Studies of the Spin Hamiltonian Parameters and the Local Structure of Tetragonal Zr$^{3+}$ Centers in Orthophosphate MPO$_4$ ($M = \text{Sc, Lu, Y}$) Crystals

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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 MPO$_4$ ($M = \text{Sc, Lu, Y}$) 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$_4$ ($M = \text{Sc, Lu, Y}$).

1. Introduction

The orthophosphates MPO$_4$ ($M = \text{Sc, Lu, Y}$) 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 applications 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 ($D_{4d}$) 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 $^2B_1$($d_{3z^2-\gamma^2}$). 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

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

where $g_s (\approx 2.0023)$ is the free-electron value. $\zeta$ 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]

\[
\zeta \approx N^2 \xi_0, \quad P \approx N^2 P_0,
\]

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in which ζ₀ and P₀ are the corresponding values of a free dⁿ ion, and N²(≈ k) is the covalence reduction factor. For a free Zr³⁺ ion, ζ₀ ≈ 500 cm⁻¹ [13]. P₀ ≈ ζ₀Nβ₀β₂ < r⁻³ > [14], and from the value of < r⁻³ > ≈ 3.16 a.u. [13] we obtain P₀ ≈ −52.5 · 10⁻⁴ cm⁻¹ for a free ⁹¹Zr³⁺ ion. The energy separations E₁ and E₂ can be written as

\[
E₁ = E(²B₂) - E(²B₁) = 10D₉,
\]

\[
E₂ = E(⁴E₂) - E(⁴E₁) = 10D₉ - 3D₄ + 5D₆.
\]

The crystal-field parameters D₉, D₄, D₂, and D₁ of the studied system in the superposition model [9] can be given as

\[
D₉ = \frac{4}{3} A₄(R₀) \sum_{i=1}^{2} \left[ \left( \frac{R₀}{R₁} \right)^{t₂} \sin^5 \theta_i \right],
\]

\[
D₂ = \frac{4}{7} A₂(R₀) \sum_{i=1}^{2} \left[ \left( \frac{R₀}{R₁} \right)^{t₂} (3 \cos^2 \theta_i - 1) \right],
\]

\[
D₁ = \frac{4}{21} A₁(R₀) \sum_{i=1}^{2} \left[ \left( \frac{R₀}{R₁} \right)^{t₂} \left( 7 \sin^4 \theta_i + 35 \cos^4 \theta_i - 30 \cos^6 \theta_i + 3 \right) \right],
\]

where the power-law exponents are t₂ ≈ 3 and t₄ ≈ 5 because of the ionic nature of the bonds [9, 15, 16]. A₂(R₀) and A₄(R₀) are the intrinsic parameters depending on the ligand, the coordination number and reference distance R₀. The values of A₄(R₀) and the ratio A₂(R₀)/A₄(R₀) ≈ 8 ~ 12 were obtained for many 3dⁿ MXₘ clusters in crystals from optical and EPR spectra studies [15 – 18]. However, for the 4dⁿ MXₘ clusters in crystals, few values of A₄(R₀) and A₂(R₀)/A₄(R₀) were reported. From the optical spectra of similar [ZrO₄]₁³⁻ clusters in a YAG:Zr³⁺ crystal [19] we estimate A₄(R₀) ≈ 1750 cm⁻¹ with R₀ ≈ 2.3 Å. It can be expected that the ratio A₂(R₀)/A₄(R₀) for 4dⁿ clusters is smaller than that for 3dⁿ clusters because (i) the ratio A₂(R₀)/A₄(R₀) is related to the ratio r₁/r₅ (ii) the ratio r₂/r₅ of a 4dⁿ ion is smaller than that of a 3dⁿ ion [13] (e.g., r₂/r₅ ≈ 0.15 and 0.27 a.u. for 4d¹ Zr³⁺ and 3d¹ Ti³⁺ ions, respectively [13]). So, we take A₂(R₀)/A₄(R₀) ≈ 5.4 for MPO₄:Zr³⁺ crystals. R₁ (i = 1 or 2) is the impurity-ligand distance and θ₁ is the angle between the R₁ and C₄ 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 MPO₄:Zr³⁺, we can reasonably let the angle θ₁ be unchanged and estimate the impurity-ligand distance R₁ from the approximate formula [20]

\[
R₁ ≈ R₉ + (r₁ - r₉)/2,
\]

where R₉ is the corresponding distance in the host crystal. The values of R₉ for MPO₄ crystals [21] are shown in Table 1. r₁ and r₉ are the ionic radius of the impurity and that of the replaced host ion. In MPO₄:Zr³⁺ crystals, r₉ ≈ 0.732, 0.85 and 0.892 Å [22] for M = Sc³⁺, Lu³⁺ and Y³⁺, respectively, and r₁(Zr³⁺) ≈ 0.89 Å, estimated by the interpolation method based on r(Zr³⁺) = 1.09 Å and r(Zr³⁺) = 0.79 Å [22]. Thus, for MPO₄:Zr³⁺ crystals the impurity-ligand distances R₁ are estimated. They and the angles θ₁ are collected in Table 1. So, in the above formulas only the parameters K and k are not known. By fitting the calculated g∥, g⊥, A∥ and A⊥ to the observed values, we obtain the same value K ≈ 1.21 and different k values (see Table 1) for the three MPO₄:Zr³⁺ 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 MPO₄:Z₃⁺ 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 MXₘ cluster the covalence increases and hence the covalence reduction factor N₂(≈ k) decreases with the decreasing M-X distance R [10, 23, 24]. Considering the different average Zr³⁺-O²⁻ distances \( \bar{R} \) of [ZrO₈]¹³⁻ clusters in MPO₄:Z₃⁺ crystals (see Table 1), one should expect an increasing value of k with an increase of the distance \( \bar{R} \). k(ScPO₄:Z₃⁺⁺) < k(LuPO₄:Z₃⁺⁺) < k(YPO₄:Z₃⁺⁺). 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 MPO₄:Z₃⁺ 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 LuPO₄:Z₃⁺⁺ and YPO₄:Z₃⁺⁺ are close to the observed values, but the calculated g∥ and g⊥ for ScPO₄:Z₃⁺⁺ agree poorly with the observed values, because the ionic radius of the impurity Zr³⁺⁺ is close to those of the replaced host ions in LuPO₄:Z₃⁺⁺ and YPO₄:Z₃⁺⁺, but the difference of the ionic radius between Zr³⁺⁺ and the replaced Sc³⁺ ion in the ScPO₄:Z₃⁺⁺ 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.