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Institute of Solid State Physics, Czechoslovakian Academy of Sciences, Prague[1])

The Crystal Field for Nd^{3+} in Garnets

By

V. NEKVASIL

A crystal field analysis of the reported optical spectra of Nd^{3+} in the series of aluminium and gallium garnets LuAG, YAG, GGG, LuGG, and YGG is presented. The reliability of the crystal field parameters determined in this way is confirmed by comparison with ESR g-values given in the literature. The results obtained represent a basis for a further study of the relation between the crystal field parameters of rare earths in garnets and the structure of the coordination dodecahedron.

Предложен анализ кристаллического поля, проведенный на основе опубликованных оптических спектров иона Nd^{3+} в гранатах-алюминатах и галлатах LuAG, YAG, GGG, LuGG и YGG. Надежность определенных такии образом параметров кристаллического поля подтверждена сравнением с доступными данными по g-факторам ЭПР. Полученные результаты представляют основу для дальнейшего изучения соотношений между параметрами кристаллического поля ионов редких земель в гранатах и структурой координационных додекаэдров.

1. Introduction

Since the first work of Hutchings and Wolf [1], the determination of the parameters of the crystal field Hamiltonian for rare earths in garnets has been a subject of wide interest. In most cases these parameters have been obtained by their fitting to the optically determined energy spectra of $4f^n$ electrons. It appears that, when the problem is treated thoroughly, the resulting crystal field parameters fit these spectra fairly well and serve also for successful predictions of various magnetic and optical properties (see, e.g., [2, 3]).

The major disadvantage connected with the above purely phenomenological approach is that it provides no information concerning the microscopic origin of the crystal field. One of the important practical consequences of this fact is the lack of the theoretical basis allowing to extrapolate the crystal field parameters obtained for a particular rare-earth ion in one host garnet lattice to other garnet structures. Such an extrapolation is desired whenever the experiment in other garnets does not provide a sufficient amount of data, especially in the study of rare-earth iron garnets, where the crystal field is accompanied by the comparable in magnitude anisotropic exchange interaction of rare earths with neighbouring irons [4].

An important step towards the understanding of the origin of the crystal field has been done by Bradbury and Newman [5]. According to their "superposition model" the crystal field acting on a paramagnetic ion can be built from the separate contributions of the O^{2-} ligands and the crystal field parameters explicitly expressed as functions of their positions. Newman and Stedman [6] have used this model for the interpretation of the crystal field of rare-earth ions in garnets, for which the parameters have been available at that time. Encouraged by the success of this work, we have started a systematic study of the crystal field interaction of one particular rare earth — neodymium — in a series of garnets.

[1]) Cukrovarnická 10, 16253 Prague 6, Czechoslovakia.

The application of Nd^{3+}: YAG in lasers has initiated the broad study of the optical properties of garnets with neodymium. The energy spectra of the lowest multiplets of this ion in twelve different garnets have been already reported [8, 9].

In this paper we report the crystal field analysis of the spectra of the ^4I term measured at 77 K in the structurally simplest garnets: $Lu_3Al_5O_{12}$ (LuAG) [10], $Y_3Al_5O_{12}$ (YAG) [11], $Gd_3Ga_5O_{12}$ (GGG) [12], $Lu_3Ga_5O_{12}$ (LuGG) [13], and $Y_3Ga_5O_{12}$ (YGG) [14]. The results for YAG have been published earlier [3].

In Section 2 we report the details of the numerical analysis of the optical spectra. The results are summarized and discussed in Section 3.

The crystal field parameters obtained in this work, together with those recently obtained in other rare-earth garnets, are analyzed on the basis of the superposition model in the following paper [7].

2. The Crystal Field Analysis

The Nd^{3+} ions in garnets enter exclusively the dodecahedral sites. The crystal field effect is treated as a perturbation of the free-ion states of $4f^3$ electrons. The Hamiltonian is written in Wybourne's form [15]:

$$\mathcal{H} = \sum_{k,q} B_{kq}(C_{kq} + C_{k,-q}) \; ; \qquad k = 2, 4, 6 \, , \qquad q = 0, 2, 4, 6 \, , \qquad q \leqq k \, , \tag{1}$$

where the B_{kq}'s are so-called crystal field parameters, the number of which is determined by the D_2 symmetry of the rare-earth site. The matrix elements of the tensor operators C_{kq} between all states belonging to ^4I term were calculated by the method proposed by Wybourne, using the tabulated reduced matrix elements [16]. As free-ion wave functions those of Rajnak were used [17].

The set of the nine crystal field parameters is obtained by the numerical solution of the inverse secular problem: Given the p eigenvalues E_l of the secular equation Hamiltonian (1),

$$|H - EI| = 0 \, , \tag{2}$$

we calculate the unknown parameters B_{kq}, determining the elements H_{ij} of the square matrix H of the order t ($t \geqq p$). For E_l we take here the experimental data deduced from the optical measurements. To solve the inverse secular problem we have applied the efficient method of "damped least-squares", which is due to Castellano and Bothner-By [18]. In order to compensate the uncertainty in the position of the free-ion energy levels, we have included them into the fitting procedure as additional variables.

The main difficulties occurring in the calculation are due to the incompleteness of the experimental energy spectra of some multiplets. In such cases the unambiguous energy level positions have only been used in the first step of the fitting procedure. The calculated parameters then allowed to locate the positions of the missing energy levels and to take some of the remaining experimental data into account. The levels involved in the final fit are taken with weight w_l equal to one, remaining levels with weight zero.

The errors associated with the calculation are treated by the standard statistical method [19]. The precision of the fit is characterized by the mean error

$$\sigma = \sqrt{\frac{\sum_l w_l(E_l(\text{exp.}) - E_l(\text{calc.}))^2}{r - s}} \, , \tag{3}$$

where r is the number of the experimental energy levels with non-zero weight and s the number of adjustable parameters. For this purpose the quantity σ serves better than $\sqrt{\sum_l w_l(E_l(\text{exp.}) - E_l(\text{calc.}))^2/(r-1)}$ used in [3]. The weight of the determination

of the α-th crystal field parameter is given by

$$w_\alpha = \frac{D}{A_{\alpha\alpha}}, \tag{4}$$

where D is the determinant of the coefficients of the normal equations and $A_{\alpha\alpha}$ denotes the cofactor of the coefficient $a_{\alpha\alpha}$ in D. The mean error associated with the α-th parameter is

$$\sigma_\alpha = \left(\frac{A_{\alpha\alpha}}{D}\right)^{1/2} \sigma . \tag{5}$$

3. Results and Discussion

The calculated parameters (with the associated errors obtained from (5) given in parentheses) for all five studied garnets are summarized in Table 1. In Tables 2 and 3 the experimental and calculated energy levels of the Nd^{3+} ion in aluminium and gallium garnets, respectively, are compared. The mean errors σ (see equation (3)) are also given.

Table 1

The crystal field parameters and free-ion energy levels for Nd^{3+} in garnets examined (in cm^{-1}). The associated mean errors are given in parentheses

	LuAG	YAG	YAG*)	GGG	LuGG	YGG
B_{20}	− 280 (29)	− 336 (50)	− 415	− 193 (37)	− 132 (9)	42 (30)
B_{22}	202 (24)	209 (35)	250	156 (29)	177 (7)	111 (17)
B_{40}	−2881 (33)	−2870 (60)	−2715	−2543 (37)	−2582 (8)	−2630 (22)
B_{42}	276 (52)	414 (73)	518	220 (78)	203 (18)	192 (38)
B_{44}	1248 (22)	1159 (37)	1018	1126 (27)	1064 (7)	1063 (23)
B_{60}	1049 (23)	994 (39)	1115	914 (27)	901 (4)	877 (15)
B_{62}	− 337 (18)	− 339 (32)	− 308	− 225 (27)	− 244 (5)	− 224 (19)
B_{64}	1675 (8)	1610 (15)	1590	1499 (9)	1516 (2)	1584 (7)
B_{66}	− 120 (13)	− 133 (21)	− 43	− 139 (16)	− 133 (3)	− 109 (11)
$E(^4I_{9/2})$	0 (1)	0 (2)		0 (1)	0 (0)	0 (1)
$E(^4I_{11/2})$	1858 (1)	1858 (2)		1862 (1)	1860 (0)	1860 (1)
$E(^4I_{13/2})$	3821 (1)	3821 (2)		3839 (2)	3847 (1)	3830 (3)
$E(^4I_{15/2})$	5839 (1)	5850 (2)		5859 (2)	5853 (0)	5854 (1)

*) Morrison et al. [20].

The fitting to the 24 experimental levels reported in YAG was already published [3]. For the sake of completeness the results are also presented here. The errors in the sign of the parameter B_{66} and in the third decimal place of the g_y value (see Tables 1 and 4), which appeared in [3], are corrected now. Since the paper [3] appeared, the crystal field parameters for this garnet have been calculated by Morrison et al. [20]. As seen from the second and third columns in Table 1, the results agree reasonably well. The remaining discrepancies are ascribed by Morrison et al. mainly to the different experimental data used in both works. While Morrison et al. have analyzed the data given by Danielmeyer et al. [21][2]) and Koningstein and Geusic [22], we have in [3] used the spectra measured by Feofilov et al. [11]. We recall here our conclusion in [3] concerning the possible misinterpretation of the observed splitting of the $^4I_{15/2}$ multiplet in [21]. This conclusion is supported by the recent effective ligand

[2]) Morrison et al. refer to the work of Tofield et al. [23], but the spectra given there are undoubtedly those of Danielmeyer et al. [21].

point-charge calculation presented by Mroczkowski and Randic [24], as well as by the comparison with the data for Nd^{3+} in other garnets [8]. Using our diagonalization procedure and the parameters of Morrison et al., we found that even these authors have interpreted the spectra of the $^4I_{15/2}$ multiplet similarly as in [3].

In the case of LuGG the calculation has been complicated by several factors. First, two different values, 2074 and 2103 cm^{-1}, for the fourth-lowest energy level in the $^4I_{11/2}$ multiplet are given in [13]. We have found the latter to be the correct one. Second, we were forced to omit all but one of the $^4I_{13/2}$ multiplet levels, as we were not able to correlate unambiguously the predicted and experimental data. As seen from Table 3, a reasonable correlation would be obtained when the 4000 cm^{-1} position would not be the Nd^{3+} level. Third, the calculation suggests that instead at 5940 cm^{-1}, there should be the level at 6503 cm^{-1}. In that case we would also get the usual picture of eight levels of the $^4I_{15/2}$ multiplet being grouped in two quartets separated by about 600 cm^{-1} [8].

Table 2

The calculated and experimental energy levels of Nd^{3+} in aluminium garnets (in cm^{-1})

multiplet	LuAG			YAG		
	E (exp.)*)	E (calc.)	ΔE	E (exp.)**)	E (calc.)	ΔE
$^4I_{9/2}$	0	2	−2	0	−1	1
	117	119	−2	131	130	1
	198	197	1	200	201	−1
	303	301	2	310	311	−1
	878	876	2	857	856	1
$^4I_{11/2}$	2004	2005	−1	2000	2003	−3
	2031	2030	1	2025	2026	−1
	2101	2098	3	2115	2106	9
	2137	2141	−4	2151	2151	0
	2487	2488	−1	2462	2469	−7
	2529	2528	1	2518	2518	0
$^4I_{13/2}$	3926	3927	−1	3921	3925	−4
	3934	3936	−2	3933	3931	2
	4026	4027	−1	4038	4038	0
	4040	4039	1	4055	4051	4
	4456	4454	2	4436	4434	2
	—	4461		—	4443	
	4506	4505	1	4495	4499	−4
$^4I_{15/2}$	5759	5755	4	5767	5764	3
	5805	5805	0	5822	5820	2
	5919	5917	2	5939	5941	−2
	5954	5957	−3	5970	5979	−9
	6583***)	6583		—	6564	
	6590	6593	−3	6590	6588	2
	6653	6652	1	6648	6646	2
	6754	6756	−2	6743	6741	2
mean error	2.9			5.0		

*) Kaminskii et al. [10].
**) Feofilov et al. [11].
***) The energy level is not included into fitting procedure because of the small experimental accuracy.

Table 3

The calculated and experimental energy levels of Nd^{3+} in gallium garnets (in cm^{-1})

multiplet	GGG			LuGG			YGG		
	E (exp.)[a]	E (calc.)	ΔE	E (exp.)[b]	E (calc.)	ΔE	E (exp.)[c]	E (calc.)	ΔE
$^4I_{9/2}$	0	0	0	0	0	0	0	−1	1
	93	92	1	97	97	0	79	78	1
	178	179	−1	185	185	0	179	181	−2
	253	253	0	259	259	0	246	246	0
	772	772	0	777	777	0	784	784	0
$^4I_{11/2}$	1994	1994	0	1996	1997	−1	1994	1995	−1
	2007	2009	−2	2010	2010	0	2007	2008	−1
	2063	2058	5	2065	2065	0	2056	2052	4
	2100	2101	−1	2103	2104	−1	2086	2089	−3
	2407	2406	1	2411	2410	1	2420	2420	0
	2433	2436	−3	2438	2437	1	2435	2433	2
$^4I_{13/2}$	3927[e]	3932		3930[e]	3943		3921[e]	3926	
	—	3936		4000[e]	3948		3985[e]	3932	
	3999	4001	−2	4016[e]	4018		3996[e]	3988	
	4015	4016	−1	4030[d, e]	4028		4030[d, e]	3995	
	4384	4384	0	4390[e]	4397		4381[e]	4392	
	4398[d]	4392		—	4406		—	4396	
	4427	4424	3	4435	4435	0	4414	4414	0
$^4I_{15/2}$	5770	5768	2	5765	5765	0	5765	5765	0
	5822	5822	0	5820	5820	0	5810	5810	0
	5914	5913	1	5913[e]	5910		5900	5898	2
	5932	5935	−3	5928[e]	5937		5920	5923	−3
	—	6504		5940[e]	6503		—	6508	
	6513[e]	6516		6513	6513	0	6520	6520	0
	6552	6553	−1	6556	6557	−1	6565	6567	−2
	6653	6651	2	6655	6655	0	6675	6674	1
mean error		3.1			1.0			2.8	

a) Bagdasarov et al. [12]. b) Bagdasarov et al. [13]. c) Kaminskii et al. [14]. d) The energy levels are not included into the fitting procedure because of the small experimental accuracy. e) The experimental energy levels are omitted because of uncertain correlation with calculation.

From Tables 2 and 3 it is seen that the experimental energy levels are reproduced practically within the accuracy of measurements, which is reported to be $\pm$ 3 cm^{-1} in YGG [14] and is probably comparable in other garnets. As, however, the number of experimental data does not considerably exceed the number of fitted parameters, this agreement says little about the physical reliability of the calculated quantities. The comparison of the theory with accurate ESR values of the components of the ground state g-tensor may serve as a test for this purpose. The calculated and experimental g-values are compared in Table 4. The agreement is seen to be especially good in aluminium garnets, while the somewhat poorer agreement in lutetium and yttrium gallium garnets may be connected with the smaller overdetermination of the inverse secular problem in these cases due to the impossibility to involve the complete spectra of the $^4I_{13/2}$ multiplet. The ESR g-values in GGG have not been reported, but the calculated values compare favourably with those in the structurally very similar EuGG.

Table 4

The calculated and experimental components of the g-tensor of the ground doublet of $^4I_{9/2}$ multiplet of Nd^{3+} in garnets

	ref.	experiment			theory		
		g_x	g_y	g_z	g_x	g_y	g_z
LuAG	[26]	1.789	1.237	3.834	1.862	1.224	3.847
YAG	[26]	1.733	1.179	3.915	1.784	1.091	3.953
	[27]	1.733	1.163	3.958			
GGG		—	—	—	2.003	1.292	3.752
LuGG	[26]	2.083	1.323	3.550	1.927	1.281	3.817
YGG	[26]	2.027	1.251	3.667	1.967	1.404	3.744
EuGG	[28]	1.965	1.190	3.820	—	—	—

The above results suggest that, despite showing the relatively smaller mean error, the crystal field parameters in LuGG and YGG are somewhat less precisely determined than in other garnets studied (see Tables 2 and 3).

4. Conclusion

It appears that the simple perturbation approach used here is adequate to the precision of the determination of the energy levels from the experiment. The inaccuracies caused by the use of this approach are probably to some extent hidden in the variable "free-ion"energy levels. Their values, given in Table 1, show a reasonably small scatter, but they are about 20 to 70 cm^{-1} smaller than the values obtained by Crosswhite et al. [25] in their many-parameter treatment of $Nd^{3+}:LaCl_3$ spectra.

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