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Measurement and crystal field analysis of energy levels of Ho^{3+} and Er^{3+} in $KGd(WO_4)_2$ single crystal

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Abstract

Optical absorption and photoluminescence spectra performed on Ho^{3+} ($4f^{10}$) and Er^{3+} ($4f^{11}$) doped $KGd(WO_4)_2$ single crystals were measured at selected temperatures between 5 and 80 K. In this monoclinic matrix, space group *C2/c* (No. 15), the lanthanide ions replacing Gd^{3+} occupy a single crystallographic site with symmetry C_2. The interpretation of these spectra and the simulation of the splitting of $^{2S+1}L_J$ levels were carried out in the frame of the phenomenological single-electron crystal field theory, through the simultaneous diagonalization of the energy matrices of the free-ion (fi) and crystal field (cf) interactions. A total of 20 fi and 14 cf adjustable parameters were considered for the reproduction of experimental energy levels and their associated wavefunctions. The simulated energy level series are in excellent accordance with the experimental data, i.e. rms deviations, $\sigma=14.5$ and 15.6 cm^{-1} for Ho^{3+} and Er^{3+}, respectively. The comparison with similar results for Pr^{3+} ($4f^2$) and Nd^{3+} ($4f^3$) allowed establishment of the variation trends of the cf parameters with the number of 4f electrons.

Keywords: Crystal and ligand fields; Optical properties; Light absorption; Luminescence; Insulators

1. Introduction

$KGd(WO_4)_2$ (hereafter KGW) single crystal, where Gd can be substituted to a large extent by other lanthanides, is an efficient laser host for the stimulated emissions of the rare-earths (RE) [1]. Despite the relevance of this system, most of the spectroscopic work so far reported has been performed at temperatures above 77 K, and consequently the energy level positions for $4f^N$ configurations usually remain ambiguously attributed. This is particularly true for Ho^{3+}, since the gap between the ground and first excited Stark levels of the $^5I_8$ multiplet is very narrow (4–8 cm^{-1}). Consequently, the interpretation of observed absorption spectra is difficult because of the coexistence, even at 5 K, of transitions starting from several levels.

In this work, polarized optical absorption (OA) and photoluminescence (PL) spectra have been measured for Ho doped KGW in the 5–80 K temperature range, and 181 energy levels of its $4f^{10}$ configuration have been now undoubtedly determined, 173 of them being used to perform the single-electron crystal field (cf) analysis for the Ho^{3+} center. This phenomenological model is described through a Hamiltonian which includes the electrostatic, spin-orbit, interconfigurational and cf interactions. The same kind of calculation has been carried out with the previously established sequence of 72 energy levels of Er^{3+} in KGW [2]. Trends in the evolution of cf parameters along the lanthanide series are shown from the comparison of cf parameters for both rare earths with those previously established for Pr^{3+} [3] and Nd^{3+} [4] in the same matrix [3].

2. Experimental techniques

Ho and Er doped KGW single crystals have been grown by the top seeded solution growth technique from mixtures of K_2CO_3, Gd_2O_3, WO_3 and Ho_2O_3 or Er_2O_3, using $K_2W_2O_7$ as solvent. Details of the growth procedures have been given previously [5]. The amount of RE substitution (either Ho or Er) ($RE_2O_3/(Gd_2O_3+RE_2O_3)$), was varied from 0.1 to 5% in the melt.

Optical absorption (OA) was performed using a Varian CARY 5E spectrophotometer. The temperature of the sample was changed in the 5–80 K range by using He-

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liquid (5–15 K) and close-cycled (10–80 K) cryostats. Photoluminescence (PL) was excited with an Ar laser. The emission is dispersed with a Spex 340E spectrometer ($f=34$ cm) and detected with a cooled Hamamatsu photomultiplier.

3. Crystal-field analysis

The method used here for calculating the energy levels of $4f^N$ configurations diagonalizes a combined Hamiltonian $H=H_{\mathrm{FI}}+H_{\mathrm{CF}}$. The free-ion part, H_{FI}, includes the electrostatic, spin-orbit and interconfigurational interactions, as well as magnetically and electrostatically correlated corrections [6]. Crystal field calculations have been carried out using a single-electron crystal field model [7] and the Hamiltonian, H_{CF}, is written as a sum of tensor operators $(C_q^k)_i$ with real B_q^k and imaginary S_q^k parameters as coefficients, whose number, 9 and 5, respectively, is the appropriate to the C_2 symmetry of the trivalent lanthanide in the host:

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

The simultaneous treatment of both free-ion and cf effects using the untruncated basis set of wavefunctions has been considered in the fitting procedure for $4f^{10}$ and $4f^{11}$ configurations. The calculations [8] have been started with cf parameters obtained previously for Pr^{3+} in KGW [3].

4. Experimental results and discussion

The description of the KGW crystalline structure and of the principal axes (*p, m* and *g*) of the optical indicatrix have been detailed elsewhere [2]. In this monoclinic crystal, with space group *C2/c* (No. 15), lanthanide ions replace the single crystallographic position of Gd^{3+}, and hence only one optical active centre is expected for both Ho^{3+} or Er^{3+} ions.

Complete energy level schemes of Ho^{3+} ($4f^{10}$) and Er^{3+} ($4f^{11}$) configurations amount to 2002 (singlets) and 182 (Kramers doublets) levels, respectively. At 5 K they can be determined by OA without significant attenuation from the matrix up to ~33 000 cm^{-1}. In the 32 000–33 000 cm^{-1} range the Gd^{3+} absorption produces sharp lines [5] that should not be confused with those corresponding to the impurities under study. The interpretation of both OA and PL spectra of Er^{3+} is relatively easy to carry out in detail because of the large separation of the $^{2S+1}L_J$ levels. In contrast, labelling energy levels of Ho^{3+} is complicated by the existence, even at 5 K, of satellite bands. These satellite bands arise from the thermal population of the first and second excited cf levels.

The 5 K OA spectra provided the energies of the Ho^{3+} multiplets from $^5I_7$ up to $^3K_6$. The energies of the ground $^5I_8$ multiplet were deduced from PL measurements and from the OA bands that are observed to grow when the temperature is raised above 5 K. Table 1 lists the energy of the 181 strongly polarized Ho^{3+} levels determined. Bands labelled *p* are mainly observed for light polarized parallel to the C_2 symmetry axis (**b** crystallographic axis) and those labelled *m* or *g* for light perpendicular to it (**ac** crystallographic plane). Following the selection rules imposed by the group theory and the experimental *p* and *m* or *g* character of the spectra, we have characterized the Ho^{3+} levels by one-dimensional irreducible representations (IR), A (*p* spectra) and B (*m* or *g* spectra).

In the fitting process Ho^{3+} levels have been separated into two submatrices, according to the values of the crystal quantum numbers $\mu=0$ and $\mu=1$, each one associated with only one IR. Table 1 includes the energies of the levels calculated using the parameters summarized in Table 3. Eight observed levels corresponding to the $^3K_7$ multiplet have not been used in the cf analysis. It is well known that ^3K levels of Ho^{3+} are peculiarly sensitive to perturbations by operators for which $k=6$, and usually the splittings of these levels are not adequately simulated [9]. Charge transfer and spin correlated crystal field models [10,11] could be included in cf fits to account these misbehaving levels. Nevertheless, these effects have not been considered in the current calculation and anyway, removing $^3K_7$ levels the mean deviation of the whole energy level sequence drops to a very good value.

In a similar way, energies of $^4I_{15/2}$ to $^4G_{7/2}$ Er^{3+} multiplets were obtained from 5 K OA spectra and the energies of the ground $^4I_{15/2}$ multiplet from PL measurements [2]. For the C_2 symmetry of the site of Er^{3+} there is only one type of level, characterized by $\mu=\pm 1/2$, i.e. degenerate in the absence of a magnetic field. The fitting method considers thus only one matrix, which includes all observed energy levels. Table 2 summarizes the sequence of 72 experimental levels along with the calculated ones using the fi and cf parameters of Table 3.

Despite of the very low symmetry of the lanthanide in this tungstate matrix, the simulations yielded energy level sequences in accordance with observed data, with very low root mean square deviations $\sigma=14.5$ and 15.6 cm^{-1} for Ho^{3+} or Er^{3+} in KGW. Moreover, in no case were large individual discrepancies between experimental and calculated energy levels found (Tables 1 and 2).

Finally, verifying the consistency of the final fitted parameters, Fig. 1 shows the evolution of calculated cf parameters with the number *N* of the 4f electrons in KGW, for the title lanthanides together those previously obtained for Pr^{3+} [3] and Nd^{3+} [4] in KGW. As expected for the same host [12], a smooth variation of cf parameters is observed through the RE series. Due to the very high

Table 1
5 K Experimental (E_o) and calculated (E_c) energy levels ($\mathrm{cm^{-1}}$) of Ho^{3+} in $KGd(WO_4)_2$[a]

$^{2S+1}L_J$	E_o	//	E_c	IR	$^{2S+1}L_J$	E_o	//	E_c	IR	$^{2S+1}L_J$	E_o	//	E_c	IR	$^{2S+1}L_J$	E_o	//	E_c	IR
										$^5G_6$	21910	*p*	21952	A	$^3H_6$	27651	*mg*	27644	B
$^5I_8$	0		3	A	$^5F_5$	15360	*mg*	15366	B		–		21954	A		27653	*p*	27644	A
	6		9	B		15365	*p*	15369	A		22025	*p*	21987	A		27703	*p*	27697	A
	11		12	A		15386	*mg*	15387	B		22030	*mg*	21996	B		27713	*mg*	27709	B
	22		36	B		15417	*mg*	15393	B		22050	*mg*	22043	B		27764	*mg*	27776	B
	48		50	A		15445	*p*	15422	A		22061	*mg*	22066	B		27770	*p*	27782	A
	75		89	B		15448	*mg*	15457	B		22062	*p*	22082	A		–		27798	A
	120		137	A		15462	*p*	15468	A		22121	*mg*	22123	B		–		27809	A
	163		155	B		15528	*p*	15545	A		22126	*p*	22131	A		–		27817	B
	–		188	B		15532	*mg*	15550	B		22180	*p*	22188	A		–		27839	A
	209		213	A		15556	*p*	15551	A		22198	*mg*	22193	B		27858	*mg*	27844	B
	229		226	A		15558	*mg*	15555	B		–		22200	A		–		27875	B
	–		228	B	$^5S_2$	18363	*p*	18369	A		22210	*mg*	22210	B		–		27878	A
	252		246	B		18377	*p*	18378	A	$^5F_1$	22233	*p*	22250	A	$^5G_2(*^5F_2)$	28097	*mg*	28124	*A*
	–		263	A		18382	*mg*	18383	B		22240	*mg*	22252	B		28167	*mg*	28177	B
	283		287	A		18402	*p*	18397	A		–		22312	B		28218	*mg*	28209	B
	–		306	B		18404	*mg*	18404	B	$^5G_5$	23858	*p*	23872	A		–		28220	A
	–		319	A	$^5F_4$	18461	*mg*	18463	B		–		23873	B		28283	*p*	28263	A
$^5I_7$	5106	*mg*	5098	B		18463	*p*	18465	A		–		23886	B	$^5G_3$ and $^3L_9$	28637	*mg*	28654	B
	5109	*p*	5101	A		18495	*p*	18488	A		23910	*p*	23899	A		28719	*p*	28701	A
	–		5105	A		18498	*mg*	18515	*A*		23915	*mg*	23903	B		28728	*mg*	28735	B
	5145	*mg*	5113	B		18513	*mg*	18533	B		23927	*p*	23940	A		28750	*p*	28740	A
	5176	*p*	5141	A		18538	*p*	18537	A		23928	*mg*	23950	B		28756	*mg*	28760	B
	5188	*mg*	5151	B		18540	*mg*	18544	B		–		23965	A		28762	*p*	28760	A
	5200	*mg*	5184	B		18576	*p*	18561	A		23979	*mg*	23978	B		28773	*mg*	28792	B
	5204	*p*	5188	A		18579	*mg*	18585	B		24002	*p*	23986	A		–		28800	B
	5206	*mg*	5204	B	$^5F_3$	20494	*mg*	20480	B		24007	*mg*	23999	B		–		28823	B
	5217	*p*	5212	A		20508	*p*	20517	A	$^5G_4$	25742	*mg*	25699	*A*		28845	*p*	28847	A
	5221	*mg*	5227	B		20538	*mg*	20524	B		25756	*mg*	25734	B		28850	*mg*	28852	B
	5236	*mg*	5239	B		20600	*p*	20579	A		25758	*p*	25753	A		–		28865	B
	5239	*p*	5245	A		20604	*mg*	20605	B		25775	*mg*	25769	B		28883	*p*	28891	A
	5271	*p*	5264	A		20630	*mg*	20628	B		25788	*p*	25788	A		–		28899	A
	5273	*mg*	5265	B		20639	*p*	20639	A		25793	*mg*	25797	B		28945	*mg*	28944	B
$^5I_6$	8609	*p*	8616	A	$^5F_2$	21016	*mg*	20988	*A*		25805	*p*	25803	A		28947	*p*	28945	A
	8614	*p*	8617	A		21035	*p*	21036	A		25810	*mg*	25836	B		–		28999	A
	8625	*mg*	8631	B		21059	*mg*	21058	B		25811	*p*	25837	A		–		29001	B
	8627	*p*	8634	A		21087	*p*	21077	A							–		29059	A
	8659	*p*	8670	A		21091	*mg*	21106	B	$^3H_5(*^5G_5)$	27422	*p*	27437	A		–		29059	B
	8663	*mg*	8671	B	$^3K_8$	21312	*p*	21326	A		–		27438	B		29123	*mg*	29115	B
	8684	*p*	8683	A		21336	*p*	21335	*B*		27460	*mg*	27475	*A*		29125	*p*	29117	A
	8687	*mg*	8697	B		–		21345	A		27476	*p*	27479	A		–		29220	B
	8696	*mg*	8709	B		21349	*p*	21348	A		27480	*mg*	27500	B		–		29221	A
	8721	*p*	8735	A		–		21354	B		27503	*mg*	27504	B		–		29227	A
	8724	*mg*	8739	B		–		21356	B		27540	*mg*	27536	B		–		29228	B
	8760	*p*	8767	A		–		21357	A		27559	*p*	27545	A	$^3F_4$ and $^3K_6$	–		29776	A
	8767	*mg*	8769	B		–		21363	A		27571	*mg*	27568	B		–		29776	B
$^5I_5$	11180	*p*	11189	A		21379	*p*	21375	*B*		27584	*p*	27575	A		–		29793	A
	–		11193	B		21386	*mg*	21386	B		27588	*mg*	27583	B		–		29809	B
	11197	*p*	11210	A		21388	*p*	21394	A							29850	*mg*	29828	*A*
	11227	*mg*	11220	B		–		21410	B							29872	*p*	29872	A
	11235	*mg*	11243	B		–		21422	A							29878	*mg*	29884	B
	11238	*p*	11254	A		–		21432	B							29907	*p*	29917	A
	11263	*p*	11255	A		–		21438	B							29924	*mg*	29930	B
	11269	*mg*	11279	B		–		21441	A							29970	*p*	29971	A
	–		11288	B		–		21443	A							29974	*mg*	29971	B
	11309	*p*	11321	A												–		29997	A
	11313	*mg*	11323	B												–		30000	B
$^5I_4$	13189	*mg*	13189	B												–		30011	A
	13194	*p*	13206	A												–		30015	A
	13255	*p*	13251	A												–		30016	B
	13305	*mg*	13305	B												30031	*mg*	30025	B
	13314	*p*	13318	A												–		30026	A
	13386	*mg*	13361	B												–		30033	B
	13400	*p*	13398	A												–		30045	B
	13448	*mg*	13417	B												–		30052	A
	13460	*p*	13447	A												–		30069	A

[a] // Indicates the polarization of the observed band, and IR the corresponding irreducible representation (italic when reversed). * Indicates strongly mixed levels.

Table 2
5 K Experimental (E_o) and calculated (E_c) energy levels (cm^{-1}) of Er^{3+} in KGd(WO$_4$)$_2$[a]

$^{2S+1}L_J$	E_o	E_c	$^{2S+1}L_J$	E_o	E_c
$^4I_{15/2}$	0	5	$^4F_{7/2}$	20445	20440
	35	39		20487	20487
	77	76		20512	20516
	127	123		20580	20574
	169	163			
	275	255	$^4F_{5/2}$	22127	22119
	343	319		22158	22144
	361	337		22193	22179
$^4I_{13/2}$	6521	6529	$^4F_{3/2}$	22473	22483
	6551	6559		22559	22565
	6577	6585			
	6607	6623	$^2H^*_{9/2}$	24504	24471
	6665	6676	($^4F_{9/2}$, $^2G_{9/2}$)	24539	24528
	6716	6736		24555	24548
	6729	6749		24586	24593
				24623	24653
$^4I_{11/2}$	10198	10184			
	10224	10207	$^4G_{11/2}$	26240	26244
	10237	10224		26256	26259
	10267	10256		26351	26339
	10289	10281		26405	26394
	10297	10299		26454	26459
				26474	26475
$^4I_{9/2}$	12399	12372			
	12440	12413	$^4G_{9/2}$	27309	27299
	12469	12465		27322	27319
	12501	12509		27348	27337
	12559	12585		27373	27374
				27388	27389
$^4F_{9/2}$	15202	15215			
	15220	15242	$^2K_{15/2}$	27431	27430
	15291	15303		27524	27523
	15335	15341		27608	27601
	15370	15393		27660	27665
				27750	27754
$^4S_{3/2}$	18329	18329		27823	27824
	18390	18381		27948	27948
				–	27982
$^2H_{11/2}$	19053	19077			
	19074	19098			
	19143	19151	$^4G_{7/2}$	28006	28007
	19181	19179		–	28027
	19215	19213		–	28042
	19226	19222		–	28047

[a] * Indicates strongly mixed levels.

Table 3
Free ion and cf parameters (cm^{-1}) for Ho^{3+} and Er^{3+} in KGd(WO$_4$)$_2$ crystals[a]

	Ho^{3+}	Er^{3+}
E^0	43 433 (1)	34932 (1)
E^1	6369 (9)	6507.2 (8)
E^2	31.12 (1)	32.06 (2)
E^3	639.46 (9)	659.73 (9)
α	19.95 (2)	18.99 (4)
β	−750 (1)	−551 (3)
γ	(1800)	(1800)
ζ	2124.3 (4)	2361.6 (9)
M^0 [b]	4.58 (3)	5.00
P^2 [c]	769 (6)	780
T^2	(400)	(300)
T^3	26 (2)	34 (2)
T^4	188 (2)	190 (4)
T^6	−198 (11)	−299 (18)
T^7	267 (11)	229 (13)
T^8	(336)	(305)
B^2_0	286 (24)	303 (28)
B^2_2	357 (17)	260 (33)
B^4_0	−724 (29)	−986 (47)
B^4_2	131 (34)	25 (63)
S^4_2	−724 (19)	−811 (30)
B^4_4	125 (29)	250 (53)
S^4_4	345 (24)	381 (38)
B^6_0	−60 (33)	36 (67)
B^6_2	256 (28)	173 (51)
S^6_2	−241 (24)	−229 (38)
B^6_4	78 (31)	5 (63)
S^6_4	−103 (38)	−14 (62)
B^6_6	−277 (26)	−173 (42)
S^6_6	133 (31)	125 (44)
S_2	259	213
S_4	457	548
S_6	191	141
S_T [d]	323	349
l Stark levels	173	72
σ [e]	14.5	15.6
Residue	30823.2	12244.8

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

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

[e] $\sigma=[\Sigma(\Delta_i)^2/(l-p)]^{1/2}$, l number of levels, p number of parameters, $\Delta_i=E_o-E_c$.

number of parameters it is risky to say that these sets are unique, but in any case the coherence found among parallel simulations performed for different lanthanides, along with the excellent fits between observed and calculated energy levels, indicate that they are, in every case, physically meaningful and consistent.

5. Conclusions

The thermal evolution of the OA spectra along with the comparison between experimental and calculated $^{2S+1}L_J$ splittings have allowed a coherent determination of the energy levels inside the transparency gap of KGW. Observed Stark levels of Pr^{3+}, Nd^{3+}, Ho^{3+} and Er^{3+} in KGW are consistently reproduced using single-electron cf formalism.

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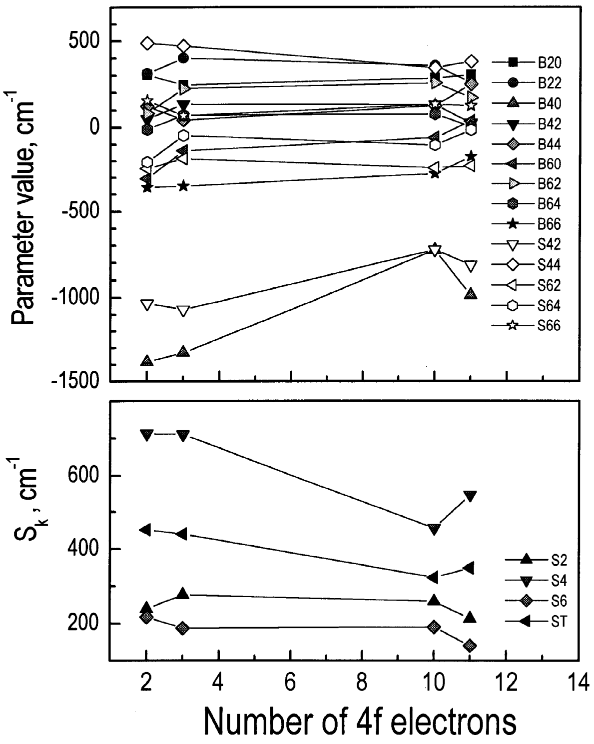

Fig. 1. Evolution of cf parameters in RE-doped KGd(WO$_4$)$_2$ host, RE = Pr^{3+} [3], Nd^{3+}.

References

[1] A.A. Kaminskii, in: Crystalline Lasers: Physical Processes and Operating Schemes, CRC Press, Boca Raton, FL, 1996, p. 68.

[2] M.C. Pujol, M. Rico, C. Zaldo, R. Solé, V. Nikolov, X. Solans, M. Aguiló, F. Díaz, Appl. Phys. B 68 (1999) 187.

[3] C. Zaldo, M. Rico, C. Cascales, M.C. Pujol, J. Massons, M. Aguiló, F. Díaz, P. Porcher, J. Phys. Cond. Matter 12 (2000) 8531.

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

[5] M.C. Pujol, R. Solé, Jna. Gavaldá, J. Massons, M. Aguiló, F. Díaz, V. Nikolov, C. Zaldo, J. Mater. Res. 14 (1999) 3739.

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

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

[8] P. Porcher, Fortran routines REEL and IMAGE for simulation of d^N and f^N configurations involving real and complex crystal field parameters, 1999 (unpublished).

[9] C. Görller-Walrand, K. Binnemans, 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.

[10] B.R. Judd, Phys. Rev. Lett. 34 (1977) 242.

[11] B.R. Judd, J. Phys. C: Solid St. Phys. 13 (1980) 2695.

[12] C. Cascales, G. Lozano, C. Zaldo, P. Porcher, Chem. Phys. 257 (2000) 29.