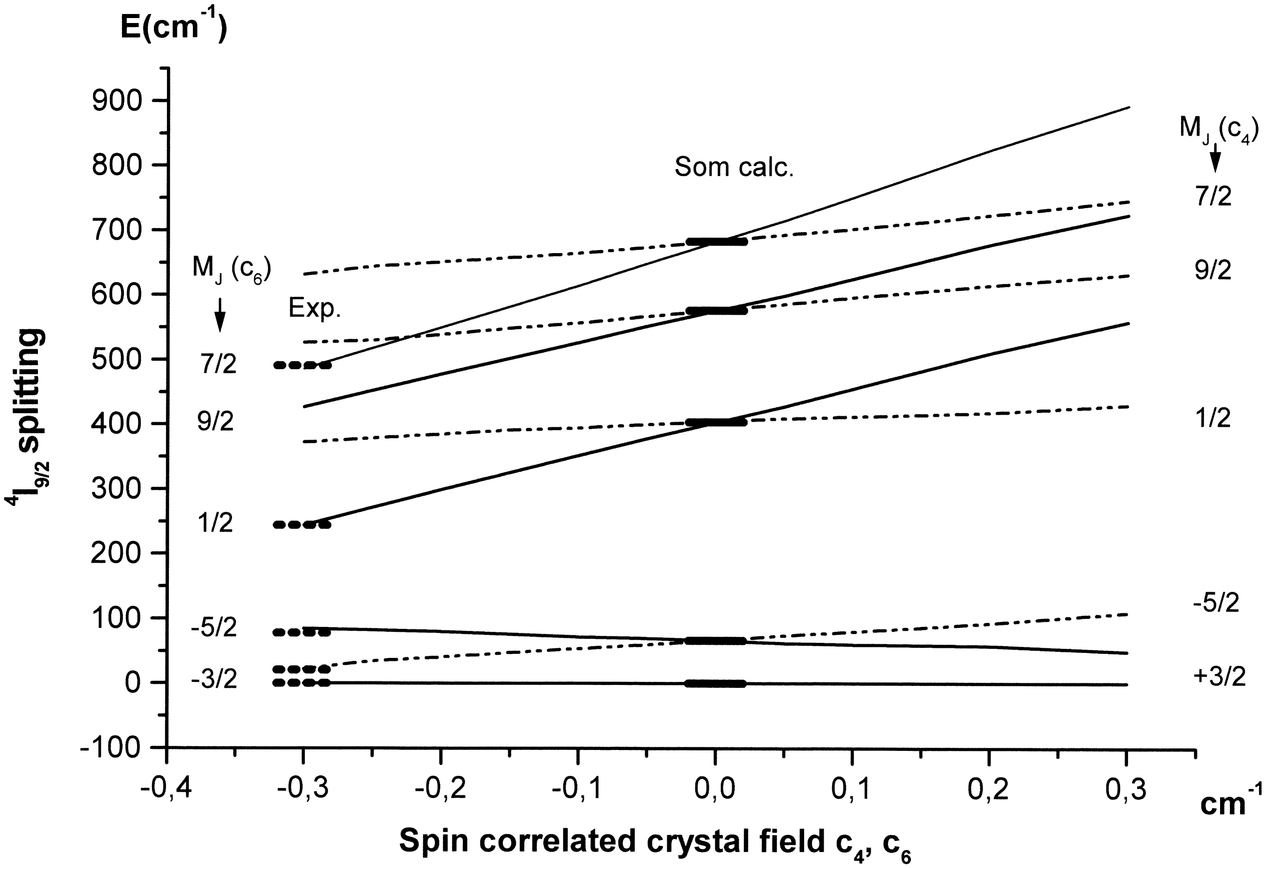

Fig. 5. Evolution of the $^4I_{9/2}$ Stark energy levels as a function of the c_4 (dotted lines) and c_6 (solid lines) parameters.

magnetic susceptibility curve. Further a fitting procedure with all parameters should be undoubtedly necessary to reproduce the position of the complete energy level scheme, although every level presents a real dependence on some cfps.

6. Conclusion

A real difficulty exists for operating in a multidimensional space. This fact implies the consideration of the simultaneous actions of all phenomenological parameters.

If the classical fitting procedure reproduces with a very good agreement the optical absorption or emission data, it is necessary to introduce other parameters such as the SCCF, to study some particular properties (magnetic susceptibility, MCD, EPR, etc.) taking into account wavefunctions. From our observations the part of the spin correlated crystal field is not negligible. We have remarked the large influence of the c_6 parameter on the $^4I_{9/2}$ splitting but also on the excited $^2H_{2,11/2}$ level well known for the strong deviation from predicted calculated values. This parameter should be a good indication of the radial function contraction. Concerning the magnetic properties, we have shown for the C_{3v} point symmetry the effect of the irreducible representations acting on the lowest Stark energy level of the ground state: this is verified for Nd_2O_2S, A-Nd_2O_3 and NdOF.

The use of the Simple Overlap Model that requires the crystallographic positions is also important. SOM calculation presents a crucial importance for the non-transparent compounds such as intermetallics or superconductors as well as for the d elements for which a very reduced number of experimental energy levels is known. This method may be regarded as a starting point to carry out practical crystal field calculation. The great difficulty becomes from the determination of the effective charge, i.e. of the covalence degree.

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