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1992 J. Phys.: Condens. Matter 4 8321

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Crystal fields in Pr^{3+} doped rare earth gallium garnets, $\text{RE}_3\text{Ga}_5\text{O}_{12}:\text{Pr}^{3+}$

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Received 18 May 1992

Abstract. The optical absorption, site selective excitation and luminescence spectra of the trivalent praseodymium ion in three rare earth gallium garnet matrices, $\text{RE}_3\text{Ga}_5\text{O}_{12}$ (REGG; RE=Y, Gd, and Pr) were detected at 4, 77 and 300 K. The $4f^2$ energy level schemes comprising 56 to 68 crystal field (CF) sublevels were simulated according to a phenomenological model taking into account both the free ion and CF effects. The model consisting of 17 parameters with 8 free ion and 9 CF parameters appropriate to the D_2 point symmetry of the RE^{3+} site reproduced the experimental energy level schemes in a satisfactory manner with RMS deviations between 17 and 23 cm^{-1} . The CF parameters vary only slightly as a function of the host matrix. The B_q^k parameter sets for PrGG and YGG: Pr^{3+} are consistent with those obtained for the other REGG and YGG: RE^{3+} , respectively.

1. Introduction

The optical properties of trivalent praseodymium (Pr^{3+} , $4f^2$ configuration) in solid state materials are among the most extensively studied in the whole rare earth series [1, 2]. The popularity of Pr^{3+} as a target for spectroscopic studies is due partly to the relatively low total degeneracy (91) of the $4f^2$ configuration (omitting the Zeeman and nuclear hyperfine interactions). With the exception of the 1S_0 level high up in the UV region at about 47 000 cm^{-1} all other energy levels are situated in the near IR and visible range and are easily accessible by spectroscopic means [3]. The overlap of the different $^{2S+1}L_J$ levels is infrequent, which, together with their low total angular momentum (J) degeneracy, facilitates the interpretation of the optical absorption and emission spectra. Finally, no computational difficulties should be anticipated even for the lowest symmetries due to treatment of only a 91×91 square matrix. The Pr^{3+} configuration is thus often considered suitable as a 'testing ground' for theoretical and experimental considerations.

Despite the real or potential industrial applications of the garnets mainly as lasers—the YAG: Nd^{3+} is currently the most used laser and Kaminskii [4] has listed 45 other potential candidates—the spectroscopic studies of the RE^{3+} doped garnets have been relatively sparse, especially when compared to the extensive work done e.g. on the $\text{LaF}_3:\text{RE}^{3+}$ system [5]. The reason might be the absence of an isostructural garnet series extending throughout the whole RE series [6]. The presence of the RE^{3+} ions in a site of low symmetry, D_2 [7], which, moreover, cannot easily be treated as

an approximately higher one, also complicates the studies. The Pr^{3+} doped garnets have received even sparser attention. The bulk of the investigations have not been concentrated on the study of the energy level scheme, the only work is by Hooge [8] on $\text{YGG}:\text{Pr}^{3+}$. The energy level schemes for the other RE^{3+} ions have been established to a certain extent, i.e. Ce^{3+} [9], Nd^{3+} [10–13], Sm^{3+} [14], Eu^{3+} [15], Dy^{3+} [10, 16, 17], Ho^{3+} [18], Er^{3+} [3, 10], and Yb^{3+} [19] in YGG as well as Nd^{3+} [20], Sm^{3+} [10], Eu^{3+} [21], Dy^{3+} [10, 17, 22], Er^{3+} [23], and Tm^{3+} [24] in the corresponding REGG.

In this paper we report the results of our study of the free ion and CF effects on the energy level scheme of the trivalent Pr^{3+} ion as a function of the host cation in RE gallium garnets, i.e. in $\text{Pr}_3\text{Ga}_5\text{O}_{12}$ (PrGG), $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG), and $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (YGG). This study utilizes the high sensitivity of the $4f^N$ energy level schemes of the RE^{3+} ions to even very slight structural modifications not only in the immediate environment of the RE^{3+} ion but also further away.

2. Experiment

2.1. Sample preparation

The rare earth gallium garnets were provided for optical studies both in the single crystal (Dr J M Desvignes [25]) and in the powder (Dr J P Coutures [26]) forms. The single crystals were obtained from a flux while the garnet powders were prepared by heating stoichiometric mixtures of corresponding oxides. The concentration of the dopant, x_{Pr} , varied from 0.1 to 50 mole % in $\text{YGG}:\text{Pr}^{3+}$ whereas in $\text{GGG}:\text{Pr}^{3+}$ the x_{Pr} was kept constant at 1 mole %. All samples were checked by x-ray diffraction analysis but only the garnet phase was found.

2.2. Optical measurements

The visible and IR absorption spectra of the Pr^{3+} ion was measured with a commercial Cary 2400 spectrometer. The transitions from the CF split ground level, $^3\text{H}_4$, to the excited $^3\text{P}_{0-2}$, $^1\text{I}_6$, $^1\text{D}_2$, $^1\text{G}_4$, and $^3\text{F}_{2-4}$ levels could be observed.

The site selective excitation spectra of the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ and $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transitions was carried out by a Lambda-Physics FL 2001/2 dye laser pumped by a SOPRA nitrogen laser; this arrangement yields a 3 mJ dye laser pulse of 12 ns duration at a repetition rate of 4 to 100 Hz. The dye laser band width was approximately 2 cm^{-1} .

The luminescence of the Pr^{3+} ion was excited either by different blue lines of a Spectra Physics argon ion laser or selectively on the $^3\text{P}_0$ and $^1\text{D}_2$ levels with the arrangement described in the preceding section. The emission—mainly from the $^3\text{P}_0 \rightarrow ^3\text{H}_{4-6}$ and $^3\text{P}_0 \rightarrow ^3\text{F}_{2-4}$ transitions—was dispersed by a 1 m Jarrell–Ash or a 1 m Jobin–Yvon HR1000 single monochromator equipped with photomultiplier detection. Weak visible emission from the $^1\text{D}_2$ level to the $^3\text{H}_j$ ground multiplet could be observed, too, as well at 300 K from the $^3\text{P}_1$ levels to the $^3\text{H}_{4-6}$ and $^3\text{F}_{2-4}$ levels. All measurements were performed at liquid helium, liquid nitrogen and room temperatures.

2.3. Crystal structure of garnets

The rare earth gallium garnets form an isostructural series with the formula $\text{RE}_3\text{Ga}_5\text{O}_{12}$. The lanthanum gallium garnet, however, has never been obtained [6]. The garnets crystallize in the cubic system with space group $\text{Ia}3\text{d}-\text{O}_h^{10}$ (number 230 in [27]) and $Z = 8$. The RE^{3+} ions reside in an eight-coordinated site of D_2 point

symmetry while 40% of the lighter host cations are in a six-coordinated (octahedral) site of S_6 point symmetry. The remaining 60% of the gallium ions lie in a four coordinated (tetrahedral) site of S_4 symmetry. The six- and four-coordinated sites are rather undistorted while the coordination around the RE^{3+} ions is much further from the ideal dodecahedron [7].

Table 1. The observed and calculated energy levels of the Pr^{3+} ion ($4f^2$ configuration) in PrGG , GGG and YGG hosts (in cm^{-1}).

$^{2S+1}L_J$	$\text{Pr}_3\text{Ga}_5\text{O}_{12}$		$\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Pr}^{3+}$		$\text{Y}_3\text{Ga}_5\text{O}_{12}:\text{Pr}^{3+}$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$^3\text{H}_4$	0	-1	0	-6	0	5
	19	13	21	8	23	7
	63	55	37	45	23	12
	—	452	—	446	—	416
	517	512	531	533	532	533
	—	549	—	565	578	590
	—	567	—	583	598	607
	706	722	643	660	626	656
	—	748	694	712	689	679
$^3\text{H}_5$	—	2251	2276	2250	—	2248
	2276	2273	2295	2303	2285	2285
	—	2322	2303	2330	2300	2299
	—	2369	—	2338	2322	2303
	2392	2386	2365	2360	2370	2391
	2525	2522	2552	2524	2578	2560
	2572	2585	2565	2611	2613	2601
	—	2589	2633	2634	2650	2641
	—	2636	2732	2689	2692	2705
	2798	2793	2750	2761	2730	2716
	—	2838	2774	2767	2749	2735
$^3\text{H}_6$	4305	4334	4291	4308	4287	4297
	—	4358	4367	4366	4333	4331
	4373	4395	—	4378	4350	4363
	4405	4401	4398	4395	4397	4410
	4437	4416	4442	4449	—	4458
	—	4517	4538	4523	4462	4464
	4569	4556	4548	4525	4534	4553
	4747	4739	—	4794	4791	4783
	—	4772	4838	4841	4824	4830
	4822	4840	—	4841	4868	4878
	—	4869	—	4854	4909	4902
	5061	5035	—	4988	—	4967
	5112	5113	5078	5069	5073	5042
	$^3\text{F}_2$	5301	5284	5302	5313	—
5342		5330	5329	5333	5350	5332
5353		5365	5362	5364	5401	5410
5377		5373	5388	5392	5464	5460
5450		5424	5458	5456	—	5534
$^3\text{F}_3$	6483	6451	6486	6467	6492	6467
	—	6478	6500	6499	6539	6557
	6531	6569	6533	6551	—	6644
	—	6694	6734	6739	6757	6771

	6741	6740	6757	6751	—	6794
	—	6761	6785	6751	6805	6796
	—	6898	6920	6956	6993	6998
3F_4	7023	7037	—	7017	7062	7063
	7053	7046	7068	7051	7101	7091
	—	7103	7088	7072	7109	7107
	—	7165	—	7122	—	7159
	7254	7303	7226	7259	7231	7266
	—	7321	7273	7264	7286	7293
	7356	7340	—	7334	—	7369
	—	7399	—	7341	7385	7394
	—	7463	—	7425	7476	7468
1G_4	9726	9732	—	9657	9718	9719
	—	9786	—	9692	—	9740
	9837	9832	—	9790	—	9797
	—	9881	—	9805	9852	9834
	10091	10079	—	9940	10001	9996
	10246	10231	—	10153	—	10123
	—	10441	—	10339	10352	10356
	—	10532	—	10404	—	10540
	—	10970	—	10904	—	10926
1D_2	16468	16468	16430	16447	16404	16416
	16480	16472	16516	16530	16539	16560
	16915	16909	16962	16953	16991	16993
	17080	17099	17063	17074	17059	17053
	17228	17226	17220	17182	17210	17177
3P_0	20577	20562	20591	20551	20597	20579
3P_1	21091	21124	21144	21155	21173	21186
	21190	21220	21201	21198	21200	21208
	21238	21242	—	21210	21243	21244
1I_6	20840	20841	20929	20941	20931	20958
	—	20880	20993	20992	20992	20966
	20930	20931	21008	21003	21031	21036
	—	20993	21041	21041	21049	21047
	21174	21184	21053	21050	—	21103
	—	21187	21060	21072	21158	21141
	21688	21660	21773	21730	21819	21813
	—	21821	21872	21855	—	21862
	21869	21889	21908	21918	21932	21944
	22067	22046	—	21976	21980	22008
	22092	22085	22008	22035	—	22038
	—	22127	—	22116	22125	22125
	22201	22225	22231	22235	22257	22236
3P_2	22340	22306	22301	22339	—	22371
	22417	22430	—	22385	—	22402
	—	22484	22461	22497	22502	22570
	22587	22598	22500	22572	22573	22594
	22634	22613	22636	22604	22638	22611
1S_0	—	46231	—	46084	—	46351

The Pr^{3+} ion can be considered to replace the RE^{3+} host cation in all three gallium garnet hosts without difficulties due to the only slight differences in the ionic

radii [28]. The insertion of the RE^{3+} ions in the Ga^{3+} site would prove to be much more difficult but cannot, however, be ruled out due to previous reports dealing with single crystals grown by the Czochralski method [29, 30].

2.4. Theoretical treatment of experimental data

The major free-ion interactions in the RE^{3+} ions with $4f^N$ configuration include the electrostatic repulsion between the 4f electrons and the coupling of their spin and orbital angular momenta. Several minor contributions can be taken into account in addition to the CF effect. A recent review [31] gives further details about the subject. The Hamiltonian used in this study was as follows:

$$H_{\text{CF}} = H_0 + \sum_{k=0,1,2,3} E_k(nf, nf)e^k + \zeta_f A_{\text{SO}} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{k=2,3,4,6,7,8} T^k t_k + \sum_{k,q,i} B_q^k C_q^k(i) \quad (1)$$

where H_0 is the spherically symmetric one-electron part of the free ion Hamiltonian, E_k and ζ_f are the electrostatic and spin-orbit integrals; e^k and A_{SO} represent the angular parts of these interactions. For configurations of two or more equivalent f electrons the two-body interaction correction terms include α , β and γ ; L is the total orbital angular momentum; $G(G_2)$ and $G(R_7)$ are the Casimir operators for the groups G_2 and R_7 , respectively. For configurations with three or more electrons the three-body configuration interaction terms parametrized with the Judd's parameters, T^k ($k = 2, 3, 4, 6, 7$ and 8), can be taken into account. The t_k in (1) are operators transforming according to the irreducible groups G_2 and R_7 .

The one-electron CF Hamiltonian H_{CF} [32] consists of a sum of products between the B_q^k parameters and the spherical tensors C_q^k appropriate to the site symmetry of the RE^{3+} ion.

$$H_{\text{CF}} = \sum_{k=0}^{\leq 6} \sum_{q \geq -k}^{\leq k} [B_q^k (C_q^k + (-1)^q C_{-q}^k) + i S_q^k (C_q^k - (-1)^q C_{-q}^k)]. \quad (2)$$

For the garnet structure there exist nine non-zero real parameters; B_0^2 , B_2^2 , B_0^4 , B_2^4 , B_4^4 , B_0^6 , B_2^6 , B_4^6 and B_6^6 [33] which are invariant under all symmetry operations of the D_2 point group of the RE^{3+} site.

The energy level calculations on the Pr^{3+} ($4f^2$) configuration employs a square matrix of size 91×91 which requires no truncation of the basis set of wave functions—even with calculations on a PC [34] since the complete matrix can usually be split into submatrices according to the symmetry of the RE^{3+} site, i.e. two matrices for the D_2 symmetry. The standard least squares calculations were carried out in order to optimize the B_q^k parameters. The root mean square deviation σ between the experimental and calculated energy level values was used as a figure of merit to describe the quality of the fit.

3. Results and discussion

3.1. Analysis of the optical spectra

The analysis of the absorption, excitation, and emission spectra of the Pr^{3+} doped RE gallium garnets yielded mutually consistent basis sets of 56 to 68 energy levels

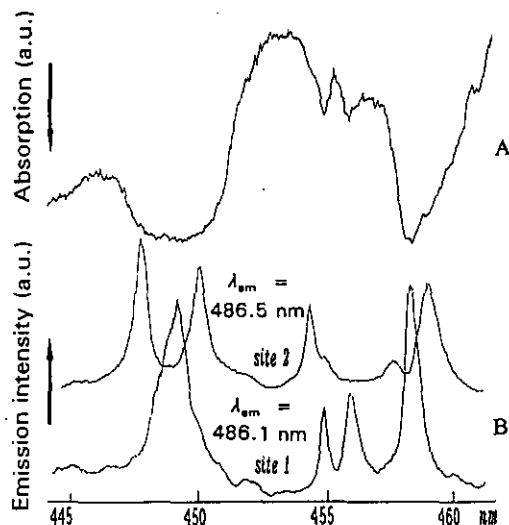


Figure 1. The absorption (A) and dye laser site selective excitation (B) spectra of YGG:Pr³⁺ at 4 K corresponding to the $^3H_4 \rightarrow ^3P_2, ^1I_6$ transitions. The emission intensity of the site 1 (taken as the regular site and thus used in the calculations) greatly exceeds that of the site 2.

for further calculations. The analysis of the spectra were afflicted by the presence of supplementary lines originating from several sites. The origin of these extra sites reported frequently in the literature [35, 36] is not completely clear, possible sources include e.g. impurity phases and defects created by different effects. For the YGG host system, two definite sites could be found by using site selective excitation by dye laser. The sites are characterized by similar CF splittings as well as by very similar decay times, 17 and 19 μ s [36]. The interpretation of the spectra could, however, be carried out reliably as shown for the $^3H_4 \rightarrow ^1I_6, ^3P_2$ transition range in figure 1. The absorption lines are rather broad and unresolved but with selective excitation by dye laser the lines belonging to the different sites could be identified. This technique, however, could not be used for the PrGG system.

The energy level schemes represent rather well all the $^{2S+1}L_J$ levels except the 1S_0 one up to 23000 cm^{-1} . The total lifting of the total angular degeneracy obtained for the energy level schemes corresponds to the D_2 point symmetry of the crystallographic RE^{3+} site. The schemes for different hosts resemble each other closely. The energy level scheme obtained for YGG:Pr³⁺ is in general agreement with that obtained by Hooge [8] but this energy level scheme could be significantly completed. Some evident misinterpretations due to the presence of the additional site could be corrected, too, by reattribution of several levels to the other site.

3.2. Energy level simulation

The phenomenological free ion model used in the simulations consists of the electrostatic Racah parameters E_k ($k = 0 - 3$), the two body interaction terms α , β , and γ as well as the spin-orbit coupling constant ζ , a total of eight parameters. All the parameters were allowed to vary freely except the γ parameter which was fixed to a usual value due to a lack of sufficient experimental data required to fit all parameters. The free ion parameters vary only very slightly from one matrix to another as should be anticipated. Accordingly, the free ion effects are to be considered in most cases matrix invariant—as far as the same $4f^N$ electron configuration is considered.

3.2.1. The REGG:Pr³⁺ system. Both the free ion and the CF simulations were carried

Table 2. The phenomenological free ion and B_q^k CF parameter values for the Pr^{3+} ion in PRGG, GGG, and YGG hosts (in cm^{-1}).

	$\text{Pr}_3\text{Ga}_5\text{O}_{12}$	$\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Pr}^{3+}$	$\text{Y}_3\text{Ga}_5\text{O}_{12}:\text{Pr}^{3+}$
E_0	5509	5541	5626
E_1	4491	4470	4491
E_2	21.17	21.53	21.47
E_3	456.0	456.8	457.5
α	20.35	21.95	21.94
β	-536	-607	-692
γ^a	[1470]	[1470]	[1470]
ζ	745	746	745
B_0^2	132	54	139
B_2^2	260	104	-67
B_0^4	389	-139	-227
B_2^4	-1820	-2115	-2202
B_4^4	-1689	-1269	-1089
B_0^6	-509	-1506	-1784
B_2^6	-366	-636	-730
B_4^6	981	977	747
B_6^6	-947	-306	-164
levels	56	62	68
RMS	20	23	17

^a Parameter fixed due to insufficient degrees of freedom in the free ion simulation.

out in a satisfactory manner for all three host lattices. No single anomalous discrepancy between the calculated and experimental energy levels could be observed and the RMS deviation remains within the usual limits, between 17 and 23 cm^{-1} . The best simulation was obtained for YGG: Pr^{3+} which also had the highest number of experimental levels available.

Simulation of the CF splitting of the $^{2S+1}L_J$ levels gave satisfactory results. The CF splitting of the 1D_2 state has been rather badly simulated in some lattices possibly due to a strong configuration interaction [37]. Our simulation of the 1D_2 state is no worse—in fact it is slightly better—than those of the other $^{2S+1}L_J$ levels.

The CF parameter values depend to a considerably greater extent on the matrix. According to a very simple reasoning the parameter values should decrease toward the heavier rare earths due to the increased nuclear charge experienced by the 4f electrons. This holds, however, mainly when the CF effect on the different dopant RE^{3+} ion is considered. In the REGG (RE = Pr, Gd and Y) host matrix series the variation of the parameters is, however, weak and also rather irregular preventing the prediction of definite tendencies.

3.2.2. The YGG: RE^{3+} system. The comparison of the CF parameter sets obtained in this work to both the YGG: RE^{3+} and REGG: RE^{3+} series shows the consistency of the present results. In the YGG: RE^{3+} series much more data are available than in the corresponding REGG: RE^{3+} series, in fact, several sets of CF parameters have been presented for the Nd^{3+} (four sets [10–13]), Sm^{3+} (two sets [14]), Dy^{3+} (three sets [10, 16, 17]), and Er^{3+} (two sets [3, 10]) ions. The general appearance of all these sets, with the notable exception of that for Eu^{3+} [15], are rather similar but significant variations occur between the sets for both Nd^{3+} and Sm^{3+} . The reasons for these differences may lie in the computational methods used as well as in the different

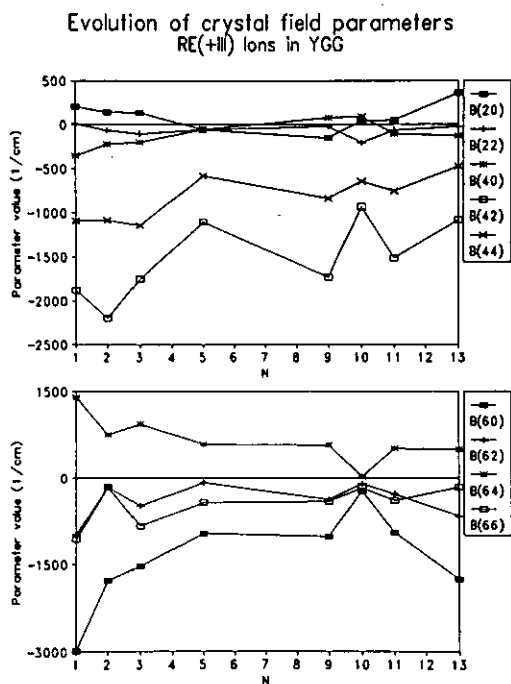


Figure 2 The evolution of the CF parameters in the YGG:RE³⁺ series. The literature data were obtained as follows: Ce [9], Nd [5], Sm [14], Dy [5], Ho [18], Er [5], and Yb [19].

experimental data or in the different interpretation of data. Older works, especially, have frequently ignored the inclusion of the J -mixing in the CF calculations which can lead to drastic differences in the values of some, but not necessarily all, CF parameters. The CF parameter values represented in figure 2 constitute a mutually consistent set where the absolute value of the parameters can be observed to decrease strongly along the RE series. This behaviour follows closely the simple theoretical trend discussed earlier.

Another tendency within the parameter sets may be of considerable interest. The absolute parameter values tend to increase slightly for the latter half of the RE series in the B_q^6 series. Since this effect cannot be found in the B_q^2 and B_q^4 series this might be an indication of the two-electron CF effects discussed previously [38, 39]. However, before any definite conclusions can be made the homogeneity of the parameter sets should be verified.

Because of the considerable inconsistency of the CF parameter set for YGG:Eu³⁺ an attempt was made to simulate the energy level scheme by using the data set from [40], too. The experimental data could be approximated by a set of B_q^k parameters consistent with those for the other YGG:RE³⁺ but due to the lack of a complete data set further efforts were not considered worthwhile. However, it was found that from the energy level scheme for YGG:Eu³⁺ several levels were missing and some others, especially those derived from weak transitions, evidently belonged to the other site(s).

3.2.3. The REGG:RE³⁺ system. The comparable sets of the B_q^k parameters for the REGG:RE³⁺ series (figure 3) are much fewer and considerably more consistent than for the YGG:RE³⁺ one (figure 2). Although three different sets have been obtained

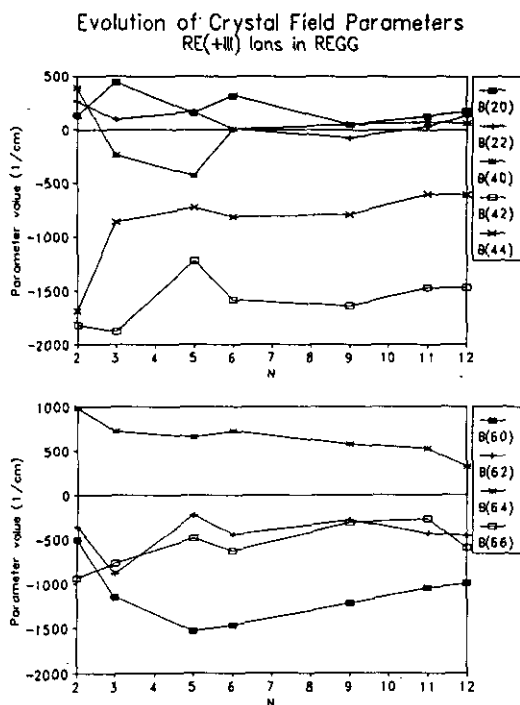


Figure 3. The evolution of the CF parameters in the REGG:RE³⁺ series. The literature data were obtained as follows: Nd [20], Sm [10], Eu [21], Dy [22], Er [23] and Tm [24].

for the Dy³⁺ ion [10, 17, 22] none of these sets reveals significant differences in the parameter values. The choice of the Dy³⁺ set presented in figure 3 can thus be considered as a matter of convenience. While a decrease in the absolute values of the parameters similar to the YGG:RE³⁺ series can also be observed in this series, there is little indication of the recovery of the parameter values in the second half of the RE³⁺ series. Accordingly, it must be concluded that the verification of the two-electron CF effects is difficult, especially when the parameter values in the REGG:RE³⁺ series seem to form a rather consistent series.

The parameter values for the Pr³⁺ ion in the PrGG host seem to differ more from the general trend than in the YGG:Pr³⁺ case. These discrepancies might either be due to the crystallographic or the electronic structure of the Pr³⁺ ion in PrGG. Since PrGG is the first one possessing a stable garnet structure the Pr³⁺ ion might be put under considerable strain within the structure and thus the CF effect may be different, too. Verification of this hypothesis would require a detailed analysis of the crystal structure which is clearly out of the scope of the present work.

The electronic structure of the Pr³⁺ ion is relatively simple—the total degeneracy is only 91—and therefore does not allow the use of all the parametrization schemes describing minor relativistic effects. This might lead to a rather low quality of the free-ion wave functions which can affect the CF parametrization trying to compensate the inadequacies of the free ion scheme. On the other hand, the next excited electron configuration to the 4f² one, 4f¹5d¹, lies very close and this fact has been shown to affect especially the CF splitting of the ¹D₂ level [37]. The inevitable omission of this configuration interaction effect may have also influenced the CF parameter set of the Pr³⁺ ion. Finally, it should be acknowledged that the sparse set of experimentally determined energy levels might be a cause to the deviation of the Pr³⁺ set from the general trend in the REGG series.

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