

Electron paramagnetic resonance parameters and local structure for Gd^{3+} in KY_3F_{10}

SHAO-YI WU^{1,2,*}, HUA-MING ZHANG¹, GUANG-DUO LU¹ and
ZHI-HONG ZHANG¹

¹Department of Applied Physics, University of Electronic Science and Technology
of China, Chengdu 610054, People's Republic of China

²International Centre for Materials Physics, Chinese Academy of Sciences,
Shenyang 110016, People's Republic of China

*Corresponding author. E-mail: shaoyi.wu@163.com

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Abstract. The electron paramagnetic resonance parameters, zero-field splittings (ZFSs) b_2^0 , b_4^0 , b_4^4 , b_6^0 , b_6^4 and the g factors for Gd^{3+} on the tetragonal Y^{3+} site in KY_3F_{10} are theoretically studied from the superposition model for the ZFSs and the approximation formula for the g factor containing the admixture of the ground $^8\text{S}_{7/2}$ and the excited $^6\text{L}_{7/2}$ (L=P, D, F, G) states via the spin-orbit coupling interactions, respectively. By analysing the above ZFSs, the local structure information for the impurity Gd^{3+} is obtained, i.e., the impurity–ligand bonding angles related to the four-fold (C_4) axis for the impurity Gd^{3+} center are found to be about 0.6° larger than those for the host Y^{3+} site in KY_3F_{10} . The calculated ZFSs based on the above angular distortion as well as the g factors are in reasonable agreement with the observed values. The present studies on the ZFSs and the local structure would be helpful to understand the optical and magnetic properties of this material with Gd dopants.

Keywords. Electron paramagnetic resonance; crystal fields and spin Hamiltonians; Gd^{3+} ; KY_3F_{10} .

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1. Introduction

Rare-earth fluorides (KR_3F_{10} , where $R=\text{Dy}^{3+}$, Er^{3+} , Yb^{3+} , denotes rare-earth ions substituting for Y^{3+} in KY_3F_{10}) with KY_3F_{10} structure have attracted a lot of attention due to their novel magnetic properties, e.g., nearly complete (Ising) anisotropy of the magnetic moments along the local symmetry axis (or C_4 axis) and three orthogonal Ising lattices [1–3]. In addition, KY_3F_{10} exhibit useful laser and luminescence properties when doped with Er^{3+} , Eu^{3+} , Ho^{3+} and Pr^{3+} [4–11]. Usually, these properties are sensitively related to the local environment (e.g., bonding length and angles) for these rare-earth impurities on the Y^{3+} site. As a

powerful tool to investigate local structures of paramagnetic impurities in crystals, electron paramagnetic resonance (EPR) technique has been applied to these ions in KY_3F_{10} [12–15]. Nevertheless, compared with the EPR investigations on the ions (e.g., Sm^{3+} , Dy^{3+} , Yb^{3+}) with non-zero orbital angular momentum in crystals, the studies on the $^8\text{S}_{7/2}$ Gd^{3+} ion with quenched angular momentum ($L = 0$) are relatively scarce due to complexity of the problem, and the measurements for Gd^{3+} ion in fluorides are even fewer. For example, EPR experiments have been carried out on Gd^{3+} -doped KY_3F_{10} [16]. For the measured EPR parameters, zero-field splittings (ZFSs) b_2^0 , b_4^0 , b_4^4 , b_6^0 , b_6^4 and the g factor at room temperature, only the rank-2 ZFS b_2^0 was theoretically analysed [16]. Up to now, however, the rank-4 and rank-6 ZFSs b_4^0 , b_4^4 , b_6^0 , b_6^4 and the g factor have not been quantitatively interpreted. Moreover, the local structure of this impurity center has not been determined, either. In general, the local structure (impurity–ligand bonding lengths and angles) of the impurity Gd^{3+} may be dissimilar to that of the host Y^{3+} in KY_3F_{10} due to their different ionic radii and thus the distinct metal–ligand interactions within the cluster.

Since (i) the EPR parameters are closely connected with the immediate environment and anisotropy of the local crystal-fields near the impurity Gd^{3+} and (ii) the spectral properties of impurity Gd^{3+} in fluorides (e.g., KY_3F_{10}) are seldom treated and poorly understood, investigations on the EPR parameters and the local structure of this center may be helpful in understanding the optical and magnetic properties of this material (or other rare-earth ion-doped KR_3F_{10}) and then have specific significance. In this work, the ZFSs b_2^0 , b_4^0 , b_4^4 , b_6^0 and b_6^4 for Gd^{3+} on the tetragonal Y^{3+} site in KY_3F_{10} are theoretically studied from the superposition model. Meanwhile, the g factor is also analysed from the approximation formula including admixture of the ground $^8\text{S}_{7/2}$ and the excited $^6\text{L}_{7/2}$ ($L = \text{P, D, F, G}$) states via the spin–orbit coupling interactions.

2. Calculations

The structure of KY_3F_{10} belongs to the space group $\text{Fm}\bar{3}\text{m}$, while the symmetry of the Y^{3+} (or the doped rare-earth ion) sites is tetragonal (C_{4v}), with the fourfold symmetry axis oriented along one of the three cubic axes. The Y^{3+} may be described as occupying the approximate face centers of a simple cubic lattice with a cube edge half the value of the full structure and located at the vertices of a network of corner-sharing octahedra [1,2,16]. Thus, the impurity Gd^{3+} is surrounded by eight nearest F^- ions forming an antiprism $[\text{GdF}_8]^{5-}$ cluster. Among the host $\text{Y}–\text{F}$ bonds, four of them are at the distance R_1 (≈ 2.329 Å), the angles θ_1 ($\approx 130.8^\circ$) and ϕ_1 ($\approx 45^\circ$), and the other four at a different distance R_2 (≈ 2.193 Å), the angles θ_2 ($\approx 60^\circ$) and ϕ_2 ($\approx 0^\circ$). Here θ_j and ϕ_j ($j = 1, 2$) denote the polar angles between R_j and Z (or C_4) and azimuth angles between R_j and the X -axes of the crystal, respectively [16]. As mentioned before, the impurity–ligand bonding length R'_j and angle θ'_j in the doped crystal may be unlike the host values R_j and θ_j , because the ionic radius r_i (≈ 0.938 Å [17]) of the host Gd^{3+} is larger than the radius r_h (≈ 0.893 Å [17]) of the host Y^{3+} . One can reasonably estimate R'_j from the approximate relationship $R'_j \approx R_j + (r_i - r_h)/2$, which have been proved to be

valid for an impurity ion in crystals by the studies of experimental superhyperfine parameters, extended X-ray absorption fine-structure (EXAFS) measurements and crystal-field spectrum analyses [18–20]. On the other hand, the host metal–ligand bonding angles θ_j can also be replaced by the local impurity–ligand bonding angles θ'_j as: $\theta'_j \approx \theta_j + \Delta\theta$, where $\Delta\theta$ denotes the local angular distortion of this center.

For a $Gd^{3+}(4f^7)$ ion in tetragonal symmetry, its ${}^8S_{7/2}$ ground state would be separated into four Kramers doublets, which can be characterized by the zero-field splittings b_2^0 , b_4^0 , b_4^4 , b_6^0 and b_6^4 . In the studies of the zero-field splittings for S-state ions in crystals, the empirical superposition model (SPM) [21–23] has been proved to be a valid method. This model assumes that the zero-field splittings can be represented by sums of independent contributions from isolated ligands of the cluster, i.e., [21,22]

$$b_n^m = \sum_{j=1}^2 \bar{b}_n(R_0)(R_0/R'_j)^{t_n} K_n^m(\theta'_j, \phi_j), \quad (1)$$

where $K_n^m(\theta_i, \phi_i)$ are the coordination factors [22,24]. t_n and $\bar{b}_n(R_0)$ ($n = 2, 4, 6$) are, respectively, the power-law exponents and the intrinsic parameters, with the reference distance R_0 .

For $Gd^{3+}-F^-$ combination, the SPM parameters $t_2 \approx 12$, $\bar{b}_2(R_0) \approx -2300 \times 10^{-4} \text{ cm}^{-1}$, $t_4 \approx 2$ and $\bar{b}_4(R_0) \approx 15 \times 10^{-4} \text{ cm}^{-1}$ were obtained from the treatments in ref. [16] and the studies on similar tetragonal $[GdF_8]^{5-}$ clusters in fluorite type MF_2 crystals ($M=Ca, Sr, Ba$) in refs [22,25]. The rank-6 parameters are approximately taken as $t_6 \approx 8$ and $\bar{b}_6(R_0) \approx 0.5 \times 10^{-4} \text{ cm}^{-1}$ due to their small magnitudes. In this work, the average metal–ligand distance $\bar{R}[(R'_1 + R'_2)/2 \approx 2.2835 \text{ \AA}]$ is taken as the reference distance, i.e., $R_0 = \bar{R}$. It can be seen from eq. (1) that the ZFSs are connected with the local structural parameters bonding length R'_j and angle θ'_j of this impurity center. It is noted that the ZFSs are more sensitively dependent upon the angles θ'_j [22,24].

Thus, there is only one unknown parameter $\Delta\theta$ in the formulas of the ZFSs. Substituting the given values into eq. (1) and fitting the calculated ZFSs to experiment, we obtain the angular distortion

$$\Delta\theta \approx 0.6^\circ. \quad (2)$$

This value means that the metal–ligand bonding angles in the host are increased by about 0.6° in the impurity center. The corresponding theoretical results (cal.^c) are compared with experiment in table 1. For comparisons, the theoretical results (cal.^b) based on the host angles (adoption of the host Y–F bonding length R_j and angle θ_j , i.e., $\Delta\theta = 0$ in eq. (2) of this work) and those (cal.^a) of the previous studies in ref. [16] are also shown in table 1.

Now we turn to the calculations of the g factor. For the ${}^8S_{7/2}$ ground state, its g factor is very close to the spin-only value g_s (≈ 2.0023) due to quenching of orbital angular momentum. The excited states ${}^6L_{7/2}$ ($L= P, D, F, G$) may have admixtures with the ground state (or one another) via the spin–orbit coupling interactions and lead to a small contribution to the g factor. Therefore, the wave function of the ground state including the admixtures among these states may be expressed as [26,27]

$$|\gamma\rangle = N[|^8S_{7/2}\rangle + \lambda_P|^6P_{7/2}\rangle + \lambda_D|^6D_{7/2}\rangle + \lambda_F|^6F_{7/2}\rangle + \lambda_G|^6G_{7/2}\rangle]. \quad (3)$$

Here $|^8S_{7/2}\rangle$ and $|^6L_{7/2}\rangle$ stand for the pure $^8S_{7/2}$ and $^6L_{7/2}$ states. λ_L are the mixing coefficients for the related excited states. N is the normalization factor. They can be determined from the spin-orbit coupling matrix elements between the states. The energy separations between various states are obtained from the free-ion parameters, i.e., the Coulomb repulsion parameters F^k ($k = 1, 2, 3$), the two-body interaction parameters α, β and γ , and the spin-orbit coupling coefficient ζ_{4f} . Thus, the g factor of the ground state can be written as [26,27]

$$g = N^2 g(^8S_{7/2}) + N^2 \sum_L \lambda_L^2 g(^8L_{7/2}), \quad (4)$$

where $g(^8S_{7/2})$ and $g(^6L_{7/2})$ denote the Lande g values for the pure $^8S_{7/2}$ and $^6L_{7/2}$ states. Obviously, $g(^8S_{7/2}) \approx g_s$. The g values for various excited states can be obtained from ref. [27]. Since these values are smaller than g_s for the pure $^8S_{7/2}$ state, the resultant g factor should be slightly lower than two. It is noted that the influence of tetragonal crystal-fields on the g factors is not considered here, since crystal-field interaction for rare-earth ions in crystals may be much weaker (about one order in magnitude smaller) than the spin-orbit coupling term. In addition, only tiny contribution to the g factor (i.e., very small anisotropy $\Delta g = g_{\parallel} - g_{\perp}$) of the $^8S_{7/2}$ ground state can be introduced by means of high-order admixture (or perturbation) via combination effect of crystal-field and spin-orbit coupling interactions. Judging from the experimental g factor [16], it is almost isotropic within the experimental errors. Therefore, we apply eq. (4) to the studies of the g factor for simplicity. From the free-ion parameters ($F^1 \approx 85669 \text{ cm}^{-1}$, $F^2 \approx 60825 \text{ cm}^{-1}$, $F^3 \approx 44776 \text{ cm}^{-1}$ and $\zeta_{4f} \approx 1508 \text{ cm}^{-1}$ [28,29]) for Gd^{3+} in similar fluorides, the g factors are calculated and shown in table 1.

3. Discussion

From table 1, one can find that the calculated ZFSs (particularly b_2^0) for Gd^{3+} in KY_3F_{10} based on the SPM and the local angles θ'_j (or the angular distortion $\Delta\theta$)

Table 1. The zero-field splittings (in 10^{-4} cm^{-1}) and the g factors for the tetragonal Gd^{3+} center in KY_3F_{10} .

	b_2^0	b_4^0	b_4^4	b_6^0	b_6^4	g_{\parallel}	g_{\perp}
Calc. ^a	998(297)	—	—	—	—	—	—
Calc. ^b	754	−21	38	1.0	2	1.992	1.992
Calc. ^c	820	−21	41	0.8	2	1.992	1.992
Expt. [16]	816(3)	−20(1)	46(7)	0.0(10)	8(10)	1.986(5)	1.987(5)

^aCalculations based on the previous treatments in ref. [16].

^bCalculations based on the host bonding lengths R_j and angles θ_j (i.e., letting $\Delta\theta = 0$ in eq. (2)) in this work.

^cCalculations based on the local angles θ'_j (i.e., including angular variation $\Delta\theta$ in eq. (2)) and bonding lengths R'_j in this work.

in eq. (2)) are in better agreement than those based on the host angles θ_j with the observed values. The above calculated b_2^0 is also qualitatively comparable with that in the previous studies [16]. This means that the related parameters adopted here and the local angular distortion $\Delta\theta$ for the studied Gd^{3+} center acquired in this work seems to be suitable. Meanwhile, the g factors are also quantitatively interpreted.

(1) The calculated b_2^0 (cal.^b) based on the host structural parameters is smaller than the experimental result. This means that the tetragonal distortion for the impurity Gd^{3+} center is somewhat underestimated by using the structural parameters for the host Y^{3+} site and not suitable for the studies of the ZFSs of $KY_3F_{10}:Gd^{3+}$. Since b_2^0 is sensitive to the immediate environment (particularly the polar angles θ'_j) around the impurity Gd^{3+} , a slight local angular variation may be expected to increase the tetragonal distortion and hence the calculated b_2^0 . Thus the increased $\Delta\theta$ for the metal–ligand bonding angles in the impurity center can be understood.

(2) The validity of the local angular variation can be further illustrated in consideration of the size mismatching substitution of Y^{3+} by Gd^{3+} . Since the ionic radius (≈ 0.938 Å [17]) of the impurity Gd^{3+} is larger than that (≈ 0.893 Å [17]) of the host Y^{3+} , local tension would be introduced due to the size mismatching substitution. Thus, the angular distortion $\Delta\theta$ can be expected to decrease the above lattice density. As for the studied KY_3F_{10} , the structure of antiprism type $[GdF_8]^{5-}$ cluster is loose along the C_4 axis and easily distorted to accommodate impurity ions. In fact, a small local lattice deformation via bending of the Gd–F bonds would modify the immediate local angle and hence the tetragonal distortion of the system. This point is also supported by the observed positive transfer hyperfine structure parameter $A_\sigma - A_\pi$, which indicates some relaxation of the Gd–F bonds [16,30]. Interestingly, similar increases in metal–ligand bonding angles (e.g., $\Delta\theta \approx 0.9^\circ$, 3.4° and 7.4° for $YGG:Dy^{3+}$, $YAG:Sm^{3+}$ and $YGG:Sm^{3+}$, respectively) were also obtained for the RO_8 (here R denotes rare-earth impurities) clusters based on the SPM studies [31], where the impurity Dy^{3+} or Sm^{3+} is also larger than the replaced Y^{3+} . Thus, the angular variation $\Delta\theta$ of the Gd^{3+} center determined in this work by analysing its EPR spectra can be regarded as reasonable. It appears that EPR analysis is effective to obtain information about angular distortion for impurity centers, which seems a complicated problem and difficult to be acquired from other (e.g., EXAFS) techniques.

(3) The g factors vary slightly from g_s , indicating that the ground state is mainly of $^8S_{7/2}$ character with tiny admixture of some excited $^6L_{7/2}$ states via the spin–orbit coupling interactions. The calculated g factors are a little larger than the experimental data [16], but very close to those ($g \approx 1.992$) for Gd^{3+} in fluorite type MF_2 crystals (where $M=Cd, Ca, Sr, Ba$) [32–34]. Interestingly, decline of ζ_{4f} by about 10% is needed so as to decrease the theoretical g factors. As mentioned before, only tiny contribution to the g anisotropy comes from the high-order admixture via combination effect of crystal-field and spin–orbit coupling interactions. Thus the nearly isotropic experimental g factors observed in ref. [16] can be understood. Then eq. (4) seems to be a valid approximation for the analysis of g factors of Gd^{3+} in crystals.

(4) There are some errors in the above calculations. (i) Some other mechanisms (e.g., relativistic mechanism, spin–spin mechanism, covalency effect and

configuration interactions [22,26,35]) are not considered for simplicity, since inclusion of the above mechanisms would strongly complicate the calculations. (ii) The error of the impurity–ligand distance R'_j obtained from the empirical formula $R'_j \approx R_j + (r_i - r_h)/2$ [18–20] would affect the results slightly. However, the above errors in R'_j would only affect (no more than 0.5%) the tetragonal distortion and the ZFSs (e.g., b_2^0) slightly, which are actually more sensitive to the polar angles θ'_j . (iii) Variations in the azimuth angles ϕ_j were not considered in the calculations. Strictly speaking, the azimuth angles ϕ_j would also suffer a slight change $\Delta\phi$ due to the above size mismatching substitution, which could induce tiny modification in the calculated b_4^4 and b_6^4 . However, because of the small magnitudes of the rank-4 and rank-6 ZFSs, the errors due to ignoring the variation of ϕ_j may be taken as negligible. For the sake of simplicity and reduction in the number of adjustable parameters, we consider only the angular distortion $\Delta\theta$ for the polar angles here. (iv) The empirical superposition model is adopted, which supposed that the zero-field splittings can be written as a sum of the independent contributions arising from the nearest ligands. This assumption may also lead to some errors. Thus, in order to make more exact investigations of the electronic states (particularly the transfer hyperfine structure parameter) for the tetragonal Gd^{3+} center in KY_3F_{10} , the more powerful density functional theory [36–38] can be applied.

4. Conclusion

In conclusion, the EPR parameters for Gd^{3+} on the tetragonal Y^{3+} site in KY_3F_{10} are theoretically studied from the superposition model for the ZFSs and the approximation formula for the g factor. The Gd–F bonding angles related to the C_4 axis in the impurity center are about 0.6° larger than those in the host. The above theoretical investigations in this work would be helpful to study optical and magnetic properties of Gd-doped KY_3F_{10} (or other KR_3F_{10} crystals).

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