Theoretical Studies of the Optical Spectra and EPR Parameters of Trigonal Yb^{3+} Center in $KMgF_3$ and $KZnF_3$ Crystals

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The optical spectra and EPR parameters of trigonal Yb^{3+} centers in $KMgF_3$ and $KZnF_3$ crystals are calculated in a unified way, based on the crystal-field theory. The results agree reasonably with the observed values. The results are discussed.

Key words: Crystal-field Theory; Electron Paramagnetic Resonance; Yb^{3+}; $KZnF_3$; $KMgF_3$.

1. Introduction

Crystals with the perovskite structure have extensive practical applications and are convenient models for investigating the optical and magnetic properties of transition metal or rare-earth metal impurity ions. Much theoretical and experimental work has been done to understand the properties of these crystals [1 – 7]. For instance, the optical and EPR spectra of trigonal Yb^{3+} centers in $KMgF_3$ and $KZnF_3$ crystals were measured many years ago [8, 9]. It is interesting that a trivalent rare-earth metal (Re^{3+}) can replace two different host cations: Mg^{2+} (or Zn^{2+}) with six coordinated F^- anions and K^+ with twelve coordinated F^- anions. Because substitution of Re^{3+} by an Mg^{2+}, Zn^{2+} or K^+ host ion gives rise to charge compensation, there may be various Re^{3+} impurity centers with different site symmetries, such as cubic, trigonal, tetragonal and orthorhombic symmetries. For example, there are three different Yb^{3+} centers including cubic, trigonal and tetragonal centers found by EPR measurements. Theoretical explanations of the optical and EPR spectra for a tetragonal Yb^{3+} center have been made in our previous work [10]. For the trigonal Yb^{3+} center, the crystal-field analysis of the optical spectra was made. The calculated electronic energy levels are consistent with the observed ones [9]. But by considering only the interaction within the ground $^2F_{7/2}$ multiplets, the EPR g factors calculated approximately from the first-order perturbation formulae agree poorly with the experimental findings [8, 9]. In this paper we use the second-order perturbation formulae of the EPR parameters for $4f^{13}$ ions in trigonal symmetry. In these formulae, the contributions to the EPR parameters due to the J-mixing between the ground $^2F_{7/2}$ and the excited $^2F_{5/2}$ states via crystal-field interactions, the interactions between the lowest Kramers doublet $\Gamma\gamma$ and the other Kramers doublets Γx via the crystal-field and angular momentum, as well as the covalence reduction effect due to the covalence of metal-ligand bonds are all considered. From these formulae and the crystal-field parameters obtained from the experimental optical spectra, the EPR g factors $g_\parallel$ and $g_\perp$ of Yb^{3+} and hyperfine structure constants $A_\parallel$ and $A_\perp$ of the $^{171}Yb^{3+}$ and $^{173}Yb^{3+}$ isotopes in $KMgF_3$ and $KZnF_3$ crystals are calculated. The calculated results agree well with the observed values. The results are discussed.

2. Calculation

The structure of the perovskite crystals belongs to the *Pm*3*m* space group [11]. The doped Yb^{3+} ion in the lattice substitutes, the monovalent K^+ sites of the tetragonal centers, and the divalent Mg^{2+} or Zn^{2+} sites of the cubic and trigonal centers [9]. A free Yb^{3+} ion has a $4f^{13}$ electronic configuration with a $^2F_{7/2}$ ground state and a $^2F_{5/2}$ excited state. The trigonal crystal-field lifts the degeneracies of $^2F_{7/2}$ and $^2F_{5/2}$ states into four and three Kramers doublets, respectively [12, 13].

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Considering the crystal-field J-mixing effect, the energy levels and wave functions of these doublets can be obtained by diagonalizing the $14 \cdot 14$ energy matrix in trigonal symmetry. The wave function of the lowest doublet $\Gamma\gamma$ can be expressed as

$$\begin{aligned}\Gamma_g\rangle \geq \sum_{\mathrm{M}_{J1}} C(^2F_{7/2};\Gamma_g \mathrm{M}_{J1})|^2F_{7/2}\mathrm{M}_{J1}\rangle \\ + \sum_{M_{J2}} C(^2F_{5/2};\Gamma_g M_{J2})|^2F_{5/2}M_{J2}\rangle,\end{aligned} \tag{1}$$

where $g=\gamma$ and $g=\gamma'$ stand for the two components of the Γ irreducible representation, M_{J1} and M_{J2} are the half-integers in the ranges $-7/2 \sim 7/2$ and $-5/2 \sim 5/2$, respectively.

The perturbation Hamiltonian for a rare-earth ion in the crystal under an external magnetic field can be written as [13]

$$\hat{H}' = \hat{H}_{\mathrm{so}} + \hat{H}_{\mathrm{CF}} + \hat{H}_{\mathrm{Z}} + \hat{H}_{\mathrm{hf}}, \tag{2}$$

where $\hat{H}_{\mathrm{so}}$ is the spin-orbit coupling interaction, $\hat{H}_{\mathrm{CF}}$ the crystal-field interaction, $\hat{H}_{\mathrm{Z}}$ the Zeeman interaction, and $\hat{H}_{\mathrm{hf}}$ the hyperfine interaction term. $\hat{H}_{\mathrm{so}}$ can be expressed as [12]

$$\hat{H}_{\mathrm{so}} = \zeta(\hat{L}\cdot\hat{S}), \tag{3}$$

where ζ is the spin-orbit coupling coefficient, and $\hat{L}$ and $\hat{S}$ are the orbital and spin momentum operators, respectively. For $4f^n$ ions, since $\hat{H}_{\mathrm{CF}}$ is much smaller than $\hat{H}_{\mathrm{so}}$, it is suitable to calculate the crystal-field matrix elements within the same $^{2S+1}\mathrm{L}_J$ configurations by means of the Stevens equivalent operator method [12, 13]. Although application of the equivalent operator may complicate the calculations of the matrix elements between the states with different $J(= 5/2$ and $7/2)$, the total calculations based on the equivalent operator method can be more convenient than those based on the irreducible tensors operator (e. g. in [9]). Thus, the former is adopted here. Then the crystal-field interaction $\hat{H}_{\mathrm{CF}}$ under trigonal symmetry in terms of equivalent operators can be expressed as [12, 13]

$$\begin{aligned}\hat{H}_{\mathrm{CF}} = B_2^0O_2^0 + B_4^0O_4^0 + B_6^0O_6^0 \\ + B_4^3O_4^3 + B_6^3O_6^3 + B_6^6O_6^6,\end{aligned} \tag{4}$$

where B_k^q are crystal-field parameters. $\hat{H}_{\mathrm{Z}}$ can be expressed in terms of the Landé factor g_J and the angular momentum operator $\hat{J}$ as [13]

$$\hat{H}_{\mathrm{Z}} = g_J\mu_{\mathrm{B}}\hat{H}\cdot\hat{J}, \tag{5}$$

and the hyperfine interaction can be denoted as $\hat{H}_{\mathrm{hf}} = PN_J\hat{N}$, where P is the dipolar hyperfine structure constant and N_J is the diagonal matrix element for $^{2S+1}\mathrm{L}_J$ state. For free Yb^{3+} isotopes, $P(^{171}\mathrm{Yb}) \approx 388.4\cdot 10^{-4}\,\mathrm{cm}^{-1}$ and $P(^{173}\mathrm{Yb}) \approx -106.5\cdot 10^{-4}\,\mathrm{cm}^{-1}$ [12, 13].

Based on the perturbation method, the perturbation formulae of the EPR parameter g factors and hyperfine structure constants $A_\parallel$ and $A_\perp$ for the $4f^{13}$ ion in trigonal symmetry can be obtained [14]:

$$\begin{aligned}
g_\parallel &= g_\parallel^{(1)} + g_\parallel^{(2)}, \\
g_\parallel^{(1)} &= 2g_J\langle\Gamma\gamma|\hat{J}_{\mathrm{z}}|\Gamma\gamma\rangle, \\
g_\parallel^{(2)} &= 2\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{\mathrm{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{J}_{\mathrm{Z}}|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)}, \\
g_\perp &= g_\perp^{(1)} + g_\perp^{(2)}, \\
g_\perp^{(1)} &= 2g_J\langle\Gamma\gamma|\hat{J}_x|\Gamma\gamma'\rangle, \quad g_\perp^{(2)} = 0,
\end{aligned} \tag{6}$$

$$\begin{aligned}
A_\parallel &= A_\parallel^{(1)} + A_\parallel^{(2)}, \\
A_\parallel^{(1)} &= 2PN_J\langle\Gamma\gamma|\hat{N}_{\mathrm{Z}}|\Gamma\gamma'\rangle, \\
A_\parallel^{(2)} &= 2P\sum_X{}' \frac{\langle\Gamma\gamma|\hat{H}_{\mathrm{CF}}|\Gamma_X\gamma_X\rangle\langle\Gamma_X\gamma_X|\hat{N}_{\mathrm{Z}}|\Gamma\gamma\rangle}{E(\Gamma_X)-E(\Gamma)}, \\
A_\perp &= A_\perp^{(1)} + A_\perp^{(2)}, \\
A_\perp^{(1)} &= 2P\,N_J\langle\Gamma\gamma|\hat{N}_X|\Gamma\gamma'\rangle, \quad A_\perp^{(2)} = 0,
\end{aligned} \tag{7}$$

where the parameters g_J, g_J', N_J, and N_J' (g_J' and N_J' occur in the expansions of the above formulae) for various states can be obtained from [12] and [13]. It is noted that the contributions to the g (or A) factors from the states with different J via $\hat{H}_{\mathrm{Z}}$ (or $\hat{H}_{\mathrm{hf}}$) are also included in the expansions of the above formulae, which are related to the parameters g_J' (or N_J'). For saving printing space, the detailed expressions for the g (or A) factors due to the J-mixing effect are not given here.

Usually, the crystal-field parameters in (4) can be evaluated from the point-charge or superposition model [15, 16] and the local structures of the studied systems. Unfortunately, the local structural parameters of the impurity centers were not known. Therefore, the crystal-field parameters are taken as adjustable parameters here, similar to the treatment in the previous work [9]. Applying the above parameters to the energy matrix, and fitting the calculated optical spectra to the observed values [9], we obtain the best fitting results

Table 1. The crystal-field energy levels (in cm^{-1}) for Yb^{3+} in $KMgF_3$ and $KZnF_3$ crystals.

		1	2	3	4	5	6	7
	Cal.[a]	0	365	408	1032	10358	10399	11087
$KMgF_3$	Cal.[b]	0	341	364	969	10358	10389	11058
	Expt. [7, 8]	0	338	364	1009	10358	10406	–
	Cal.[a]	0	377	411	1045	10371	10417	11119
$KZnF_3$	Cal.[b]	0	352	372	990	10371	10405	11087
	Expt. [7, 8]	0	349	–	1047	10371	10419	–

[a] Calculations based on the fitted crystal-field parameters in terms of the irreducible tensor operator method in [8].

[b] Calculations based on the fitted crystal-field parameters [(8) and (9)] in terms of the equivalent operator method in this work.

of the crystal-field parameters and spin-obit coupling coefficient

$$\begin{aligned} &B_2^0 \approx 63\ \mathrm{cm}^{-1}, \quad B_4^0 \approx -1430\ \mathrm{cm}^{-1}, \\ &B_4^3 \approx 1945\ \mathrm{cm}^{-1}, \quad B_6^0 \approx -160\ \mathrm{cm}^{-1}, \\ &B_6^3 \approx -30\ \mathrm{cm}^{-1}, \quad B_6^6 \approx 32\ \mathrm{cm}^{-1}, \\ &\zeta \approx 2905\ \mathrm{cm}^{-1}, \end{aligned} \tag{8}$$

for $KMgF_3$:Yb^{3+}, and

$$\begin{aligned} &B_2^0 \approx 56\ \mathrm{cm}^{-1}, \quad B_4^0 \approx -1450\ \mathrm{cm}^{-1}, \\ &B_4^3 \approx 1991\ \mathrm{cm}^{-1}, \quad B_6^0 \approx -150\ \mathrm{cm}^{-1}, \\ &B_6^3 \approx -25\ \mathrm{cm}^{-1}, \quad B_6^6 \approx 32\ \mathrm{cm}^{-1}, \\ &\zeta \approx 2908\ \mathrm{cm}^{-1}, \end{aligned} \tag{9}$$

for $KZnF_3$:Yb^{3+} (note: the conversion between the crystal-field parameters based on the Stenvens operator and the irreducible tensor operator notations, i. e. Wybourne formulations, can be obtained from [12, 17]). Thus, the theoretical optical spectra are obtained by diagonalizing the energy matrix based on the above crystal-field parameters. Comparisons between the calculated and experimental energy levels are shown in Table 1. Note that the energy labels stand for the energy differences between the lowest Kramer doublet (labeled as 1) and the other higher Kramer doublets (labeled as $2 \sim 7$), due to the trigonal crystal-field splittings of the $^2F_{7/2}$ and $^2F_{5/2}$ configurations. The fitted data in [8] are also collected in Table 1.

Table 2. The EPR parameters of Yb^{3+} in $KMgF_3$ and $KZnF_3$ crystals (the hyperfine structure constants A_i are in units of 10^{-4} cm^{-1}).

		$g_\parallel$	$g_\perp$	$A_\parallel$ (^{171}Yb)	$A_\perp$ (^{171}Yb)	$A_\parallel$ (^{173}Yb)	$A_\perp$ (^{173}Yb)
	Cal.[a]	1.99	2.98				
$KMgF_3$	Cal.[b]	1.846	2.892	479.0	749.9	131.3	205.6
	Expt. [8]	1.84	2.90	–	–	–	–
	Cal.[a]	1.96	2.99				
$KZnF_3$	Cal.[b]	1.814	2.905	470.5	753.3	129.0	206.4
	Expt. [8]	1.82	2.90	–	–	–	–

[a] Calculations based on the fitted crystal-field parameters in terms of the irreducible tensor operator method in [8].

[b] Calculations based on the fitted crystal-field parameters [(8) and (9)] in terms of the equivalent operator method in this work.

Considering the covalence reduction effect, the orbital angular momentum $\hat{L}$ in (6) and (7) should be multiplied by an orbital reduction factor k. In order to reduce the number of adjustable parameters, the value $k(\approx 0.949)$ for Yb^{3+} in zircon-type crystal [14] can be approximately adopted here. Thus, from above parameters and formulae, the g factors $g_\parallel$, $g_\perp$ of Yb^{3+} and the hyperfine structure constants $A_\parallel$, $A_\perp$ of ^{171}Yb and ^{173}Yb isotopes in both crystals are calculated. The calculated EPR parameters are compared with those of the observed values in Table 2.

3. Discussion

From the Table 1 it can be seen that the calculated energy levels in this work agree better than those in [9] with the observed values. So the crystal-field parameters adopted in this paper are reasonable. The difference between the two sets of the crystal-field parameters and the energy levels may be due to the process of fitting as well as the adopted (equivalent and tensor) operator methods. From the Table 2 one can find that by using the second-order perturbation formulae the EPR g factors $g_\parallel$, $g_\perp$ for Yb^{3+} in $KMgF_3$ and $KZnF_3$ crystals are also consistent with the experimental findings. This means that the formulae of the g factors including the second-order perturbation terms and the covalency reduction effect (i. e., including of the factor k) adopted in the present work can be regarded as more reasonable.

As experimental values of the hyperfine structure parameters $A_\parallel$, $A_\perp$ of $^{171}Yb^{3+}$ and $^{173}Yb^{3+}$ in $KMgF_3$ and $KZnF_3$ are not reported, the corresponding calculated values remain to be verified.

Compared with the experimental hyperfine structure parameters for Yb^{3+} in other crystals, such as CaF_2, $LiYF_4$ and YPO_4 (see Table 3), we can find that the relationship $g_\parallel/g_\perp \approx A_\parallel/A_\perp$ is approximately valid for all the systems, as supported by [12]. Moreover, the ratios are also close to each other, suggesting that the theoretical hyperfine structure parameters $A_\parallel$ and $A_\perp$ obtained for $KMgF_3$ and $KZnF_3$ in this work can be regarded as reasonable. Obviously, these values need to be further checked with experimental investigations.

			$^{171}Yb^{3+}$		$^{173}Yb^{3+}$		
Host	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$A_\parallel$	$A_\perp$	Refs.
CaF_2	2.420(4)	3.802(3)	–	–	169	272	Expt. [18, 19]
$LiYF_4$	1.3308(6)	3.917(3)	338(2)	1028(4)	92.5(5)	284(1)	Expt. [20]
$LiYF_4$	1.330(2)	3.903(3)	347(2)	1018(2)	95(2)	279(2)	Expt. [21]
YPO_4	1.526(1)	3.120(3)	408(4)	827(7)	111(1)	235(2)	Expt. [22]
$KMgF_3$	1.846	2.892	479.0	749.9	131.3	205.6	Cal. [this work]
$KZnF_3$	1.814	2.905	470.5	753.3	129.0	206.4	Cal. [this work]

Table 3. EPR parameters of Yb^{3+} in other crystals (the hyperfine structure constants A_i are in units of 10^{-4} cm^{-1}).

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