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Investigations of the spin-Hamiltonian parameters and defect structures for Gd^{3+} ions in YMO_4 (M=V, P, As) crystals

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ABSTRACT

A 56×56 energy matrix containing the ground multiplet $^8S_{7/2}$ and the excited multiplets $^6L_{7/2}$ (where L=P, D, F, G, H, I) for $4f^7$ ion Gd^{3+} at a tetragonal crystal field and under an external magnetic field is constructed. By diagonalizing the energy matrix, the spin-Hamiltonian parameters (g factors $g_{\|}$, $g_{\perp}$ and zero-field splittings b_2^0, b_4^0, b_4^4, b_6^0, b_6^4) for Gd^{3+} ion at the tetragonal Y^{3+} site of YMO_4 (M=V, P, As) crystals are calculated. The calculated results are in reasonable agreement with the experimental values. The defect structures of Gd^{3+} centers in YMO_4 crystals are estimated from the calculation. The results are discussed.

1. Introduction

YMO_4 (M=V, P, As) form an isomorphous series of compounds with zircon-type structure. They doped with rare earth ions can find a wide applications as solid-state laser, phosphor and luminescence materials [1–6]. The spectroscopic studies of rare earth ions doped into YMO_4 crystals have been paid considerable attention. For instance, the electron paramagnetic resonance (EPR) spectra of Gd^{3+} at tetragonal Y^{3+} sites of YMO_4 crystals were measured and their spin-Hamiltonian parameters (g factors $g_{\|}$, $g_{\perp}$ and zero-field splittings b_2^0, b_4^0, b_4^4, b_6^0, b_6^4) were given [7]. Newman and Urban [8,9] studied roughly the rank-two zero-field splitting b_2^0 and rank-four zero-field splittings b_4^0, b_4^4 using the empirical superposition model. However, the theoretical calculations for all these spin-Hamiltonian parameters have not yet been reported. The goal of this investigation is to calculate these spin-Hamiltonian parameters together from a diagonalization (of energy matrix) method. From the calculation, all these spin-Hamiltonian parameters can be explained in a unified way. Since the spin-Hamiltonian parameters of a paramagnetic impurity in crystals are fairly sensitive to its immediate environment, the calculation can also provide information on the defect structures of Gd^{3+} impurity centers in YMO_4 crystals. The results are discussed.

2. Theoretical calculations

Gd^{3+} ion in YMO_4 crystal substitutes for the Y^{3+} ion and occupies the 8-fold coordinated dodecahedral site with tetragonal (D_{2d}) symmetry [7]. The tetragonal crystal field splits the ground multiplet $^8S_{7/2}$ of the free $4f^7$ ion Gd^{3+} into four Kramers doublets. The external magnetic field used in the EPR experiment splits further the four doublets into eight singlet states with $J=-7/2, -5/2, -3/2, -1/2, 1/2, 3/2, 5/2, 7/2$. It is known that the EPR spectra of a paramagnetic ion in crystal are characterized by spin-Hamiltonian parameters. For $4f^7$ ion in a tetragonal site, the spin-Hamiltonian parameters includes g factors $g_{\|}$, $g_{\perp}$ and zero-field splittings b_2^0, b_4^0, b_4^4, b_6^0, b_6^4, and the corresponding effective spin-Hamiltonian is [7,10]

$$H_s = g_{//}\beta B_z S_z + g_{\perp}\beta(B_x S_x + B_y S_y) + \frac{1}{3}b_2^0 O_2^0 + \frac{1}{60}(b_4^0 O_4^0 + b_4^4 O_4^4) + \frac{1}{1260}(b_6^0 O_6^0 + b_6^4 O_6^4) \quad (1)$$

in which O_m^n are the spin operators represented in Ref. [11]. The relationships among the spin-Hamiltonian parameters and the energy levels of the above eight singlets can be obtained in terms of the eigenvalues of spin Hamiltonian H_s.

In the case of the external magnetic field $B\|Z$-axis (i.e., C_4 axis), the off-diagonalization matrix elements of H_s are considerably smaller than the diagonal elements, so the second-order perturbation theory may be adequate here. By neglecting the high-order approximation terms (i.e., those including parameters $P=(b_4^4)^2/20g_{\|}\beta B$),

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we have [10]

$$\Delta E_1(\|) = \Delta E(\frac{3}{2}\rightarrow\frac{1}{2}) - \Delta E(-\frac{1}{2}\rightarrow-\frac{3}{2}) = 2(2b_2^0 - 12b_4^0 + 14b_6^0)$$

$$\Delta E_2(\|) = \Delta E\left(\frac{5}{2}\rightarrow\frac{3}{2}\right) - \Delta E\left(-\frac{3}{2}\rightarrow-\frac{5}{2}\right) = 2(4b_2^0 - 10b_4^0 - 14b_6^0)$$

$$\Delta E_3(\|) = \Delta E\left(\frac{7}{2}\rightarrow\frac{5}{2}\right) - \Delta E\left(-\frac{5}{2}\rightarrow-\frac{7}{2}\right) = 2(6b_2^0 + 20b_4^0 + 6b_6^0)$$

$$g_{\|} = \frac{\Delta E(\frac{1}{2}\rightarrow-\frac{1}{2})}{\beta B_Z} \tag{2}$$

If the external magnetic field changes to be normal to z-axis and along the x-axis, in the similar way, we have [10]

$$\Delta E_1(\perp) = \Delta E\left(\frac{3}{2}\rightarrow\frac{1}{2}\right) - \Delta E\left(-\frac{1}{2}\rightarrow-\frac{3}{2}\right) = 2b_2^0 + 9b_4^0 + \frac{35}{4}b_6^0 + 3b_4^4 + \frac{7}{4}b_6^4$$

$$\Delta E_2(\perp) = \Delta E\left(\frac{5}{2}\rightarrow\frac{3}{2}\right) - \Delta E\left(-\frac{3}{2}\rightarrow-\frac{5}{2}\right) = 4b_2^0 + \frac{15}{2}b_4^0 - \frac{35}{4}b_6^0 + \frac{5}{2}b_4^4 - \frac{7}{4}b_6^4$$

$$\Delta E_3(\perp) = \Delta E\left(\frac{7}{2}\rightarrow\frac{5}{2}\right) - \Delta E\left(-\frac{5}{2}\rightarrow-\frac{7}{2}\right) = 6b_2^0 - 15b_4^0 + \frac{15}{4}b_6^0 - 5b_4^4 + \frac{3}{4}b_6^4$$

$$g_{\perp} = \frac{\Delta E(\frac{1}{2}\rightarrow-\frac{1}{2})}{\beta B_x} \tag{3}$$

Thus, the spin-Hamiltonian parameters can be given by calculating the energy levels of the eight singlets of $^8S_{7/2}$.

As has been said before, the splittings of the multiplet $^8S_{7/2}$ into eight singlets are due to Gd^{3+} ion in a tetragonal crystal-field and under an external magnetic field. In this system, the Hamiltonian should be

$$H = H_f + H_{CF} + H_{Ze} \tag{4}$$

where H_f is the free-ion term which expression is given in Ref. [12]. The crystal-field interaction term H_{CF} and Zeeman (or magnetic) interaction term H_{Ze} are given by [12,13]

$$H_{CF} = B_2^0C_2^0 + B_4^0C_4^0 + B_4^4(C_4^4 + C_4^{-4}) + B_6^0C_6^0 + B_6^4(C_6^4 + C_6^{-4}) \tag{5}$$

$$H_{Ze} = g_J\beta JB \tag{6}$$

in which B_k^q represent the crystal field parameters, C_k^q denote the Racah spheric operators and the rest notations are standard [13].

In consideration of the splittings of the ground multiplet $^8S_{7/2}$ of Gd^{3+} arising mainly from the interactions of it with the low-lying excited multiplets with the same $J=7/2$ [8,9,14–16], for simplicity, we found the 56×56 energy matrix of the Hamiltonian in Eq. (4) by taking into account the ground multiplet $^8S_{7/2}$ and excited multiplets $^6L_{7/2}$ (L=P, D, F, G, H, I) with the aid of the equivalent operator and/or irreducible tensor operator method. Thus, the energy levels of eight singlets of $^8S_{7/2}$ and hence the spin-Hamiltonian parameters $g_{\|}$, $g_{\perp}$ and b_m^n can be calculated from the diagonalization (of energy matrix) method.

In the energy matrix, we take the free-ion parameters of Gd^{3+} as the mean values acquired for Gd^{3+} ions in a great number of crystals [12]. These values are the Coulomb repulsion $F^2\approx85300\ cm^{-1}$, $F^4\approx60517\ cm^{-1}$ and $F^6\approx44731\ cm^{-1}$, the two-body and three-body interaction parameters $\alpha\approx18.95\ cm^{-1}$, $\beta\approx-620\ cm^{-1}$, $\gamma\approx1658\ cm^{-1}$, $T^2\approx308\ cm^{-1}$, $T^3\approx43\ cm^{-1}$, $T^4\approx51\ cm^{-1}$, $T^6\approx-298\ cm^{-1}$, $T^7\approx338\ cm^{-1}$ and $T^8\approx335\ cm^{-1}$, the spin-orbit parameter $\zeta=1504\ cm^{-1}$, the Marrin integrals $M^0\approx2.99\ cm^{-1}$, $M^2\approx1.67\ cm^{-1}$, $M^4\approx1.14\ cm^{-1}$, and the parameters related to the electrostatic correlated magnetic interaction $P^2\approx542\ cm^{-1}$, $P^4\approx407\ cm^{-1}$ and $P^6\approx271\ cm^{-1}$. The crystal-field parameters B_k^q in energy matrix, as those for $3d^n$ and $4f^n$ ions in many crystals, can be calculated from the empirical superposition model [17–20]. In the model, the parameters B_k^q are assumed to come from a sum of axially symmetry of n ligands. For $4f^n$ ions in a tetragonal (D_{2d}) 8-fold coordinated site, from the model, we have

$$B_2^0 = 4\bar{A}_2(R_0)\sum_{i=1}^{2}\left[\left(\frac{R_0}{R_i}\right)^{t_2}(3\cos^2\theta_i - 1)\right]$$

$$B_4^0 = 4\bar{A}_4(R_0)\sum_{i=1}^{2}\left[\left(\frac{R_0}{R_i}\right)^{t_4}35\cos^4\theta_i - 30\cos^2\theta_i + 3\right]$$

$$B_4^4 = 2\sqrt{70}\bar{A}_4(R_0)\sum_{i=1}^{2}\left[\left(\frac{R_0}{R_i}\right)^{t_4}\sin^4\theta_i\right]$$

$$B_6^0 = 4\bar{A}_6(R_0)\sum_{i=1}^{2}\left[\left(\frac{R_0}{R_i}\right)^{t_6}(231\cos^6\theta_i - 315\cos^4\theta_i + 105\cos^2\theta_i - 5)\right]$$

$$B_6^4 = 6\sqrt{14}\bar{A}_6(R_0)\sum_{i=1}^{2}\left[\left(\frac{R_0}{R_i}\right)^{t_6}(11\cos^2\theta_i - 1)\sin^4\theta_i\right] \tag{7}$$

in which t_k ($k=2, 4, 6$) are the power-law exponents. As in some $4f^n$ ions in crystals, we take $t_2\approx5$, $t_4\approx6$ and $t_6\approx10$ [21,22] here. $\bar{A}_k(R_0)$ denote the intrinsic crystal-field parameters with the reference distance R_0. R_i ($i=1, 2$) and θ_i are the structural data of the studied Gd^{3+} center. Since for Gd^{3+} in YMO_4 crystals, the eight neighboring O^{2-} ions can be divided into two groups. The four O^{2-} ions in each group have the same metal-ligand distance R_i and angle θ_i (between R_i and C_4 axis). The structural data R_i^h and θ_i^h for the host YMO_4 crystals [8] are collected in Table 1. It is believed that the defect structural data of impurity center in crystal are unlike the corresponding data in the host crystal because of the size and/or nature mismatch. For the impurity-ligand distance R in impurity center, we can estimate it from an approximate formula [23] $R=R_h+(r_i-r_h)/2$, where r_i and r_h are, respectively, the ionic radius of impurity and that of the replaced host ion. For Gd^{3+} in YMO_4 crystals, from r_i (=0.938 Å [24]) and r_h (=0.893 Å [24]) and R_i^h (see Table 1), we obtain the values of R_i (see Table 1). Since the angle θ_i in the impurity center may differ from the corresponding angle θ_i^h in the host crystals, we introduce the parameters $\Delta\theta_i$ to characterize the angular distortion due to the substitution. Thus, we have $\theta_i\approx\theta_i^h+\Delta\theta_i$. Thus, in the energy matrix, we have five adjustable parameters $\bar{A}_k(R_0)$ and $\Delta\theta_i$. They are obtained through fits to the experimental values of spin-Hamiltonian parameters (note: to compare the adjustable

Table 1
The structural data of Gd^{3+} ion in YMO_4 (M=V, P, As) crystals.

	$YVO_4:Gd^{3+}$	$YPO_4:Gd^{3+}$	$YAsO_4:Gd^{3+}$
R_1^h (Å)[a]	2.291	2.313	2.300
R_2^h (Å)[a]	2.433	2.374	2.412
R_1 (Å)	2.314	2.336	2.323
R_2 (Å)	2.456	2.397	2.435
θ_1^h (deg.)[a]	78.1	76.33	77.08
θ_2^h (deg.)[a]	32.83	30.22	31.88

[a] Ref. [8].

Table 2
The intrinsic crystal field parameters $\bar{A}_k(R_0)$ (in cm^{-1}) and angular distortions $\Delta\theta_i$ for Gd^{3+} ion in YMO_4 (M=V, P, As) crystals.

	$\bar{A}_2(R_0)$	$\bar{A}_4(R_0)$	$\bar{A}_6(R_0)$	$\Delta\theta_1$ (deg.)	$\Delta\theta_2$ (deg.)
YVO_4:Gd3+	980	62	32	0.06	1.06
YPO_4:Gd3+	960	68	29	0.96	2.76
$YAsO_4$:Gd3+	802	76	23	0.28	2.79