The g Factors and Defect Structure of Orthorhombic Dy^{3+} Ions in CdF_2 Crystals

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The electronic paramagnetic resonance g factors g_x, g_y and g_z of an orthorhombic Dy^{3+} center in CdF_2 are studied by the perturbation formulae of the g factors for a $4f^9$ ion in orthorhombic symmetry. In these formulae, the contributions to g factors due to J-mixing among the ground ${}^6H_{15/2}$, the first excited ${}^6H_{13/2}$ and the second excited ${}^6H_{11/2}$ states via crystal-field interaction, lead to admixtures among the states with the same J-value via spin-orbit coupling. In addition, the admixtures between the lowest Kramers doublet $\Gamma\gamma$ and other 20 Kramers doublets Γx within the states ${}^6H_J$ ($J = 15/2$, 13/2 and 11/2) via crystal-field and orbital angular momentum interactions are considered. In the above orthorhombic center, the impurity Dy^{3+} is associated with co-doped crystals with alkali metal ions in the [110] axis. By analyzing the g factors, we find that the impurity Dy^{3+} ion does not reside in the ideal Cd^{2+} site but moves towards the co-doped alkali metal ion along the [110] direction by a displacement $\Delta Z \approx 0.272$ Å.

Key words: Crystal-Field Theory; Electron Paramagnetic Resonance; Superposition Model; Dy^{3+}; CdF_2.

1. Introduction

Fluoride crystals with fluorite structure, named MF_2 ($M = Ca^{2+}$, Sr^{2+}, Cd^{2+}, etc.), doped with rare-earth (Re) ions, are not only important optical materials but also wide-used laser hosts. Many experimental and theoretical works have appeared in the past years [1 – 6]. In fact, there may be various Re^{3+} impurity centers with different site symmetries, such as cubic, trigonal, tetragonal and orthorhombic symmetries in $MF_2{:}Re^{3+}$ crystals due to the charge compensating effect [7, 8]. The study of the defect structure of the impurity center is interesting and important. Previous theoretical studies deal usually with axial symmetry. Studies dealing with lower orthorhombic symmetry are scarce. For example, the electron paramagnetic resonance (EPR) g factors for orthorhombic Dy^{3+} ions in CdF_2 crystals were observed by Chang and Cohen decades ago [9]. But until now these experimental results have not been explained and the local structure of the impurity ion has remained unknown.

In this paper we use the perturbation formulae of g factors for the $4f^9$ ion in orthorhombic symmetry. In these formulae, the contributions to g factors due to (i) the J-mixing among the ground ${}^6H_{15/2}$, the first excited ${}^6H_{13/2}$ and the second excited ${}^6H_{11/2}$ states via crystal-field interactions, (ii) the mixtures among the states with the same J-value via spin-orbit interaction and (iii) the admixtures between the lowest Kramers doublet $\Gamma\gamma$ and other 20 Kramers doublets Γx via crystal-field and orbital angular momentum interactions as well as the covalence reduction effect are taken into account. In the treatments, the related crystal-field parameters are calculated by using the superposition model. Based on these studies, the displacement of the orthorhombic Dy^{3+} center in CdF_2 is determined. The results are discussed.

2. Calculations

The structure of the CdF_2 crystal is of the well-known fluorite type with lattice constants of 5.388 Å. The eight fluorine ions reside at the corners of a cubic

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lattice, and the Cd^{2+} ions are at the centers of the alternate cubes. The symmetry of the local crystalline field at the Cd sites is eight coordinated cubic (T_d site group) symmetry. When an impurity Dy^{3+} enters the lattice of CdF_2, Dy^{3+} may substitute the host Cd^{2+} ion, and its local symmetry can be trigonal, tetragonal or orthorhombic due to the cases of charge compensating effect. In crystals that are co-doped with alkali metals such as Na, Li or K, the impurity centers with orthorhombic symmetry will be favored [9, 10].

For a $4f^9$ ion in orthorhombic symmetry, the orthorhombic crystal-field lifts the degeneracies of $^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ states into eight, seven and six Kramers doublets, respectively [11, 12]. The basis function of the lowest lying doublet $\mathit{\Gamma}\gamma$ can be obtained by diagonalizing the 42×42 energy matrix in orthorhombic symmetry, based on the J-mixing among the above ^6H_J ($J = 15/2$, 13/2 and 11/2) states via crystal-field interaction. In addition, considering the admixtures among the states or levels with the same J-values (i. e., the admixtures among $^6H_{15/2}$, $^6I_{15/2}$ and $^2K_{15/2}$, that among $^6H_{13/2}$, $^4I_{13/2}$ and $^4H_{13/2}$, and that among $^6H_{11/2}$, $^4I_{11/2}$ and $^4G_{11/2}$) via spin-orbit coupling interaction, the basis function of the lowest doublet $\mathit{\Gamma}\gamma$ (or γ', where γ and γ' stand for the two components of $\mathit{\Gamma}$ irreducible representation) can be obtained [13]:

$$\begin{aligned}
|\mathit{\Gamma}\gamma^{(\gamma')}\rangle = {} & \sum_{\mathrm{M}_{J1}} C(^6\mathrm{H}_{15/2};\mathit{\Gamma}\gamma^{(\gamma')}\mathrm{M}_{J1})N_{15/2}(|^6\mathrm{H}_{15/2}\mathrm{M}_{J1}\rangle + \lambda_{\mathrm{I}}|^4\mathrm{I}_{15/2}\mathrm{M}_{J1}\rangle + \lambda_{\mathrm{I}}{}'\,|^4\mathrm{I}_{15/2}\mathrm{M}_{J1}\rangle) \\
& + \sum_{\mathrm{M}_{J2}} C(^6\mathrm{H}_{13/2};\mathit{\Gamma}\gamma^{(\gamma')}\mathrm{M}_{J2})N_{13/2}(|^6\mathrm{H}_{13/2}\mathrm{M}_{J2}\rangle + \lambda_{\mathrm{I}}{}''\,|^4\mathrm{I}_{13/2}\mathrm{M}_{J2}\rangle + \lambda_{\mathrm{H}}|^4\mathrm{H}_{13/2}\mathrm{M}_{J2}\rangle) \\
& + \sum_{\mathrm{M}_{J3}} C(^6\mathrm{H}_{11/2};\mathit{\Gamma}\gamma^{(\gamma')}\mathrm{M}_{J3})N_{11/2}(|^6\mathrm{H}_{11/2}\mathrm{M}_{J3}\rangle + \lambda_{\mathrm{I}}{}'''\,|^4\mathrm{I}_{11/2}\mathrm{M}_{J3}\rangle + \lambda_{\mathrm{F}}|^6\mathrm{F}_{11/2}\mathrm{M}_{J3}\rangle + \lambda_{\mathrm{G}}|^4\mathrm{G}_{11/2}\mathrm{M}_{J3}\rangle),
\end{aligned} \tag{1}$$

where N_i and λ_i are the normalization factors and mixing coefficients, M_{J1}, M_{J2} and M_{J3} are in the ranges $-15/2 \sim 15/2$, $-13/2 \sim 13/2$ and $-11/2 \sim 11/2$, respectively. They can be determined from the spin-orbit coupling matrix elements and perturbation method.

The perturbation Hamiltonian for a rare-earth ion in the crystal under an external magnetic field can be written as [14]

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

where $\hat{H}_{\mathrm{CF}}$, $\hat{H}_{\mathrm{so}}$, $\hat{H}_{\mathrm{Z}}$ are the crystal-field, spin-orbit coupling and Zeeman interactions, respectively. The latter can be expressed in terms of the Landé factor g_J and the angular momentum operator $\hat{J}$ as $\hat{H}_{\mathrm{Z}} = g_J \mu_{\mathrm{B}} \hat{H} \cdot \hat{J}$ [11]. $\hat{H}_{\mathrm{so}}$ can be expressed as $\hat{H}_{\mathrm{so}} = \zeta(\hat{L} \cdot \hat{S})$, where ζ is the spin-orbit coupling coefficient, and $\hat{L}$ and $\hat{S}$ are the orbital and spin angular momentum operators, respectively. The crystal-field interaction $\hat{H}_{\mathrm{CF}}$ can be written in terms of the Steven equivalent operators in orthorhombic symmetry [14]:

$$\begin{aligned}
\hat{H}_{\mathrm{CF}} = {} & B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_2^2 O_2^2 \\
& + B_4^2 O_4^2 + B_6^2 O_6^2 + B_4^4 O_4^4 + B_6^4 O_6^4 + B_6^6 O_6^6,
\end{aligned} \tag{3}$$

where B_k^q are crystal-field parameters.

The contributions to the g factors come mainly from the first-order perturbation terms, as pointed out in [11, 15]. However, the other irreducible representations $\mathit{\Gamma}x$ may mix with the ground $\mathit{\Gamma}\gamma$ doublet via crystal-field and angular momentum interactions and so make the second-order contributions. Based on the perturbation method, the perturbation formulae of the EPR g factors for the lowest Kramers doublet of the $4f^9$ ion in orthorhombic symmetry can be obtained, i. e., [12]

$$\begin{aligned}
& g_x = g_x{}^{(1)} + g_x{}^{(2)}, \\
& g_x{}^{(1)} = g_J \langle \mathit{\Gamma}\gamma | \hat{J}_X | \mathit{\Gamma}\gamma' \rangle, \quad g_x{}^{(2)} = 0, \\
& g_y = g_y{}^{(1)} + g_y{}^{(2)}, \\
& g_y{}^{(1)} = g_J \langle \mathit{\Gamma}\gamma | \hat{J}_Y | \mathit{\Gamma}\gamma' \rangle, \quad g_y{}^{(2)} = 0, \\
& g_z = g_z{}^{(1)} + g_z{}^{(2)}, \\
& g_z{}^{(1)} = 2 g_J \langle \mathit{\Gamma}\gamma | \hat{J}_Z | \mathit{\Gamma}\gamma \rangle, \\
& g_z{}^{(2)} = 2 {\sum_x}' \frac{\langle \mathit{\Gamma}\gamma | \hat{H}_{\mathrm{CF}} | \mathit{\Gamma}x\gamma_x \rangle \langle \mathit{\Gamma}x\gamma_x | \hat{L}_z | \mathit{\Gamma}\gamma \rangle}{E(\mathit{\Gamma}x) - E(\mathit{\Gamma})},
\end{aligned} \tag{4}$$

where the parameters g_J and $g_J{}'$ [note: $g_J{}'$ occurs in the expansions of (4)] for various states can be obtained from [11, 14].

According to the superposition model [16, 17], the crystal-field parameters can be expressed as

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

where the coordination factor $K_k^q(\theta_j, \phi_j)$ can be obtained from the local structural data of the studied sys-

Table 1. The EPR g factors of an orthorhombic Dy^{3+} center in CdF_2 crystal.

	g_x	g_y	g_z
Cal.	2.1024	10.4228	8.6165
Expt.	2.1025	10.1846	8.6613

tem. t_k and $\bar{A}_k$ are the power-law exponents and intrinsic parameters with the reference distance R_0, respectively. For the $(DyF_8)^{5-}$ cluster, $\bar{A}_4 \approx 90.3\ \mathrm{cm}^{-1}$ and $\bar{A}_6 \approx 26.6\ \mathrm{cm}^{-1}$ (with $R_0 \approx 2.333$) [17], and $\bar{A}_2 \approx 395\ \mathrm{cm}^{-1}$ (with $R_0 \approx 2.366$) [8] were reported. The exponents $t_2 \approx 7$, $t_4 \approx 12$, $t_6 \approx 11$ and the orbital reduction factor $k \approx 0.956$ were also obtained in [12, 13].

The free-ion parameters of Coulomb repulsion ($E^0 \approx 55395\ \mathrm{cm}^{-1}$, $E^1 \approx 6158\ \mathrm{cm}^{-1}$, $E^2 \approx 30.43\ \mathrm{cm}^{-1}$ and $E^3 \approx 622.75\ \mathrm{cm}^{-1}$), the two-body interaction parameters ($\alpha \approx 17.92\ \mathrm{cm}^{-1}$, $\beta \approx -612.15\ \mathrm{cm}^{-1}$ and $\gamma \approx 1679.85\ \mathrm{cm}^{-1}$) and the spin-orbit coupling coefficient ($\zeta_{4f} \approx 1914\ \mathrm{cm}^{-1}$) in the energy matrix were obtained in [18].

Because the ionic radius and the charge of the impurity Dy^{3+} are different from those of the host Cd^{2+} ion, the impurity-ligand distance R in the doped crystal would be unlike the cation-anion distance R_H in the host CdF_2 crystal. R can be reasonably estimated from the approximate formula [19, 20]

$$R = R_H + (r_i - r_h)/2, \tag{6}$$

where r_i and r_h are the ionic radii of the impurity and the host ion, respectively. For $CdF_2{:}Dy^{3+}$, $r_i \approx 0.908$ Å and $r_h \approx 0.97$ Å [21].

As mentioned before, charge compensation can be achieved by replacing one nearest neighbor Cd^{2+} ion by a co-doped alkali metal ion (such as Li^+, Na^+ and K^+) in one of [110] axes. For the reason of electrostatic attraction between the impurity Dy^{3+} and the univalent cation (whose effective charge may be regarded as $-$e), the Dy^{3+} ion would not locate on the ideal Cd^{2+} site, but shift away from the center of the $(DyF_8)^{5-}$ cube by a distance ΔZ along the [110] direction (note: the displacement direction towards the co-doped alkali metal ion is defined as position). Thus, the local structural parameters R_j. θ_j and ϕ_j for the impurity center are determined from the displacement ΔZ and the local geometrical relationships (note: the principal axes of the system were taken as $X//[\bar{1}10], Y//[001]$ and $Z//[110]$).

Now, substituting the above parameters into (4) and fitting the calculated g factors to the observed values, we obtain the displacement of the Dy^{3+} ion, i. e.,

$$\Delta Z \approx 0.272\ \text{Å}. \tag{7}$$

The corresponding theoretical g factors are compared with the observed values in Table 1.

3. Discussion

From Table 1 one can find that the calculated g factors for the orthorhombic Dy^{3+} center in CdF_2 crystal based on the displacement ΔZ are reasonably consistent with the experimental values. So the perturbation formulae of the g factors and the related parameters adopted in this work can be regarded as suitable. Thus, the EPR g factors are reasonably explained, and the local structural parameters are also obtained for the orthorhombic Dy^{3+} center. Obviously, the calculated method is also effective to other similar $MF_2{:}Re^{3+}$ systems.

Because of the effective negative charge of the co-doped alkali metal ion, the impurity Dy^{3+} should be shifted towards the neighboring alkali metal ion due to the electrostatic attraction. So, the sign of the displacement $\Delta Z > 0$ is understandable.

In the calculations, the adopted impurity-ligand distance R obtained from the empirical formula in (6) may be actually disturbed by other unknown and complicated factors, which would lead to some errors in the crystal-field parameters and the final results. However, the strict determination of the real impurity-ligand distance in doped crystals is very difficult. Fortunately, some theoretical investigations on experimental superhyperfine constant and extended X-ray absorption fine structure (EXAFS) measurements have verified that the empirical formula (6) is approximately valid for various systems. Thus, the errors of the calculated g factors and the displacement ΔZ due to the variation of the adopted R in this work can be considered as unimportant. On the other hand, the displacements of fluorine ions (which can be divided into three different kinds of magnitudes) are not considered, and this may bring some errors in the theoretical results. Based on the calculations, inclusion of the displacements of the ligands equivalently leads to modifications of the intrinsic parameters and the power-law exponents by about 10%, i. e., the errors for $\bar{A}_2$, $\bar{A}_4$ and $\bar{A}_6$ are estimated to be around ± 40, ± 10 and $\pm 2\ \mathrm{cm}^{-1}$, and those for t_k are roughly ± 1. Then, the fitted displacement ΔZ of Dy^{3+} and the results of the g factors would also vary by 5% or so. Therefore, one can more safely adopt $\Delta Z \approx 0.272(14)$ Å in (7), and the calculated g_x, g_y and g_z in Table 1 with corresponding errors of about ± 0.1133, ± 0.3648 and ± 0.3619, respectively. In view of the above points, the structural parameters (impurity displacement ΔZ) obtained in this work remain to be checked by future experimental studies.

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