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Energy Levels and Crystal-Field Calculations of Trivalent Ytterbium in Yttrium Aluminum Garnet and Yttrium Gallium Garnet

By

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The splitting of the two ^2F states of Yb^{3+}:YAlG and Yb^{3+}:YGaG, have been determined from fluorescence and absorption spectra at low temperatures. The levels of the ground states of Yb^{3+}:YAlG are at: 0, 388, 613, 778 cm^{-1}, those of Yb^{3+}:YGaG at 0, 308, 567, and 672 cm^{-1}. Crystal field calculations yield the following values for Yb^{3+}:YAlG; $A_2^0 = 270$ cm^{-1}, $A_4^0 = -165$ cm^{-1}, $A_4^4 = -1155$ cm^{-1}, $A_6^0 = 21$ cm^{-1}, $A_6^4 = -304$ cm^{-1} and for Yb^{3+}:YGaG: $A_2^0 = 110$ cm^{-1}, $A_4^0 = -125$ cm^{-1}, $A_4^4 = -1250$ cm^{-1}, $A_6^0 = 10$ cm^{-1} and $A_6^4 = -142$ cm^{-1}. A satisfactory agreement has been found for calculated and observed splitting patterns.

Die Aufspaltung der ^2F-Zustände von Yb^{3+}:YAlG (I) und Yb^{3+}:YGaG (II) wurde bei tiefen Temperaturen aus Fluoreszenz- und Absorptionsspektren bestimmt. Die Niveaus des Grundzustandes von (I) liegen bei 0, 388, 613, 778 cm^{-1}, die von (II) bei 0, 308, 567 und 672 cm^{-1}. Die Ligandenfeldtheorie ergibt folgende Werte für die Kristallfeldparameter: für (I) $A_2^0 = 270$ cm^{-1}, $A_4^0 = -165$ cm^{-1}, $A_4^4 = -1155$ cm^{-1}, $A_6^0 = 21$ cm^{-1}, $A_6^4 = -304$ cm^{-2} und für (II) $A_2^0 = 110$ cm^{-1}, $A_4^0 = -125$ cm^{-1}, $A_4^4 = -1250$ cm^{-1}, $A = 10$ cm^{-1} und $A_6^4 = -142$ cm^{-1}. Die Übereinstimmung zwischen berechneter und beobachteter Aufspaltung war befriedigend.

La division, par le champ de ligandes, des états $^2F_{7/2}$ et $^2F_{5/2}$ dans Yb^{3+}:YAlG et Yb^{3+}:YGaG a été déterminée des spectres de fluorescence et d'absorption. Les sous-niveaux de l'état fordamental se situent à 0, 388, 613, 778 cm^{-1} dans Yb^{3+}:YAlG, à 0, 308, 567, 672 cm^{-1} Yb^{3+}:YGaG. Le calcul fournit les valeurs suivantes pour les parametres: Yb^{3+}:YAlG $A_2^0 = 270$ cm^{-1}, $A_4^0 = -165$ cm^{-1}, $A_4^4 = -1155$ cm^{-1}, $A_6^0 = 21$ cm^{-1}, $A_6^4 = -304$ cm^{-1}; Yb^{3+}:YGaG $A_2^0 = 110$ cm^{-1}, $A_4^0 = -125$ cm^{-1}, $A_4^4 = -1250$ cm^{-1}, $A_6^0 = 10$ cm^{-1} et $A_6^4 = -142$ cm^{-1}. L'accord entre les spectres calculé et observé est satisfaisant.

I. Introduction

The determination of the position of Stark components of the $^2F_{5/2}$ and $^2F_{7/2}$ states of the trivalent ytterbium ion in garnet host lattices, has been the subject of some investigations [*1 – 3, 6, 12 – 13, 15 – 17*]. Considerable attention has been paid to the theoretical interpretation of the spectrum of Yb^{3+} in $Y_3Ga_2(GaO_4)_3$ [Yb^{3+}:YGaG]. PAPPALARDO and WOOD [*12*] and WOOD [*17*] for instance reported the four Kramers' doublets of the ground state at 0, 112, 308 and 550 cm^{-1}. These positions do not agree with susceptibility data [*1, 3*]. In a very recent paper HUTCHINGS and WOLFE [*5*] assembled all available experimental data and in employing a crystal field calculation, found that the ground state should be split in four Stark levels at 0, 517, 697 and 796 cm^{-1} in obvious disagreement with WOODS assignment. Much less attention has been paid to the spectrum Yb^{3+}:YAlG [*17*].

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In some recent papers, KONINGSTEIN and GEUSIC [7 – 9] showed that the crystal field which the ions Nd^{3+}, Eu^{3+}, Tb^{3+} and Er^{3+} experience in the host lattice YAlG deviates slightly from tetragonal symmetry. Employing crystal field parameters $A_n^m = \langle r^n \rangle B_n^m$ for Yb^{3+}:YAlG which are approximately equal to the values reported for Er^{3+}:YAlG [9] it thus becomes possible to calculate the splitting of the $^2F_{7/2}$ and $^2F_{5/2}$ manifolds of Yb^{3+}:YAlG. These calculations reveal that the calculated and observed splitting patterns of the $^2F_{5/2}$ state are in agreement; however, this is not the case for the ground state.

In an attempt to understand these discrepancies we have re-examined the optical spectra of Yb^{3+}:YAlG and Yb^{3+}:YGaG at 300° K and 77° K while new absorption and fluorescence measurements were made at 4.2° K and 1.9° K. From the new experimental data we have determined the position of the four Stark components of the $^2F_{7/2}$ states. Crystal field calculations yielded parameters which values were acceptable if compared with values of these parameters reported in previous communications. The experimental results suggest that not all Yb^{3+} ions do replace the Y^{3+} ions in the garnet host lattices.

II. Experimental procedure

Absorption and fluorescence spectra of Yb^{3+}:YAlG have been studied at 300° K, 77° K, 4.2° K and 1.9° K. A ½ meter Jarrell Ash spectrometer was used to record the absorption spectrum, while a 1 meter Jarrell Ash spectrometer was used to examine the fluorescence spectrum. The fluorescence was excited with a filtered Hg light source. All spectra were recorded under an average resolution of $< 1\ cm^{-1}$. The samples of Yb^{3+}:YAlG and Yb^{3+}:YGaG contained 3 – 10 at % Yb^{3+}, while spectrum were also studied of the compound YbAlG.

III. Experimental results

The fluorescence spectrum of Yb^{3+}:YAlG at 1.9° K is shown in Fig. 1. Transitions of the fluorescence spectrum at 77° K and even more so at 1.9° K should originate in the lowest lying level of the $^2F_{5/2}$ state and terminate in Stark components of the $^2F_{7/2}$ state. Instead of a maximum of four transitions one observes about 10 lines. The strong emission at 10324 cm^{-1} coincides with a strong absorption at that frequency in the absorption spectrum of this particular sample. This emission line which has not been observed by WOOD [17] terminates in the ground state. Like the fluorescence spectrum, the absorption spectrum at 77° K and 4.2° K shown in Fig. 2 reveals the presence of many extra lines. The fine structure which appears on the low frequency side of the peak absorptions at 10634 cm^{-1} and 10610 cm^{-1} does not disappear in the low temperature absorption spectrum. These bands cannot be assigned to transitions which originate in vibrational levels on the electronic ground state or other Stark component of the $^2F_{7/2}$ state. We suspect that these extra lines may be due to transitions of 4f electrons of Yb^{3+} ions which occupy positions in the host lattice other than the yttrium site.

The strong emission line and absorption band at 10324 cm^{-1} do not show this complicated fine structure. The fluorescence spectrum at 1.9° K as shown in Fig. 1 gives thus direct information about the position of the Stark components of the $^2F_{7/2}$ state. If one assumes that the strong fluorescence lines (and also absorption bands) belong to the transitions of 4f electrons of ytterbium ions which occupy the appropriate site for rare earth ions in YAlG then the positions of the Stark components are directly mapped out (see Fig. 2). Evidence for the existence of a

Stark component at 387 cm^{-1} above the ground state was also obtained by studying the absorption spectrum of YbAlG at 77° K. Transitions from a series of levels positioned at ~380 cm^{-1} to an excited state at 10630 cm^{-1} could be detected.

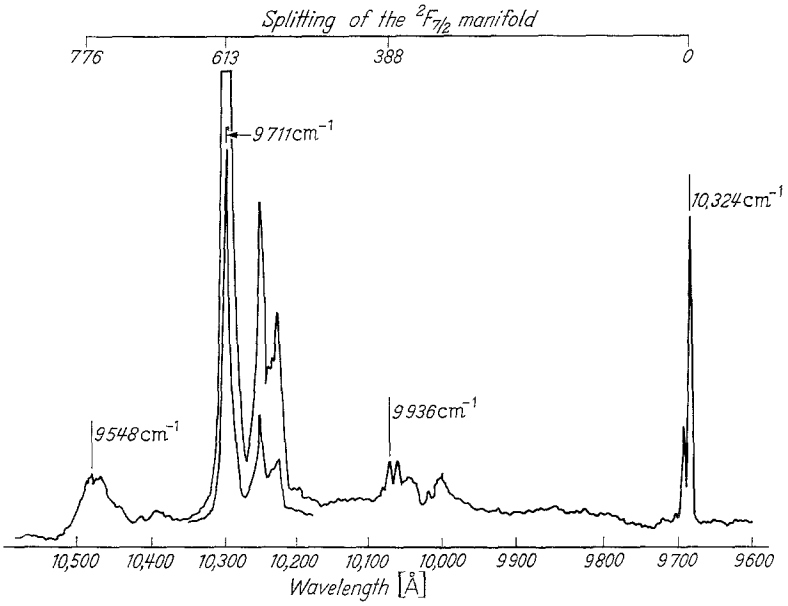

Fig. 1. The fluorescence spectrum of Yb^{3+}:YAlG at 1.9° K. The emission line at 10324 cm^{-1} represents the transition between the lowest lying level of the $^2F_{5/2}$ manifold and the ground state. Also indicated are the positions of the other Stark components of the $^2F_{7/2}$ ground manifold

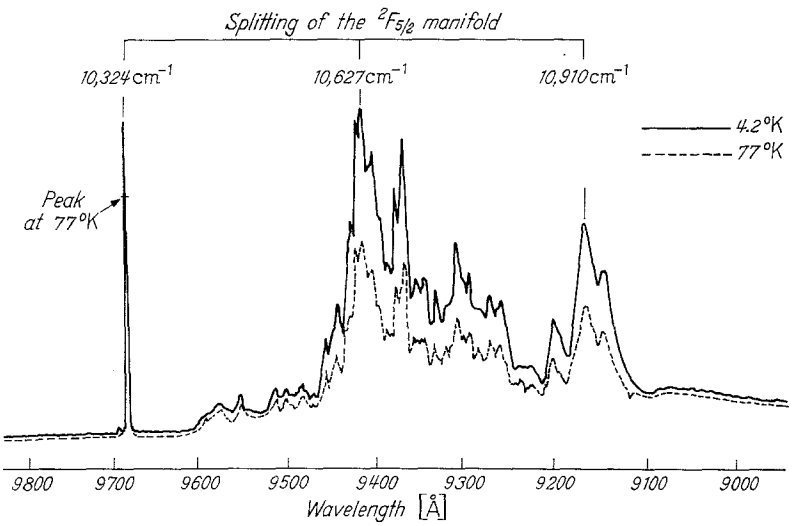

Fig. 2. The absorption spectrum of Yb^{3+}:YAlG at 77° K and 4.2° K

Wood [17] has reported levels of the ground manifold at 0, 140, 390* and 620 cm^{-1}. Our experiments do not show the presence of a level at 140 cm^{-1}. It shall be

* There appears to be an arithmetical error in Fig. 2, Ref. 17. Dr. Wood thought it a good idea to point this out.

shown that crystal field calculations predict only levels above 400 cm^{-1}. It is very well possible that a level at 140 cm^{-1} above the ground manifold is associated with transitions of ytterbium ions which do not occupy the appropriate sites for rare earth ions in YAlG.

The fluorescence spectrum of Yb^{3+}:YGaG has also been investigated. Although quite similar, the fluorescence spectrum at 4.2° K is less complicated than that of Yb^{3+}:YAlG. Three lines at 9702 cm^{-1}, 9762 cm^{-1} and 10329 cm^{-1} have the same intensity distribution as the lines at 9548 cm^{-1}, 9711 cm^{-1} and 10324 cm^{-1} of the fluorescence spectrum of Yb^{3+}:YAlG. The line at 10329 cm^{-1} coincides with an absorption at approximately that frequency reported by PAPPALARDO and WOOD which was assigned to the transition of the ground state and the lowest lying level of the $^2F_{5/2}$ state. According to these authors, the energy difference between the two lowest lying level Stark components of the $^2F_{5/2}$ state is 290 cm^{-1}. Hence transition of the fluorescence spectrum at 4.2° K should predominately arise in the level of Yb^{3+}:YGaG at 10329 cm^{-1}.

The lines at 9762 cm^{-1} and 9702 cm^{-1} terminate then in levels which are 567 cm^{-1} and 627 cm^{-1} above the ground state of Yb^{3+}:YGaG. From an intensity comparison of the fluorescence spectra follows that the corresponding levels of Yb^{3+}:YAlG at 0, 613 and 788 cm^{-1} are of Yb^{3+}:YGaG at 0, 567 and 627 cm^{-1}. The over-all splitting of the ground manifold of Yb^{3+}:YGaG is thus smaller than the splitting of this manifold of Yb^{3+}:YAlG. This has also been observed for identical J manifolds of Eu^{3+} and Nd^{3+} in these host lattices. An estimate can be made of the position of the fourth and missing component of the $^2F_{7/2}$ state of Yb^{3+}:YGaG. The centers of gravity of the $J = 5/2$ and $J = 7/2$ manifolds of Yb^{3+}:YAlG are at 10618 cm^{-1} and 444 cm^{-1}. The centers of gravity of these manifolds of Yb^{3+}:YGaG are at 10562 cm^{-1} and $x + 567 + 627$ cm^{-1}, where x is the energy of the missing level. If one assumes that the spin orbit coupling constant λ is the same for the Yb^{3+} ion in both host lattices then the center gravity of the $J = 7/2$ manifold of Yb^{3+}:YGaG should be at: $10562 - (10618 - 444) = 308$ cm^{-1}. Relating the two expressions for the center of gravity one evaluates a value of 358 cm^{-1} for the position of the fourth Kramers doublet. It should be remembered that a change of 0.1% in λ results in a change of $\sim$50 cm^{-1} in the calculated position of this level.

IV. The Crystal field for Yb^{3+}:YAlG

The experimental results on the split manifold of Yb^{3+}:YAlG indicate that the $J + 1/2$ fold degeneracy of the $^2F_{5/2}$ and $^2F_{7/2}$ states is removed by the crystalline field. This is in agreement with previous results on the ions Nd^{3+} and Er^{3+} in the same host lattice.

The author [7 – 9] has shown that the symmetry of the crystal field which some of the trivalent Lanthanide ions experience in YAlG and YGaG deviates slightly from tetragonal symmetry. If A_2^2, A_4^2, A_6^2 and A_6^6 are also small for Yb^{3+}:YAlG and Yb^{3+}:YGaG then the perturbing Hamiltonian H_C due to the crystal field can then be written as:

$$H_C = \alpha A_2^0 O_2^0 + \beta [A_4^0 O_2^0 + A_4^4 O_4^4] + \gamma [A_6^0 O_6^0 + A_6^4 O_6^4] \quad (1)$$

where

$$A_n^m = \langle r^n \rangle B_n^m$$

O_n^m are angular momentum operators.

α, β and γ are operator equivalent constants [*4—13*].

Values of the second and fourth order parameters are most easily obtained from the splitting of a $J = 5/2$ manifold. In a previous paper on crystal field calculations for Nd^{3+}:YAlG it was shown [7] how values of the second and fourth order crystal field parameters may be evaluated from the splitting of a $J = 5/2$ manifold in a tetragonal field.

Equations 4a, b, 5 (a – d) and 6 given in Ref. 7 have been applied to the position of the Stark components of the $^2F_{5/2}$ state of Yb^{3+}:YAlG. One evaluates $A_2^0 = 270\ cm^{-1}$, $A_4^0 = -165\ cm^{-1}$ and $A_4^4 = \pm 1155\ cm^{-1}$. Values of the sixth order parameters are evaluated from the splitting of the $^2F_{7/2}$ state of Yb^{3+}:YAlG.

Table 1. *Energy levels of* Yb^{3+}:YAlG

OBS (cm^{-1})	calc (cm^{-1})	Δ (cm^{-1})	Assignment	Energy (cm^{-1})
0	0	0		
388	399	11	$^2F_{7/2}$	0
613	612	1		
778	789	11		
10324	10324	0		
10622	10622	0	$^2F_{5/2}$	10173
10910	10910	0		

Average Deviation 8 cm^{-1}
Spin-orbit coupling $\lambda = -2907\ cm^{-1}$

From the relations given by Eqs. 7a, 7b and 7c the following values are obtained: with $A_2^0 = 270\ cm^{-1}$, $A_4^0 = -165\ cm^{-1}$, $A_4^4 = -1155\ cm^{-1}$, $A_6^0 = 21\ cm^{-1}$ and $A_6^4 = -304\ cm^{-1}$. The calculated splitting patterns of the $^2F_{7/2}$ and $^2F_{5/2}$ states of Yb^{3+}:YAlG with crystal field parameters given above is compared with the observed splitting in Tab. 1.

V. Energy levels and Crystal field for Yb^{3+}:YGaG

The same type of calculations have also been applied to the splittings of the $J = 5/2$ and $J = 7/2$ manifolds of Yb^{3+}:YGaG. One evaluates the

Table 2. *Energy levels of* Yb^{3+}:YGaG

OSB (cm^{-1})	calc (cm^{-1})	Δ (cm^{-1})	Assignment	Energy (cm^{-1})
0	0	0		
308[a]	322	14	$^2F_{7/2}$	0
565	550	17		
627	627	0		
10315[a]	10315	0		
10605[a]	10605	0	$^2F_{5/2}$	10186
10765[a]	10765	0		

Average Deviation 3 cm^{-1}
Spin-orbit coupling $\lambda = -2910\ cm^{-1}$

[a] Values reported by Wood and Pappalardo.

crystal field parameters: $A_2^0 = 110\ cm^{-1}$, $A_4^0 = -125\ cm^{-1}$, $A_4^4 = -1250\ cm^{-1}$, $A_6^0 = 10\ cm^{-1}$ and $A_6^4 = -142\ cm^{-1}$. The fourth Stark component of the $^2F_{7/2}$ state is calculated at $322\ cm^{-1}$ above the ground state which is in reasonable agreement with an estimated value of $358\ cm^{-1}$ given in the above. WOOD concluded from absorption measurements at different temperatures that low lying levels of the ground manifold are at $112\ cm^{-1}$ and $308\ cm^{-1}$. We believe that the level at $112\ cm^{-1}$ is associated with transitions of ytterbiums which do not occupy the appropriate sites in the gallium garnet host. Furthermore, the concentration of ytterbium ions which occupy these improper sites is less then the concentration of the rare earth ions which replace the yttrium ions. This for instance can be seen from the absorption spectrum of Yb^{3+}:YAlG at 4.2° K (Fig. 2). The intensities of the bands decrease if the peak absorptions move away from the absorptions which are due to $^2F_{7/2} - {}^2F_{5/2}$ transitions of ytterbium ions which occupy the proper site. The level at $308\ cm^{-1}$ is probably the position of the fourth stark component of the $^2F_{7/2}$ manifold of Yb^{3+}:YGaG. A comparison of calculated and observed splitting of the two J manifolds of Yb^{3+}:YGaG is given in Tab. 2. HUTCHINGS and WOLFE concluded from crystal field calculations that levels of the $^2F_{7/2}$ state of Yb^{3+}:YGaG are at 0, 517, 697 and 797 cm^{-1}. These results are in disagreement with the experimental and theoretical results presented in this article. It is perhaps worthwhile to note that the signs of our parameters A_2^0, A_4^0 and A_6^0 are in agreement with the results of a point charge calculations reported by these authors.

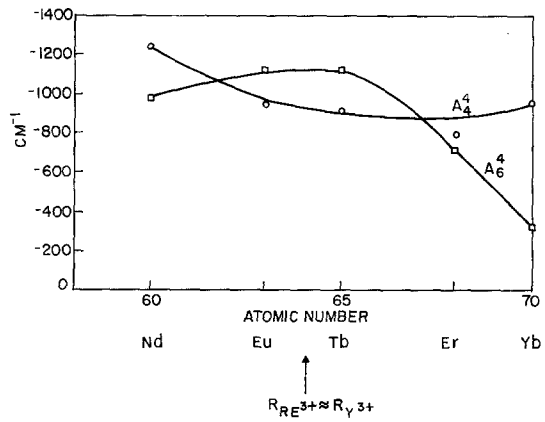

Fig. 3. Values of the crystal field parameters A_2^0, A_4^0 and A_6^0 for different rare earth ions in YAlG

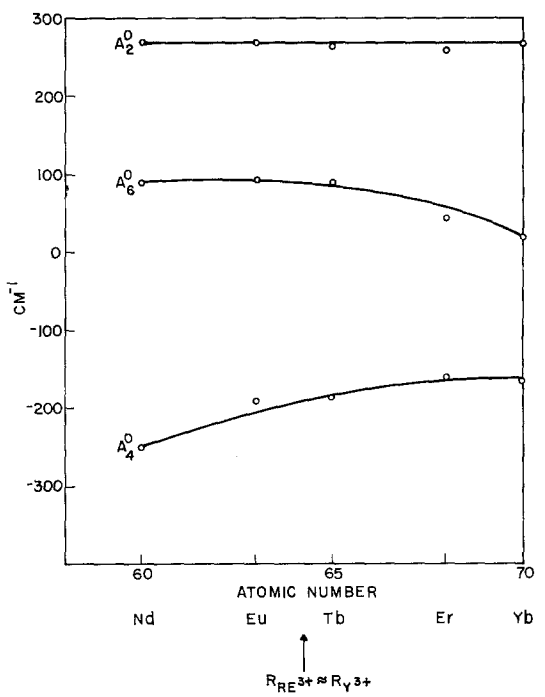

Fig. 4. Values of the parameters A_4^4 and A_6^4 for the different rare earth ions in YAlG

In some earlier publications we have given values of crystal field parameters

of the ions Nd^{3+}, Eu^{3+}, Tb^{3+} and Er^{3+} in YAlG. It is interesting to compare the A_n^m s of the different ions in the host lattice YAlG. This comparison can be seen in Figs. 3 and 4 where the plots are shown of the parameters as a function of the atomic member of the rare earth ions. The parameter A_6^4 is most sensitive, A_2^0 is least sensitive to a change in the value of Z in the series of the Lanthanides. If all trivalent rare earth ions experience a crystal field of the same symmetry then the ratios A_4^4/A_4^0 and A_6^4/A_9^0 should be constant. This is not the case if YAlG is the host lattice. Both ratios increase in fact slowly. The radii of the trivalent ions decrease as the atomic number Z increases, while $r_{Yb^{3+}} \approx r_{Y^{2+}}$. It is very well possible that this change of the radius of the central rare earth ion causes a reorientation of the closest neighbors. This in turn results in a change of the ratios mentioned in the above.

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References

[1] AYANT, Y., and J. THOMAS: Compt. Rend. **248**, 387 (1959).
[2] BALL, M., G. GARTON, M. J. M. LEASK, and W. P. WOLFE: Proc. Intern. Conf. Low Temp. Physics 7th Toronto Ont. **1960**, 128 (1961).
[3] BRUMAGE, W. H., C. C. LIN, and J. H. VAN VLECK: Physic Rev. **132**, 608 (1963).
[4] ELLIOTT, R. J., and K. W. H. STEVENS: Proc. Roy. Soc. **A 218**, 553 (1953).
[5] HUTCHINGS, M. T., and W. P. WOLFE: J. chem. Physics **41**, 617 (1964).
[6] JUDD, B. R.: Proc. Roy. Soc. **A 227**, 552 (1955).
[7] KONINGSTEIN, J. A., and J. E. GEUSIC: Physic Rev. **136**, A 711 (1964).
[8] — Physic Rev. **136**, A 717 (1964).
[9] —, and J. E. GEUSIC: Physic Rev. **136**, A 726 (1964).
[10] — The Energy Levels of Trivalent Europium in Yttrium Gallium Garnet (to be published in J. chem. Physics).
[11] —, and D. L. WOOD: Energy Levels of Nd^{3+}:YGaG (to be published).
[12] PAPPALARDO, R., and D. L. WOOD: J. chem. Physics **33**, 1734 (1960).
[13] SIEVERS, A. J., and M. TINKHAM: Physic Rev. **124**, 321 (1961).
[14] STEVENS, K. W. H.: Proc. Physic Soc. **A 65**, 209 (1952).
[15] WICKERSHEIM, K. A., and R. L. WHITE: Physic Rev. Letters **4**, 123 (1960).
[16] — Physic Rev. **122**, 1376 (1961).
[17] WOOD, D. L.: J. chem. Physics **39**, 1671 (1963).

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