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Zero-field splitting and g-factor studies for $3d^5$ ions in tetragonal and trigonal symmetry

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Abstract

In this paper, the rigorous analytical expressions for the zero field splittings *D*, *a*, *F* and g-factors of a $3d^5$ ion in tetragonal and trigonal crystal fields are derived. In the derivations, the energy levels equivalence between microscopic Zeeman interaction and phenomenological spin-Hamiltonian was used. The deduced expressions do not depend on any interaction model and are universal expressions. As some examples, we studied the specific examples of $MnCO_3$, $Rb_2CdF_4:Mn^{2+}$ and $KZnF_3:Mn^{2+}$. Good agreement between calculation and experiments shows that the formulas are reasonable.

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1. Introduction

The ground state properties of the transition metal ions in crystals are well described by the electron paramagnetic resonance (EPR) and zero-field splitting (ZFS) parameters which appear in the phenomenological spin Hamiltonian (SH) [1–4]. For the $3d^5$ configurations, the ground state has a large spin of 5/2 and none orbital angular momentum. In cubic symmetry, the ground state splits into two sublevels and only one ZFS parameter *a* has a non-zero value. Exact calculations show that the non-zero parameter *a* equals to the difference between the two sublevels. In tetragonal and trigonal crystal fields, there are three ZFS parameters (*D*, *a* and *F*)

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which cannot be neglected. However, there are only two energy differences. This leads to the difficulty of the ZFS problem for the $3d^5$ ions in tetragonal and trigonal crystal fields. Until now, no satisfactory theoretical calculation has been made to solve the problem. During the past long period of time, a large number of theoretical and experimental works have been made for the ZFS of $3d^5$ ions in crystals [5–17]. Most of these theoretical works are confined in cubic symmetry crystal and only discussed the rank-2 parameters D and E [5–10]. In the tetragonal and trigonal symmetry field, some of the parameters are neglected in the Refs. [5–7].

Yu et al. [11–13] studied the ZFS parameters D, a and F of $3d^5$ ions in tetragonal and trigonal symmetries by means of the high-order perturbation method suggested by Macfarlane [14] and Zdansky [15] and the intermediate-field coupling scheme [16]. Zhao et al. have developed an analytical expression of the parameters D, a, F of $3d^5$ ions in tetragonal and trigonal symmetries on the basis of the complete diagonalization procedure (CDP) method [17]. In their calculations, the equivalence between the CDP and SH is employed not only in energy but also in wavefunction. The equivalence of the wavefunctions between CDP and SH has been critically commented by Rudowicz [18].

In order to develop an exact theoretical calculation for the ZFS parameters of $3d^5$ configurations in tetragonal and trigonal symmetry field, in the present paper, the Zeeman splitting of a $3d^5$ ion in tetragonal and trigonal symmetries with an external magnetic field is utilized. It is found that the ZFS parameters D, a, F and EPR parameter g can be expressed as a function of the Zeeman splitting. The developed expressions are universal expressions and do not depend on any interaction model. It is interesting that the results in this paper are very close to that calculated by Zhao et al. [17]. In the present paper the hyperfine structure is not involved. The hyperfine structure of some $3d^5$ ions in crystals will be discussed in our later work.

2. ZFS and g-factors formulas

2.1. Zeeman splitting of the ground state

For a $3d^5$ ion in crystal field, the microscopic Hamiltonian (MH) is

$$H = H_{ee} + H_{so} + H_{crys} + H_M \tag{1}$$

with

$$H_M = \mu_B \vec{B} \cdot \sum_i (\vec{l}_i + 2.0023\vec{s}_i), \tag{2}$$

where H_{ee} denotes the electron–electron repulsion potential, H_{so} is the spin–orbit interaction of the d-electrons, H_{crys} is the crystal filed potential, H_M is the Zeeman interaction, μ_B is Bohr magneton, $\vec{B}$ is the external magnetic field strength, $\vec{l}_i$ and $\vec{s}_i$ denote the orbit and spin angular momentum of the ith d-electron, respectively.

The ground state of a $3d^5$ ion is ^6S, which splits into three levels in tetragonal and trigonal crystal field. If the external magnetic field $\vec{B} \neq 0$, the ^6S state would further split into six sublevels which relate to the effective spin $S_z^{eff} = \pm\frac{5}{2}$, $\pm\frac{3}{2}$ and $\pm\frac{1}{2}$, respectively.

2.2. ZFS and g-factors in tetragonal symmetry

In the tetragonal symmetry crystal field, the phenomenological SH of the $3d^5$ configuration can be written as [2–4]

$$\begin{aligned} H = {} & D[S_z^2 - S(S+1)] + \frac{a}{6}[S_x^4 + S_y^4 + S_z^4 \\ & - S(S+1)(3S^2 + 3S - 1)/5] \\ & + \frac{F}{180}[35S_z^4 - 30S(S+1)S_z^2 \\ & + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2] \\ & + \mu_B g_{||} B_z S_z + \mu_B g_\perp (B_x S_x + B_y S_y), \end{aligned} \tag{3}$$

where D, a and F are the ZFS parameters. $g_{||}$ and $g_\perp$ are the EPR g-factors. S_x, S_y and S_z denote the component of the spin angular momentum, B_x, B_y and B_z denote the external magnetic field strength. x, y and z denote the cubic crystalline axis, z denotes the symmetry principal axis.

Appling the SH to the ground state and solving the secular equation with external magnetic field $B_x = B_y = 0, B_z \neq 0$ and $B_x \neq 0, B_y = B_z = 0$, the