Chapter 1

Magnetism of the Rare-Earth Ions in Crystals

1. *Magnetism of the Rare-Earth ions in Crystals*

In this chapter we present the basic facts regarding the physics of magnetic phenomena of rare-earth ions in crystals. We discuss the theory of quantized angular momentum and the theory of the crystal field (CF) splitting of the electronic energy levels of the rare-earth ions in these crystals as required to give a better understanding for the material discussed in detail in later chapters in this book. Additional data and analyses can be found in corresponding references, which expand on topics that are discussed in each of the chapters in this book.

1.1. *Electronic Structure and Energy Spectra of the "Free" Rare-Earth Ions*

In rare earth (RE) compounds, the lanthanide ions (from Ce to Yb) are usually found in the trivalent state RE^{3+}. The ground electronic configuration of the RE ions may be written as [Xe]$4f^n$, where [Xe] = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 p^6$ is the closed-shell configuration of the noble gas xenon, and n is the number of electrons in the unfilled $4f^n$ shell, ranging from $n = 1$ for Ce^{3+} to $n = 13$ for Yb^{3+}. The characteristic magnetic moment for each RE ion leads to an interaction between that ion and an applied external magnetic field H, producing interesting magnetic and magnetooptical features in the RE compounds.

Over the years, methods of numerical analysis have been developed to calculate the energy states of "free" RE ions (that is, for ions that are not in a ligand or crystal-field environment). These methods allow evaluation of the multiplicities of states and the energy-level positions of excited electronic configurations relative to the ground state. Energy intervals for $4f^n$, $4f^{n-1}5d$, $4f^{n-1}6s$, and other excited electronic configurations for free RE ions are presented in Refs. [1,2]. Also presented are energy level schemes for the energy levels of the $4f^n$ configuration for all trivalent RE ions. From these results it follows that the excited RE ion configurations, such as $4f^{n-1}5d$, $4f^{n-1}6s$, are separated from the $4f^n$ ground state by an energy interval typically on the order of 10^5 cm^{-1}.

The repulsion between the equivalent $4f$ electrons within the shell, usually called the correlation Coulomb interaction of the RE ion, splits the states into *terms* characterized by the orbital (L) and spin (S) momenta. A *term* with fixed values of L and S has $(2L + 1)(2S + 1)$ degenerate states distinguished by the m_L and m_S projections of the orbital and spin momenta. The wave functions of these degenerate states are given by $|\gamma LSm_Lm_S\rangle$, where $-L \le m_L \le L$, $-S \le m_S \le S$ and the index γ distinguishes between terms with the same L and S. Neighboring terms are separated from each other by an energy interval on the order of 10^4 cm^{-1} [3-5].

To determine the ground term of the $4f^n$ electronic configuration, one usually applies Hund's rules and the Pauli exclusion principle [4,6]. Hund's first two rules assert:

1) For a given electronic configuration the *term* (i.e., a quantum state with fixed $\boldsymbol{L}$ and $\boldsymbol{S}$) with maximum multiplicity (i.e., with maximum $\boldsymbol{S}$) has the lowest energy.

2) For a given multiplicity (i.e., $\boldsymbol{S} = \boldsymbol{S}_{\max}$), the *term* with the largest value of $\boldsymbol{L}$ has the lowest energy.

For instance, let us apply Hund's rules for the determination of the ground term of the rare-earth Tb^{3+} ion that has eight electrons in the unfilled $4f^8$ electronic configuration. In this regard, we can construct **Table 1.1** for the orbital (m_l) and spin (m_s) momentum projections of the eight f electrons. Hund's first rule indicates that the first seven electrons will fill states of the same spin momentum (m_s); Hund's second rule indicates that the eighth electron will fill one of the remaining (opposite-spin) states having the largest angular momentum (m_l). This is shown in **Table 1.1**. In spectroscopic language, the ion Tb^{3+} has a ground term of ^{7}F, where the conventional notation is $^{(2S+1)}L$ with $(2S + 1)$ being the *multiplicity.*

The quantum degeneracy of the RE ion terms is removed by the spin-orbit interaction W_{SO} that has a value on the order of 10^3 cm^{-1}. The effective Hamiltonian of the spin-orbit interaction that describes the splitting of the term with fixed values of L and S has the form,

$$\hat{H}_{LS} = \xi \cdot \hat{L} \cdot \hat{S}\,, \tag{1.1}$$

Table 1.1. Arrangement of the orbital (m_l) and spin (m_s) momentum projections in the $4f^8$ electronic configuration of Tb^{3+}. The maximum number of f electrons in the shell is $N = 14$.

m_l / m_s	−3	−2	−1	0	+1	+2	+3
↑	↑	↑	↑	↑	↑	↑	↑
↓	↓						↓

where $\widehat{L}$ and $\widehat{S}$ are the operators of the orbital and spin momenta, respectively, and ξ is the spin-orbit coupling constant defined by the well-known Goudsmit formula [5]. From a qualitative point of view, the spin-orbit interaction W_{SO} corresponds to the magnetic interaction between the spin magnetic momentum and the magnetic field caused by the motion of the $4f$ electron around the nucleus. In the one-electron approximation, W_{SO} can be written as [7],

$$W_{SO} = \frac{\hbar^2 e^2 \left(\vec{l} \cdot \vec{s}\right)}{2m^2 c^2 \cdot r^3}, \tag{1.2}$$

where $\hbar$ is the Plank constant, m and e are the mass and charge of the electron, c is the speed of light, r is the radius of electron orbit, and l and s are the orbital and spin moments of the electron, respectively.

The spin-orbit interaction splits the $^{(2S+1)}L$-terms into multiplets characterized by the total angular momentum J (with $|L - S| \leq J \leq L + S$) whose wavefunctions are spherical functions expressed in terms of $|J,M_J>$ [8]. Each multiplet is many-fold degenerate in terms of its angular momentum projection M_J; this degeneracy can be removed by an external action (relative to the RE ion), such as crystalline electric or magnetic fields. In the case of an applied external magnetic field, H, a complete lifting of the degeneracy takes place, with the $^{(2S+1)}L_J$ multiplet split into $(2J + 1)$ equidistant sublevels. The energy interval between sublevels is defined by the magnetic field intensity and by the value of the g-factor. We write the Hamiltonian (1.1) in the form,

$$\widehat{H}_{LS} = \frac{1}{2}\xi \cdot \left(\widehat{J}^2 - \widehat{L}^2 - \widehat{S}^2\right). \tag{1.3}$$

For the diagonal matrix elements that define the multiplet energy E we obtain,

$$E(J) = \frac{1}{2}\xi \cdot \left[J(J+1) - L(L+1) - S(S+1)\right]. \tag{1.4}$$

From this expression, the Lande' "rule of intervals" is determined as,

$$E(J) - E(J-1) = \frac{1}{2}\xi \cdot \left[J(J+1) - J(J-1)\right] = \xi \cdot J, \tag{1.5}$$

which gives the difference in energy between neighboring multiplets having the same L and S [3].

The nomenclature of the multiplets in a term depends on the sign of the spin-orbit coupling constant ξ. For the "heavy" RE ions (from Tb^{3+} to Yb^{3+}) with the $4f$ shell more than half filled $\xi < 0$, so the lowest-energy multiplet will have the largest possible value of J for a given L and S, that is, $J_0 = L_0 + S_0$. For the "light" RE ions (from Ce^{3+} to Gd^{3+}) with less than a half-filled $4f$ shell, $\xi > 0$. In this case, the lowest-energy multiplet will have the smallest possible value of J for a given L and S, that is, $J_0 = |L_0 - S_0|$. This is known as Hund's third rule, which asserts that:

3) For the less-than-half filled shell, the state with the smallest allowed value of J is the lowest energy state; for the more-than-half filled shell, the state with the largest allowed value of J is the lowest energy state.

A general scheme for the energy spectrum for the $4f^n$ configuration of the free rare earth ion based on these energy terms is presented in **Figure 1.1**. The ground term for each trivalent RE ion and the ground and first excited multiplets associated with each of these terms in the $4f^n$ configuration are presented in **Table 1.2**.

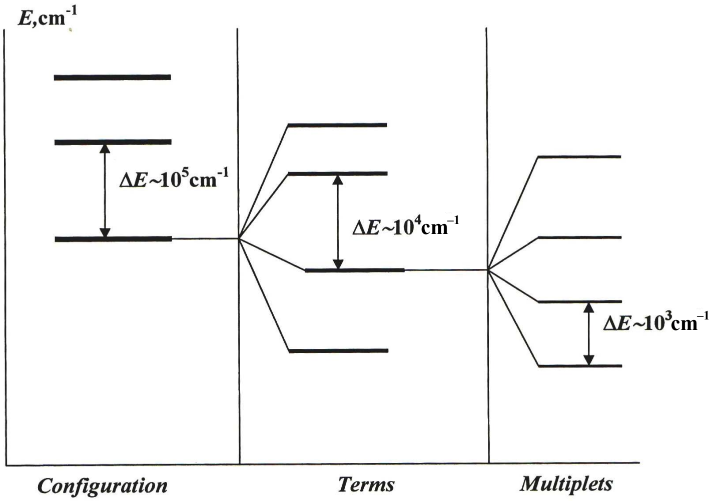

Figure 1.1. Splitting scheme for the energy levels of the free rare-earth ions [3].

Table 1.2. Ground and first excited energy levels of the free RE ions.

RE^{3+}	Ground electronic configuration	Ground term	Ground multiplet	First excited multiplet	$E_1 - E_0$ (cm^{-1})
Ce	$4f^1$	^2F	$^2F_{5/2}$	$^2F_{7/2}$	2200
Pr	$4f^2$	^3H	$^3H_4$	$^3H_5$	2200
Nd	$4f^3$	^4I	$^4I_{9/2}$	$^4I_{11/2}$	1800
Pm	$4f^4$	^5I	$^5I_4$	$^5I_5$	1600
Sm	$4f^5$	^6H	$^6H_{5/2}$	$^6H_{7/2}$	1000
Eu	$4f^6$	^7F	$^7F_0$	$^7F_1$	350
Gd	$4f^7$	^8S	$^8S_{7/2}$	–	–
Tb	$4f^8$	^7F	$^7F_6$	$^7F_5$	2300
Dy	$4f^9$	^6H	$^6H_{15/2}$	$^6H_{13/2}$	3400
Ho	$4f^{10}$	^5I	$^5I_8$	$^5I_7$	5000
Er	$4f^{11}$	^4I	$^4I_{15/2}$	$^4I_{13/2}$	6400
Tm	$4f^{12}$	^3H	$^3H_6$	$^3H_5$	8200
Yb	$4f^{13}$	^2F	$^2F_{7/2}$	$^2F_{5/2}$	10100

The classification of free RE ion states is based on the Russell-Saunders approximation (also called normal- or *LS*-coupling), which requires that the energy separation between the terms be much greater than the value of the term-splitting into multiplets by the spin-orbit interaction. For the ground term of the $4f^n$ configuration, this approximation is generally valid. However, significant deviation from *LS*-coupling is observed for excited RE ion states [3,4]. Nevertheless, *LS*-coupling is still a sufficiently good approximation to calculate the energy spectra and the classification of states for both the ground $4f^n$ configuration and the lower states of the first excited $4f^{n-1}5d$ and $4f^{n-1}6s$ configurations of the free RE ions. As shown by the results from direct calculations (see, for example, Refs. [9,10]), the energy value of the *d* electron interaction with the *f* electrons of the $4f^{n-1}$ "core" of the $4f^{n-1}5d$ configuration is on the order of 10^4 cm^{-1}, while the value of the spin-orbit interaction for the *d* electron is on the order of 10^3 cm^{-1}. The lower states of the $4f^{n-1}5d$ (or $4f^{n-1}6s$) configuration of the free RE ion can be described in the *LS*-coupling approximation as vector sums of the quantum numbers *L* and *S* that characterize the ground state of the $4f^{n-1}$ "core" with the quantum numbers *l* and *s* of the "valence" 5*d* (or 6*s*) electron [4,5,7].

1.2. *Paramagnetism of the "Free" RE Ions*

Let us consider the interaction between the "free" RE ion (as defined in Sec. 1.1) with an external magnetic field *H*. An interaction Hamiltonian of the ion with an external magnetic field (denoted the Zeeman Hamiltonian) is usually written as,

$$\hat{H}_Z = \mu_B \left(\hat{L} + 2\hat{S} \right) \vec{H} = \mu_B \left(\hat{J} + \hat{S} \right) \vec{H} \ . \tag{1.6}$$

If the field *H* is directed along the *z*-axis of the coordinate system, the Hamiltonian can be written in the following form,

$$\hat{H}_Z = \mu_B \left(\hat{J}_Z + \hat{S}_Z \right) H \ . \tag{1.7}$$

Based on the state wave functions, $|LSJM_J>$, that are distinct for each state, we can write the matrix elements for this Hamiltonian as [3],

$$\left\langle LSJM_J \left| \hat{H}_Z \right| LSJM_J \right\rangle = g_J \mu_B M_J H \ , \tag{1.8}$$

where $g_J = 1 + \dfrac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$ is the Lande' factor for the multiplet of the RE ion,

and

$$\left\langle LS(J+1)M_J \left| \hat{H}_Z \right| LSJM_J \right\rangle = -g'_J \mu_B H \left[(J+1)^2 - M_J^2 \right]^{1/2} \tag{1.9}$$

where $g'_J = \left[\dfrac{(J+L+S+2)(L-J+S)(J-L+S+1)(J+L-S+1)}{4(J+1)^2(2J+1)(2J+3)} \right]^{1/2}$.

Let us consider now the behavior of an ensemble of free RE ions in an external magnetic field. In this case, the magnetic field tends to orient the magnetic moments $\vec{M}$ of the ions, whereas the thermal motion tends to disorient them. As $\vec{M}$ is spatially quantized, the energy of the interaction between the magnetic moment $\vec{M}$ of the RE ion with the