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Spectroscopic analysis of lithium terbium tetrafluoride

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The absorption spectra of Tb^{3+} in LiTbF_4 have been recorded in the spectral interval from 4000 to 25000 cm^{-1} and for temperatures between 2.3 and 150 K. This covers the transitions from the ground multiplet 7F_6 to the multiplets 7F_3 , 7F_2 , 7F_1 , 7F_0 , and 5D_4 . The transitions were predominantly of electric-dipole nature, but small contributions of magnetic-dipole nature were seen. The crystal-field splitting was temperature dependent—the reason for this is not completely understood. No experimental evidence for a crystallographic phase transition was found. The energy levels of the ground 7F term were calculated by diagonalizing an effective spin-orbit and crystal-field Hamiltonian in an LS basis. $H = \sum \lambda_i (\vec{L} \cdot \vec{S})^i + \sum \alpha_i \sum B_{im} O_{im}$, where the parameters λ_i are functions of the spin-orbit parameter ζ and the Slater parameter F_2 . The O_{im} and α_i are Racah operators and reduced matrix elements, respectively. The rare-earth site in LiTbF_4 possesses S_4 symmetry, which allows six crystal-field parameters. ζ and the six B_{im} were varied to obtain the best agreement with the experimentally observed levels. Keeping $F_2 = 434 \text{ cm}^{-1}$ fixed, a fit with a standard deviation of 12 cm^{-1} was obtained at 10 K with the following parameters: $\zeta = 1698 \text{ cm}^{-1}$, $B_{20} = 445 \text{ cm}^{-1}$, $B_{40} = -761 \text{ cm}^{-1}$, $B_{44} = 1120 \text{ cm}^{-1}$, $B_{60} = 4 \text{ cm}^{-1}$, and $B_{64} = 761 + i609 \text{ cm}^{-1}$. Although the ground LS term of Tb^{3+} is rather isolated, the term mixing is significant, which is also the case for the multiplet mixing. Even for the ground multiplet the J mixing cannot be ignored.

I. INTRODUCTION

The characteristics of the tripositive rare-earth ions (R^{3+}) doped in LiYF_4 have been studied in numerous works. The main reason for this is the interesting optical properties of these systems.

For the rare earth heavier than Sm it is possible to grow $\text{LiY}_{1-x}\text{R}_x\text{F}_4$ crystals for any value of x . Until now, however, most of the attention has been focused on the crystals dilute in R content. Only recently, crystals dense in R have been investigated, and it has mainly been the magnetic properties which have been examined.¹⁻⁶ Especially the features of the systems in the temperature region where the ordered phase appears⁷⁻¹⁰ have been investigated.

Approximate crystal-field parameters have been determined from susceptibility and magnetization measurements,^{2,5} but only a few direct spectroscopic observations of the crystal-field splitting of the energy levels of R^{3+} in LiR_xF_4 have been made.^{8,11}

The reason why works on crystals dilutely doped with R have been predominant is that for optical applications one is often limited to such systems due to destructive R - R interaction, i.e., concentration quenching of the fluorescence. There are, however, exceptions, one of which is the $\text{LiY}_{1-x}\text{R}_x\text{F}_4$ system. Long-lived (5 msec) green fluorescence has been reported¹² from Tb^{3+} in $\text{LiY}_{0.5}\text{Tb}_{0.25}\text{Gd}_{0.25}\text{F}_4$ and measurements¹³ on Tb^{3+} in LiTbF_4 show that the lifetime of the green light is still longer than 1 msec.

Therefore, it is of interest to know in detail the

energy-level scheme of R^{3+} in the dense crystal, and here I report on the results for the whole 7F term and the lowest 5D_4 multiplet for the case of Tb^{3+} .

II. THEORY

A. Free Tb^{3+} ion

The ground configuration of the free Tb^{3+} ion has eight $4f$ electrons outside closed orbitals. The next configuration, which is a $4f^75d$, is approximately $60\,000 \text{ cm}^{-1}$ above the $4f^8$ configuration according to Dieke.¹⁴ Thus, for the lowest levels of the ground configuration, the configuration mixing is small, and for these levels it is a good approximation to do all the energy calculations within the $4f^8$ configuration.

In this configuration the ground LS term is the rather isolated 7F . The width of the 7F term is 6000 cm^{-1} and the next term, which is a 5D , is situated about $20\,000 \text{ cm}^{-1}$ above. In 5D the lowest multiplet 5D_4 is rather isolated and acts as the upper fluorescence level in Tb^{3+} . While for the 7F term the term mixing is small, this is not true for the other terms. The configuration extends to about $150\,000 \text{ cm}^{-1}$, and above $25\,000 \text{ cm}^{-1}$ the classification of the levels is somewhat uncertain.

Although the term mixing for 7F is moderate, the Landé interval rule for the spin-orbit splitting is not well fulfilled, so it is necessary to introduce even this slight mixing in the calculations. The L and S quantum numbers are in this way no longer really good quantum numbers contrary to J . The spin-orbit coupling splits the ground term in seven

TABLE I. Crystal-field splittings of J multiplets in S_4 symmetry.

J	Γ_1	Γ_2	Γ_3	Γ_4
0	1	0	0	0
1	1	0	1	1
2	1	2	1	1
3	1	2	2	2
4	3	2	2	2
5	3	2	3	3
6	3	4	3	3

multiplets with $J=0, 1, \dots, 6$, where 7F_6 is the ground multiplet.

B. Tb^{3+} ion in a crystal with S_4 symmetry

$LiTbF_4$ crystallizes in the tetragonal scheelite structure. The Tb^{3+} ion is on a site having S_4 symmetry with respect to the crystal as a whole, but almost D_{2d} symmetry with respect to the eight nearest-neighbor F^- ions. In S_4 symmetry the J multiplets split up as shown in Table I, where Γ_1 , Γ_2 , Γ_3 , and Γ_4 refer to the notation of Koster *et al.*¹⁵

The Γ_3 and Γ_4 representations are related by time-reversal symmetry, and the eigenvalues for states transforming according to these representations will therefore be degenerate. In the following they will be named by $\Gamma_{3,4}$.

The crystal field mixes the multiplets slightly (less than 10%), causing J to be not exactly a good quantum number. Therefore, it is necessary to take J mixing into account in the calculations of the energies of the levels. This, however, does not change the transformation properties of the associated states.

C. Selection rules for S_4 symmetry

The two most significant contributions to the transitions between the levels are the electric and magnetic dipole interaction with the applied electromagnetic radiation. The electric dipole transitions are parity forbidden within a single configuration, so they occur only due to configuration mixing. Still, for the rare earths they are, in general, stronger than the magnetic dipole transitions.

Thus, calculation of transition strengths requires knowledge of configuration mixing, which is difficult to determine. On the contrary, separation of allowed and forbidden transitions can be done entirely on group-theoretical grounds. The selection rules for electric and magnetic dipole transitions in S_4 symmetry are given in Table II.

TABLE II. Selection rules in S_4 symmetry: (a) electric dipole transitions, (b) magnetic dipole transitions. The π spectrum has the electric polarization parallel to the c axis. The σ spectrum has the electric polarization perpendicular to the c axis.

(a)	Γ_1	Γ_2	$\Gamma_{3,4}$
Γ_1		π	σ
Γ_2	π		σ
$\Gamma_{3,4}$	σ	σ	π
(b)	Γ_1	Γ_2	$\Gamma_{3,4}$
Γ_1	σ		π
Γ_2		σ	π
$\Gamma_{3,4}$	π	π	σ

D. Model Hamiltonian

As stated in Secs. IA–IC the configuration mixing is neglected in the calculations, whereas the mixing of LS terms and of J multiplets is taken into account by using a generalized spin-orbit Hamiltonian and by diagonalizing the entire LS matrix of the ground term.

Following Karayianis¹⁶ the effective spin-orbit operator to order p is given by

$$H_{so} = \sum_{i=1}^p \lambda_i (\vec{L} \cdot \vec{S})^i, \quad (1)$$

where the parameters λ_i are given by

$$\lambda_i = \zeta \sum_{m=i}^p \left(\frac{\zeta}{F_2} \right)^{m-i} \Lambda_{im}(N), \quad (2)$$

where ζ is the spin-orbit parameter and F_2 is a Slater parameter. $\Lambda_{im}(N)$, where N is the number of f electrons, are reduced matrix elements. They depend on the radial part of the wave functions only through the ratios F_4/F_2 and F_6/F_2 , which are wave function insensitive. The parameters Λ are given by Karayianis.¹⁶

The crystal-field operator is given by

$$H_c = \sum_i \alpha_i(L) \sum_m B_{im} O_{im}(L), \quad (3)$$

where $O_{im}(L)$ are Racah operator equivalents and $\alpha_i(L)$ are reduced matrix elements. In S_4 symmetry the only nonvanishing crystal-field parameters are B_{20} , B_{40} , B_{44} , B_{60} , and B_{64} , where B_{44} and B_{64} are complex. By proper choice of the coordinate system one can make one of them—for example, B_{44} —real, leaving six crystal-field parameters to be determined.

III. EXPERIMENTAL PROCEDURE

A. Crystal preparation

Single crystals of pure LiTbF_4 and of LiYF_4 doped with 10% Tb were grown by spontaneous crystallization from the melt as described by Laursen and Holmes.¹⁷ The crystals were oriented by x-ray technique. Slabs about 1 mm thick were cut with faces perpendicular to an a axis for the polarized spectra and with faces perpendicular to the c axis for the axial spectrum. The slabs were mounted so that the angle between the crystal axis and the polarization axis was less than 2° (in fact, the spectra were rather insensitive to small deviations between the directions of the polarization and the crystal axes).

B. Apparatus

The absorption spectra were recorded using a modified Zeiss MM12 double monochromator. In the relevant spectral region it was possible to achieve a spectral resolution of 6 cm^{-1} . A Glan prism was used as polarizer.

For low-temperature measurements two cryostats were available. The first one, where the crystal was placed directly in the pumped liquid helium, was used for temperatures below 4.2 K. The other one, where the crystal was placed in a stream of helium gas, was used for temperatures above 4.2 K. In the first cryostat the temperature was determined from the He pressure. In the second the temperature was measured with an Au-Fe vs Cromel thermocouple, which had a resolution of 1 K. The temperature stability of the flow cryostat was $\pm 1 \text{ K}$.

C. Absorption spectra

The absorption spectra for polarized light for Tb^{3+} in LiTbF_4 were recorded in the region from 4000 to $25\,000 \text{ cm}^{-1}$ ($2.5\text{--}0.4 \mu\text{m}$), which covers the transitions from the 7F_6 ground multiplet to the four highest multiplets of the ground term ($J = 0, 1, 2, 3$) and to the lowest 5D_4 multiplet.

The spectra were recorded for different temperatures between 2.3 and 150 K. However, for temperatures higher than 100 K, the positions of most of the lines were difficult to determine because the spectra were smeared out due to overlapping with many new lines.

1. Transitions within the ground term

At 10 K, which is well above the Curie point $T_C = 2.87 \text{ K}$,⁷ only the ground state, which is a quasi-doublet made up of two levels transforming according to Γ_2 of S_4 (Laursen and Holmes¹⁷), is populated. As shown in Fig. 1 one finds at this tempera-

FIG. 1. Absorption spectra at 10 K for transition from the ground state to 7F_3 , 7F_2 , 7F_1 , and 7F_0 of Tb^{3+} in LiTbF_4 . The π -polarized, the σ -polarized, the axial, and the reference spectrum are shown. The arrows indicate the magnetic dipole transitions.

ture for each of the two polarizations four strong absorption lines in the spectral region, where transitions to the 7F_0 - 7F_3 multiplets are expected.

This is in agreement with the transitions being of electric dipole nature. π transitions from the Γ_2 ground levels to $\Gamma_1(^7F_0)$, $\Gamma_1(^7F_1)$, $\Gamma_1(^7F_2)$, and $\Gamma_1(^7F_3)$ lead to four lines. σ transitions from Γ_2 to $\Gamma_{3,4}(^7F_1)$, $\Gamma_{3,4}(^7F_2)$, and two $\Gamma_{3,4}(^7F_3)$ give four lines, while the Γ_2 to Γ_2 transitions are not electric dipole allowed in S_4 symmetry.

In addition to these strong lines there are also some weak lines in the spectra. The transitions from Γ_2 to $\Gamma_{3,4}$ can be seen in the π spectrum, whereas the Γ_2 to Γ_1 transitions cannot be seen in the σ spectrum. This indicates that there are also magnetic dipole transitions present—and that the lines are not due to misorientation of the crystal (compare with Table II). The magnetic dipole transitions from Γ_2 to Γ_2 are allowed in the σ spectrum. Experimentally one also finds two weak lines in the σ spectrum corresponding to two of the four possible Γ_2 to Γ_2 transitions. The two other lines should be found in regions, where they are difficult to recover due to the strong lines and noise. A few other very weak lines in the spectra must be due to impurities in the crystal.

As a verification of the nature of the transitions, the axial spectrum was recorded. In the axial spectrum one should find the electric dipole transitions of the σ spectrum and the magnetic dipole transitions of the π spectrum. Thus, in the axial spectrum only Γ_2 to $\Gamma_{3,4}$ transitions are to be seen. This is what is found experimentally (see

TABLE III. Experimental positions of the 7F levels, which it has been possible to determine, and calculated positions of all the levels. All values are in cm^{-1} .

J	Γ	Experimental values at $T =$					Calculated values (10 K)
		10 K	40 K	50 K	60 K	100 K	
0	1	5917	5917	5915	5913	5909	5923
1	3, 4	5690	5689	5688	5685	5681	5714
	1	5592	5591	5590	5588	5586	5603
2	2	5385					5371
	3, 4	5285	5284	5283	5282	5278	5285
	2	5067					5064
	1	5035	5035	5034	5034	5033	5024
3	2	4532					4536
	3, 4	4524	4524	4522	4522	4516	4528
	1	4473	4473	4472	4472	4470	4478
	3, 4	4406	4406	4405	4404	4404	4404
	2	4333					4324
4	1						3845
	3, 4						3630
	2						3572
	1						3539
	3, 4						3400
	2						3399
	1						3325
5	2						2403
	3, 4						2390
	1						2339
	3, 4						2162
	1						2148
	1						2130
	3, 4						2089
	2						2087
6	2						401
	3, 4						390
	1						376
	1			217			223
	3, 4			166			175
	2			136			135
	1			124			119
	3, 4			107			108
	2			0			2
	2	0	0	0	0	0	0

Fig. 1).

At higher temperatures more levels of the ground multiplet become populated. Already at about 25 K the transitions from the first excited level ($\Gamma_{3,4}$) can be seen in the spectra, even if the relative population of this level is only around 3×10^{-3} . As the temperature is further increased, more and more lines appear in the spectra. By analyzing the spectra at temperatures up to 100 K, it has been possible to determine the energies of the seven lowest levels of the ground multiplet and

of the two remaining Γ_2 levels of 7F_3 and 7F_2 . The positions of the experimentally determined lines of the ground LS term are listed in Table III.

The experimental linewidths of the electric dipole transitions from the ground quasidoublet are 10–20 cm^{-1} , with an instrumental resolution of about 6 cm^{-1} . The lines are not much broader at higher temperatures, but the lines are getting weaker due to depopulation of the ground state, and some of them become disturbed by new lines.

Some of the lines, which according to the theory

FIG. 4. Experimental position of the transition from the ground state to 7F_0 of Tb^{3+} in LiTbF_4 as a function of the temperature around T_C , where LiTbF_4 orders magnetically.

2.7 to 3.0 K. This is in agreement with the fact that the crystal orders ferromagnetically below 2.87 K.⁷ As shown in Fig. 4 the shift of the line corresponding to absorption to 7F_0 is $3.5 \pm 1 \text{ cm}^{-1}$ at 2.3 K. The ordering causes the ground quasi-doublet to split proportional to the magnetization into an $M_J = +6$ and an $M_J = -6$ level, of which only the lowest is well populated.

For an Ising system the shift at 0 K should be equal to $k_B \theta$, where θ is the asymptotic paramagnetic Curie temperature, assuming that in the ordered phase the domains are long thin needles along the c axis. Holmes *et al.*¹ give $\theta = 3.60 \pm 0.1 \text{ K}$ ($\theta_{\text{dipolar}} = 3.97 \text{ K}$) and thus a shift of $2.5 \pm 0.1 \text{ cm}^{-1}$ is expected. The observed shift seems somewhat higher than this, similar to what has been

FIG. 5. π - and σ -polarized absorption spectra at 10 K for the transitions from the ground state to 5D_4 of Tb^{3+} in LiTbF_4 .

TABLE IV. Experimental positions in cm^{-1} of the 5D_4 levels.

J	Γ	Experimental values (10 K)
4	2	20 666
	1	20 654
	3, 4	20 641
	2	20 589
	1	20 580
	3, 4	20 571
	1	20 561

found in LiHoF_4 (Battison *et al.*⁹) in which case the deviation might be explained by the large hyperfine interaction in Ho^{3+} . This is not possible in the case of Tb^{3+} in LiTbF_4 , where the total hf splitting is 0.3 cm^{-1} .

2. Transitions to the 5D_4 multiplet

In the region around $20\,600 \text{ cm}^{-1}$ three lines in the π spectrum and two lines in the σ spectrum were found at low temperatures, as shown in Fig. 5. They are due to transitions from the ground state to the three Γ_1 levels and two $\Gamma_{3,4}$ levels of the 5D_4 multiplet. The two Γ_2 levels of 5D_4 were found by examining the warm-up spectra. The experimental line positions of 5D_4 are listed in Table IV.

IV. CALCULATIONS

A. Fitting procedure

The energy levels of the ground LS term were calculated using the model described in Sec. IID. The six crystal-field parameters and the spin-orbit parameter ζ were varied, until the best agreement with the 19 experimentally observed levels was obtained.

It is not relevant to let F_2 vary freely, since this parameter primarily must give the correct configuration splitting. However, the fitting was tried with several F_2 values between 434 cm^{-1} given by Wybourne¹⁸ and the "smoothed" value 417 cm^{-1} given by Karayianis.¹⁶ The result was not very sensitive to the F_2 value, but the best initial fit was obtained with $F_2 = 434 \text{ cm}^{-1}$. This value was used in the remaining calculations.

In order to get an LS term splitting in good agreement with the experiments, it was necessary to use an effective spin-orbit Hamiltonian including three terms [$p = 3$ in Eq. (1)]. Note, however, that the number of fitting parameters is independent of the number of these terms. As experimental data for the 7F_5 and 7F_6 multiplets have not been

obtained, it is especially important not to use more free parameters in the fitting procedure than dictated by the underlying physics.

Setting $\text{Im}B_{64}$ equal to zero and fitting only five crystal-field parameters gave almost as good agreement as when all six crystal-field parameters were allowed to vary freely. This is what might be expected from the fact that the rare-earth ion is on a site of nearly D_{2d} symmetry, where all crystal-field parameters should be real. The final fittings, however, were done using all six crystal-field parameters.

B. Results

The fitting procedure was carried out at five temperatures between 10 and 100 K. (For the lines only known experimentally at one temperature, a temperature dependence similar to the other lines was assumed.) As shown in Fig. 6 the crystal-field parameters were strongly temperature dependent. This was not the case for the ζ parameter. ζ was found to be 1698 cm^{-1} for all temperatures lower than 100 K, where it was 1700 cm^{-1} . The uncertainty of ζ was less than 2.5 cm^{-1} . Wybourne¹⁸ gives a free-ion value of 1705 cm^{-1} for Tb^{3+} . In crystals the spin-orbit coupling strength may differ from the free-ion value due to the coupling to the crystal field.

In the fittings a standard deviation of 12 cm^{-1} was obtained. The standard deviation is given by

$$S = \left(\sum_{i=1}^{19} \frac{(\Delta E_i)^2}{19-6} \right)^{1/2}. \quad (4)$$

The calculated energy levels at 10 K are given in Table III and the crystal-field parameters at 10 K in Table V. The calculated position of the lowest $\Gamma_{3,4}$ level of the ground multiplet is 108 cm^{-1} at 10 K and 100 cm^{-1} at 100 K. Holmes *et al.*²

FIG. 6. Crystal-field parameters at the Tb^{3+} site in LiTbF_4 as a function of temperature. The sign of $\text{Im}B_{64}$ is unknown. The lines through the points are only for visual aid.

TABLE V. Crystal-field parameters in cm^{-1} . It is not possible to determine the sign of $\text{Im}B_{64}$ with the methods referred to here. The first column gives the values obtained in this work, when the parameters are fitted inside the 7F term. The uncertainties correspond for the given model to an uncertainty on the experimental data of about 5 cm^{-1} . The second column gives the values obtained by Holmes *et al.* (Ref. 2) by neutron-scattering and by susceptibility measurements. The third column gives the values obtained in this work, when the parameters are fitted inside the 7F_6 multiplet.

	Fitted to the 7F term at 10 K	Fitted to the susceptibility	Fitted to the 7F_6 multiplet at 10 K
B_{20}	445 ± 10	316 ± 30	474
B_{40}	-761 ± 30	-673 ± 130	-433
B_{44}	1120 ± 40	628 ± 130	1080
B_{60}	4 ± 200	-338 ± 250	64
$\text{Re}B_{64}$	761 ± 130	82 ± 60	744
$ \text{Im}B_{64} $	609 ± 130	92 ± 60	286

find the same levels at 106 and 98 cm^{-1} , respectively, by inelastic neutron scattering. Good agreement is also found for the next $\Gamma_{3,4}$ level, where the calculated values are 175 and 165 cm^{-1} , and the experimental values from the inelastic neutron scattering are 169 and 161 cm^{-1} .

V. DISCUSSION

A. Crystal field

As shown in Table V the spectroscopically determined B parameters at 10 K differ rather much from those found by Holmes *et al.*² by fitting to the susceptibility in the temperature range 5–300 K and to a few levels of the ground multiplet. The temperature dependence found (Fig. 6) indicates that a detailed comparison between these two sets of parameters cannot be undertaken.

The spectroscopically determined B parameters give splittings of the ground multiplet—when diagonalizing within the whole LS term—which is in good agreement with the seven lowest levels, which it has been possible to determine experimentally. As seen from Fig. 7 the calculated positions of both the remaining three high-lying levels as well as the seven lower-lying levels are in semiquantitative agreement with the experimental splittings for Tb^{3+} doped in CaWO_4 given by Wortman.¹⁹

On the other hand, when diagonalizing only within the ground multiplet, but with B parameters found by fitting to the whole LS term, some of the levels come out wrong, differing as much as 50 cm^{-1} from the experimental values. This indicates

FIG. 7. Splittings of the ground multiplet of Tb³⁺. (I) Experimentally determined for Tb³⁺ doped in CaWO₄ (Ref. 19). (II) Calculated for Tb³⁺ in LiTbF₄ by diagonalizing the entire *LS* matrix of the ground term. (III) Calculated for Tb³⁺ in LiTbF₄ with the same parameters as in II, but diagonalizing only the *J* matrix of the ground multiplet. (IV) Calculated for Tb³⁺ in LiTbF₄ with the parameters of Holmes *et al.* (Ref. 2).

that even for the ground multiplet, *J* mixing is significant. If the *B* parameters are fitted inside the ground multiplet only, the *B* values given in the third column of Table V are obtained. (Because of six parameters being available for fitting of 10 levels, the fit is perfect to within 1 cm⁻¹.) It is clearly seen that the set of *B* parameters are model dependent to a degree which is significant in relation to a quantitative discussion of experimentally determined properties. Still, it is remarkable that the order of all the levels is the same for all four cases depicted in Fig. 7. This must be due to the circumstance that the different interactions are of such relative strengths that the *LS* description as well as the *J* description are both good enough for a quantitatively correct discussion of at least the lowest multiplet.

When the splitting of the ground multiplet is calculated using the parameters given by Holmes *et al.*,² it is clear from Fig. 7 that the three highest levels have too low energies, whereas the others fit very well.

The last fact is mainly due to the clamping of the lowest $\Gamma_{3,4}$ levels to the positions obtained by

the neutron-scattering results, whereas the low value of the total splitting is connected to the low value of B_{20} . B_{20} is, however, almost tied to the difference between the reciprocal susceptibilities $\chi_{||}^{-1}$ and $\chi_{\perp}^{-1}$ at "high" temperatures. At 300 K this high-temperature limit is approached, and therefore the value of B_{20} , obtained by Homes *et al.*,² can be regarded as approximately correct for $T \approx 300$ K. In this connection it is noteworthy that if the temperature dependence of B_{20} observed in the spectroscopic results persists up to room temperature, the value of B_{20} will be lowered to about 360 cm⁻¹ at this temperature. Yet, because of the significant but partly unknown temperature variation of all the *B*'s, we shall defer at this stage to make a detailed comparison with the susceptibility data in the whole temperature range 4–300 K.

The calculated splitting Δ in the paramagnetic phase of the two Γ_2 levels spanning the ground quasidoublet is 1.9 cm⁻¹, which is higher than the values given by Holmes *et al.*² (1.3 cm⁻¹), by Magariño *et al.*¹¹ (≈ 1 cm⁻¹), and (for Tb³⁺ diluted in LiYF₄) by Laursen and Holmes¹⁷ (0.93 cm⁻¹). Calculation with *B* parameters fitted inside the ground multiplet gives a value of 1.5 cm⁻¹ for Δ .

The splitting Δ is, for Tb³⁺ in a Scheelite-crystal, strongly sensitive primarily to $\text{Im}B_{64}$. If a value of $\Delta \approx 1$ cm⁻¹ is considered the most reliable, this will therefore point to a somewhat lower value of $\text{Im}B_{64}$ than that obtained from the term fitting.

B. Temperature dependence of the spectrum

Four features concerning the temperature dependence of the level positions have been found experimentally. (i) A small shift of the lines takes place in a narrow temperature region around 50 K. (ii) The crystal-field splittings show a large continuous decrease in the temperature region 50–100 K. There is indication that this decrease continues to higher temperatures. (iii) The temperature effects are much less pronounced in a diluted system. (iv) At no temperature do the data indicate that additional crystal-field parameters are necessary in order to explain the level positions. This means that a transition to a lower rare-earth site symmetry is very unlikely.

Als-Nielsen *et al.*⁷ have determined the structure of LiTbF₄ at 100 K and at room temperature by neutron diffraction. They find that the crystal structure is very stable, although one coordinate of the fluorine ions is changed about 0.25% from 100 K to room temperature. The thermal expansion is small and anisotropic. The structure has not been determined below 100 K, where the spectroscopic data indicate that something more inter-

esting happens.

In the scheelite structure (space group $I4_1/a$) there exist three degrees of freedom in the fluorine positions. The first fluorine can—apart from physical constraints—be placed arbitrarily in the unit cell, whereas the remaining fluorines are fixed by the symmetry requirements. Further the fluorines probably give the dominant contribution to the crystal-field energy of the $4f$ electrons of the R^{3+} ions. This coupling, together with the possibility of changing the fluorine positions without breaking the space-group symmetry, should in general (i.e., for all LiRF_4 systems) lead to temperature-dependent properties. The magnitude of the effect is difficult to predict, but qualitatively a smooth temperature dependence might be expected.

The temperature dependence of the experimental data for LiTbF_4 indicates, however, the existence of a characteristic transition temperature T_i around 50 K. The nature of the transition is not clear. Speculatively, the continuous character of the transition and the constancy of the B 's below T_i

might be caused by the fluorine system being trapped in positions corresponding to local D_{2d} symmetry at the R^{3+} sites. This is possible without breaking the global S_4 symmetry of the R^{3+} site or the space-group symmetry. However, there would still exist two degrees of freedom for configurational changes in the fluorine system. Finally the cooperative nature of the phenomena—which is indicated by the weakening of the effect in a diluted system—is understandable, because each fluorine ion makes significant contributions to the crystal-field energy on at least two R^{3+} sites.

In contrast to the temperature dependence observed for LiTbF_4 , Battison *et al.*⁹ found no temperature dependence for Ho^{3+} in LiHoF_4 for those transitions which they examined.

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