Investigations of the EPR *g* Factors for Er^{3+} in $CaMoO_4$

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The electron paramagnetic resonance (EPR) *g* factors $g_\parallel$ and $g_\perp$ for Er^{3+} in $CaMoO_4$ are theoretically investigated by using the perturbation formulas of the *g* factors for a $4f^{11}$ ion in tetragonal symmetry. In these formulas, the contributions to the *g* factors arising from the second-order perturbation terms and the admixture of various states are considered. The crystal-field parameters for the tetragonally distorted tetrahedra are determined by using the superposition model and the structural data of the impurity Er^{3+} on the host Ca^{2+} site in $CaMoO_4$. The calculated *g* factors agree with the observed values. The validity of the results is discussed.

Key words: Electron Paramagnetic Resonance (EPR); Crystal- and Spin Hamiltonians; Er^{3+}; $CaMoO_4$.

1. Introduction

$CaMoO_4$ is among the group of scheelite-type structure with $C_{4h}{}^6$ point symmetry ($I4_1$/a space group). Recently, $CaMoO_4$ has attracted great interest because of its application in silica-supported catalysts [1], as dispersive element in electronically tunable lasers [2] and mixed electron-hole-ion conductor [3, 4]. Particularly, this kind of compounds can be easily doped with rare earth ions and grown to large crystals which are the candidates of solid state laser materials [5, 6]. In order to study the electronic energy transfer mechanisms among the rare earth ions as well as the effect of crystal-fields, temperature and pressure on the properties of these materials, extensive investigations have been carried out by means of high pressure Raman and X-ray excited luminescence spectroscopies [7 – 9]. The electron paramagnetic resonance *g* factors for Er^{3+} in $CaMoO_4$ were measured by EPR technique decades ago [10, 11]. Until now, however, these experimental results have not been theoretically studied. Since information about the electronic properties of Er^{3+} ions in $CaMoO_4$ may be useful to understand the properties of this material (or other scheelite-type compounds), theoretical investigations on the EPR *g* factors of the above Er^{3+} impurity center are significant. In this paper, we investigate theoretically the *g* factors for Er^{3+} in $CaMoO_4$ by using the perturbation formulas of the *g* factors for a $4f^{11}$ ion in tetragonal symmetry. In these formulas, the contributions to the g factors arising from the second-order perturbation terms and the admixture of various states are taken into account. The validity of the results is discussed.

2. Calculation

In scheelite-type $CaMoO_4$, the Ca^{2+} site is coordinated to eight nearest-neighbour oxygen ions which are grouped into two sets of tetragonally distorted interpenetrating tetrahedra. The site symmetry for Ca^{2+} is S_4 [12, 13]. Trivalent rare earth ions (e. g., Er^{3+}) tend to locate on Ca^{2+} sites and conserve the tetragonal (S_4) site symmetry, because charge compensation is regarded as distant from the impurity center [13]. For an Er^{3+}($4f^{11}$) ion in a tetragonal (S_4) site without inversion symmetry, the $^4I_{15/2}$ ground state may be split into eight Kramers doublets. The lowest doublet can be $(\Gamma_5+\Gamma_6)$ or $(\Gamma_7+\Gamma_8)$, corresponding to the cubic (T_d) representation Γ_6 or Γ_7, with an average value $\bar{g}$ [= $(g_\parallel+2g_\perp)/3$] of about 6.8 or 6 [15], respectively (note: the above notation for T_d [15] is an exchange of that for octahedral cubic $\mathrm{O_h}$ symmetry in [16, 17]). According to the observed $\bar{g}(\approx 6)$ for Er^{3+} in $\mathrm{CaMoO_4}$ [10, 11], the lowest doublet should be $(\Gamma_7+\Gamma_8)$. Therefore, the perturbation formulas of the g factors for a $4\mathrm{f}^{11}$ ion in tetragonal symmetry can be expressed as [18]

$$\begin{aligned} g_\parallel &= g_\parallel^{(1)} + g_\parallel^{(2)}, \\ g_\parallel{}^{(1)} &= 2g_J\langle\Gamma\gamma|\hat{J}_\mathrm{Z}|\Gamma\gamma\rangle, \\ g_\parallel{}^{(2)} &= 2\sum_x{}' \frac{\langle\Gamma\gamma|\hat{H}_\mathrm{CF}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{J}_\mathrm{Z}|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)}, \end{aligned} \tag{1}$$

$$\begin{aligned} g_\perp &= g_\perp^{(1)} + g_\perp^{(2)}, \\ g_\perp{}^{(1)} &= g_J\langle\Gamma\gamma|\hat{J}_+|\Gamma\gamma'\rangle, \\ g_\perp{}^{(2)} &= 0. \end{aligned} \tag{2}$$

Here g_J is the Lande factor and $\hat{J}$ is the orbital angular momentum operator. $\hat{H}_\mathrm{CF}$ denotes the crystal-field interaction. The parameters g_J for various ${}^{2S+1}\mathrm{L}_J$ configurations are collected in [16, 17]. It is noted that the nondiagonal elements g'_J may occur in the expansions of (1) and (2) for the interactions between different ${}^{2S+1}\mathrm{L}_J$ configurations. In the above formulas, besides the contributions to the g factors from the first-order perturbation terms, we also include the contributions from the second-order perturbation terms, which result from the admixture of the lowest $(\Gamma_7+\Gamma_8)$ doublet with the other fourteen irreducible representations Γ_x [i.e., six $(\Gamma_5+\Gamma_6)$ and eight $(\Gamma_7+\Gamma_8)$] due to the tetragonal splitting of the ground ${}^4\mathrm{I}_{15/2}$ and the first excited ${}^4\mathrm{I}_{13/2}$ states via crystal-field $\hat{H}_\mathrm{CF}$ and orbital angular momentum $\hat{J}$ interactions [18, 19]. As for (2), the second-order perturbation contribution $g_\perp{}^{(2)}$ vanishes because none of the fourteen Γ_x has a non-zero matrix element with the lowest $(\Gamma_7+\Gamma_8)$ doublet, for both $\hat{H}_\mathrm{CF}$ and the x or y component of $\hat{J}$ operators. In the above formulas, the basic function $\Gamma\gamma^{(\gamma')}$ (where γ and γ' denote the two components of the Γ irreducible representation) contains admixtures of various states, namely the admixture between the ground ${}^4\mathrm{I}_{15/2}$ and the excited ${}^4\mathrm{I}_{13/2}$ states via $\hat{H}_\mathrm{CF}$ interaction, the admixture among ${}^2\mathrm{K}_{15/2}$, ${}^2\mathrm{L}_{15/2}$, and ${}^4\mathrm{I}_{15/2}$ and that among ${}^2\mathrm{K}_{13/2}$, ${}^2\mathrm{I}_{13/2}$ and ${}^4\mathrm{I}_{13/2}$ via spin-orbit coupling interaction. So, the expression for $\Gamma\gamma^{(\gamma')}$ may be written as [18, 19]

$$\begin{aligned} |\Gamma\gamma^{(\gamma')}\rangle = {} & \sum_{M_{J1}} C({}^4\mathrm{I}_{15/2};\Gamma\gamma^{(\gamma')}\mathrm{M}_{J1})\mathrm{N}_{15/2}(|{}^4\mathrm{I}_{15/2}\mathrm{M}_{J1}\rangle + \lambda_K|{}^2\mathrm{K}_{15/2}\mathrm{M}_{J1}\rangle + \lambda_L|{}^2\mathrm{L}_{15/2}\mathrm{M}_{J1}\rangle) \\ & + \sum_{M_{J2}} C({}^4\mathrm{I}_{13/2};\Gamma\gamma^{(\gamma')}\mathrm{M}_{J2})\mathrm{N}_{13/2}(|{}^4\mathrm{I}_{13/2}\mathrm{M}_{J2}\rangle + \lambda'_K|{}^2\mathrm{K}_{13/2}\mathrm{M}_{J2}\rangle + \lambda_I|{}^2\mathrm{L}_{13/2}\mathrm{M}_{J2}\rangle), \end{aligned} \tag{3}$$

where M_{J1} and M_{J2} are, respectively, in the ranges of $-15/2$ to $15/2$ and $-13/2$ to $13/2$. The coefficients $C({}^4\mathrm{I}_{15/2};\Gamma\gamma^{(\gamma')}\mathrm{M}_{J1})$ or $C({}^4\mathrm{I}_{13/2};\Gamma\gamma^{(\gamma')}\mathrm{M}_{J2})$ can be obtained by diagonalizing the 30×30 energy matrix including the ${}^4\mathrm{I}_{15/2}$ and ${}^4\mathrm{I}_{13/2}$ states. N_i and λ_i are the normalization factors and the mixing coefficients, respectively. They can be determined by using the spin-orbit coupling matrix elements and the perturbation method.

As mentioned before, the Ca^{2+} site occupied by the impurity Er^{3+} has the S_4 local symmetry. However, the $\mathrm{D}_{2\mathrm{d}}$ symmetry is proved to be a good approach due to the rather small distortion from $\mathrm{D}_{2\mathrm{d}}$ to S_4 [20, 21], as treated for some trivalent rare earth ions in similar scheelite-type $\mathrm{LiYF_4}$ by many authors [22, 23]. So we still take the $\mathrm{D}_{2\mathrm{d}}$ approximation here for simplicity. According to [16, 17], the crystal-field interaction $\hat{H}_\mathrm{CF}$ for a $4\mathrm{f}^{11}$ (Er^{3+}) ion in tetragonal $(\mathrm{D}_{2\mathrm{d}})$ symmetry can be written in terms of the Stevens operator equivalents, i. e.,

$$\hat{H}_\mathrm{CF} = B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_4^4O_4^4 + B_6^4O_6^4. \tag{4}$$

Here B_k^q (where $k=2,4,6$; $|q|\le k$) are the crystal-field parameters. From the superposition model [24], they can be expressed as

$$B_k^q = \sum_{j=1}^{2} \bar{A}_k(R_0)(R_0/R_j)^{t_k}K_k^q(\theta_j,\phi_j), \tag{5}$$

where $K_k^q(\theta_j,\phi_j)$ are the coordination factors [24, 25], which can be obtained from the local structural data of the studied defect centers. t_k and $\bar{A}(R_0)$ are, respectively, the power-law exponents and the intrinsic parameters (with the reference distance R_0). The Ca^{2+} ion in $\mathrm{CaMoO_4}$ is coordinated to eight nearest O^{2-} ions, with four of them at the distance R_1 and angles

Table 1. The EPR g factors for the tetragonal Er^{3+} center in $CaMoO_4$.

	$g_\parallel$	$g_\perp$
Cal.[a]	1.043	8.452
Cal.[b]	1.141	8.452
Expt. [10, 11]	1.176	8.55

[a] Calculation by considering the contributions from only the first-order perturbation terms. [b] Calculation by considering the contributions from both the first- and second-order perturbation terms.

θ_1 and ϕ_1, and the other four at the different distance R_2 and angles θ_2 and ϕ_2, where θ_j and ϕ_j ($j = 1,2$) are, respectively, the polar angles and the azimuthal angles of the metal-ligand distances R_j related to the Z (or fourfold) and X axes of the crystal [20, 21]. For the Ca^{2+} site in $CaMoO_4$, $R_1 \approx 2.472$ Å, $\theta_1 \approx 67.55°$, $\phi_1 \approx -36.03°$, $R_2 \approx 2.460$ Å, $\theta_2 \approx 141.05°$ and $\phi_2 \approx -29.67°$ [21]. According to [21, 26], the power-law exponents $t_2 \approx 3.5$, $t_4 \approx t_6 \approx 6$ and the intrinsic parameters $\bar{A}_2(R_0) \approx 400$ cm^{-1}, $\bar{A}_4(R_0) \approx 50(2)$ cm^{-1}, and $\bar{A}_6(R_0) \approx 17(3)$ cm^{-1} [with the reference bonding length $R_0 \approx 2.466$ Å, which is very close to the average metal-ligand distance $\bar{R}(\approx 2.466$ Å) in the studied $CaMoO_4$] were obtained for Er^{3+} in scheelite $CaWO_4$. So, they are also adopted for the Er^{3+} center in this work, except that we take $\bar{A}_4(R_0) \approx 50.2$ cm^{-1} and $\bar{A}_6(R_0) \approx 21.1$ cm^{-1} here for $CaMoO_4$ in consideration of the small difference between the structural data for $CaMoO_4$ and $CaWO_4$ [21]. The free-ion parameters of the Coulombic repulsion ($F^2 \approx 97504$ cm^{-1}, $F^4 \approx 70746$ cm^{-1} and $F^6 \approx 48042$ cm^{-1}), the two-body interaction parameters ($\alpha \approx 20.95$ cm^{-1}, $\beta \approx -689$ cm^{-1} and $\gamma \approx 1839$ cm^{-1}) and the spin-orbit coupling coefficient ($\zeta_{4f} \approx 2339$ cm^{-1}) in the energy matrix were obtained for Er^{3+}-doped $CaWO_4$ [27]. They can be approximately adopted here. In view of the covalency between the 4f orbitals of the Er^{3+} ion and the 2p orbitals of O^{2-} for the Er^{3+}-O^{2-} bonds in $CaMoO_4$, the orbital reduction factor $k(\approx 0.979)$ for the similar Er^{3+}-O^{2-} bond in MgO: Er^{3+} [16] and that (≈ 0.979) for Yb^{3+} in scheelites [28] can also be applied here. Substituting these parameters into (1) and (2), the g factors for the Er^{3+} center in $CaMoO_4$ are calculated and compared with experiment in Table 1.

3. Discussion

From Table 1 one can find that the calculated g factors for Er^{3+} in $CaMoO_4$ based on the perturbation formulas of the g factors for $4f^{11}$ ions in tetragonal symmetry agree with the observed values, suggesting that the perturbation formulas and the related parameters adopted in this work are reasonable. There are several points that may be discussed here:

1. The observed axial g factors reveal the tetragonal symmetry of the Er^{3+} center in $CaMoO_4$. It is noted that there are two possible cases which would lower the local symmetry of the impurity center, i. e., vicinal charge compensation and off-center displacement of the impurity ion. On the one hand, charge compensation ions may be far enough from the impurity center and then influence on the local symmetry may be negligible [13]. On the other hand, Kiel and Mims [20] found that impurity ions (e. g., divalent or trivalent $3d^n$ ions) smaller than 0.8 Å would be unstable at the Ba^{2+} (with the ionic radius of about 1.34 Å [29]) site in scheelite-type $BaWO_4$ and then are off-center displaced away from the ideal cation site, based on the Born-Mayer theory of ionic bonding. However, for the studied tetragonal center in $CaMoO_4$, the impurity Er^{3+} (with the ionic radius of about 0.881 Å [29]) is not sufficiently small to be unstable at the host Ca^{2+} site. Consequently, both possible cases are excluded and the local tetragonal symmetry of the host Ca^{2+} site is therefore conserved in the studied system.

2. According to our calculations, the contributions to $g_\parallel$ arising from the second-order perturbation terms are about 9% those from the first-order perturbation terms. So, in order to explain the g factors for Er^{3+} centers in crystals more satisfactorily, the second-order perturbation contributions should be taken into account. Based on the above studies, the importance of the contributions due to the second-order perturbation terms is related to the tetragonal crystal-fields, i.e., both the numerators and the denominators in (1) increase with the increase of the strength of the crystal-fields. Meanwhile, the contributions arising from some irreducible representation Γ_x are very small or cancel one another. On the whole, the total contributions to $g_\parallel$ from the second-order perturbation terms are approximately 9% those from the first-order perturbation ones. On the other hand, the contributions to the g factors from the admixtures of various states are about 5%, which is smaller than those from the second-order perturbation terms. Obviously, higher excited states (e.g., $^4I_{11/2}$, $^4I_{9/2}$ etc.) would have even smaller influence.

3. It is noted that there may be some errors in our calculations. (i) The free-ion parameters for the similar $CaWO_4$ in [27] have fitting errors. Nevertheless, these errors have only slight influence (no more than

2%) on the energy separations between the ground $^4I_{15/2}$ and the excited states ($^4I_{13/2}$, $^2K_{15/2}$, $^2L_{15/2}$, $^2K_{13/2}$, $^2I_{13/2}$ et. al.) and bring still smaller errors (no more than 1%) to the parameters N_i and λ_i in (3). Since the basic function $\Gamma\gamma$ and the calculated g factors are mainly related to the crystal-field splitting of the ground $^4I_{15/2}$ state, the calculation errors of the g factors due to the fitting errors of the free-ion parameters are expected to be less than 2%. (ii) The effective impurity-ligand distance may be dissimilar to the corresponding metal-ligand distances R_j due to the difference in charge and ionic radius between the impurity Er^{3+} and the replaced Ca^{2+} in $CaMoO_4$. However, the above errors in R_j would only slightly affect the tetragonal distortion and the crystal-field parameters B_k^q, which are more sensitive to the polar angles θ_j. Even if the host metal-ligand distances R_j are replaced by the impurity-ligand distances R'_j from the approximate formulas $R'_j \approx R_j + (r_i - r_h)/2$ (where r_i is the ionic radius of the impurity Er^{3+} and r_h (≈ 0.99 Å) the radius of the host Ca^{2+} [29]) [30, 31], the calculated g factors would change by less than 2%. (iii) For simplicity, the D_{2d} approach instead of S_4 symmetry is adopted to describe the crystal-field interaction of (4) in this work. In fact, even though one takes the exact S_4 symmetry, the magnitudes of the imaginary parts of the rank-4 and rank-6 crystal-field parameters are very small, as shown in [21, 32, 33], and so their contributions to the coefficient $C(^4I_{15/2};\Gamma\gamma^{(\gamma')}M_{J1})$ or $C(^4I_{13/2};\Gamma\gamma^{(\gamma')}M_{J2})$ in $\Gamma\gamma$ and the g factors are expected to be no more than 4%. (iv) Even in the approach of D_{2d} symmetry, the angular distortions for the polar angles θ_j due to the size and charge mismatching substitution of Ca^{2+} by Er^{3+} are not considered in the calculations. Since the host Ca^{2+} is replaced by the slightly smaller impurity Er^{3+}, local relaxation around the impurity can be introduced. On the other hand, the local relaxation may be largely counteracted by the extra positive charge of Er^{3+} and hence stronger electrostatic attraction between Er^{3+} and the ligands. As a result, the $[ErO_8]^{13-}$ cluster should be relatively stable and then the angular distortion can be regarded as negligible in $CaMoO_4$. (v) The errors due to adoption of the superposition model parameters for the similar $CaWO_4$:Er^{3+} can also affect the calculated g factors. According to the studies, the errors of the theoretical g factors are expected to be no more than 3% whereas the parameters $\bar{A}_k$ and t_k change by 10%. In addition, part of the effects of the above errors (i.e., points (i)∼(iv)) on the final g factors can be assumed to be absorbed in the parameters $\bar{A}_4(R_0)$ and $\bar{A}_6(R_0)$. In consideration of the above analyses, the theoretical calculations and the results in this work can still be regarded as reasonable.

In conclusion, the EPR g factors of the tetragonal Er^{3+} center in $CaMoO_4$ are theoretically investigated by using the perturbation formulas of the g factors for a $4f^{11}$ ion in tetragonal symmetry. According to the above studies, the experimental EPR data [10, 11] for $CaMoO_4$:Er^{3+} can be reasonably attributed to the impurity Er^{3+} occupying the host Ca^{2+} site with approximately tetragonal (D_{2d}) point symmetry. Similarly, the theoretical formulas and the methods of this work can also be applied to Er^{3+} in other tetragonal scheelite-type ABO_4 compounds.

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