ELSEVIER

Journal of Alloys and Compounds 303–304 (2000) 349–354

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Measurement and simulation of the energy levels of R=Pr^{3+} and Nd^{3+} in $GaRGe_2O_7$

G. Lozano[a], C. Cascales[a,*], C. Zaldo[a], P. Porcher[b]

[a]*Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain*

[b]*Laboratoire de Chimie Appliquée de l'Etat Solide, UMR 7574-CNRS, ENSCP, 11 rue P. et M. Curie, F-75231 CX05, Paris, France*

Abstract

The optical absorption spectra of $GaRGe_2O_7$, R=Pr, Nd, have been measured, on polycrystalline powders, at 9 K. These compounds are monoclinic, space group $P2_1/c$, and in them R^{3+} occupies a single crystallographic position with C_1 point symmetry. From the crystal field analysis of the spectra, energy level schemes and an expression of the associated wavefunctions for the $4f^2$ and $4f^3$ configurations have been derived. The semi-empirical simple overlap model is used to calculate an initial set of crystal-field parameters from the crystal structure. The fitting of experimental Stark level energies and the phenomenological calculation of crystal-field parameters were performed for the approximate $C_s(C_2)$ symmetry. Very satisfactory correlations were obtained between calculated and experimental levels, with root mean square deviations $\sigma=14.1$ and 15.7, respectively, and despite the very low symmetry of R^{3+} in the matrix, the similarity of both sets of crystal-field parameters indicates the consistence of these calculations.

Keywords: Rare earth germanates; Crystal field analysis; Crystal field parameters

1. Introduction

Structures containing only one crystallographic rare-earth site offer a good opportunity for a systematic study of the spectroscopic properties of the trivalent lanthanides. The family of germanates $MRGe_2O_7$, in which M and R represent trivalent metals, Al, Ga or Fe, and rare-earth ions, respectively, constitutes an interesting host from this point of view. Among them, those with Al or Ga, R=La–Dy [1,2] were found in the early 1980s to present a monoclinic $AlNdGe_2O_7$ structure type, S.G. $P2_1/c$ (No. 14). The main feature of this structure is the presence of chains of edge-sharing flexed RO_9 tricapped trigonal prisms running along the *a* axis, linked alternately through an edge or a corner from isolated GaO_5 distorted trigonal bipyramids in the *c* direction, Fig. 1. Since these germanates are isomorphic along the whole R^{3+} series, a comparison of their spectroscopic properties can be established. Some studies of photoluminescence and stimulated emission were carried out [2] for the Nd^{3+}-containing compounds.

The crystal field model has been successfully used in the analysis of $4f^N$ configurations of rare-earth ions in solids [3,4], whose energy levels are reproduced through a hamiltonian which involves both free-ion and crystal-field operators. A satisfactory simulation of the experimental energy levels can be achieved if the number and quality of the operators is adequate. The most interesting trivalent lanthanide would be certainly neodymium because of its relatively large number of energy levels (182 Kramers doublets), but not too large in terms of the size of the secular determinant we need to diagonalize. The difficulty of obtaining proper crystal field parameters, CFPs, from neodymium data alone can be lifted using an isomorphous europium compound to provide phenomenological starting CFP values, or through an initial set of calculated parameters from the several ab initio crystal field models, and thus fitting them along with the free-ion parameters in the hamiltonian to the large number of experimental neodymium levels. Such a procedure provides the energy level scheme but also good quality wavefunctions which can be used to simulate other physical properties depending on them and the energies only [5–7].

The current work presents the results of the study of the optical absorption spectra at 9 K for trivalent Pr and Nd on $GaRGe_2O_7$. From these experimental data the crystal-field analysis and the simulation of their energy level schemes were accomplished considering the approximate $C_s(C_2)$ point symmetry for R, for which nine real plus five

---

*Corresponding author. Fax: +34-913-720-623.

E-mail address: ccascales@estafeta.icmm.csic.es (C. Cascales)

0925-8388/00/$ – see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(00)00610-1

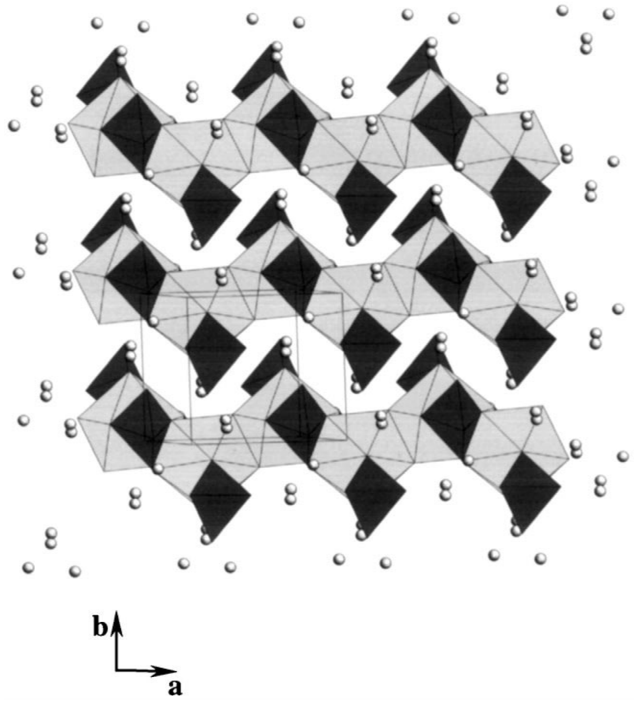

Fig. 1. Projection on the *ab* plane of the $GaRGe_2O_7$ structure showing the RO_9 chains running along the *a* axis. Large (light gray) and small (dark gray) polyhedra correspond to tricapped trigonal prisms RO_9 and trigonal bipyramids GaO_5, respectively. Spheres represent positions of Ge.

complex CFPs are involved. A set of CFPs calculated using a semi-empirical model from crystallographic data was utilized as the starting point in the simulation of these configurations. In this case the true C_1 symmetry of R in the germanate matrix was considered.

2. Experimental details

$GaRGe_2O_7$ (R=Pr, Nd) were prepared as pure polycrystalline powders by solid state reaction from analytical grade mixtures of Ga_2O_3, GeO_2 and Pr_6O_{11} or Nd_2O_3 at molar ratios Ga:R:Ge=1:1:2. A slight deficiency of the R-oxide with regards to the stoichiometric required amounts was used in order to counteract the losses of GeO_2, especially as a vitrified product. Samples were ground and heated in air to 1150°C for 1 week with intermediate regrindings. Standard X-ray powder diffraction analysis indicated that final samples were well crystallized and appeared, to the limits of the technique, free of other crystalline phases.

In order to study the thermal evolution of this structure, neutron powder diffraction (NPD) patterns of a $GaLaGe_2O_7$ sample were collected at 1.7 K and room temperature on the D1B powder diffractometer, at the Institut Laue-Langevin of Grenoble, using a wavelength of 1.595 Å. Further details and the crystallographic refinement process followed can be found elsewhere [8].

The absorption spectra of pure $GaRGe_2O_7$, R=Pr, Nd, were obtained by using a CARY 5E spectrophotometer. Measurements were carried out at 9 K on dispersed $GaRGe_2O_7$ in KBr pellets. The spectral range extended from 4000 up to 31,000 cm^{-1}, the absorption edge of the matrix.

3. Energy level scheme simulation

In the development of a complete hamiltonian for $4f^N$ configurations, the central-field approximation allows us to consider separately the hamiltonian corresponding to the gaseous free ion, H_{FI}, and to the crystal field interactions which arise when the ion is in a condensed phase, H_{CF}. The interactions primarily responsible for the free-ion structure can be written [9] as:

$$\begin{aligned}H_{FI} = H_0 &+ \sum_{k=0,1,2,3} E_k e^k + \zeta_{4f} A_{SO} + \alpha L(L+1) \\ &+ \beta G(G_2) + \gamma G(R_7) + \sum_{k=0,2,4} M^k m_k + \sum_{i=2,4,6} P^i p_i \\ &+ \sum_{k=2,3,4,6,7,8} T^k t_k\end{aligned}$$

which includes the spherically symmetric one-electron term of the hamiltonian, the electrostatic repulsion between equivalent f electrons, the spin–orbit interaction, and terms considering higher-order corrections. Judd's parameters T^λ account for non-negligible three-body interactions for configurations having more than two electrons. Magnetically correlated corrections such as spin–spin and spin-other-orbit interactions can be simulated through the M^k ($k = 0, 2, 4$) parameters, also called Marvin integrals, and the electrostatically correlated spin–orbit interactions are described by the P^i ($i = 2, 4, 6$) integrals. Thus, 14 free-ion parameters can describe adequately the $4f^2$ configuration of Pr^{3+}, whereas for the $4f^3$ configuration of Nd^{3+} the T^λ parameters are introduced, too.

The crystal-field term, H_{CF}, takes into account the effect of the electrostatic interactions arising from the surrounding ions on the f electrons. In the presence of a crystalline electric field the degeneracy of each state of the free ion will be lifted according to the site symmetry of the rare earth in the crystal lattice. Calculations are usually carried out within the single-particle crystal-field theory, and following Wybourne's [10] formalism, the crystal-field hamiltonian is expressed as a sum of products of spherical harmonics and CFPs:

$$\begin{aligned}H_{CF} = \sum_{k=2}^{4,6} \sum_{q=0}^{k} &\left[B_q^k (C_q^k + (-1)^q C_{-q}^k)\right. \\ &\left.+ iS_q^k (C_q^k - (-1)^q C_{-q}^k)\right].\end{aligned}$$

A few configurations ($4f^{1,\,2,\,3,\,11,\,12,\,13}$) can be treated without truncations, others ($4f^{6,\,7}$) have to be truncated, but, on the whole, coherent results are found for the values of the CFPs of different lanthanides, utilized as crystal field probes in the same site of isostructural compounds. The number of the non-zero B^k_q and S^k_q phenomenological CFPs depends on the crystallographic point-site symmetry of the lanthanide ion. In the studied germanates R^{3+} occupies a crystallographic position with the lowest C_1 point symmetry. The serial development of this crystal field potential keeps non-zero all of the 27 CFPs, which constitutes non-realistic conditions of simulation. Thus, the well-known problem [11–13] of the analysis of optical data for lanthanide ions with low point-group symmetries emerges in the present parametrization scheme. Obviously, in the absence of polarization emission measurements on single crystals, it is very difficult if not impossible to unravel the optical spectra unambiguously. Even if these measurements were possible and this had been done, it is not straightforward to fit the data with a total hamiltonian. The number of adjustable parameters is very large, and in this case it is generally admitted that nonlinear least square fits are unreliable, and several minima may exist that are indistinguishable from one another insofar as the quality of the fit is concerned. Since the optimized parameter set is very dependent on the chosen starting values, imposing theoretical constraints can alleviate these difficulties. The free-ion parameters will not vary much for a lanthanide ion in different systems, and in any case are available in the literature [9], in contrast to the CFPs, which may show a large variation depending on the host crystal. Various theoretical models of the crystal-field interactions [14] can be used to provide one convenient set of starting values for CFPs in the search for the corrected minimum. Another method is the initial consideration of a higher but close to the true symmetry in order to reduce the number of involved CFPs, i.e. the so-called descending symmetry procedure [10]. Moreover, to verify the consistency and reliability of the final fitted parameters, simultaneous simulations performed for different $4f^N$ configurations, either in the same [9] or in an isostructural crystalline matrix [4,15,16], should provide sets of CFPs with only smooth variations.

For these reasons and in order to compare therefore with phenomenological values, the semi-empirical simple overlap model, SOM [17], was applied to calculate the initial set of CFPs from the crystal structure. This model has been tested [18] over a wide variety of R^{3+} compounds, in single crystal or polycrystalline form, for which the point symmetry of the site occupied by the rare-earth was ranging from the high cubic O_h to the very low triclinic C_1 symmetries, and whose experimental CFPs and free-ion interactions are known as precisely as possible. The model is based on effective charges, located around the middle of the R^{3+}-ligand distance, which are assumed to be proportional to the magnitude of the overlap, ρ, between rare earth and ligand wavefunctions. CFPs are written as

$$B^k_q = \langle r^k \rangle \sum_{\mu} \rho_{\mu} \left(\frac{2}{1 \pm \rho_{\mu}} \right)^{k+1} A^k_q(\mu),\ \rho_{\mu} = \rho_0 \left(\frac{R_0}{R_{\mu}} \right)^{3.5}.$$

The sum over μ is restricted to the first neighbors, i.e. over all ligands of the first coordination sphere, consequently the required crystallographic data are restricted to the closest ligand positions and thus $\langle r^k \rangle$ radial integrals [19] are not corrected from the spatial expansion. ρ varies for each ligand as a function of the distance from the central ion and is referred to the closest ligand. A^k_q is the lattice sum and it takes into account the symmetry properties of the metal site, including the effective charge attributed to the ligand. The sign $\pm$ of the denominator stands for differentiating the type of ligand: when a single type of ligand is considered, a minus sign corresponding to the normal shift of the charge barycenter from the middle of the bonding distance should be taken, and when different ligands are present the minus sign corresponds to the most covalent one.

Comparisons between experimental and semi-empirical SOM CFPs, for the true C_1 symmetry, were made through the corresponding crystal field strengths S_k, for the CFPs of rank k, and the total crystal field strength, S_T [20], defined as follows:

$$S_k = \left\{ 1/(2k+1) \left[(B^k_0)^2 + 2\sum_q \left[(B^k_q)^2 + (S^k_q)^2 \right] \right] \right\}^{1/2} \quad S_T = \left[\frac{1}{3} \sum_k S^2_k \right]^{1/2}.$$

In these comparisons the two adjustable parameters required for the model adopted the typical values of -0.8 for the effective charge of the oxygen [11] (effective charges for lanthanides, as well as for Ge are not considered for the model, which takes into account *only* the first neighbours), and values between 0.06 and 0.08 for the overlap ρ [21,22].

The simulation of schemes of crystal field energy levels has been performed by the programs REEL and IMAGE [23]. Instead of C_1, the approximate C_s (or C_2) point symmetry, which involves 14 CFPs, was used for the simulations of both configurations. Anyway, the great number of parameters introduced forced us to be particularly careful on the meaning of the obtained values. For this reason, depending on the observed energy levels and on their sensibility to a given parameter, some of them should be fixed to so-called standard values, corresponding to calculated ones or to those found in a matrix yielding the richest information. Among them, γ will be fixed since the levels in which its effect is really of importance are not experimentally observed ($^1S_0$ and $^2F(2)$ terms of Pr and Nd, respectively, for instance). For the same reason T^2 and T^8 could not be varied freely. M^k and P^i cannot be freely varied, and they are always maintained in standard and/or related ratios, which can be the pseudo-relativistic Hartree–Fock [24] calculated ones $M^2/M^0 = 0.5582$, $M^4/M^0 = 0.3785$, $P^4/$

$P^2 = 0.6667$ and $P^6/P^2 = 0.4899$, or more or less 'adapted' ones $P^4/P^2 = 0.75$ and $P^6/P^2 = 0.50$ [25] or $M^2/M^0 = 0.56$, $M^4/M^0 = 0.31$, $P^4/P^2 = 0.50$ and $P^6/P^2 = 0.10$ [9] see Table 1.

To test the consistency of the final fitted parameters, the set obtained for $PrGaGe_2O_7$ has been utilized as a starting point to perform the crystal-field analysis for $NdGaGe_2O_7$.

The correct procedure for the simulation of the energy level schemes involves the simultaneous treatment of both the free-ion and CF effects using the untruncated basis set of wavefunctions. The best fit of parameters was obtained in each case by the least-squares refinement between the observed and calculated energy level values through a minimization of the rms function $\sigma = [\Sigma(\Delta_i)^2/(n-p)]^{1/2}$, where Δ_i is the difference between observed and calculated energies, n is the number of levels fit and p is the number of parameters freely varied.

Table 1
Free ion and crystal field parameters (C_s) for $RGaGe_2O_7$, R = Pr^{3+}, Nd^{3+} [a]

	Pr	Nd
E^0	9497 (1)	23,644 (1)
E^1	4474 (2)	4782.2 (7)
E^2	22.16 (1)	23.40 (1)
E^3	463.0 (1)	480.51 (7)
α	23.32 (6)	17.79 (3)
β	−709 (6)	−556 (3)
γ	[1470]	[1490]
ζ	739(1)	868.3 (6)
T^2	–	[305]
T^3	–	38 (2)
T^4	–	74 (2)
T^6	–	−246 (5)
T^7	–	290 (5)
T^8	–	[350]
$M^{0,b}$	[0.80]	[0.80]
$P^{2,c}$	[200]	[200]
B^2_0	−285 (14)	−421 (11)
B^2_2	226 (8)	91 (13)
B^4_0	768 (23)	482 (43)
B^4_2	303 (25)	355 (33)
S^4_2	−399 (22)	−115 (41)
B^4_4	−304 (24)	−298 (36)
S^4_4	−182 (26)	−339 (33)
B^6_0	121 (38)	556 (51)
B^6_2	574 (31)	725 (25)
S^6_2	−112 (40)	−341 (37)
B^6_4	501 (33)	458 (31)
S^6_4	200 (40)	427 (42)
B^6_6	−445 (26)	−336 (31)
S^6_6	168 (54)	−258 (51)
Levels	50	110
σ	14.1	15.7
Residue	5804.1	21,017.7

[a] Values in parentheses refer to estimated standard deviations in the indicated parameter. Values in square brackets were not allowed to vary in the parameter fitting.

[b] M^0, M^2, M^4 were constrained by the ratios $M^2 = 0.5625\ M^0$, $M^4 = 0.3125\ M^0$.

[c] P^2, P^4, P^6 were constrained by the ratios $P^4 = 0.75\ P^2$, $P^6 = 0.50\ P^2$. All data are in cm^{-1} units.

4. Results and discussion

The J-manifolds of R^{3+} in this germanate matrix are split in the maximum number of Stark components, singlets for Pr^{3+} and Kramers doublets for Nd^{3+}. The lack of selection rules for electric and magnetic dipole transitions for the C_1 symmetry allows to draw quite complete sequences of crystal-field levels, in the visible part of the spectrum, especially for the Nd-compound.

Well resolved transitions in the absorption spectrum of Nd^{3+} in $GaNdGe_2O_7$ at 9 K, Fig. 2, originate from the lowest Stark component of the $^4I_{9/2}$ ground state manifold. A pattern with 110 energy levels is considered in the fitting procedure. For $GaPrGe_2O_7$ a set of 50 transitions was observed, including an almost full sequence for $^1D_2$, $^3P_{0,1,2}$ levels and some components of $^1I_6$.

SOM CFPs have been calculated for C_1, the true symmetry for the R^{3+} site, and in this case the crystal field potential involves a large number of CFPs, 27, far away

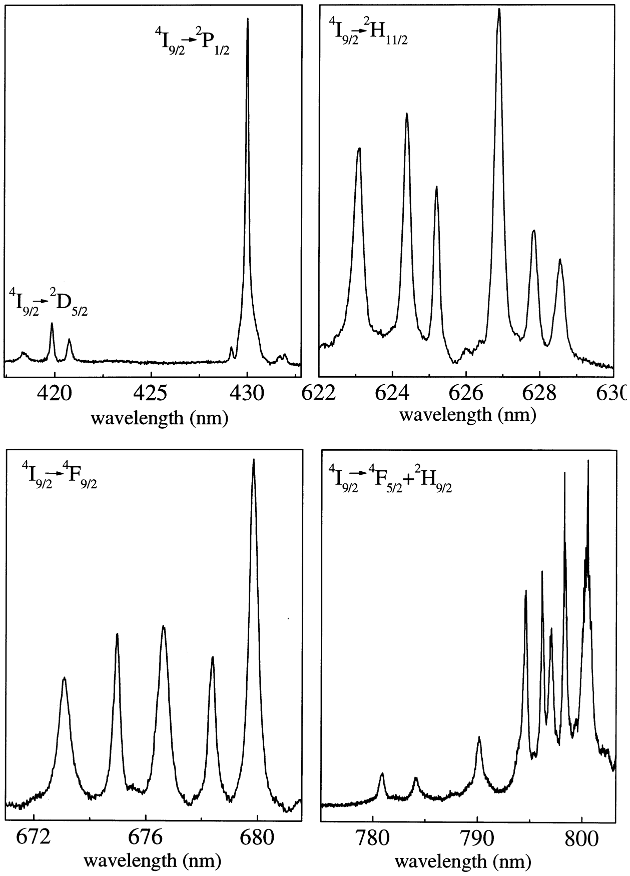

Fig. 2. Selected parts of the optical absorption spectrum of $GaNdGe_2O_7$, at 9 K.

from the 14 experimentally obtained for the approximate C_s (C_2) symmetry. Thus, in order to compare them, the use of their corresponding crystal field strength S_k parameters is a more reasonable approach. A good correlation can be observed between phenomenological S_k values and those reproduced by the model, Table 2, especially for S_2, for which the better result would suppose $\rho \sim 0.07$ for both compounds. S_T would require, however, a stronger overlap, the ρ values being anyway characteristic for f cations. Because of the particular sensitivity of B_0^2 (S_2) to the magnitude of the electrostatic interactions, that is, a small variation of the metal–ligand distance inducing a strong variation in the CFP values, the crystallographic structure in which SOM is based has been determined from powder neutron diffraction data at 1.7 K. A proper comparison of semi-empirical CFPs and energy level schemes deduced from 9 K measurements is, in this way, possible.

Large individual discrepancies between experimental and calculated energy levels have not been detected in any case [7]. Despite the very low symmetry of R in this germanate matrix, the simulations yielded energy level schemes in good agreement with the experimental data, $\sigma = 14.1$ and 15.7 cm^{-1} for Pr and Nd compounds, respectively, Table 1.

In contrast to many Pr-compounds, in which energy levels of the $^1D_2$ multiplet are poorly fitted [26], a good concordance is obtained between the observed and calculated Stark levels of this multiplet for $PrGaGe_2O_7$. For the Nd-compound, almost all crystal-field levels obtained in the fitting procedure, which uses as a starting point the set of CFPs obtained for Pr, are close to their experimental values, including those of the $^2H(2)_{11/2}$ multiplet.

On the other hand, there is a general similarity between sets of parameters for both compounds, which is seen from Table 1. Due to the very high number of parameters it is impossible or at least very risky to say that these parameter sets are unique, but in any case the agreement between them indicates that they are physically meaningful and consistent.

The oversimplified SOM model seems to be useful providing reasonable estimations of crystal field strength parameters from crystallographic data. However, taking into account the lack of symmetry of the R^{3+} site in this germanate host, a careful evaluation of results from SOM should be considered, because they provide only a *global* estimation of the magnitude of the crystal field strength. Anyway, SOM offers a good possibility, especially when the point symmetry of the rare-earth involves a reduced number of non-zero parameters, this kind of calculation being of particular interest when opaque materials are to be considered.

Table 2
Comparison between SOM-calculated and observed crystal field strength parameters (cm^{-1}) in $GaRGe_2O_7$, R = Pr, Nd

S_k	SOM (C_1)			Pr (C_s)	Nd (C_s)
	$\rho = 0.06$	$\rho = 0.07$	$\rho = 0.08$		
S_2	151.7	183.6	217.7	191.4	196.7
S_4	218.6	268.2	322.4	386.4	319.4
S_6	231.7	288.3	351.6	365.2	465.8
S_T	203.7	250.8	302.8	326.2	345.3

Acknowledgements

The authors acknowledge the financial support of DGESIC under project No. PB97-1200 and TIC96-1039. They are also indebted to the Institut Laue Langevin, Grenoble, for neutron scattering facilities offered.

References

[1] K. Jarchow, K.H. Klaska, H. Schenk-Strauss, Z. Krystallogr. 172 (1985) 159.

[2] A.A. Kaminskii, B.V. Mill, A.V. Butashin, E.L. Belokoneva, K. Kurbanov, Phys. Status Solidi a 103 (1987) 575.

[3] C. Cascales, R. Sáez Puche, P. Porcher, J. Solid State Chem. 114 (1995) 52.

[4] C. Cascales, P. Porcher, R. Sáez Puche, J. Phys. Condens. Matter 8 (1996) 6413.

[5] C. Cascales, R. Sáez Puche, P. Porcher, Chem. Phys. 240 (1999) 291.

[6] C. Cascales, P. Porcher, R. Sáez Puche, J. Alloys Comp. 250 (1997) 391.

[7] G. Lozano, C. Cascales, C. Zaldo, P. Porcher, Chem. Mater., in press.

[8] C. Cascales, L. Bucio, E. Gutiérrez Puebla, I. Rasines, M.T. Fernández Díaz, Phys. Rev. B 57 (1998) 5240.

[9] W.T. Carnall, G.L. Goodman, K. Rajnak, R.S. Rana, J. Chem. Phys. 90 (1989) 3443.

[10] B.G. Wybourne, Spectroscopic Properties of Rare Earths, Wiley, New York, 1965.

[11] C.A. Morrison, R.P. Leavitt, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 5, North Holland, Amsterdam, 1996, p. 461, and references cited therein.

[12] C. Görller-Walrand, K. Binnemans, Rationalization of crystal-field parametrization, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 23, North Holland, Amsterdam, 1996, p. 121.

[13] G.W. Burdick, S.M. Crooks, M.F. Reid, Phys. Rev. B 59 (1999) 7789.

[14] D. Garcia, M. Faucher, Crystal field in non-metallic (rare earth) compounds, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 21, North Holland, Amsterdam, 1995, p. 263, and references cited therein.

[15] J. Huang, J. Loriers, P. Porcher, G. Teste de Sagey, P. Caro, C. Levy-Clement, J. Chem. Phys. 80 (1984) 6204.

[16] V.S. Mironov, L.E. Li, J. Alloys Comp. 279 (1998) 83.

[17] O.L. Malta, S.J.L. Ribeiro, M. Faucher, P. Porcher, J. Phys. Chem. Solids 52 (1991) 587.

[18] P. Porcher, M. Couto dos Santos, O. Malta, Phys. Chem. Chem. Phys. 1 (1999) 397.

[19] A.J. Freeman, J.P. Desclaux, J. Magn. Magn. Mater. 12 (1979) 11.

[20] N.C. Chang, J.B. Gruber, P.R. Leavitt, C.A. Morrison, J. Chem. Phys. 76 (1982) 3877.
[21] J.D. Axe, G. Burns, Phys. Rev. 152 (1966) 331.
[22] D. Garcia, M. Faucher, J. Chem. Phys. 82 (1985) 5554.
[23] P. Porcher, Fortran routines REEL and IMAGE for simulation of d^N and f^N configurations involving real and complex crystal field parameters, (1989), unpublished.
[24] G.M. Copland, D.J. Newman, C.D. Taylor, J. Phys. B: Atom. Mol. Phys. 4 (1971) 1388.
[25] H.M. Crosswhite, H. Crosswhite, J. Opt. Soc. Am. 1 (1984) 246.
[26] D. Garcia, M. Faucher, J. Chem. Phys. 90 (1989) 5280.