Studies of the Spin Hamiltonian Parameters and the Local Structure of Tetragonal Zr^{3+} Centers in Orthophosphate MPO_4 (M = Sc, Lu, Y) Crystals

Gui-Qiang Qu[a], Wang Fang[a], and Wen-Chen Zheng[a,b]

[a] Department of Material Science, Sichuan University, Chengdu 610064, P. R. China
[b] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China

Reprint requests to W.-C. Z.; E-mail: zhengwc1@163.com

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The spin Hamiltonian parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) of Zr^{3+} on the tetragonal M^{3+} (M = Sc, Lu, Y) sites of zircon-type orthophosphate MPO_4 crystals are calculated by high-order perturbation formulas of d^1 ions in tetragonal symmetry. The crystal-field parameters are estimated by the superposition model and reasonable local structural data of impurity centers. The results show good agreement with the experimental values. It appears that in the case of size mismatch, the explanation of the spin Hamiltonian parameters of a paramagnetic impurity in crystals should take the impurity-induced local lattice relaxation into account.

Key words: EPR; Spin Hamiltonian Parameters; Crystal-Field Theory; Defect Structure; Zr^{3+}; MPO_4 (M = Sc, Lu, Y).

1. Introduction

The orthophosphates MPO_4 (M = Sc, Lu, Y) form an isomorphous series of compounds with zircon-type structure. They and other zircon-type compounds doped with rare-earth and transition metal ions have gained considerable interest because of their application in lasers and luminescent materials [1 – 4]. Many optical and EPR spectral studies of doped MPO_4 crystals were made [5 – 8]. For example, the EPR spectra of the $4d^1$ configuration ion Zr^{3+} in MPO_4 crystals were measured and their spin Hamiltonian parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) were given in [8]. The Zr^{3+} ion in MPO_4 crystals replaces the M^{3+} ion and is in an eight-fold coordinated site with tetragonal (D_{2d}) symmetry. Until now no theoretical explanations (in particular those related to the structure of impurity centers) for these spin Hamiltonian parameters were given. Abraham et al. [8] thought that these spin Hamiltonian parameters were not accounted for by previously published second-order perturbation expressions. In the present paper, we calculate these spin Hamiltonian parameters by high-order perturbation formulas of the d^1 ion in tetragonal symmetry. In the calculations, the crystal-field parameters are estimated by the superposition model [9] and reasonable local structure data of impurity centers. The results are discussed.

2. Calculation

For a d^1 configuration ion, a cubic crystal-field will split the five-fold degeneracy energy level ^2D into an orbital doublet $^2E(D)$ and triplet $^2T_2(D)$. In the eight-fold coordinated site under study, the energy level $^2E(D)$ is lower. Adding the tetragonal distortion, the $^2E(D)$ level is split into two different orbital singlets $^2A_1$ and $^2B_1$, and the $^2T_2(D)$ is split into a doublet $^2E(T)$ and a singlet $^2B_2$. From the observed g factors of $MPO_4{:}Zr^{3+}$ [8] one finds that the ground state is $^2B_1(|d_{x^2-y^2}\rangle)$. By the spin Hamiltonian theory, the third-order perturbation formulas of $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ for a d^1 ion in tetragonal symmetry can be expressed as

$$\begin{aligned} g_\parallel &= g_s - \frac{8k\zeta}{E_1} - \frac{(g_s+k)\zeta^2}{E_2^2} - \frac{4k\zeta^2}{E_1E_2}, \\ g_\perp &= g_s - \frac{2k\zeta}{E_2} - \frac{(g_s/2-k)\zeta^2}{E_2^2} - \frac{2g_s\zeta^2}{E_1^2}, \\ A_\parallel &= P\left[-K - \frac{4}{7} + (g_\parallel - g_s) + \frac{3}{7}(g_\perp - g_s)\right], \\ A_\perp &= P\left[-K + \frac{2}{7} + \frac{11}{14}(g_\perp - g_s)\right], \end{aligned} \tag{1}$$

where g_s (≈ 2.0023) is the free-electron value. ζ and P are the spin-orbit coupling parameter and dipolar hyperfine structure constant in the crystal. k and K are the orbital reduction factor and the core polarization constant. Because of the covalence reduction effect for d^n ions in crystals, we have [10 – 12]

$$\zeta \approx N^2\zeta_0, \quad P \approx N^2P_0,$$

	R_1^{h} (Å) [21]	R_2^{h} (Å) [21]	R_1 (Å)	R_2 (Å)	$\bar{R}$ (Å)	θ_1 (deg) [21]	θ_2 (deg) [21]	k
$ScPO_4$:Zr^{3+}	2.150	2.277	2.229	2.356	2.293	103.17	31.62	0.911
$LuPO_4$:Zr^{3+}	2.264	2.346	2.284	2.366	2.325	103.47	30.95	0.934
YPO_4:Zr^{3+}	2.313	2.374	2.3115	2.3725	2.342	103.67	30.22	0.944

Table 1. The structural data and the orbital reduction factor k for MPO_4:Zr^{3+} (M = Sc, Lu, Y) crystals.

Table 2. The spin Hamiltonian parameters of MPO_4:Zr^{3+} (M = Sc, Lu, Y) crystals.

		$ScPO_4$:Zr^{3+}	$LuPO_4$:Zr^{3+}	YPO_4:Zr^{3+}
$g_{\parallel}$	Cal.[a]	1.892	1.849	1.830
	Cal.[b]	1.870	1.844	1.830
	Expt. [8]	1.871	1.844	1.832
$g_{\perp}$	Cal.[a]	1.948	1.936	1.933
	Cal.[b]	1.938	1.934	1.933
	Expt. [8]	1.936	1.933	1.932
$A_{\parallel}$ (10^{-4} cm^{-1})	Cal.[a]	91.5	96.3	98.3
	Cal.[b]	92.8	96.6	98.3
	Expt. [8]	92.7	98.5	100.8
$A_{\perp}$ (10^{-4} cm^{-1})	Cal.[a]	46.2	47.9	48.5
	Cal.[b]	46.6	47.9	48.5
	Expt. [8]	49.9	52.1	52.9

[a] Calculated using the structural data of host crystals.

[b] Calculated, using the defect structural data of impurity centers.

in which ζ_0 and P_0 are the corresponding values of a free d^n ion, and N^2 ($\approx k$) is the covalence reduction factor. For a free Zr^{3+} ion, $\zeta_0 \approx 500$ cm^{-1} [13]. $P_0 \approx g_e g_N \beta_e \beta_N < r^{-3} >$ [14], and from the value of $< r^{-3} > \approx 3.16$ a.u. [13] we obtain $P_0 \approx -52.5 \cdot 10^{-4}$ cm^{-1} for a free $^{91}Zr^{3+}$ ion. The energy separations E_1 and E_2 can be written as

$$\begin{aligned} E_1 &= E(^2B_2) - E(^2B_1) = 10D_q, \\ E_2 &= E(^2E_2) - E(^2B_1) = 10D_q - 3D_s + 5D_t. \end{aligned} \tag{2}$$

The crystal-field parameters D_q, D_s and D_t of the studied system in the superposition model [9] can be given as

$$\begin{aligned} D_q &= \frac{4}{3}\bar{A}_4(R_0)\sum_{i=1}^{2}\left[\left(\frac{R_0}{R_i}\right)^{t_4}\sin^4\theta_i\right], \\ D_s &= -\frac{4}{7}\bar{A}_2(R_0)\sum_{i=1}^{2}\left[\left(\frac{R_0}{R_i}\right)^{t_2}(3\cos^2\theta_i - 1)\right], \\ D_t &= -\frac{4}{21}\bar{A}_4(R_0)\sum_{i=1}^{2}\left[\left(\frac{R_0}{R_i}\right)^{t_4}(7\sin^4\theta_i + 35\cos^4\theta_i \right. \\ &\qquad \left. - 30\cos^2\theta_i + 3)\right], \end{aligned} \tag{3}$$

where the power-law exponents are $t_2 \approx 3$ and $t_4 \approx 5$ because of the ionic nature of the bonds [9, 15, 16]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters depending on the ligand, the coordination number and reference distance R_0. The values of $\bar{A}_4(R_0)$ and the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 8 \sim 12$ were obtained for many 3d^n MX_m clusters in crystals from optical and EPR spectra studies [15 – 18]. However, for the 4d^n MX_m clusters in crystals, few values of $\bar{A}_4(R_0)$ and $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ were reported. From the optical spectra of similar $[ZrO_8]^{13-}$ clusters in a YAG:Zr^{3+} crystal [19] we estimate $\bar{A}_4(R_0) \approx 1750$ cm^{-1} with $R_0 \approx 2.3$ Å. It can be expected that the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ for 4d^n clusters is smaller than that for 3d^n clusters because (i) the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is related to the ratio $\langle r_2\rangle/\langle r_4\rangle$ and (ii) the ratio $\langle r_2\rangle/\langle r_4\rangle$ of a 4d^n ion is smaller than that of a 3d^n ion [13] (e.g., $\langle r_2\rangle/\langle r_4\rangle \approx 0.15$ and 0.27 a.u. for 4d^1 Zr^{3+} and 3d^1 Ti^{3+} ions, respectively [13]). So, we take $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 5.4$ for MPO_4:Zr^{3+} crystals. R_i (i = 1 or 2) is the impurity-ligand distance and θ_i is the angle between the R_i and C_4 axis. In general, the local structural data of impurity centers are unlike the corresponding data in the host crystal because of the size and/or charge mismatch. For the studied MPO_4:Zr^{3+}, we can reasonably let the angle θ_i be unchanged and estimate the impurity-ligand distance R_i from the approximate formula [20]

$$R_i \approx R_i^{\mathrm{h}} + (r_i - r_{\mathrm{h}})/2, \tag{4}$$

where R_i^{h} is the corresponding distance in the host crystal. The values of R_i^{h} for MPO_4 crystals [21] are shown in Table 1. r_{i} and r_{h} are the ionic radius of the impurity and that of the replaced host ion. In MPO_4:Zr^{3+}crystals, $r_{\mathrm{h}} \approx 0.732$, 0.85 and 0.892 Å [22] for M^{3+} = Sc^{3+}, Lu^{3+} and Y^{3+}, respectively, and $r_{\mathrm{i}}(Zr^{3+}) \approx 0.89$ Å, estimated by the interpolation method based on $r(Zr^{+}) \approx 1.09$ Å and $r(Zr^{4+}) \approx 0.79$ Å [22]. Thus, for MPO_4:Zr^{3+} crystals the impurity-ligand distances R_i are estimated. They and the angles θ_i are collected in Table 1. So, in the above formulas only the parameters K and k are not known. By fitting the calculated $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ to the observed values, we obtain the same value $K \approx 1.21$ and different k values (see Table 1) for the three MPO_4:Zr^{3+} crystals. The calculated spin Hamiltonian parameters are compared with the experimental values in Table 2.

In addition, for comparison, we also calculate the spin Hamiltonian parameters for MPO_4:Zr^{3+} crystals by using the structural data in the host crystals. The calculated results are also shown in Table 2.

3. Discussion

It is agreed that for a MX_m cluster the covalence increases and hence the covalence reduction factor $N^2(\approx k)$ decreases with the decreasing M-X distance R [10, 23, 24]. Considering the different average Zr^{3+}-O^{2-} distances $\bar{R}$ of $[ZrO_8]^{13-}$ clusters in MPO_4:Zr^{3+} crystals (see Table 1), one should expect an increasing value of k with an increase of the distance $\bar{R}$, $k(ScPO_4{:}Zr^{3+}) < k(LuPO_4{:}Zr^{3+}) < k(YPO_4{:}Zr^{3+})$. Our calculated values of k (see Table 1) are consistent with this expectation and can be regarded as suitable.

The calculated spin Hamiltonian parameters for MPO_4:Zr^{3+} crystals, using the defect structural data of impurity centers, show good agreement with the experimental values (see Table 2). If the structural data of the host crystals are applied, the calculated results of $LuPO_4$:Zr^{3+} and YPO_4:Zr^{3+} are close to the observed values, but the calculated $g_\parallel$ and $g_\perp$ for $ScPO_4$:Zr^{3+} agree poorly with the observed values, because the ionic radius of the impurity Zr^{3+} is close to those of the replaced host ions in $LuPO_4$:Zr^{3+} and YPO_4:Zr^{3+}, but the difference of the ionic radius between Zr^{3+} and the replaced Sc^{3+} ion in the $ScPO_4$:Zr^{3+} crystal is larger. So, in the cases of size or/and charge mismatch, the reasonable explanations of spin Hamiltonian parameters for a paramagnetic impurity in crystals should take the impurity-induced local lattice relaxation into account.

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