Predicting the position of the spin-forbidden band for Tb^{3+} ions in crystal hosts

Predicting the position of the spin-forbidden band for Tb³⁺ ions in crystal hosts

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Abstract

The energy difference ΔE between the spin-allowed and spin-forbidden states of Tb³⁺ in crystals is studied. The environmental factor h_e representing the character of the host is redefined by using the chemical band of complex crystals. The relationship between h_e and ΔE is found to be a linear relation. The results show that the energy difference between the spin-forbidden and spin-allowed states for Tb³⁺ ions in crystals can be predicted from the environmental factor.

1. Introduction

Recently, a lot of studies on the ultraviolet (UV) and vacuum ultraviolet (VUV) spectroscopic characteristics of $4f^8$–$4f^7 5d$ transitions of the Tb³⁺ ions in inorganic compounds have been reported [1–5]. The positions of the energy levels of the $4f^7 5d$ electronic configuration depend strongly on the host; they may change by several thousands of wavenumbers among different compounds. In the Tb³⁺ absorption spectra or excitation spectra, a broad band that is assigned to the spin-allowed fd transition can be observed. In general, the band is constituted of several broad peaks because of the crystal field splitting of the excited energy levels. In addition, in some hosts, a weak band can be observed on the lower-energy side of the broad band, which is assigned to a spin-forbidden transition [6]. Up to now, there have been few theoretical reports on the spin-forbidden transition, but it is important for analysing the spectroscopic characteristics of $4f^8$–$4f^7 5d$ transitions of the Tb³⁺ ions.

In the free ion state, the energy level structure of the $4f^7(^8S)5d$ configuration is relatively simple, only ^8S from $4f^7$ coupling with d of ^9D_J (higher-spin state $S = 4$) and ^7D_J (lower-spin state $S = 3$). The transition between the ground state $^7F_6$ ($S = 3$) and the higher-spin fd state is spin forbidden; its band is weaker than the fully allowed fd band. In addition, there are other peaks from f–f transitions of the $4f^8$ configuration in the band range. Hence, it is difficult to observe and analyse the weak spin-forbidden band. Dorenbos [7, 8] collected data

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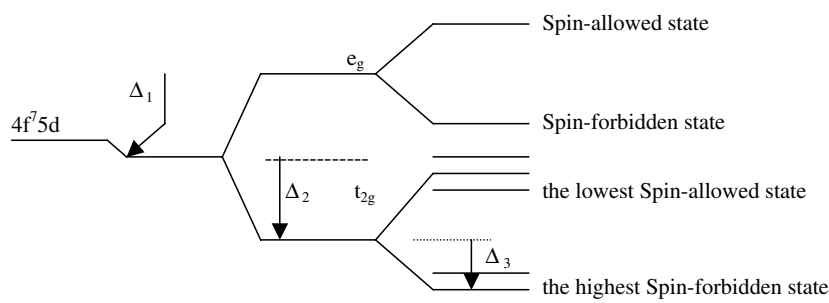[1] Author to whom any correspondence should be addressed.

Figure 1. A schematic energy level diagram for the Tb^{3+} ion in a cubic crystal field.

on the position of the most intense spin-forbidden transition band for Tb^{3+} in a wide variety of inorganic compounds, and gave an average value of the energy difference between the lowest spin-allowed fd and the most intense spin-forbidden state bands as 6300 ± 900 cm^{-1} for 19 compounds. But the values of ΔE are very different for the various compounds; for example $\Delta E = 3400$ cm^{-1} for $LaPO_4$ [7] and $\Delta E = 8177$ cm^{-1} for $YLiF_4$ [9]. For any compound, the average value cannot be used to predict the ΔE value and the position of the weak spin-forbidden band of Tb^{3+} cannot be determined. In fact, the value of ΔE is closely connected with the crystal field environment surrounding Tb^{3+}, which varies with microscopic parameters.

In this paper, the environmental factor of the host, h_e, is redefined and calculated by using chemical bond theory of complex crystals [10, 17]; the relation between h_e and ΔE is studied. The calculated values of ΔE are in reasonable agreement with the experimental values given by other workers [4, 5, 8, 24, 25]; the maximum error between the experimental and calculated values for $Y_3Al_5O_{12}$ is 451 cm^{-1}. The positions of the spin-forbidden transition of Tb^{3+} in inorganic crystals can now be predicted.

2. Analysis and theoretical method

In general, the positions of the energy levels in crystals are lower than in the free ion state. Figure 1 displays the energy level diagram of the $4f^7 5d$ configuration of Tb^{3+} in a cubic crystal field. It is shown that the energy level decline results from three factors for Tb^{3+}. Δ_1 denotes the decline of the energy centroid of the d orbit, Δ_2 denotes the decline due to crystal field splitting, and Δ_3 denotes changes of all relevant interactions of ^7D_J or ^9D_J terms except those associated with the crystal field. Evidently, Δ_1 and Δ_2 do not contribute to ΔE. In Δ_3, the relevant interactions include primarily Coulomb interaction between 4f and 5d electrons, spin–orbit interaction of 4f electrons, and spin–orbit interaction of 5d electrons. The two latter interactions undergo small changes compared with the former for the lowest spin-allowed fd and the most intense spin-forbidden states in different crystals. So the energy difference ΔE is due to the change of the Coulomb interaction between 4f and 5d electrons, which can be shown from their energy expressions [11]:

$$E_{sa} = 3G_1 + 12G_3 + 66G_5 \tag{1}$$
$$E_{sf} = -21G_1 - 84G_3 - 462G_5 \tag{2}$$

where E_{sa} and E_{sf} denote the Coulomb interaction between the 4f and 5d electrons for ^7D and ^9D terms respectively; G_1, G_3, G_5 are exchange integral parameters of the Coulomb interaction, whose values in the free ion state have been given in [12]. The energy difference

can be denoted as follows:

$$\Delta E = E_{\mathrm{sa}} - E_{\mathrm{sf}} = 24G_1 + 96G_3 + 528G_5. \tag{3}$$

If the parameters G_1, G_5 are replaced with G_3 by means of the ratios $G_1/G_3 = 7.788$, $G_5/G_3 = 0.144$ [12], expressions (3) are changed to

$$\Delta E = 358.94G_3. \tag{4}$$

The values of G_K ($K = 1, 3, 5$) are different in different hosts because of the nephelauxetic effect [13], which is related to the reduction of the interelectron repulsion between the d and f electrons. According to Jørgensen's suggestion, the nephelauxetic ratio β between the phenomenological value of the exchange integral parameter of Tb^{3+} in the host and that foe the free ion can be written [13] as

$$\frac{G_3}{G_3^0} = \beta = 1 - kh_{\mathrm{e}} \tag{5}$$

where G_3^0 is the exchange integral parameter for the free ion state, k is a factor depending only on the central atom, and h_{e} is a factor depending only on the ligands.

Hence,

$$\begin{aligned} G_3 &= \beta G_3^0 \\ \Delta E &= 358.94\beta G_3^0 = \beta\,\Delta E^0 = \Delta E^0 - kh_{\mathrm{e}}\,\Delta E^0 \end{aligned} \tag{6}$$

where ΔE^0 is a constant, denoting the energy difference between ^7D and ^9D states in the free ion; k is also constant in any crystal for Tb^{3+}. Thus, the relationship between h_{e} and ΔE is found to be a linear relation.

Our group has given the expression for h_{e} in the past [14]. Considering that the electric charge of ligands is different in different crystals, we redefined the environmental factor:

$$h_{\mathrm{e}} = \left[\sum f_{\mathrm{c}}(i)\alpha(i)Q(i)^2 \right]^{1/2} \tag{7}$$

where $f_{\mathrm{c}}(i)$ is the fractional covalency of the chemical bond from Tb^{3+} to the ith ligand, $\alpha(i)$ is the polarizability of the ith chemical bond volume, $Q(i)$ is the charge presented by the ith neighbouring anion in the bond subformula. The latter can be calculated using chemical bond theory of complex crystals; the detailed theoretical method can be found elsewhere [10, 17]. In this paper, only a brief description is given.

According to the chemical bonding of complex crystals, in a complex crystal $A_aB_bD_dG_g$ (crystal molecular formula) any kind of chemical bond A–B can be written as:

$$\frac{N(\mathrm{B}-\mathrm{A})\cdot a}{N_{\mathrm{CA}}}\mathrm{A}\frac{N(\mathrm{A}-\mathrm{B})\cdot b}{N_{\mathrm{CB}}}\mathrm{B} \tag{8}$$

where A, B, D, and G represent the different constituent elements in the crystal formula and a, b, d, and g represent the number of the corresponding elements. $N(\mathrm{I}-\mathrm{J})$ is the number of I ions in the coordination group of a J ion. N_{CA} and N_{CB} are the nearest-coordination numbers for each element in the crystal. In a subformula equation of a complex crystal, the charge Q presented by each coordination anion can be obtained from the valence conservation and electric neutrality of the subformula.

Having listed the subformula equation of a complex crystal and given the charge presented by each ion, we can obtain the number of effective valence electrons of each ion:

$$(Z_{\mathrm{A}}^{\mu})^* = Z_{\mathrm{A}}^{\mu}q_{\mathrm{A}}^{\mu}. \tag{9}$$

Z_A^μ is the number of valence electrons of the A ion; q_A^μ is the effective charge of each valence electron of each A ion. The effective valence electron density associated with the bond μ is

$$(N_e^\mu)^* = (n_e^\mu)^* / v_b^\mu \tag{10}$$

where

$$(n_e^\mu)^* = (Z_A^\mu)^* / N_{CA}^\mu + (Z_B^\mu)^* / N_{CB}^\mu \tag{11}$$

$$v_b^\mu = (d^\mu)^3 \Big/ \sum_v (d^\mu)^3 N_b^v. \tag{12}$$

v_b^μ is the chemical bond volume of type-μ bonds; d^μ is the nearest-neighbouring distance. According to the PV theory [15], the susceptibility of any bond is described as

$$\chi^\mu = \frac{1}{4\pi} \left[\frac{\hbar \Omega_p^\mu}{E_g^\mu} \right]^2. \tag{13}$$

Ω_p^μ is the plasma frequency

$$(\Omega_p^\mu)^2 = [4\pi (N_e^\mu)^* e^2 / m] D_\mu A_\mu \tag{14}$$

where D_μ and A_μ are the correction factors defined in [16]. e and m are the electronic charge and mass respectively.

In equation (2), E_g^μ is the average energy band gap between the bonding and antibonding states, and can be separated into homopolar E_h^μ and heteropolar C^μ parts:

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \tag{15}$$

where

$$E_h^\mu = \frac{39.74}{(d^\mu)^{2.48}}, \tag{16}$$

$$C^\mu = 14.4 b^\mu \exp(-k_s^\mu r_0^\mu) \left[\frac{(Z_A^\mu)^*}{r_0^\mu} - n \frac{(Z_B^\mu)^*}{r_0^\mu} \right] \tag{17}$$

where n is the number ratio of two elements B and A in the subformula. $r_0^\mu = d^\mu / 2$; $\exp(-k_s^\mu r_0^\mu)$ is the Thomas–Fermi screening factor;

$$k_s^\mu = \left(\frac{4 k_F^\mu}{\pi a_B} \right)^{1/2}; \tag{18}$$

$$k_F^\mu = [3\pi^2 (N_e^\mu)^*]^{1/3}; \tag{19}$$

a_B is the Bohr radius. b^μ is a correction factor depending on the crystal structure. If the refractive index of a crystal is known, the values of b^μ and C^μ can be obtained by using equations (13), (15), (17) and the following equation:

$$\chi = (\varepsilon - 1)/4\pi = \sum_\mu F^\mu \chi^\mu = \sum_\mu N_b^\mu \chi_b^\mu \tag{20}$$

where ε is the dielectric constant, which can be obtained from the index of refraction, n ($\varepsilon = n^2$). F^μ is the fraction of bonds of type μ composing the crystal. χ is the total linear susceptibility of a crystal.

The fractional ionicity f_i^μ and covalence f_c^μ of the individual bond can be determined as

$$f_i^\mu = \frac{(C^\mu)^2}{(E_g^\mu)^2} \qquad f_c^\mu = \frac{(E_h^\mu)^2}{(E_g^\mu)^2}. \tag{21}$$

According to the Lorentz formula,

$$\frac{(\varepsilon^\mu - 1)}{(\varepsilon^\mu + 2)} = \frac{4}{3} \pi \alpha_0^\mu. \tag{22}$$

Table 1. The experimental and calculated values of the energy difference ΔE (10^3 cm^{-1}).

Crystal	Site of substitution	ε^{a}	h_e	$\Delta E_{exp}{}^{b}$	$\Delta E_{cal}{}^{c}$
$LiYF_4$	Y^{3+}	2.11	0.20	8.18	8.21
CaF_2	Ca^{2+}	2.06	0.39	7.93	7.65
YPO_4	Y^{3+}	2.96	0.62	7.37	6.97
$K_3La(PO_4)_2$	La^{3+}	2.72*	0.64	7.11	6.91
YBO_3	Y^{3+}	2.89*	0.53	7.04	7.24
$Y_3Ga_5O_{12}$	Y^{3+}	3.71	0.79	6.10	6.47
$Y_3Al_5O_{12}$	Y^{3+}	3.31	0.74	6.17	6.62
$YAl_3B_4O_{12}$	Y^{3+}	3.06*	1.41	4.83	4.64
$YAlO_3$	Y^{3+}	3.71	0.89	—	6.18
$LiLuF_4$	Lu^{3+}	2.08*	0.22	—	8.15

[a] $\varepsilon = n^2$, dielectric constant; n: index of refraction; *: estimate values.
[b] ΔE_{exp}: the experimental values of ΔE.
[c] ΔE_{cal}: the calculated values of ΔE.

The polarizability coefficient of the μ-bond, α_0^{μ}, can be obtained; this denotes the polarizability of the μ bond per cubic ångström. The polarizability of the type-μ bond volume can be written as

$$\alpha_b^{\mu} = v_b^{\mu}\alpha_0^{\mu}. \tag{23}$$

If the crystal structure and the refractive index are known, the environmental factor h_e can be calculated by using the above chemical bond theory of complex crystals. For example, in $LiYF_4$, the ions Tb^{3+} occupy the Y^{3+} site. On the basis of the detailed cell parameters of $LiYF_4$ [18], we can calculate the bond lengths of the Y–F bond and the Li–F bond, and the coordination numbers of F, Y, and Li ions, which are 3, 8, and 4 respectively. $LiYF_4$ can be decomposed using equation (2):

$$LiYF_4 = YF_{8/3} + LiF_{4/3}.$$

In a subformula equation for a complex crystal, the charge Q presented by each coordination anion can be obtained from the valence conservation and electric neutrality of the subformula. In this equation, the charges presented by Y and Li equate to their valence charges: 3+ and 1+ respectively. So the charges presented by F ions are 1.125 in the Y–F bond and 0.75 in the Li–F bond. The refractive index of $YLiF_4$ ($n = 1.3467$) is used in equation (20); then, E_h^{μ} and C^{μ} can be calculated from (13), (15)–(17), and (20): 5.21 and 34.20 respectively. f for the Y–F bond is 0.0226. The polarizability of the type Y–F bond volume can be obtained from (13), (20), (22), (23): 0.1785. So the environmental factor h_e of $YLiF_4$ can be obtained: $h_e = (8 \times 0.0226 \times 0.1785 \times 1.125^2)^{1/2} = 0.20$.

3. Results

Table 1 displays the calculated values of h_e and the corresponding ΔE for ten kinds of crystal. The structures of these crystals have been reported in [18–23]. The second column shows values of the dielectric constant $\varepsilon = n^2$, where n is the refractive index, which is used in equation (20), with an average of values reported in the literature or estimated in terms of values for crystals with similar structure. The energy difference ΔE between the lowest energy level of the spin-allowed fd and the most intense spin-forbidden states of Tb^{3+} in these hosts can be obtained from reported experimental spectra and data [4, 5, 8, 24, 25]. For $Y_3Al_5O_{12}$, there are two values of ΔE: one is 5632 cm^{-1}, from [7]; the other is 6166 cm^{-1}, from [24].
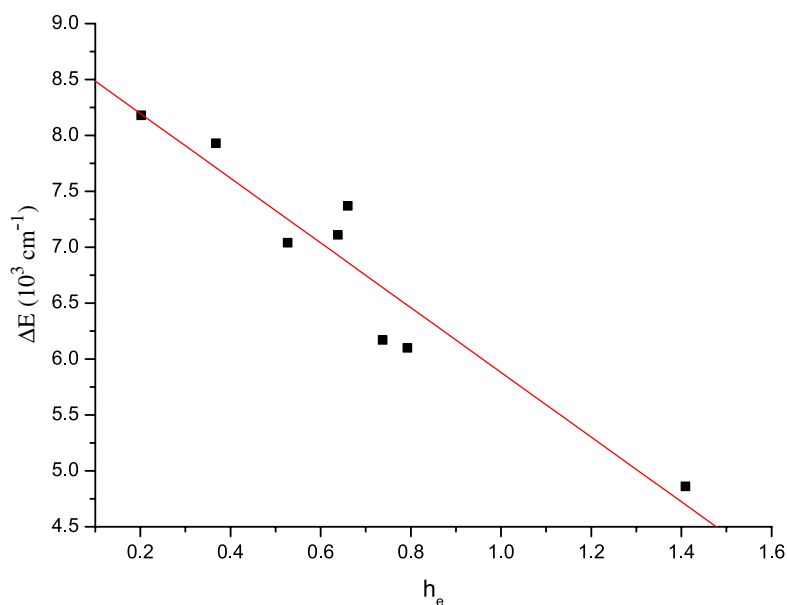
Figure 2. The relation between the energy difference ΔE and the environmental factors h_e.
(This figure is in colour only in the electronic version)

Although further experimental verification is required, the latter agree with the general trend in figure 2 to some extent.

Plotting ΔE versus h_e (see figure 2), we certainly find a linear relation between ΔE and h_e; the simulation equation can be written as

$$\Delta E = 8.80 - 2.95 h_e. \tag{24}$$

By using expression (24), ΔE for the Tb^{3+} ion was calculated for the eight crystals listed in table 1. A reasonable agreement between experimental and calculated values is obtained. The maximal error is 451 cm^{-1}, for $Y_3Al_5O_{12}$:Tb^{3+}. The error is enough small for us to be confident of the position of the spin-forbidden transition.

In the free state, $f_c(i) = 0$, $\alpha(i) = 0$. In that case, expression (24) can be written as

$$\Delta E_0 = 8.80 \ (10^3 \ \text{cm}^{-1}). \tag{25}$$

Evidently, 8.8×10^3 cm^{-1} is the energy difference between the lowest spin-allowed fd and the most intense spin-forbidden states of Tb^{3+} in the free ion state.

Using the value of the lowest spin-allowed fd peak and expression (24), the fd spin-forbidden band of any crystal can be given. In table 1, the calculated values of h_e for the crystals $YAlO_3$, $LuLiF_4$ are given. ΔE is predicted to be 6.18 and 8.15 (10^3 cm^{-1}) respectively for the two crystals.

4. Conclusions

In this paper, the reason for the energy difference between the lowest energy level of the spin-allowed fd and the most intense spin-forbidden states of Tb^{3+} in crystals has been discussed: it is the nephelauxetic effect. The environmental factor h_e is redefined, and a good linear relationship between h_e and ΔE is obtained, which can be used to predict the values of ΔE

for crystals. If the lowest spin-allowed fd peaks in crystals are known, the position of spin-forbidden band can be obtained.

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