Theoret. chim. Acta (Berl.) 5, 327—335 (1966)

Crystal-field Studies of trivalent Thulium in Yttrium Aluminum Garnet

J. A. KONINGSTEIN

E. W. R. Steacie Building of Chemistry, Carleton University, Ottawa, Ontario (Canada)

Received March 21, 1966

CF parameters have been calculated from the splitting of some of the manifolds of Tm^{3+} in Yttrium Aluminum Garnet (YAlG). Values of these parameters are: $A_2^0 = 270\ cm^{-1}$, $A_2^2 = \pm 95\ cm^{-1}$, $A_4^0 = -170\ cm^{-1}$, $A_4^2 = \pm 410\ cm^{-1}$, $A_4^4 = -1020\ cm^{-1}$, $A_6^0 = 30\ cm^{-1}$, $A_6^2 = \pm 115\ cm^{-1}$, and $A_6^4 = -475\ cm^{-1}$. There are indications that these parameters do not describe the splitting patterns of excited states with higher energy.

Aus der Aufspaltung entarteter Zustände von Tm^{3+} in YAlG sind Kristallfeldparameter berechnet worden. Die Werte dieser Parameter sind: $A_2^0 = 270\ cm^{-1}$, $A_2^2 = \pm 95\ cm^{-1}$, $A_4^0 = -170\ cm^{-1}$, $A_4^2 = \pm 410\ cm^{-1}$, $A_4^4 = -1020\ cm^{-1}$, $A_6^0 = 30\ cm^{-1}$, $A_6^2 = \pm 115\ cm^{-1}$, und $A_6^4 = -475\ cm^{-1}$. Es gibt Anzeichen dafür, daß diese Parameter nicht das Aufspaltungsmuster angeregter Zustände höherer Energie beschreiben.

On a calculé les paramètres du champ cristallin à partir de la séparation obtenue par levée de dégénerescence pour les niveaux de Tm^{3+} dans le grenat d'yttrium aluminium (YAlG). Les valeurs de ces paramètres sont: $A_2^0 = 270\ cm^{-1}$, $A_2^2 = \pm 95\ cm^{-1}$, $A_4^0 = -170\ cm^{-1}$, $A_4^2 = \pm 410\ cm^{-1}$, $A_4^4 = -1020\ cm^{-1}$, $A_6^0 = 30\ cm^{-1}$, $A_6^2 = \pm 115\ cm^{-1}$ et $A_6^4 = -475\ cm^{-1}$. Il existe des indications selon lesquelles ces paramètres ne décrivent pas l'aspect des séparations des états excités d'énergies plus élevées.

1. Introduction

During the last few years considerable attention has been paid to magnetic [*1*–*7*] and spectroscopic properties [*8*–*18*] of trivalent rare earth ions in Garnet host lattices. The lanthanide ions which replace the Yttrium ions occupy the orthorhombic (*c*) sites in the unit cell [*19*]. Consequently one should accept the fact that the symmetry of the crystal field which the ions experience is orthorhombic.

A first attempt to fit some spectroscopic splitting patterns of Er^{3+} in Yttrium Gallium Garnet (YGAG) was made by PAPPALARDO [*8*] in employing a crystal field of cubic symmetry. Also PAPPALARDO [*9*] and WOOD [*9, 10*] used such a field to explain splittings of *LSJ* manifolds of Yb:YGaG. In a series of papers, KONINGSTEIN and GEUSIC [*12, 14*] and more recently KONINGSTEIN [*13, 15, 17, 18*], a study was presented of energy levels and crystal field calculations of the trivalent ions Nd, Eu, Tb, Er, Tm, Yb in YAlG; Nd, Eu, Yb in YGaG and Eu in EuIG. The result of the studies indicate that the symmetry of the crystal field is indeed orthorhombic, but that the field deviates only slightly from tetragonal symmetry.

The spectroscopic data of Yb^{3+} in Garnets seem to be in disagreement with some magnetic susceptibility data by VAN VLECK [*4*] et al. These measurements for instance do indicate that the first excited state should be around 700 cm^{-1}. Fluorescence and absorption measurements reveal the presence of a level at

~ 300 cm^{-1}. HUTCHINGS and WOLFE [*20*] assembled experimental data and performed a calculation of crystal field parameters based on the point charge approximation. They also disputed the presence of a Stark level at 300 cm^{-1}. Recently the author completed a spectroscopic study of Yb^{3+} in the Aluminum and Gallium Garnets [*17*]. The absorption and fluorescence spectra at low temperatures showed that not all the Yb^{3+} ions occupy the appropriate orthorhombic sites in YAlG. From an intensity comparison of the fluorescence spectrum of Yb:YAlG it can be estimated that $\sim 50\%$ of the Yb^{3+} ions do not occupy these orthorhombic sites. These ions give rise to a series of ground states (see Fig. 1, Ref. [*17*]) which are ~ 560 cm^{-1} above the groundstate of the Yb^{3+} ions occupying the appropriate sites in YAlG. A determination of the position of the first excited Stark level of the $^2F_{7/2}$ manifold of the latter ions by means of magnetic susceptibility measurements is apt to be obscured by the presence of these states. The population of these states do not follow BOLTZMANN's distribution law.

The Thulium ion is bounded by the Er and Yb ions in the periodic table. Abnormalities have not been observed in the spectrum of Er:YAlG [*14*].

The purpose of this communication is to report spectroscopic data of Tm:YAlG. A study of the absorption spectra showed that also in the case of Tm:YAlG the rare earth ions do not always occupy the appropriate orthorhombic sites. A crystal field analysis of this ion in the Aluminum Garnet host lattice revealed that drastic changes occur in the values of the crystal field (CF) parameters A_2^2, A_4^2 and A_6^2 of Tm:YAlG, when these values are compared with similar A_n^m's of Eu^{3+} and Tb:YAlG. The calculations suggest that the symmetry of the crystal field of rare earth ions in YAlG deviates more and more from pure tetragonal symmetry as the atomic number Z increases in the series of the Lanthanides.

2. Experimental

Absorption spectra of a single crystal of Tm:YAlG—which contained ~ 5 at % of the rare earth ion—were recorded in the infrared, visible, and UV spectral regions at different temperatures of the sample. Spectra were studied with different spectrometers. The spectral resolution in most spectral regions was ~ 1 cm^{-1}.

3. Results

From the temperature dependence of absorption bands we could establish the position of the first excited state of the $^3H_6$ ground manifold of Tm:YAlG at 28 cm^{-1}. Hence the transitions of the absorption spectra at 4.2 °K arise predominantly from the level of the ground state. The energy of the excited states is thus directly obtained from such spectra. In cases where a transition occurred which did not seem to originate in the ground state an absorption measurement at 1.9 °K was usually sufficient to make the correct assigments.

The approximate positions of the centers of the J manifolds of the trivalent Tm^{3+} ion are all well known, although there seems to be some doubt as to the location of the $^1I_6$ state [*21, 22*]. In following the calculations of GRUBER and CONWAY [*23*], the position of levels of $^1I_6$ should be below the levels of $^3P_{0,\,1,\,2}$ manifolds and at approximately 33000 cm^{-1}. We have observed two absorption bands close together (at 4.2 °K) at 34370 cm^{-1} and 34425 cm^{-1}, one band at 35343 cm^{-1}, again two rather strong absorptions at 36399 cm^{-1} and 36428 cm^{-1}

respectively, and one band at 37507 cm^{-1}. $^3H_6 - {}^1I_6$ transitions are assigned to the first two absorption bands, and the $^3H_6 - {}^3P_{0,\,1,\,2}$ transitions to the absorptions towards shorter wavelengths.

A close examination of some of the low temperature spectra revealed that some of the bands appear to have fine structure. The fine structure which occurs on both sides of such bands does not disappear on cooling of the sample to 1.9 °K. This is an indication that the shoulders appearing at higher wavelengths are not due to transitions which originate in Stark components of the ground manifold or vibrational levels of these states. Exactly the same features were observed in the absorption spectra of the ytterbium ion in garnet host lattices [*17*].

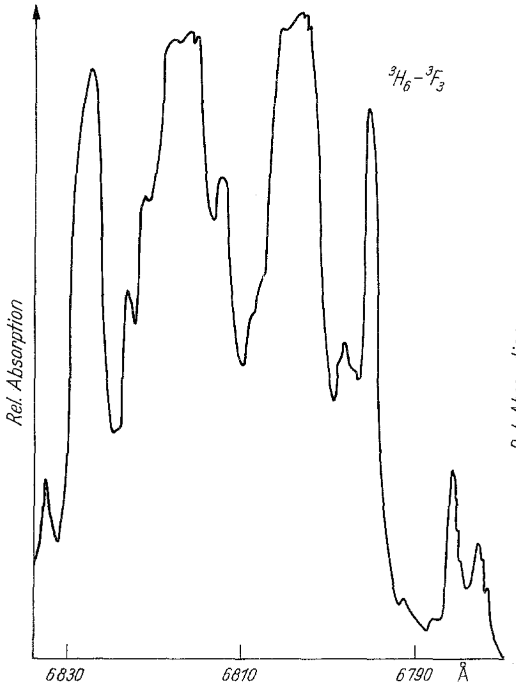

Fig. 1

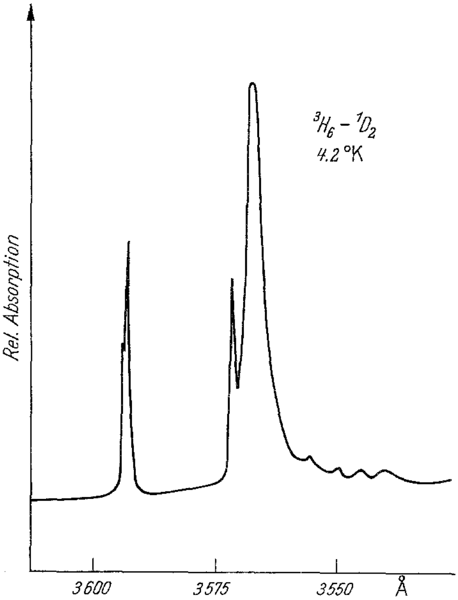

Fig. 2

Fig. 1. The absorption spectrum of Tm: YAlG at 4.2 °K in the spectral region of 6830 — 6790 Å

Fig. 2. The absorption spectrum of Tm: YAlG at 4.2 °K in the spectral region of 3600 — 3550 Å

The possibility exists that not all Tm^{3+} ions occupy the appropriate orthorhombic yttrium sites in YAlG. Such ions experience crystal fields which are different from that of the bulk of the rare earth ions which do occupy the yttrium sites. The absorption spectra of these ions are not equivalent.

It might be of interest to note that these multiple spectra have not been observed for Er, Tb, Eu and Nd:YAlG. It has been found that changes occur in the values of some of the crystal field parameters as the atomic number Z of rare earth ions in Garnet host lattices increases [*17*]. These changes are particularly pronounced if one compares crystal field parameters of Er:YAlG with parameters of Yb:YAlG. The radii of these ions are smaller than that of the yttrium ion. It has also been pointed out that from changes of the values of the ratios $A_4^4/5A_4^0$

and $A_6^4/21A_6^0$ the conclusion can be drawn that the closest neighbours of the rare earth ions experience the effect of the change in size of the radius of these ions. It is possible that the neighbouring ions try to find the energetically most favourable positions by rearranging themselves. For the cases of Tm^{3+} and also Yb^{3+} however, this perhaps cannot be completely accomplished. Consequently the strength of the bond between the central ions and ligands decreases. This, in turn, may at a certain moment cause the departure from the yttrium site of some of these trivalent rare earth ions. The crystal field analysis of Tm:YAlG (see Section IV) suggests that in the process of rearrangement of the neighbouring ions, the crystal field deviates more and more from a field of near tetragonal symmetry.

The appearance of the multiple absorption spectra mentioned above in the spectral region of 8000 Å – 6850 Å was rather disturbing. It, in fact, did not allow us to locate the correct positions of the Stark components of the $^3F_3$ and $^3F_4$ manifolds. The transitions of $^3H_6 - {}^3F_3$ are shown in Fig. 1. A group of four absorption bands showed up in the spectral region of 3600 Å – 3500 Å. They are shown in Fig. 2. Two of the lines are separated by 7 cm^{-1} and we believe that this again is due to the effect discussed above. The transitions are assigned to $^3H_6 - {}^1D_2$. A group of four absorptions shown in Fig. 3 between 4800 Å and 4600 Å is due to $^3H_6 - {}^1G_4$. From the position of the bands it can be calculated that the overall splitting of the $^1G_4$ manifold is at least 971 cm^{-1}. In this case we do not observe multiple spectra.

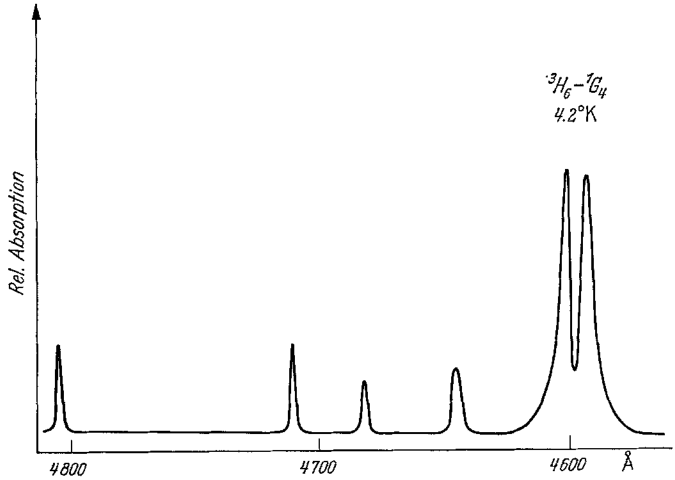

Fig. 3. The absorption spectrum of Tm: YAlG at 4.2 °K in the spectral region of 4800 — 4600 Å

Five absorptions between 6600 Å and 6450 Å belong to $^3H_6 - {}^3F_2$ transitions. The band at lower energy has two shoulders which do not disappear upon cooling of the sample to 1.9 °K. Transitions to some of the Stark components of $^3H_5$ manifold and to all levels of the $^3H_4$ manifold were recorded in the spectral regions of 1.18 μ – 1.16 μ and 1.80 μ – 1.63 μ. The positions of some of the Stark levels of the ground manifold have been inferred from the temperature dependence of absorption bands due to $^3H_6 - {}^1D_2$ and $^3H_6 - {}^1G_4$ transitions. The positions of many of the Stark components of all except one J manifold are given in Tab. 1.

Table 1. *Position of energy levels of* Tm:YAlG

Obs. energy in cm^{-1}	Center (10^{+3} cm^{-1})	Assign-ment	Calculated centers[a] (10^{+3} cm^{-1})
0, 28, 43, 270, 490	0	$^3H_6$	0
5557, 5769, 5834, 5903, 5941, 6043, 6120, 6167, 6181	5.770	$^3H_4$	5.77
8341, 8346, 8489, 8516, 8557	8.125	$^3H_5$	7.71
12604, 12634, (12701) 12739, 12746, 12882, 13113	12.611	$^3F_4$	11.81
(14641) 14652, (14662) (14666) (14674), 14685 (14692) 14701, (14715) 14722, 14742, 14748	14.543	$^3F_3$	14.36
(15171) (15178) 15188, 15236, 15256, 15282, 15424	15.112	$^3F_2$	15.02
20800, 21219, 21375, 21525, 21728, 21777	21.239	$^1G_4$	20.08
(27851) 27858, 28022, 28058	27.752	$^1D_2$	28.60
34370, 34425	34.232	$^1I_6$	34.67
35343	35.178	$^3P_0$	36.84
36399, 36428	36.248	$^3P_1$	37.50
37507	37.342	$^3P_2$	38.82

---

[a] The position of the "free ion" manifold centers have been calculated with the analytical expressions given by GRUBER and CONWAY [*23*].

4. Crystal-field analysis of $^3F_2$ and $^3H_4$manifolds

In some recent publications [*12—18*] it has been demonstrated that the splitting of J manifolds of a number of rare earth ions in YAlG could be explained on the basis of a crystalline field of tetragonal symmetry. The data on the splitting patterns of the $^3H_4$ and $^3F_2$ manifolds of Tm:YAlG suggest that the $2J+1$ fold degeneracy has been completely removed by the crystal field. The crystal field potential $V(r_k,\theta_k,\varphi_k)$ produced by the surrounding ions on the position of the k^{th} $4f$ electron of the Tm^{3+} ion gives rise to a term H_c in the total Hamiltonian. H_c can be written as:

$$H_c = -e\sum_k V(r_k,\theta_k,\varphi_k) \tag{1}$$

where $\sum_k$ is a summation over all 12 electrons. r_k is the expectation value of the radius of the $4f$ orbit. The crystal field potential is usually expanded in terms of spherical harmonics.

$$V(r_k,\theta_k,\varphi_k) = \sum_n\sum_m\sum_k B_n^m \cdot r^n \cdot Y_n^m\,(\theta_k,\varphi_k) \tag{2}$$

where B_n^m are constants and determined by the position of the neighbours around the central ion; $Y_n^m\,(\theta_k,\varphi_k)$ are spherical harmonics; $n \leqq 6$ and even for f electrons.

The pertubing Hamiltonian for Tm:YAlG can now be written as:

$$\begin{aligned} H_c = {} & \alpha A_2^0 O_2^0 + \alpha A_2^2\,(O_2^2 + O_2^{-2}) + \beta A_4^0 O_4^0 + \beta A_4^2\,(O_{21}^2 + O_4^{-2}) + \beta A_4^4\,(O_4^4 + O_4^{-4}) + \\ & + \gamma A_6^0 O_6^0 + \gamma A_6^2\,(O_6^2 + O_6^{-2}) + \gamma A_6^4\,(O_6^4 + O_6^{-4}) + \gamma A_6^6\,(O_6^6 + O_6^{-6})\ , \end{aligned} \tag{3}$$

where $A_n^m = \, < r^n > B_n^m$ with $< r^n > \, = \int [R(r)]^2 \cdot r^{n+2}\,dr$. O_n^m are angular momentum operators [*27*]. α, β and γ are operator equivalent constants [*23*]. Although all nine CF parameters should in principle be employed to reproduce the splittings patterns of the J manifolds of Tm:YAlG, presently the effect of the parameter A_6^6 is ignored.

Some of the J manifolds of trivalent rare earth ions are doubly degenerate if the ions experience a crystal field of tetragonal symmetry. For such a field $A_2^2 = A_4^2 = A_6^2 = A_6^6 = 0$. The spectra of the ions Eu^{3+} and Tb^{3+} in yttrium aluminum garnet revealed the presence of pairs of fluorescence lines and absorption bands. The number of these pairs agreed with the number of doubly degenerate Stark levels of the J manifolds mentioned above. The splitting within the pairs is thus a measure of the deviation of the CF field from pure tetragonal symmetry. Pairs of absorption bands are also observed in the spectrum of Tm:YAlG, however, the separation of the components is larger than in the case of Eu:YAlG or Tb:YAlG [13]. This is a clear indication that the deviation from tetragonal symmetry is more pronounced for Tm:YAlG than for Eu:YAlG.

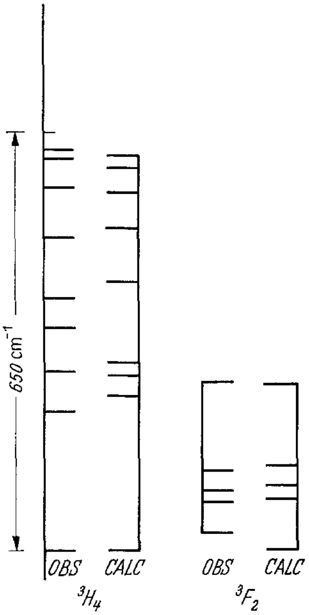

Fig. 4

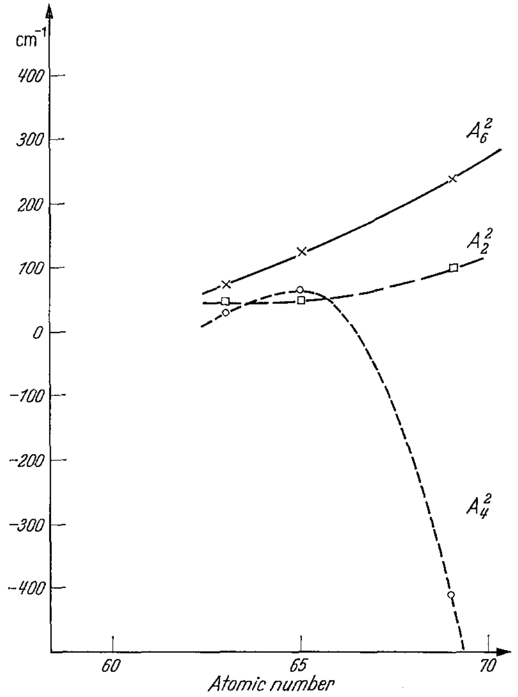

Fig. 5

Fig. 4. A comparison of observed and calculated splitting patterns of the $^3H_4$ and $^3F_2$ manifolds of Tm: YAlG

Fig. 5. Values of the parameters A_2^2, A_4^2 and A_6^2 for various trivalent rare earth ions in YAlG

In the crystal field analysis of Tm:YAlG we have made use of the data obtained for other rare earth ions in this host lattice [17]. Hence from the plot of the A_n^m's versus the atomic number Z, approximate values can be obtained for some of the second, fourth and sixth order terms of the expansion Eq. (3). In an earlier communication a method was proposed to infer values of the parameter A_n^2 ($n = 2, 4, 6$) from the splitting of a $J = 4$ manifold in a field of near tetragonal symmetry [15]. Without going into details, it can be shown that from the splitting of a $J = 2$ manifold in such a field, a relation can be obtained which enables one to compute values of A_2^2 and A_4^2. All experimental results of the Stark components of the $^3F_2$ and $^3H_4$ manifolds of Tm:YAlG have been employed to calculate the crystal field parameters. From the splitting of the $^3F_2$ manifold it became immediately clear that the values of A_2^0, A_4^0 and A_4^4 were extremely close (within 10 cm^{-1}) to the values predicted from the plot mentioned above.

The position of the centers of the doublets of the $^3H_4$ manifold were calculated with the previously computed values of A_2^0, A_4^0, A_4^4 and values of A_6^0 and A_6^4 taken again from the plot. They agreed to within a few wavenumbers with the experimental data. As far as the A_n^2 ($n = 2, 4, 6$) was concerned, only two relations in the three unknowns could be evaluated from $^3H_4$ and $^3F_2$ data. Thus for every value of, for example, A_2^2, values of A_4^2 and A_6^2 can be calculated. Together with the knowledge of the other crystal field parameter this makes it possible to cumpute the complete splitting patterns of the $^3H_4$ and $^3F_2$ manifolds. The best fit between the experimental and calculated splitting patterns of these manifolds can be seen in Fig. 4. Values of the A_n^m's uses in the computation are given in Tab. 2. The discrepancies are believed to be due to inaccurate values of the operator equivalent constants [*23*]. From a re-examination of the spectra of Eu:YAlG and Tb:YAlG values of A_2^2, A_4^2 and A_6^2 could be inferred. A comparison of these parameters of various rare earth ions in YAlG can be seen in Fig. 5. The appearance of the multiple spectra of Tm:YAlG, which was discussed in section III, and the larger values of the parameter A_2^2, A_4^2 and A_6^2 for this ion, are related to each other. They both indicate the occurence of a rather sudden change in the symmetry of the crystal field for rare earth ions in YAlG which have radii smaller than the radius of the Yttrium ion. This is in agreement with the change in the values of some of the other A_n^m's as a function of the atomic number Z of the rare earth ion in the YAlG host lattice [*17*].

Table 2. *Crystal field parameters* A_n^m *(in* cm^{-1}*) for* Tm:YAlG

A_2^0	A_4^0	A_4^4	A_6^0	A_6^4	A_2^2	A_4^2	A_6^2
270	−170	$6\,A_4^0$	32.5	$-15.2\,A_6^0$	±100	±410	±115

5. Crystal-field analysis of other Excited States

Not all the positions of the Stark levels of $^1G_4$, $^1D_2$, $^1I_6$ and $^3P_{0,1,2}$ manifolds have been located. Only four absorptions were recorded in the spectral regions where transitions to $^1D_2$ manifold levels should occur. The calculations of the splitting pattern have been carried out in different stages, each of which is shown in Fig. 6. It can be seen in that figure that with the crystal field parameters of Tab. 2, the computed overall splitting apparently approaches the value of the observed splitting of the $^1D_2$ manifold. Smaller values of the parameters A_2^2 and A_4^2 result in an even better fit. Although this calculation seems to yield the desired results, it may not be the correct analysis for this manifold. From Fig. 2 it can be seen that the absorption band at higher energy is the strongest of the group. Also the half-width of this line is about twice as large as the width of the other lines. The possibility exists that this band is a doublet and that a crystal field analysis has to be carried out corresponding to stage III of Fig. 6. The correct values of the

CF parameters are now: $A_2^0 = 287$ cm^{-1}, $A_4^0 = -222$ cm^{-1} and $A_4^4 = 60\,A_4^0$, but $A_2^2 = A_4^2 \approx 0$. For Eu:YAlG it was also concluded that the value of the parameter A_2^2 decreases with increasing energy of the excited states. We suspect that some significance has to be attached to the above because the calculated overall splitting of the $^1G_4$ manifold with CF parameters given in Tab. 2 is considerably smaller than the data indicate. Larger values of A_2^0, A_4^0, A_4^4 and probably also A_6^0 and A_6^4 are thus necessary to explain the $^1G_4$ manifold splitting.

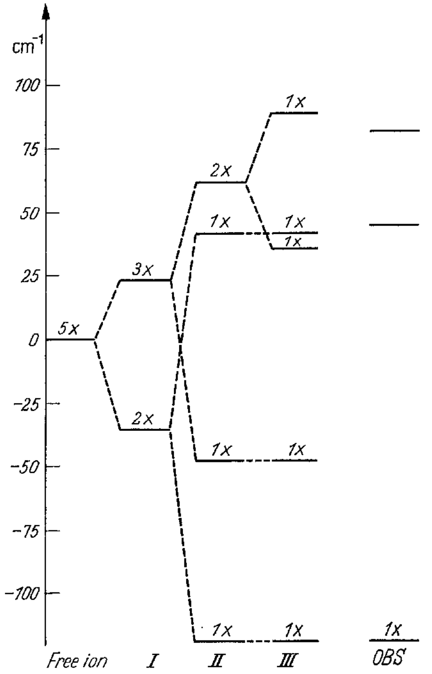

Fig. 6. The computation of the splitting pattern of the $^1D_2$ manifold of Tm: YAlG. Stage I: splitting in a crystal field of pure cubic symmetry with $A_4{}^0 = -170$ cm^{-1}; Stage II: splitting pattern in a field of tetragonal symmetry with values of *CF* parameters: $A_2{}^0 = 270$cm^{-1}, $A_4{}^0 = -170$cm^{-1}, $A_4{}^4 = 6\,A_4{}^0$; Stage III: splitting in a field of rhombic symmetry. Same *CF* parameters as in II, but now $A_2{}^2 = 100$ cm^{-1}, $A_4{}^2 = -410$ cm^{-1}. The numbers indicate the degeneracy of each level

The limited amount of experimental data on the $^3P_{0,\,1,\,2}$ manifold splittings does not allow one to obtain more information concerning the values of some of the CF parameters.

6. The positions of the centers of gravity of J manifolds

The calculation of the position of *LSJ* manifolds of a f^2 configuration has been outlined in a paper by Spedding [22]. For the f^{12} configuration of Tm^{3+} one can use the same secular equations with the only difference that the sign in front of the spin orbit interaction term ζ has to be changed. Gruber and Conway [23] who performed these calculations, obtained a plot of the energy of the *J* manifolds of Tm^{3+} as function of the ratio ζ/F_2, where F_2 is a Slater integral. From this plot the following values have been inferred for Tm:YAlG: $F_2 = 480$ cm^{-1} and $\zeta = 1248$ cm^{-1}. The centers of gravity of the "free ion" positions of the *J* manifolds of Tm^{3+} from the results of Tm:YAlG are shown in the last column of Tab. 1. The average deviation of observed and calculated centers is ± 275 cm^{-1}. F_2 decreases in value as the position of the centers of gravity of the *LSJ* manifolds increases in energy. The value of F_2 for the $^1G_4$ state does not seem to follow this trend. The position of the $^1G_4$ state depends quite drastically on the amount of intermediate coupling. This raises some questions as to the validity of the operator equivalent constants and might explain the large values of the A_n^m's which are necessary to describe the splitting pattern of the $^1G_4$ manifold of Tm:YAlG.

7. Conclusions

A crystal field analysis has been carried out for Tm^{3+} in Yttrium Aluminum Garnet. The values of the CF parameters A_n^m are in agreement with the values of some parameters of other rare earth ions in this host lattice. The symmetry of the crystal field for Tm:YAlG, however, deviates more from tetragonal symmetry than that of Eu, Tb or Nd:YAlG. There are indications that the CF parameters for excited states are not equal to the values of these parameters for lower lying states.

Acknowledgements. The author is grateful to Dr. L. G. van Uitert of the Bell Telephone Laboratories Inc. for supplying the crystals which were used in the investigations.

He also wishes to extend his thanks to Drs. Amberg and Kruus for critical reading of the manuscript.

References

[*1*] Wolf, W. P., and J. H. van Vleck: Phys. Rev. **118**, 1490 (1960).
[*2*] — M. Ball, M. T. Hutchings, M. J. M. Leask, and A. F. G. Wyatt: J. phys. Soc. Japan **17**, B-1, 443 (1961).
[*3*] Perel, J., and M. Schieber: Japan. J. Appl. Phys. **1** (1966).
[*4*] Brumage, W. H., C. C. Lin, and J. H. van Vleck: Phys. Rev. **132**, 608 (1963).
[*5*] Cohen, R. L.: Phys. Letters **5**, 177 (1963).
[*6*] Geller, S., J. P. Remeika, R. C. Sherwood, H. J. Williams, and E. G. Espimona: Phys. Rev. **A 137**, 1034 (1965).
[*7*] Schieber, M. M., C. C. Lin, and J. H. van Vleck: To be published.
[*8*] Pappalardo, R.: Z. Physik **173**, 374 (1963).
[*9*] —, and D. L. Wood: J. chem. Phys. **33**, 1734 (1960).
[*10*] Wood, D. L.: J. chem. Phys. **39**, 1671 (1963).
[*11*] Wickersheim, K. A., and R. L. White: Phys. Rev. Letters **4**, 123 (1960).
[*12*] Koningstein, J. A., and J. E. Geusic: Phys. Rev. **A 136**, 711 (1964).
[*13*] — Phys. Rev. **A 136**, 717 (1964).
[*14*] —, and J. E. Geusic: Phys. Rev. **A 136**, 726 (1964).
[*15*] — J. chem. Phys. **42**, 1423, 3195 (1965).
[*16*] Dreyfus, B., M. Veysie, and J. Verdone: J. Phys. Chem. Solids **26**, 107 (1965).
[*17*] Koningstein, J. A.: Theoret. chim. Acta (Berl.) **3**, 271 (1965).
[*18*] — Crystal field analysis of excited states of Nd:YGaG and Nd:AlG. To be published in: J. chem. Phys.
[*19*] Geller, S., and M. A. Gilles: Phys. Chem. Solids **3**, 30 (1957).
[*20*] Hutchings, M. T., and W. P. Wolf: J. chem. Phys. **41**, 617 (1964).
[*21*] Jørgensen, C. K.: Acta Chim. Scand. **9**, 540 (1955).
[*22*] Spedding, F. H.: Phys. Rev. **58**, 255 (1940).
[*23*] Gruber, J. B., and J. G. Conway: J. chem. Phys. **32**, 1178 (1960).
[*24*] Stevens, K. W. H.: Proc. Phys. Soc. (Lond.) **A 65**, 209 (1952).
[*25*] Elliott, R. J., and K. W. H. Stevens: Proc. Roy. Soc. (London) **A 218**, 553 (1953).
[*26*] Judd, B. R.: Proc. Roy. Soc. (London) **A 227**, 552 (1955).
[*27*] Baker, T. M., B. Bleaney, and W. Hayes: Proc. Roy. Soc. (London) **A 297**, 141 (1958).

Prof. J. A. Koningstein
E. W. R. Steacie Building of Chemistry
Carleton University
Ottawa, Ontario, Canada