Studies of the Zero-field Splitting for Mn^{2+} in 6H-$RbMgF_3$ Crystal

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By using the spin-orbit coupling mechanism and the empirical superposition model, the zero-field splittings *D* of Mn^{2+} ions on both Mg^{2+} sites in hexagonal 6H-$RbMgF_3$ crystal are calculated from the structural data of both Mg^{2+} sites. The calculated results of both methods confirm the suggestion that Mn^{2+} in 6H-$RbMgF_3$ occupies the Mg^{2+} (I) site (which has D_{3d} site symmetry) and the zero-field splitting *D* of 6H-$RbMgF_3$: Mn^{2+} is explained reasonably.

Key words: Electron Paramagnetic Resonance; Crystal-Field Theory; Superposition Model; Mn^{2+}; 6H-$RbMgF_3$.

1. Introduction

Fluoroperovskites ABF_3 can be used as laser crystals when doped with transition-metal and rare earth ions, and so they have attracted much attention [1 – 6]. The structure of a fluoroperovskite depends upon the tolerance factor $t = (r_A + r_F)/[\sqrt{2}(r_B + r_F)]$, where r is an ionic radius [7]. Fluoroperovskite $RbMgF_3$, since the tolerance factor $t \approx 1.01 > 1$, has a 6H-type hexagonal structure in which there are two crystallographically distinct types of Mg^{2+} ions [7, 8]. Both Mg^{2+} ions are surrounded by octahedra of F^- ions. One of them, Mg^{2+} (I), exhibits D_{3d} site symmetry, while the other, Mg^{2+} (II), occupies a site having C_{3V} symmetry [8]. When a $3d^n$ ion enters the 6H-$RbMgF_3$ crystal, it may occupy the Mg^{2+} (I) or Mg^{2+} (II) sites. The EPR spectra of Mn^{2+} ions in 6H-$RbMgF_3$ crystal were reported [9]. Since the spectra can be described by a spin Hamiltonian containing a zero-field splitting $D \approx 91.6 \cdot 10^{-4}$ cm^{-1}, Mn^{2+} occupies only one Mg^{2+} site. Dance and Kerkouri [9] suggested that Mn^{2+} occupies the Mg^{2+} (I) site in 6H-$RbMgF_3$ crystal. In order to confirm the suggestion and to explain the zero-field splitting of 6H-$RbMgF_3$: Mn^{2+}, in this paper, we calculated the zero-field splittings *D* based on the structural data related to both Mg^{2+} sites in 6H-$RbMgF_3$ crystal from the microscopic spin-orbit coupling mechanism and the empirical superposition model.

2. Calculation

The zero-field splitting of the ^{6}S-state (or $3d^5$) ions in the crystal can be calculated by the microscopic mechanisms [10, 11] and the empirical superposition model [12]. Because of the lack of orbital angular momentum in the ^{6}S ground state, the microscopic mechanisms of zero-field splitting for $3d^5$ ions in crystals are complex, and there are many mechanisms which contribute to the zero-field splitting [10, 11, 13]. Among these mechanisms, the spin-orbit coupling mechanism is regarded as the dominant one [10, 11, 13, 14]. According to this mechanism, the high-order (fourth- and sixth-order) perturbation formula of zero-field splitting *D* for $3d^5$ ions in trigonal symmetry can be expressed as [14]

$$
\begin{aligned}
D &\approx D^{(4)} + D^{(6)}, \\
D^{(4)} &\approx 3\zeta^2(-B_{20}^2 - 21\zeta B_{20})/(70P^2D') \\
&\quad + \zeta^2(-10B_{40}^2 + 7B_{43}^2)/(126P^2G) \\
D^{(6)} &\approx -B_{20}^2\zeta^2[175B_{43}^2 + (24B_{20}^2 - 25B_{40})^2] \\
&\qquad /(360150P^2D'^2F) - 9\zeta^2B_{40}^2/(2450P^3D'^2) \\
&\quad - B_{20}^2\zeta^2(11B_{43}^2 + 10B_{40}^2)/(735P^3D'G) \\
&\quad + \zeta^2[7B_{20}B_{43}^2(25B_{40} - 68B_{20}) \\
&\qquad\quad + 10B_{20}B_{40}(B_{20} + B_{40})(24B_{20} - 25B_{40})] \\
&\qquad /(36015P^2D'FG)
\end{aligned}
$$

$$\begin{aligned}
&-5\zeta^2(B_{40}^2-7B_{43}^2/10)(29B_{43}^2+10B_{40}^2)\\
&\quad/(3969P^3G^2)\\
&+\zeta^2[-5(B_{40}^2-7B_{43}^2/10)(15B_{40}^2-14B_{43}^2)\\
&\qquad+7B_{20}B_{43}^2(57B_{20}-120B_{40})\\
&\qquad-75B_{20}B_{40}^2(B_{20}+2B_{40})]\\
&\quad/(21609P^2G^2F), \qquad (1)
\end{aligned}$$

where ζ is the spin-orbit coupling parameter. B_{kl} are the trigonal field parameters. P, D', G and F are the zero-order energy separations. They are

$$\begin{aligned}
&P=7B+7C,\ D'=17B+5C,\\
&G=10B+5C,\ F=22B+7C,
\end{aligned} \qquad (2)$$

where B and C are the Racah parameters.

The empirical superposition model can be used for the analyses of the crystal-field parameters and zero-field splittings [12]. From the superposition model, related to the crystal-field parameters, the trigonal field parameters B_{kl} can be written as

$$B_{20}=3A_2(R_0)\sum_{i=1}^{2}(2\cos^2\theta_i-1)(R_0/R_i)^{t_2},$$

$$B_{40}=3A_4(R_0)\sum_{i=1}^{2}(35\cos^4\theta_i-30\cos^2\theta+3)(R_0/R_i)^{t_4},$$

$$B_{43}=-\sqrt{35}A_4(R_0)\sum_{i=1}^{2}\sin^3\theta\cos\theta_i(R_0/R_i)^{t_2}, \qquad (3)$$

where R_i are the impurity-ligand distances and θ_i are the angles between the R_i and C_3 axis. For the host 6H-$RbMgF_3$ crystal, the structural parameters R_i^H and θ_i, related to both Mg^{2+} sites, were determined [9] and are shown in Table 1. Since the ionic radius r_i (≈ 0.97 Å [15]) of the impurity Mn^{2+} differs from the radius r_h (≈ 0.86 Å [15]) of the replaced Mg^{2+} ion, the impurity-ligand distances R_i in 6H-$RbMgF_3$: Mn^{2+} should be unlike the corresponding distances R_i^H in the host crystal. We can estimate reasonably the distances R_i from the empirical formula [16, 17] $R_i=R_i^H+(r_i-r_h)/2$. Thus, the impurity-ligand distances R_i for Mn^{2+} on both Mg^{2+} sites can be obtained and are also shown in Table 1. In (3), t_2 and t_4 are the power-law exponents. We take $t_2\approx 3$ and $t_4\approx 5$ because of the ionic nature of the bonds [12, 18]. $\overline{A_2}(R_0)$ and $\overline{A_4}(R_0)$ are the intrinsic parameters with the reference distance $R_0[\approx\overline{R}\approx(R_1+R_2)/2]$. For $3d^n$ ions on octahedral sites, $\overline{A_4}(R_0)=3Dq/4$ [12, 18], where Dq is the cubic field parameter. The ratio $\overline{A_2}(R_0)/\overline{A_4}(R_0)$ is in the range of $9\sim 12$ for $3d^n$ ions in crystals [18–20], and we take the average value, i.e., $\overline{A_2}(R_0)/\overline{A_4}(R_0)\approx 10.5$. The parameters B, C and Dq can be obtained from the optical spectra of the studied system. No optical spectra data of the studied 6H-$RbMgF_3$: Mn^{2+} crystal have been reported. So we estimate them from the optical spectra of similar systems. Since $KMnF_3$ and 6H-$RbMgF_3$ crystals have the same $(MnF_6)^{4-}$ cluster and a similar Mn^{2+}-F^- distance R (for $KMnF_3$, $R\approx 2.095$ Å [21]), the optical spectra of both crystals may be similar. So, we apply the optical spectra of $KMnF_3$ [21] here:

$$B\approx 829\ \text{cm}^{-1},\ C\approx 3130\ \text{cm}^{-1},\ Dq\approx 786\ \text{cm}^{-1}. \quad (4)$$

Table 1. The structural data of 6H-$RbMgF_3$: Mn^{2+} crystal. [a] Ref. [8].

	R_1^H (Å)[a]	R_1^H (Å)[a]	R_1 (Å)	R_2 (Å)	θ_1 (deg.)[a]	θ_2 (deg.)[a]
Site I	2.034	2.034	2.089	2.089	56.16(21)	56.16(21)
Site II	2.027	1.987	2.082	2.042	48.15(14)	57.65(14)

Table 2. The zero-field splitting D of 6H-$RbMgF_3$: Mn^{2+} crystal.

	Cal.[a]	Cal.[b]	Cal.[c]	Cal.[d]	Expt. [9]
D (10^{-4} cm^{-1})	85(10)	74(17)	−93(10)	−94(14)	91.6

[a] Calculation using the structural data for Mn^{2+} on the Mg^{2+} (I) site from the microscopic spin-orbit coupling mechanism. [b] Calculation using the structural data for Mn^{2+} on the Mg^{2+} (I) site from the superposition model. [c] Calculation using the structural data for Mn^{2+} on the Mg^{2+} (II) from the microscopic spin-orbit coupling mechanism. [d] Calculation using the structural data for Mn^{2+} on the Mg^{2+} (II) site from the superposition model.

The spin-orbit coupling parameter ζ in crystals can be estimated by the formula [14] $\zeta\approx N^2\zeta_0$, where N ($\approx\sqrt[4]{B/B_0}$, B_0 is the corresponding value in the free state) is the average covalence reduction factor and ζ_0 is the spin-orbit coupling parameter of the free $3d^n$ ion. For the free Mn^{2+} ion [22], we have $B_0\approx 873$ cm^{-1} and $\zeta_0=347$ cm^{-1}, thus we obtain $\zeta=330$ cm^{-1}.

Substituting all these parameters into the above formulas, the zero-field splittings D for Mn^{2+} on both Mg^{2+} sites are calculated. The results are shown in Table 2.

The empirical superposition model has also been used to explain successfully the zero-field splittings for S-state ions in crystals. From the model related to zero-field splitting [12, 23], for $3d^5$ ions in trigonal symmetry we have [12]

$$D=3/2\sum_{i=1}^{2}\overline{b_2}(R_0)(R_0/R_i)^{t_2}(3\cos^2\theta_i-1), \qquad (5)$$

where $\overline{b_2}(R_0)$ is the intrinsic zero-field splitting parameter. The reference distance R_0 is taken as a typical bond distance in compounds of the paramagnetic ion [23]. t_2 is the power-law exponent. For $(MnF_6)^{4-}$ clusters, $\overline{b_2}(R_0) \approx -0.034(3)$ cm^{-1} with $R_0 \approx 2.1$ Å and $t_2 \approx 7$ are obtained by combining the crystallographic data with the EPR data for Mn^{2+} ions in many crystals [23]. Applying these parameters and the structural data given in Table 1 in (5), the zero-field splittings D for Mn^{2+} on the two Mg^{2+} sites in 6H-$RbMgF_3$ crystals are calculated. The results are also shown in Table 2.

3. Discussion

From Table 2 one finds that for Mn^{2+} on the sites Mg^{2+} (I) and (II) in 6H-$RbMgF_3$ crystal, the calculated zero-field splittings D from the microscopic spin-orbit coupling mechanism and the empirical superposition model are close to each other. So, the two methods are effective for studies of the zero-field splittings of $3d^5$ ions in crystals.

Within the range of error [note: the calculated errors are due to the errors of the angles θ_i and the error of $\overline{b_2}(R_0)$], by both methods the calculated D-values for Mn^{2+} on the Mg^{2+} (I) site in 6H-$RbMgF_3$ agree with the observed value. The signs of calculated D-values for Mn^{2+} on the Mg^{2+} (II) site from both methods are opposite to that of the observed value. So, the suggestion for Mn^{2+} on site (I) in 6H-$RbMgF_3$ crystal, given in [9], is validated, and the zero-field splitting D for 6H-$RbMgF_3$: Mn^{2+} is explained reasonably.

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