Covalent bonding and J–J mixing effects on the EPR parameters of Er^{3+} ions in GaN crystal*

Rui-Peng Chai(柴瑞鹏)†, Long Li(李隆), Liang Liang(梁良), and Qing Pang(庞庆)

Department of Physics, Xi'an University of Architecture and Technology, Xi'an 710055, *China*

(Received 1 December 2015; revised manuscript received 18 March 2016; published online 1 June 2016)

The EPR parameters of trivalent Er^{3+} ions doped in hexagonal GaN crystal have been studied by diagonalizing the 364×364 complete energy matrices. The results indicate that the resonance ground states may be derived from the Kramers doublet Γ_6. The EPR g-factors may be ascribed to the stronger covalent bonding and nephelauxetic effects compared with other rare-earth doped complexes, as a result of the mismatch of ionic radii of the impurity Er^{3+} ion and the replaced Ga^{3+} ion apart from the intrinsic covalency of host GaN. Furthermore, the J–J mixing effects on the EPR parameters from the high-lying manifolds have been evaluated. It is found that the dominant J–J mixing contribution is from the manifold $^2K_{15/2}$, which accounts for about 2.5%. The next important J–J contribution arises from the crystal–field mixture between the ground state $^4I_{15/2}$ and the first excited state $^4I_{13/2}$, and is usually less than 0.2%. The contributions from the rest states may be ignored.

Keywords: EPR parameters, covalent bonding effect, J–J mixing effect, rare-earth ion Er^{3+}

PACS: 76.30.–v, 75.10.Dg, 31.15.–p, 76.30.Kg **DOI:** 10.1088/1674-1056/25/7/077601

1. Introduction

In recent years much attention has been paid to the investigation of rare-earth (RE) doped GaN semiconductors, due to their potential in micro- and optoelectronics devices applications.[1–11] Of particular interest has been the electrical and optical properties of trivalent Er^{3+} in GaN host,[5–11] since the 1.54 μm luminescence center arising from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is in the region of minimal loss in optical fibers.

It is well known that the open 4f shell of the trivalent $4f^{11}$ ion Er^{3+} is spatially protected from the 5s and 5p shells due to a greater radial extent. Accordingly, the central RE ions are less affected by the surrounding ligand ions when doped in a certain host, thus resulting in a larger spin–orbit interaction than the crystal field if compared with $3d^N$ transition-metal complexes.[12–16] However, the case may be different for the RE doping from one host to another because of the distinct features between the central ion and the ligand ion, e.g., ionic radius, charge, mass, etc.

To gain a better insight into the local structures and optical properties of the RE materials, electronic paramagnetic resonance (EPR) is regarded as a suitable tool to investigate the interrelation between the electronic structure and molecular structure. For instance, Palczewska *et al.* has performed the EPR measurement on Er^{3+}-doped single GaN crystal, and the corresponding EPR parameters $g_{\parallel} = 2.861 \pm 0.003$, $g_{\perp} = 7.645 \pm 0.003$, $A_{\parallel} = (110 \pm 5) \times 10^{-4}$ cm^{-1}, and $A_{\perp} = (290 \pm 5) \times 10^{-4}$ cm^{-1} were obtained.[17] It should be noted that a rule of average g-factor $g_{\rm av} = 1/3(g_{\parallel} + 2g_{\perp})$, obtained from experiment, may be applied to predict the assignment of the lowest Kramers doublet by comparing with the theoretical one.[18–20] Namely, if the average g-factor $g_{\rm av} \approx 6.0$, where the contributions from all high excited states are ignored and only the pure $^4I_{15/2}$ manifold is taken into account, the ground resonance states may be assigned to Kramers doublet Γ_7 in $T_{\rm d}$ symmetry, while the lowest states may be attributed to Γ_6 if $g_{\rm av} \approx 6.8$ for the same site symmetry.[21] The rule is appropriate for an axial C_{3v} or C_{4v} symmetry.[22,23] Consequently, Palczewska *et al.* assigned the ground states to Γ_7 for the tetrahedral Er^{3+} center in GaN epilayers based on the fact that the experimental average g-factor ($g_{\rm av} \approx 6.05$) is approximately equal to the expected $g_{\rm av}$ of the doublet Γ_7.[17] In order to account for these EPR parameters, Maâlej *et al.* recently carried out a theoretical study on the EPR parameters of the Er^{3+} ions in GaN crystal by means of the first-order perturbation method,[24] where only the ground manifold $^4I_{15/2}$ is included. They also claimed that the lowest Kramers doublet belongs to the Γ_7 based on the calculated average g-factor $g_{\rm av} \approx 6.14$. However, to the best of our knowledge, the experimental $g_{\rm av}$ of the most Er^{3+}-doped complexes is generally less than the expected value 6.0 or 6.8 for the ground Kramers doublet Γ_7 or Γ_6, respectively.[19] Hence, the average g-factor $g_{\rm av}$ for the hexagonal Er^{3+} center in GaN seems to be somewhat abnormal if the ground doublet is Γ_7. For that matter, it is necessary to perform a detailed theoretical analysis on the EPR parameters of GaN:Er^{3+} system to examine the actual assignment associated with the ground Kramers doublet.

In this work, we will perform a quantitative theoretical

*Project supported by the Foundation of Education Department of Shaanxi Province, China (Grant No. 16JK1461).

†Corresponding author. E-mail: chairuipeng2005@163.com

© 2016 Chinese Physical Society and IOP Publishing Ltd

study on the J–J mixing effects, arising from the high-lying excited states (such as the terms $^4I_{13/2}$, $^2K_{15/2}$, $^2L_{15/2}$, etc.), on the EPR parameters based on a complete energy matrix method, where all excited states are included. Furthermore, the relation between the EPR g-factors and the orbit reduction factor k reflecting the covalent bonding and nephelauxetic effects is studied systematically. The plausible abnormal g-factors particularly for the average g-tensor g_{av} of the Er^{3+} ion in GaN are reasonably expounded.

2. Theoretical method

In general, the perturbation Hamiltonian for a $4f^{11}$ configuration ion Er^{3+} in an axial crystal field can be expressed as[25–29]

$$\begin{aligned}\hat{H} &= \sum_{k=1,2,3} E^k e_k + \zeta_{4f}\sum_i \boldsymbol{l}_i\cdot\boldsymbol{s}_i + \alpha L(L+1) + \beta G(G_2)\\ &\quad + \gamma G(R_7) + \sum_{\substack{k=2\\k\neq 5}}^{8} T^k t_k + \sum_{k,q,i} B_q^k C_q^k(i),\end{aligned} \tag{1}$$

where the former six terms on the right represent the spherically symmetric free-ion parts, and the latter term represents the crystal field potential function. The operators and parameters appearing in Eq. (1) are written and defined according to the conventional meaning.[29] The photoluminescence excitation studies suggest that the Er^{3+} ion occupies the substitutional Ga^{3+} site with approximate C_{3v} site symmetry when doped in the hexagonal GaN host,[5] and the local structure of the studied system has been plotted in Fig. 1. The crystal field potential for the trigonal C_{3v} symmetry is as follows:

$$\begin{aligned}\hat{H}_{CF} &= B_0^2C_0^2 + B_0^4C_0^4 + B_0^6C_0^6 + B_3^4(C_3^4 - C_{-3}^4)\\ &\quad + B_3^6(C_3^6 - C_{-3}^6) + B_6^6(C_6^6 + C_{-6}^6).\end{aligned} \tag{2}$$

To study the EPR parameters without spoiling the overall coupling of the various interactions, the actual Zeeman operator has been included in Eq. (1) instead of the approximate operator-equivalent technique, when it is subjected to an external magnetic field $\boldsymbol{H}$. The general matrix elements of the Zeeman operator $\hat{H}_{ZEE}$ in the intermediate coupling scheme $|\gamma SLJM_J\rangle$ may be expressed as[30]

$$\begin{aligned}&\left\langle f^N\gamma SLJM_J\left|\sum_i \beta\boldsymbol{H}\cdot(k\boldsymbol{l}_i + g_s\boldsymbol{s}_i)_q^{(1)}\right|f^N\gamma' S'L'J'M_J'\right\rangle\\ &= (-1)^{J-M_J}\beta H\begin{pmatrix} J & 1 & J'\\ -M_J & q & M_J'\end{pmatrix}\\ &\quad\times\langle\gamma SLJ\|kL + g_sS\|\gamma' S'L'J'\rangle.\end{aligned} \tag{3}$$

Likewise, the magnetic hyperfine interaction $\hat{H}_{HF}$, which arises from the interaction between the unfilled electrons and nucleus, may be written as

$$\hat{H}_{HF} = \frac{2\beta\beta_N\mu_N}{I}\sum_i \frac{\boldsymbol{N}_i\cdot\boldsymbol{I}}{r_i^3}, \tag{4}$$

where $\boldsymbol{N}_i = k\boldsymbol{l}_i - \boldsymbol{s}_i + 3\boldsymbol{r}_i(\boldsymbol{r}_i\cdot\boldsymbol{s}_i)/r_i^2$, β and β_N are the Bohr magneton and nuclear magneton, respectively; μ_N is the value of the nuclear magnetic moment in nuclear magnetons, and I represents the nuclear spin.[31] The constants required for the following calculations are $I = 7/2$, $\mu_N = -0.5647$, and $\langle r^{-3}\rangle = 10.6$ a.u. for the $^{167}Er^{3+}$ isotope.[32] By recoupling these angular momenta, the $\boldsymbol{N}_i$ may be expressed as

$$\boldsymbol{N}_i = k\boldsymbol{l}_i - \sqrt{10}(\boldsymbol{sC}^2)_i^{(1)}, \tag{5}$$

where the sum runs over all the unfilled electrons. The EPR parameters of the trigonal Er^{3+} center in GaN can be studied by using spin Hamiltonian[33]

$$\begin{aligned}\hat{H}_S &= \beta H_z g_\parallel S_z + \beta g_\perp(H_xS_x + H_yS_y)\\ &\quad + A_\parallel I_zS_z + A_\perp(S_xI_x + S_yI_y),\end{aligned} \tag{6}$$

where $S = 1/2$ is taken up. By now, the correlation between the EPR parameters and the perturbation Hamiltonian has been established by complete energy matrices.

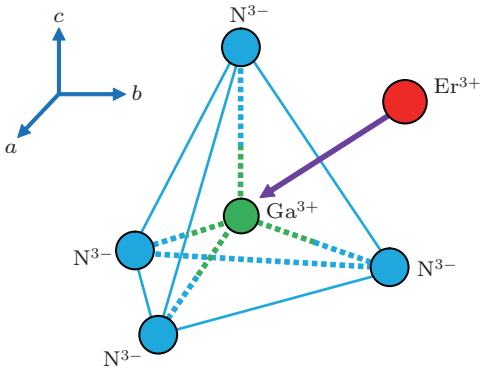


Fig. 1. (color online) Local structure of hexagonal $(GaN_4)^{9-}$ cluster in the GaN crystal. The central cation Ga^{3+} is replaced by the Er^{3+} ion with approximate C_{3v} symmetry when Er^{3+} is embedded in GaN host.

3. Calculations and discussion

In this work, a refined least-squares fitting method, rather than the regular fitting routine, has been developed by simulating the EPR parameters and optical spectra simultaneously, which may reflect the macro- and microscopic optical properties of the GaN:Er^{3+} system, respectively. In order to reduce the number of adjustable parameters in our calculations, all free-ion parameters except the spin–orbit coupling parameter ζ are taken as the same values as the free-ion parameters of Er^{3+} obtained by Carnall *et al*,[34] in view of the fact that the small change of free-ion parameters only affects the displacement of the centre of gravity of various manifolds, and hardly affects the Stark splitting and the EPR parameters. The obtained crystal–field parameters together with the free-ion parameters are tabulated in Table 1. The comparison between the theoretical values and experimental values of the Stark energy levels of the manifolds $^4I_{15/2}$ and $^4I_{11/2}$ is listed in Table 2

by diagonalizing the 364×364 complete energy matrices. The calculated and experimental values of the EPR parameters including the g-factors $g_{\parallel}$, $g_{\perp}$, and hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$ are projected in the Table 3. From Table 2 it can be found that the calculated Stark splittings are in good agreement with the observed values, though the third level (No. Z3) of $^4I_{15/2}$ and the second level (No. A2) of $^4I_{11/2}$ show a slightly large deviation (but not more than 5.0 cm^{-1}). The errors can be expected because the spin-correlated crystal–field interaction of perturbation Hamiltonian has been ignored considering the absence of the complete optical spectra.[35,36] However, there are moderate deviations for the EPR g-factors as shown in Table 3, if the covalent bonding and nephelauxetic effects characterized by an average orbital reduction factor k are not taken into account, viz., $k = 1$. Just as pointed out by Maâlej *et al.*,[24] the J–J mixing effects between the ground states and excited states (e.g., $^4I_{13/2}$, $^2K_{15/2}$, $^2L_{15/2}$) by the coupling of the crystal–field, spin–orbit, and the orbital angular momentum interactions should be evaluated in order to get some insight into the actual effects from the high-lying manifolds. For this purpose, the eigenfunctions of the lowest Kramers doublet comprised of the ground manifold $^4I_{15/2}$ and the predominant excited manifolds $^4I_{13/2}$, $^2K_{15/2}$, and $^2L_{15/2}$ are obtained and tabulated in Table 4. Note that the coefficients for each state satisfy the following relation: if one state of the Kramers doublet is expressed as

$$\psi = \sum_i a_i |J, M_J\rangle + \sum_i b_i |J', M_J'\rangle + \sum_i c_i |J'', M_J''\rangle + \cdots, \tag{7}$$

then its Kramers conjugate state is

$$\psi' = \sum_i a_i (-1)^{J+M_J} |J, -M_J\rangle + \sum_i b_i (-1)^{J'+M_J'} |J', -M_J'\rangle + \sum_i c_i (-1)^{J''+M''} |J'', -M_J''\rangle + \cdots. \tag{8}$$

With the aid of the operator-equivalent technique developed by Stevens *et al.*,[37] the J–J mixing effects on the EPR parameters from the manifolds $^4I_{15/2}$, $^4I_{13/2}$, $^2K_{15/2}$, and $^2L_{15/2}$ have been evaluated and collected in Table 3 (lines 1–5). It is shown from Table 3 that the leading J–J contribution to the g-factors, in addition to the ground $^4I_{15/2}$, arises from the excited manifold $^2K_{15/2}$, which accounts for about 2.5%. However, the second important contribution comes from the crystal–field mixing effect between the ground $^4I_{15/2}$ and the first excited state $^4I_{13/2}$, where the ratio is less than 0.2% and the J–J contribution to $g_{\perp}$ is nearly twice larger than that to $g_{\parallel}$. The next J–J mixing contribution is from the state $^2L_{15/2}$ which merely accounts for about 0.023% for $g_{\parallel}$ and 0.022% for $g_{\perp}$, respectively. Moreover, the contribution from the first excited state $^4I_{13/2}$ to the EPR parameters is least compared with the above terms, which may be ascribed to the weaker crystal–field strength than the spin–orbit interaction for the RE complexes. The J–J contribution to the g-factors from the rest states, such as the terms $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, and $^2K_{13/2}$, may be almost negligible. The case for the hyperfine structure

Table 1. The free-ion parameters and crystal–field parameters for Er^{3+} in GaN crystal. The values of all parameters are expressed in units of cm^{-1}.

Parameter[a]		Parameter	
E^1	6636.0	T^6	–160
E^2	32.91	T^7	358
E^3	652.06	T^8	0.0
ζ_{4f}	2363.1		
α	22.549	B_{20}	–16.1
β	–814.58	B_{40}	720.7
γ	1553.9	B_{43}	–25.0
T^2	0.0	B_{60}	–185.5
T^3	75.0	B_{63}	–20.7
T^4	155	B_{66}	–289.9

[a]The free-ion parameters were obtained by Carnall *et al.*[34]

Table 2. The calculated and experimental Stark levels of the hexagonal Er^{3+} centres in GaN.

Stark level	No.	E^{Calc}/cm^{-1}	E^{Expt}/cm^{-1} [35,36]
$^4I_{15/2}$	Z1	0.0	0.0
	Z2	4.4	4.5
	Z3	38.4	33.9
	Z4	103.5	–
	Z5	132.9	–
	Z6	134.8	–
	Z7	167.6	–
	Z8	193.2	–
$^4I_{11/2}$	A1	10114.8	10115.6
	A2	10128.2	10132.9
	A3	10137.4	10138.7
	A4	10152.6	10150.5
	A5	10156.3	10153.0
	A6	10165.6	10168.1

Table 3. The theoretical and experimental EPR parameters for the Er^{3+} centers in single GaN crystal. The hyperfine structure parameters $A_{\parallel}$ and $A_{\perp}$ are in units of 10^{-4} cm^{-1}.

g-factors	$g_{\parallel}$	$g_{\perp}$	g_{av}^d	$A_{\parallel}$	$A_{\perp}$
$g(^4I_{13/2}\|^4I_{13/2})^a$	0.000315	0.001088			
$g(^4I_{15/2}\|^4I_{15/2})$	–3.464816	8.135542			
$g(^2K_{15/2}\|^2K_{15/2})$	–0.091034	0.212923			
$g(^2L_{15/2}\|^2L_{15/2})$	–0.000817	0.001880			
$g(^4I_{13/2}\|^4I_{15/2})$	–0.003299	0.016300			
Cal.[b]	–3.55801	8.37189	6.76726	130.09	305.34
Cal.[c]	–3.17645	7.47650	6.04315	109.27	276.49
Expt.[17]	2.861(3)	7.645(3)	6.050(3)	110(2)	290(2)

[a]The lines 1–5 represent the g-factors from the different terms based on the obtained eigenfunctions.

[b]Calculated using the orbital reduction factor $k = 1$ by diagonalizing the complete energy matrices.

[c]Calculated using the orbital reduction factor $k \approx 0.84$ by diagonalizing the complete energy matrices.

[d]The value of average g-tensor $g_{av} = (|g_{\parallel}| + 2|g_{\perp}|)/3$.

constants $A_{\parallel}$ and $A_{\perp}$ is similar to the EPR g-factors. It follows that the J–J mixing effects from the high manifolds indeed cannot contribute more to the final EPR parameters. Furthermore, we consider that the lowest resonance states may originate from the Kramers doublet Γ_6 based on the evaluated average g-tensor $g_{\rm av} \approx 6.76$ when the orbit reduction factor k is taken as 1.0. However, the noticeable deviation of the calculated g-factors from the measured values needs to be expounded if the above conjecture on the ground state assignment is reasonable.

Table 4. The eigenfunctions of the lowest Kramers doublet for Er^{3+} ions in GaN crystal.

$\left\|^{2S+1}L_J, M_J\right\rangle_i$	$\left\|^{2S+1}L_J, \mp 1/2\right\rangle$	$\left\|^{2S+1}L_J, \pm 5/2\right\rangle$	$\left\|^{2S+1}L_J, \mp 7/2\right\rangle$	$\left\|^{2S+1}L_J, \pm 11/2\right\rangle$	$\left\|^{2S+1}L_J, \mp 13/2\right\rangle$
$C_i(^4I_{13/2};\Gamma_6^{\alpha(\beta)}M_J)$[a]	–0.00039	∓0.01115	±0.00695	–0.00042	–0.00031
$C_i(^4I_{15/2};\Gamma_6^{\alpha(\beta)}M_J)$	±0.00885	0.56840	0.80361	∓0.04225	±0.01168
$C_i(^2K_{15/2};\Gamma_6^{\alpha(\beta)}M_J)$	∓0.00153	–0.09744	–0.13802	±0.00730	∓0.00204
$C_i(^2L_{15/2};\Gamma_6^{\alpha(\beta)}M_J)$	∓0.00016	–0.00971	–0.01386	±0.00075	∓0.00022

[a]The $C_i(\Gamma_6^{\alpha(\beta)}M_J)$ represent the preceding coefficients of the states $\left|^{2S+1}L_J, M_J\right\rangle_i$.

Early studies have indicated that trivalent erbium ion Er^{3+} will occupy the position of Ga^{3+} site with local C_{3v} symmetry when implanted in GaN host.[5] However, there is considerable difference of the ionic radii for the impurity ion Er^{3+} and the replaced cation Ga^{3+} of host ($r_{Er^{3+}} \approx 0.89$ Å, $r_{Ga^{3+}} \approx 0.62$ Å). More overlap of electronic cloud between the central Er^{3+} ion and the ligand ions N^{3-} in the GaN:Er^{3+} system can be expected as a result of the larger ionic radius of impurity Er^{3+}, and thus produce a stronger covalent bonding effect to some extent apart from the dominant covalency of host GaN. In the paper, in order to evaluate the covalent and nephelauxetic effects characterized by an average orbital reduction factor k as a whole,[38,39] the calculated results of the EPR g-factors ($g_{\parallel}$, $g_{\perp}$, $g_{\rm av}$) as a function of the orbital reduction factor k are obtained and collected in Table 5, and the dependences of EPR g-factors are also plotted in Fig. 2. As shown by Fig. 2, the EPR g-factors are very sensitive to the orbital reduction factor k. The g-factors will increase linearly along with the increase of the factor k. Furthermore, we find that the agreement of the calculated g-factors may be further improved if the orbital reduction factor k is taken as 0.84, which reflect the stronger covalent bonding effect as expected. In particular, as for the average g-tensor $g_{\rm av}$, the theoretical value is in accord with the experimental value. At the same time, it is of interest to note that the calculated hyperfine structure parameter $A_{\parallel}^{\rm Cal}$ $(= 109.27 \times 10^{-4}\ {\rm cm}^{-1})$ is in excellent agreement with the experimental value $A_{\parallel}^{\rm Exp}$ $(= 110 \times 10^{-4}\ {\rm cm}^{-1})$ if the same reduction factor $k = 0.84$ is used, whereas the calculated $A_{\parallel} = 130.09 \times 10^{-4}\ {\rm cm}^{-1}$ when the orbital reduction effect is not taken into account. It is concluded that the stronger covalent bonding and nephelauxetic effects may be mainly responsible for the large deviation of the $g_{\rm av}$ from the predicted value because of the mismatch of ionic radii. Our recent studies on the Er^{3+} ion implanted in $ScVO_4$ crystal also show that there is more covalent effect on the EPR parameters if the ionic radius of central ion Er^{3+} is bigger than the substituted ion of host, where a comparable orbit reduction factor $k \approx 0.826$ has been obtained based on a more detailed theoretical analysis.[27] Of course, to evaluate the effect of the hybridization of 4f states with the states of N^{3-} ions on the EPR parameters with care, more theoretical studies based on the first-principle calculations are needed. However, we do not mean to undertake it in the present study, since the mechanism controlling the atomic rearrangement has not been established, and the overall optical spectra data have not been reported yet, when the Er^{3+} is doped in single GaN crystal.

Table 5. The EPR g-factors ($g_{\parallel}$, $g_{\perp}$, $g_{\rm av}$) as a function of the orbital reduction factor k for Er^{3+} ions doped in GaN.

k	$g_{\parallel}$	$g_{\perp}$	$g_{\rm av}$
0.60	2.60412	6.13334	4.95693
0.64	2.69951	6.35721	5.13798
0.68	2.79490	6.58107	5.31901
0.72	2.89029	6.80493	5.50005
0.76	2.98568	7.02879	5.68109
0.80	3.08106	7.25265	5.86212
0.84	3.17645	7.47650	6.04315
0.88	3.27184	7.70036	6.22419
0.92	3.36723	7.92420	6.40521
0.96	3.46262	8.14805	6.58624
1.00	3.55801	8.37189	6.76726

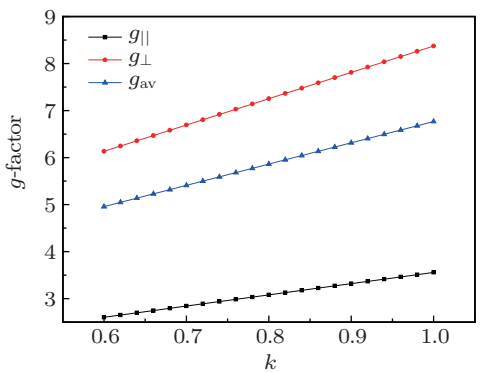


Fig. 2. (color online) Dependence of the EPR g-factors ($g_{\parallel}$, $g_{\perp}$, $g_{\rm av}$) on the orbital reduction factor k for the GaN: Er^{3+} system.

4. Conclusion

A complete theoretical method has been established by diagonalizing the 364×364 energy matrix to study the EPR parameters of the trivalent Er^{3+} ions doped in hexagonal GaN crystal. The results show that the ground states may be derived from the Kramers doublet Γ_6 for the GaN: Er^{3+} system, and the strong covalent bonding and nephelauxetic effects, as a result of the mismatch of ionic radii of the impurity Er^{3+} and replaced Ga^{3+} ion, may be mainly responsible for the larger deviation of the average EPR g-tensor g_{av} from the theoretical value ($g_{av} \approx 6.8$) as expected. Moreover, the J–J mixing contribution to the EPR parameters from the high-lying excited states has been evaluated. Differing from the previous studies, it is found that the predominant J–J mixing contribution is the state $^2K_{15/2}$, which accounts for about 2.5%, and the second major J–J contribution arises from the crystal–field mixture between the ground state $^4I_{15/2}$ and the first excited state $^4I_{13/2}$, and is usually less than 0.2%. The next J–J mixing contribution is from the state $^2L_{15/2}$ which merely accounts for about 0.023% for $g_{\|}$ and 0.022% for $g_{\perp}$, respectively. The contributions from the rest states such as the $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, and $^2K_{13/2}$ may be ignored. It follows that the J–J mixing effects from the high manifolds could not really add more contribution to the final EPR parameters, which may be due to the larger spin–orbit coupling interaction than the crystal–field interaction for the RE-doped complexes.

References

[1] Gruber J B, Burdick G W, Woodward N T, Dierolf V, Chandra S and Sardar D K 2011 *J. Appl. Phys.* **110** 043109
[2] Dammak M, Kammoun S, Maalej R, Koubaa T and Kamoun M 2007 *J. Alloys Compd.* **432** 18
[3] Metcalfe G D, Readinger E D, Shen H, Woodward N T, Dierolf V and Wraback M 2009 *J. Appl. Phys.* **105** 053101
[4] Dorenbos P and van der Kolk E 2006 *Appl. Phys. Lett.* **89** 061122
[5] Stachowicz M, Kozanecki A, Ma C G, Brik M G, Lin J Y, Jiang H X and Zavada J M 2014 *Opt. Mater.* **37** 165
[6] Al tahtamouni T M, Stachowicz M, Li J, Lin J Y and Jiang H X 2015 *Appl. Phys. Lett.* **106** 121106
[7] Svane A, Christensen N E, Petit L, Szotek Z and Temmerman W M 2006 *Phys. Rev. B* **74** 165204
[8] Yang Y and Pitzer R M 2010 *J. Phys. Chem. A* **114** 7117
[9] George D K, Hawkins M D, Mclaren M, Jiang H X, Lin J Y, Zavada J M and Vinh N Q 2015 *Appl. Phys. Lett.* **107** 171105
[10] Ugolini C, Feng I W, Sedhain A, Lin J Y, Jiang H X and Zavada J M 2012 *Appl. Phys. Lett.* **101** 051114
[11] Nepal N, Zavada J M, Dahal R, Ugolini C, Sedhain A, Lin J Y and Jiang H X 2009 *Appl. Phys. Lett.* **95** 022510
[12] Chai R P, Kuang X Y, Li C G and Zhao Y R 2011 *Chem. Phys. Lett.* **505** 65
[13] Mishra I, Kripal R and Misra S 2012 *Chin. Phys. Lett.* **29** 037601
[14] He L M, Ji Y, Wu H Y, Xu B, Sun Y B, Zhang X F, Lu Y and Zhao J J 2014 *Chin. Phys. B* **23** 077601
[15] Dwivedi P, Kripal R and Shukla S 2010 *Chin. Phys. Lett.* **27** 017601
[16] Wang L X, Kuang X Y, Li H F, Chai R P and Wang H Q 2010 *Acta Phys. Sin.* **59** 6501 (in Chinese)
[17] Palczewska M, Wolos A, Kaminska M, Grzegory I, Bockowski M, Krukowski S, Suski T and Porowski S 2000 *Solid State Commun.* **114** 39
[18] Lea K R, Leask M J M and Wolf W P 1962 *J. Phys. Chem. Solids* **23** 1381
[19] Ammerlaan C A J and de Maat-Gersdorf I 2001 *Appl. Magn. Reson.* **21** 13
[20] Chai R P, Kuang X Y, Liang L and Yu G H 2015 *J. Phys. Chem. Solids* **80** 1
[21] Watts R K and Holton W C 1968 *Phys. Rev.* **173** 417
[22] Wu S Y and Dong H N 2008 *J. Alloys Compd.* **451** 248
[23] Wu S Y and Dong H N 2006 *J. Lumin.* **119** 517
[24] Maâlej R, Kammoun S, Dammak M and Kammoun M 2008 *Mater. Sci. Eng. B* **146** 183
[25] Newman D J and Ng B 2000 *Crystal Field Handbook* (Cambridge: Cambridge University Press) pp. 6–43
[26] Newman D J and Ng B 1989 *Rep. Prog. Phys.* **52** 699
[27] Chai R P, Hao D H, Kuang X Y and Liang L 2015 *Spectrochim. Acta Part A* **150** 829
[28] Gruber J B, Sardar D K, Russell lll C C, Yow R M, Zandi B and Kokanyan E P 2003 *J. Appl. Phys.* **94** 7128
[29] Carnall W T 1992 *J. Chem. Phys.* **96** 8713
[30] Judd B R 1963 *Operator Techniques in Atomic Spectroscopy* (New York: McGraw-Hill Book Co) pp. 25–46
[31] Wybourne B G 1965 *Spectroscopic Properties of Rare Earths* (New York: John Wiley & Sons, Inc.) p. 39
[32] Vishwamittar and Puri S P 1974 *Phys. Rev. B* **9** 4673
[33] Abragam A and Bleaney B 1986 *Electron Paramagnetic Resonance of Transition Ions* (New York: Dover Publications, Inc.) pp. 277–341
[34] Carnall W T, Fields P R and Sarup R 1972 *J. Chem. Phys.* **57** 43
[35] Glukhanyuk V, Przybylińska H, Kozanecki A and Jantsch W 2006 *Opt. Mater.* **28** 111
[36] Glukhanyuk V, Przybylińska H, Kozanecki A and Jantsch W 2006 *Opt. Mater.* **28** 746
[37] Stevens K W H 1952 *Proc. Phys. Soc. London, Sect. A* **65** 209
[38] Jørgensen C K 1962 *Absorption Spectra and Chemical Bonding in Complexes* (Oxford, London, New York, Paris: Pergamon Press) p. 296
[39] Reisfeld R C and Jørgensen C K 1977 *Laser and Excited State of Rare Earths* (Berlin, Heidelberg, New York: Splinger-Verlag) p. 123