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ENERGY LEVELS OF THE FREE ION Nd^{3+} AND Nd^{3+} IN $Y_3Al_5O_{12}$

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In the present paper quantum states are assigned to experimentally determined energy levels on the basis of our calculations and further information on levels of the free Nd^{3+} ion in physical literature. In the absorption spectra $Nd^{3+}:Y_3Al_5O_{12}$ measured at 9.5 K in the region 3800—30500 cm^{-1} 111 levels of the crystal field splitting were detected. On the basis of the perturbation theory, following rigorously the crystal field model, impurity ions were approximated by point charges. Further parameters A_k^q of the crystal field $Nd^{3+}:Y_3Al_5O_{12}$ were calculated in orthorhombic symmetry (D_2) for the multiplets ^4I and ^4F by means of the best fitting procedure.

ЭНЕРГЕТИЧЕСКИЕ УРОВНИ СВОБОДНОГО ИОНА Nd^{3+} И Nd^{3+} В $Y_3Al_5O_{12}$

В работе, исходя из рассчитанных, а также других доступных данных об энергетических уровнях свободного иона Nd^{3+}, сделана попытка сопоставить экспериментально определенным уровням соответствующие квантовые состояния. В спектре поглощения $Nd^{3+}:Y_3Al_5O_{12}$, измеренном при температуре 9,5 °K в диапазоне 3800—30500 $см^{-1}$, было обнаружено 111 линий, расщепленных полем кристалла. Для отдельных ионов было сделано приближение в виде точечных зарядов на основе теории возмущений и в соответствии с моделью внутреннего поля кристалла. Проведена также оптимизация параметров A_k^q поля кристалла $Nd^{3+}:Y_3Al_5O_{12}$ с ромбической симметрией для мультиплетов ^4I и ^4F.

I. INTRODUCTION

An yttrium aliminium garnet $Y_3Al_5O_{12}$ (YAG) doped with rare earth (RE) ions TR^{3+} (Nd, Gd, No, Er, Tu, Yb) attracts considerable attention as a material suitable for quantum optics equipments. This application has resulted in an increasing interest in the physical characteristics of this material. It is impossible to describe the function properties of Nd^{3+} : YAG lasers, as well as other garnet-based lasers, without the exact knowledge of the mentioned parameters [1]. Our attention was directed to the determination of the energy levels spectra of the impurity ion Nd^{3+} on the basis of an analysis of the absorption spectra of Nd^{3+} : YAG obtained at 9.5 K and also to the calculation of terms of the free Nd^{3+} ion. The analysis of the energy spectra splitting by the crystal field (CF) was performed by the procedure of the best fit of CF parameters A_k^q of the orthorhombic (D_2) symmetry. Next, the program is given for the calculation of values of $3-j$ symbols for the method of Racah operators, which is used in the procedure of the best fit.

II. METHOD

The method of Elliott, Judd and Runciman [3] for RE ions of the configuration f^n based on the Racah tensor operators [4], [5], and $3-j$ and $6-j$ symbols tabulated by Rotenberg et al. [2], were used. Their expression for the matrix elements of U_q^k in a slightly changed notation are defined as $(4\pi/2k-1)^{1/2}Y_k^q$, rewritten in terms of the $3-j$ symbols and the $6-j$ symbols are the following:

$$(f^n\alpha SLJM\,|U_q^k|\,f^n\alpha' S'L'J'M') = (-1)^{J-M}\begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \tag{1}$$

$$(-1)^{S+L'+J+k}(2J+1)(2J'+1)^{1/2}\begin{Bmatrix} L & J & S \\ J' & L' & k \end{Bmatrix}$$

$$(f^n\alpha SL\,\|U^k\|\,f^n\alpha' S'L'),$$

where for the RE ions within a given configuration only $k=2, 4, 6$ need to be considered. The expression $(:\ :\ :)$ is a $3-j$ symbol, $\{:\ :\ :\}$ is a $6-j$ symbol, α, α' denote the remaining quantum numbers required to specify the state. A last member on the right-hand side of equation (1) is the reduced or double bar matrix element.

The complete Hamiltonian including the free ion and the CF energy is of the following form [6]

$$H = H_{el} + H_{LS} + H_{KP}, \tag{2}$$

where

$$H_{el} = \sum_{ij}\frac{e^2}{r_{ij}} \tag{3}$$

is the Coulomb repulsion of the outer electrons of the free ion summed over all the pairs of electrons.

$$H_{LS} = \sum_{i=j}^{n}\lambda_i(l_i\,.\,s_i) \tag{4}$$

is the spin-orbit coupling of $4f$ electrons. λ_i is the spin-orbit constant for the i-th electron.

$$\begin{aligned} H_{KP} = {} & \alpha(A_2^0\langle r^2\rangle O_2^0 + A_2^2\langle r^2\rangle O_2^2) + \beta(A_4^0\langle r^4\rangle O_4^0 + \\ & + A_4^2\langle r^4\rangle O_4^2 + A_4^4\langle r^4\rangle O_4^4) + \gamma(A_6^0\langle r^6\rangle O_6^0 + \\ & + A_6^2\langle r^6\rangle O_6^2 + A_6^4\langle r^6\rangle O_6^4 + A_6^6\langle r^6\rangle O_6^6) \end{aligned} \tag{5}$$

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is the CF energy of the D_2 symmetry with the RE ion [7], where A_k^q are CF parameters, $\langle r^k \rangle = \int [R(r)^2 r^{k+2}\, dr$ signifies the k-th power of the $4f$ electron orbit radius and O_k^q, s are angular momentum operators.

III. EXPERIMENT

The transparent synthetic garnet Nd^{3+} : YAG of rose colour was grown by the Czochralsky method in Monokrystaly Turnov. The concentration of Nd^{3+} ions built into the crystal is evaluated to be 0.5 at %. The sample studied has a dimension of $10 \times 10 \times 3$ mm.

Measurements of the absorption spectra in the region from 3800 to 30500 cm^{-1} at the liquid helium temperature (LHeT) were carried out with the aid of the registration spectrometers Optica Milano 4 CF with the accuracy of the wavelength scale in the region UV – VIS ± 0.2 nm and 0.5 nm in the near infra red (NIR) at the Institute of Solid State Physics, Czechoslovak Academy of Sciences in Prague. In the present paper the abbreviation LHeT stands for liquid 9.5 K ± 1.0 K temperature as described in the following.

The measurements at LHeT were carried out in two stages. For the NIR region from 3800 cm^{-1} to 10000 cm^{-1} and for the VIS region from 10000 cm^{-1} to 30500 cm^{-1}. The values of the Nd^{3+} : YAG as obtained from the presented measurements can be seen in Table 1.

IV. CALCULATIONS

All the calculations described in this chapter were performed on a digital computer Siemens 4004/150 at the Computing Centre of the Comenius University.

For the calculation of the free ion spectra of the trivalent Nd a special program was suggested. The numerical results were used in the analysis of the Nd^{3+} : YAG spectra.

On the basis of Elliott's, Judd's and Runciman's work, [3] using the methods of Racah, the spin-orbit interaction including intermediate coupling together with the electrostatic interactions of f^3 in the one matrix for the same value of J and for various values of L, S were calculated. The electrostatic interactions for the configuration f^3 were calculated by Racah [4]. For the purpose of this paper the matrix elements tabulated by Nielson and Koster [9] were expressed in terms of the parameters E^1, E^2 and E^3, being the linear combinations of the Slater radial integrals defined by Racah [8]. In our calculation of free ion energy levels of the trivalent Nd the values of the parameters E^1, E^2 and E^3 (by Wybourne [10]) were used. Judd and Loudon [11] published the spin-orbit matrix elements. For matrix diagonalizations the method of the real symmetry matrix diagonalization by Jacobi [12, 13] was chosen. The products of this diagonalization are, besides the energy eigenvalues, the matrices of the eigenvectors as well.

Table 1

Energy levels of Nd^{3+} : YAG at 9.5 K.

Term	Energy level cm^{-1}	Term	Energy level cm^{-1}	Term	Energy level cm^{-1}
$^4I_{13/2}$	3918	$\beta^2H_{9/2}$	12586	$^4G_{5/2}$	16854
	3922		12628		16996
	3928		12707		17053
	4029		12789	$\beta^2G_{7/2}$	17251
	4043		12870		17272
	4442	$^4F_{7/2}$	13377		17340
	4507		13440		17595
$^4I_{15/2}$	5780	+	13571	$^4G_{7/2}$	18759
	5802	$^4S_{3/2}$	13593		18843
	5919		13623		18862
	5949	$^4F_{9/2}$	14626		18878
	6561		14680	$^2K_{13/2}$	18902
	6574		14801		19020
	6630		14820		19198
	6720		14920		19332
$^4F_{3/2}$	11423	$\beta^2H_{11/2}$	15738		19361
	11509		15829		19513
$^4F_{5/2}$	12359		15858		19588
	12425		15949		
	12527		15972		
			16089		
$\beta^2G_{9/2}$	19637	$^4G_{11/2}$	21828	$^4D_{5/2}$	28500
	19658		21896		28739
	19697		21939		28912
	19865		22059	$^4D_{1/2}$	29079
	20100		22078	$^2L_{15/2}$	29225
$^2K_{15/2}$	20734		22127		29731
	20787	$^2P_{1/2}$	23125		29885
	20811	$\beta^2D_{5/2}$	23657		29978
	20824		23603		30084
	21003		23818		30207
	21074	$^2P_{3/2}$	26226		30405
	21118		26267		30538
	21152	$^4D_{3/2}$	27583		
$\beta^2D_{3/2}$	21193		27685		
	21203	$^2I_{11/2}$	27823		
$^4G_{9/2}$	21582		28001		
	21636		28083		
	21702		28198		
	21727		28272		
	21800		28362		

By using the method of the Racah operators it is inevitable to know also the values of the $3-j$ symbols. The program of their evaluation was elaborated on the basis of the expression for the $3-j$ symbol [2]

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3} \times \tag{7}$$

$$\times \frac{(j_1+j_2-j_3)!\,(j_1-j_2+j_3)!\,(-j_1+j_2+j_3)!^{1/2}}{(j_1+j_2+j_3+1)!} \times$$

$$\times (j_1+m_1)!\,(j_1-m_1)!\,(j_2+m_2)!\,(j_2-m_2)!\,(j_3+m_3)!\,(j_3-m_3)! \times$$

$$\times \sum_k \frac{(-1)^k}{k!\,(j_1+j_2-j_3-k)!\,(j_1-m_1-k)!\,(j_2+m_2-k)!} \times$$

$$\times \frac{1}{(j_3-j_2+m_1+k)!\,(j_3-j_1-m_2+k)!}.$$

The values of the individual $3-j$ symbols were calculated with double precision (i.e. exactly to 14 valid places).

For the CF analysis of the D_2 symmetry of the nearest neighbour of the impurity ion Nd^{3+} in the YAG the modified fitting procedure by Kalavský [14] was used. This procedure enables the best fit of a given theoretical function of a set of theoretical parameters to the course of the experimentally obtained curve. The calculation starts from the estimated values of the parameters. With one described fitting procedure, unlike in [15, 16], the whole manifold of multiplets was best fitted. The J-mixing was not taken into account in this case.

V. DISCUSSION

We can say that the calculation of free Nd^{3+} ion spectra helped us in the analysis of the absorption spectra of the Nd^{3+} : YAG single crystal. Comparing the results of our calculations with those of Wybourne [17] in Table 2 it can be seen at first sight that our results are in good agreement with Wybourne's [17].

The first disagreement of Wybourne's theory with our calculations appears in the order of the ${}^4G_{5/2}$ and ${}^2G_{7/2}$ levels, which appear in the reversed order. We are sure that the results of our calculations are correct because of a good agreement with experimental spectra. The other point where Wybourne's theory fails is the order of the energy levels of ${}^4G_{7/2}$, ${}^2K_{13/2}$, ${}^2G_{9/2}$, ${}^4G_{9/2}$, ${}^2K_{15/2}$, ${}^2D_{3/2}$ (according to our calculations) and ${}^2K_{13/2}$, ${}^4G_{7/2}$, ${}^4G_{9/2}$, ${}^2K_{15/2}$, ${}^2D_{3/2}$, ${}^2G_{9/2}$ (according to Wybourne's theory). The energy levels ${}^4G_{7/2}$ and ${}^2K_{13/2}$ should appear in the reversed order and the level of the ${}^4G_{9/2}$ should be shifted to the left side of spectra. Let us present the results of Carlson's and Dieke's [18] calculations: The order of the energy levels should be ${}^2K_{13/2}$, ${}^4G_{7/2}$, ${}^2G_{7/2}$, ${}^2K_{15/2}$ and ${}^4G_{9/2}$: We shall return to this problem later in this paper.

Table 2

Calculated energy levels of the free ion Nd^{3+}. In the column (G) there are values of the present paper and in the column (W) the values calculated by Wybourne [17] are given comparation.

Term	Term Energy cm^{-1} (G)	Term Energy cm^{-1} (W)	Term	Term Energy cm^{-1} (G)	Term Energy cm^{-1} (W)
${}^4I_{9/2}$	0	0	$\beta{}^2D_{5/2}$	23803	23880
${}^4I_{11/2}$	1919	1928	${}^2P_{3/2}$	26383	26348
${}^4I_{13/2}$	3958	3976	${}^4D_{3/2}$	28602	28641
${}^4I_{15/2}$	6081	6099	${}^4D_{5/2}$	28935	28836
${}^4F_{3/2}$	11513	11524	${}^2I_{11/2}$	29008	28694
${}^4F_{5/2}$	12603	12607	${}^4D_{1/2}$	29250	29276
$\beta{}^2H_{9/2}$	13108	12612	${}^2L_{15/2}$	29397	29413
${}^4S_{3/2}$	13446	13454	${}^2I_{13/2}$	30052	30070
${}^4F_{7/2}$	13671	13611	${}^2L_{17/2}$	30916	30932
${}^4F_{9/2}$	14581	14903	${}^4D_{7/2}$	31068	31004
$\beta{}^2H_{11/2}$	15794	15885	$\alpha{}^2H_{9/2}$	33257	32729
${}^4G_{5/2}$	17438	17356	$\alpha{}^2H_{11/2}$	33542	34119
$\beta{}^2G_{7/2}$	18096	17354	$\alpha{}^2D_{3/2}$	33676	33771
${}^4G_{7/2}$	18807	19320	$\alpha{}^2D_{5/2}$	35209	34970
${}^2K_{13/2}$	18960	18978	$\beta{}^2F_{7/2}$	39449	41114
$\beta{}^2G_{9/2}$	19384	21255	$\beta{}^2F_{5/2}$	41070	39665
${}^4G_{9/2}$	20134	19720	$\alpha{}^2G_{7/2}$	48398	49006
${}^2K_{15/2}$	21009	21027	$\alpha{}^2G_{9/2}$	48544	48153
$\beta{}^2D_{3/2}$	21271	21247	$\alpha{}^2F_{5/2}$	68013	69874
${}^4G_{11/2}$	22203	21826	$\alpha{}^2F_{7/2}$	70227	68693
${}^2P_{1/2}$	23129	23147			

In the region of 3800—30500 cm^{-1}, where our measurements were performed, we should expect a splitting of the energy levels of the Nd^{3+} ion starting at the ${}^4I_{13/2}$ term and diminishing at the ${}^2L_{15/2}$ term. This should represent a set of 12 multiplets thus introducing 26 terms into the spectra. The 26 terms are split into 112 energy levels in the CF of a tetragonal or a lower symmetry after the $(J+1/2)$-fold degeneracy has been completely removed. We have succeeded in identifying 111 absorption maxima attributed to transitions from the basic energy level to the higher levels (Table 1). The only missing line is one of the doublet ${}^4S_{3/2}$, which we have not been able to identify (see Fig. 1) in spite of the fact that the line was found in Koningstein's and Geusic's [19] spectra. The authors of [19] have the value of 7 cm^{-1} for the distance between the ${}^4S_{3/2}$ doublet components.

In the spectral region as plotted in Fig. 2 we have followed our calculations of the free Nd^{3+} ion energies. Koningstein [20] was not able to distinguish the

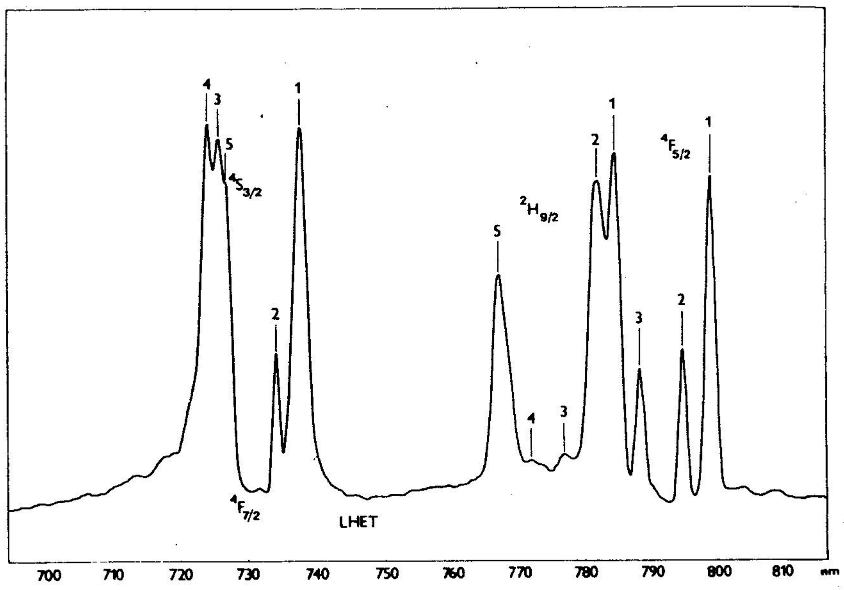

Fig. 1

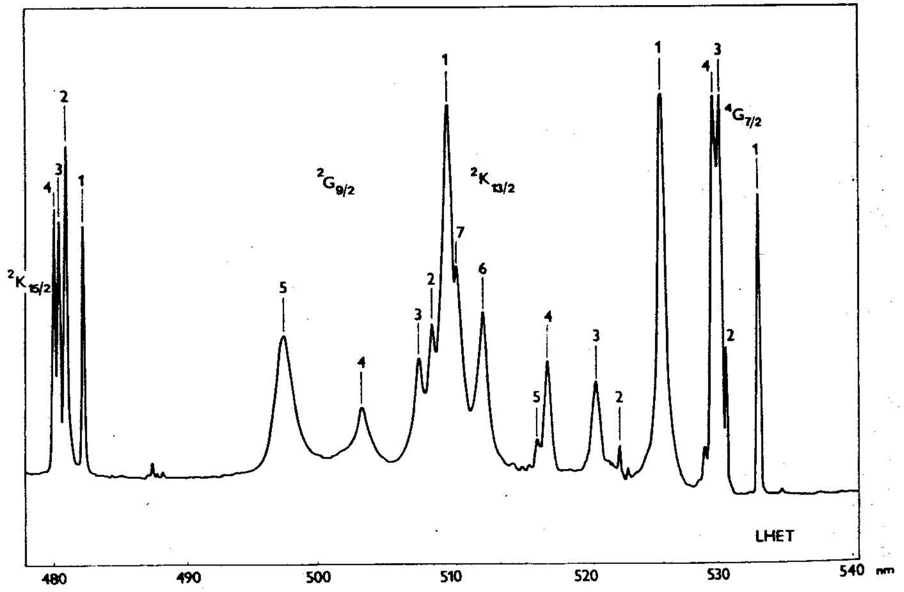

Fig. 2

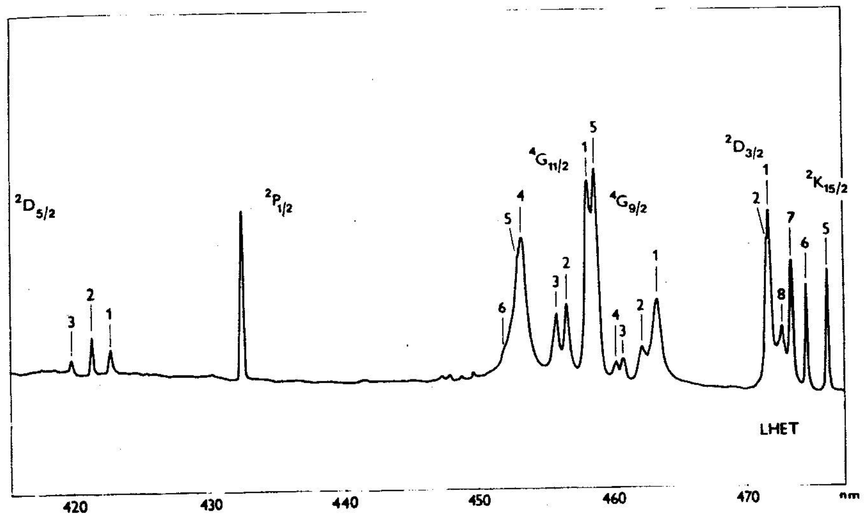

Fig. 3

spectral lines N° 2 of the $^4G_{7/2}$ term and the N° 2 of the $^2K_{13/2}$ term in his experimental spectra. In spite of [20] we have been able to identify all the 16 lines in our spectra. The number of the 16 lines corresponds to the complete removal of the $(J + 1/2)$-fold degeneracy in the tetragonal or even lower symmetry crystal field. As we have found, the order of spectral lines attributed to the proper terms should be $^4G_{7/2}$, $^2K_{13/2}$ and $^2G_{9/2}$, the wave number increasing from right to left.

In the region from 20700 to 22000 cm^{-1}, as seen in Fig. 3., there appears a great deal of discrepancies between experiment and theory. An absorption band which can be attributed to the $^2D_{3/2}$ term (according to [16, 20]) appears in our spectra in the form of an asymmetric absorption line subdued to a slightly marked splitting into a triplet (see lines N° 4, 5 and 6 of Fig. 3), attributed to the term of $^4G_{11/2}$. A new distribution of spectral lines with respect to the rising value of wave numbers should be: $^2K_{15/2}$, $^2D_{3/2}$, $^4G_{9/2}$ and $^4G_{11/2}$. The term $^4G_{9/2}$ was attributed to lines, occuring in the vicinity of 20700 cm^{-1} in spite of [19, 20] (measured at LHeT) or [15] (measured at LNT), who attributed the term of $^4G_{9/2}$ to lines at the position 20700 cm^{-1} approximately. According to our free ion calculations, the term $^4G_{9/2}$ should be placed in the neighbourhood of 20134 cm^{-1}, which is in discrepancy with our above mentioned organization of energy levels for the Nd^{3+} ion in the crystal field. The reasons, which led us to the above mentioned organization of the levels are the following: The wrong attribution of an unsplit energy band to the $^2D_{3/2}$ term according to [20]. The troubles Koningstein [20] had not only with the above mentioned $^2D_{3/2}$ term, but also with the order of all the four terms, discussed in the preceding part of our paper. We have concluded (after the analysis of LNT [15] and LHeT spectra and with excluding the lines generated by thermal transitions) that the full number of the 21 spectral lines in our experimental spectra must be attributed to the four terms.

With the program described in the fourth part of this paper the CF parameters A_k^q for the CF of D_2 symmetry (5) were the best fitted. Stedman, Cade [21] solved the problem also for CF of Nd^{3+} : YAG. In [21] they determined CF parameters with the best fitting, the D_2 symmetry was supposed to take place in the YAG, the J-mixing was ignored for the relatively well separated terms, concretely $^4I_{9/2}$, $^4I_{11/2}$, $^4F_{3/2}$, $^4F_{9/2}$ and $^2H_{11/2}$.

Voronko et al. [22] investigated the changes of the energy levels splitting of the Er^{3+}, Eu^{3+} and Nd^{3+} ions with the aim to determine the symmetry of the nearest-neighbour RE ions among the various substances of the garnet structure type $M_3Al_5O_{12}$ (M = Lu, Yb, Tu, Er, Y, Ho, Dy, Tb). In accordance with [22] for Nd^{3+} : YAG by means of the terms for splitting $^4F_{3/2}$, $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$ the CF parameters for the D_2 symmetry were determined.

Nekvasil [23] performed the CF analysis of the optical spectra of Nd^{3+} : YAG measured by Feofilov et al. [24]. They fitted the CF parameters of the energy levels of the ^4I multiplets including the J-mixing by the least-squares method according to the program suggested by Grűnberg et al. [25].

In Table 3 there are compared the values of the CF parameters A_k^q of the D_2 symmetry, the standard deviations δ_k of the energy levels of single terms or multiplets for measured E_n and for calculated E_v.

Table 3

The values of the parameters A_k^q of the symmetry D_2 and the values of mean square errors δ_k. (The label 1+ takes place — for $^4I_{11/2}$, 2+ — for ^4I, 3+ — for ^4F).

cm⁻¹	Stedman Cade [21]	Voronko a kol. [22]	Nekvasil [23]	Present paper
A_2^0	239	± 150	− 168	− 258
A_2^2	291	± 230	256	662
A_4^0	− 303	− 100	− 359	− 465
A_4^2	− 245	− 186	327	− 1164
A_4^4	1185	− 1100	1212	− 2529
A_6^0	107	30	62	27
A_6^2	49	0	− 217	− 121
A_6^4	1151	− 635	1130	257
A_6^6	− 152	802	126	71
δ_k	33.0^{1+}	$130.0^{2+,3+}$	3.7^{2+}	59.9^{2+} 74.9^{3+}

Concluding we can say that the tetragonal symmetry of the nearest-neighbours of the impurity Nd^{3+} ion in YAG is responsible for the reality of the single terms of the multiplet ^4F [15, 20]. For the multiplet ^4I the agreement between calculated and measured energy levels of tetragonal symmetry is not so good as in [15, 20]; therefore, in this work, also the lower D_2 symmetry was assumed. The results showed here that the agreement between experiment and calculation neglecting the J-mixing, is not satisfactory from the terms $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$.

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