Investigation of the EPR Parameters and Defect Structure of Ni\(^{2+}\) Ions in RbMgF\(_3\) Crystals

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By means of the complete energy matrix diagonalization procedure of 3d\(^2\)/3d\(^8\) ions in trigonal symmetry and using the superposition model, the electron paramagnetic resonance (EPR) parameters for Ni\(^{2+}\) ions in RbMgF\(_3\) crystals with C\(_3\)\(_v\) and D\(_{3d}\) symmetry are studied. From the investigation, the defect structures of these paramagnetic impurity centers are obtained and the EPR parameters are explained reasonably. – PACS numbers: 76.30.Fc, 61.72.Bb, 71.70.Ch

Key words: EPR Parameters; Defect Structure; Crystal-Field Theory; RbMgF\(_3\):Ni\(^{2+}\) Crystals.

1. Introduction

The electron paramagnetic resonance (EPR) parameters (zero-field splitting parameter \(D\) and \(g\)-factors \(g_\|\) and \(g_\perp\)) of rare-earth and transition-metal ions in crystals are related to the crystal structure. A number of studies [1 – 3] has been carried out to calculate the optical spectra and the EPR spectra. For 3d\(^8\) ions in RbMgF\(_3\) crystals, the EPR parameters were measured by Najia twenty years ago [4], and Najia pointed out that the Ni\(^{2+}\) ion can occupy two magnesium positions which were detected by EPR. In a recent study, the EPR parameters are explained by using the parameterization \(d\) orbital by Xu [5], but Xu neglects the factual effect of the local structure distortion when Ni\(^{2+}\) is doped in RbMgF\(_3\). Thus, until now no theoretical studies, which are related to the EPR parameters and defect structure of these impurity centers, have been made. Considering that the EPR parameters (particularly the zero-field splitting parameter \(D\)) are sensitive to the immediate environment of the paramagnetic ion, the studies can not only give the theoretical explanations of these EPR parameters, but also gain some useful information about the defect structures of these impurity centers in RbMgF\(_3\) crystals.

In this paper, the relationship between the zero-field splitting parameter \(D\), the \(g\)-factors and the crystal structure of Ni\(^{2+}\) in RbMgF\(_3\) crystals has been established on the basis of the superposition model [6, 7] and the complete energy matrix diagonalization procedure (CDP) [3, 8]. \(D\) and \(g\)-factors, with the defect structure being taken into account, have been investigated. The calculated results are in excellent agreement with experimental findings.

2. Theoretical Model of \(C_{3v}/D_{3d}\) Symmetry

According to the detection by EPR spectroscopy, the local structure of the \([\text{MgF}_6]^{4–}\) group in the host crystal RbMgF\(_3\) has trigonal symmetry (\(C_{3v}\)) or \(D_{3d}\)), and both magnesium positions can be occupied by Ni\(^{2+}\) ions [4]. Therefore, we consider two kinds of theoretical models in our studies.

2.1. The Displaced Model of the \(C_{3v}\) Symmetry

Owing to the differences in mass and ionic radius of Mg\(^{2+}\) and Ni\(^{2+}\), the bond lengths \(R_1\) and \(R_2\) in the doped crystal must differ from \(R_{H1}\) and \(R_{H2}\) in the host crystal. According to the studies of Zheng [9], if the host cation is replaced by an impurity with different charge or/and ionic radius, one can expect that the impurity ion does not occupy exactly the original site, but is displaced \(\Delta Z\) towards the bigger oxygen triangle along the \(C_3\) axis. Here, we assume that our studies resemble those of Zheng (see Fig. 1).

So the formulas of the bond lengths and bond angles of the \([\text{NiF}_6]^{4–}\) group are

\[
R_i = (\Delta Z + R_{H1}^2 + 2\Delta Z \cdot R_{H1} \cos \theta_{H1})^{1/2},
\]

\[
\cos \theta_i = \frac{R_{H1} \cos \theta_{H1} + \Delta Z}{R_i},
\]

where \(i = 1, 2\) and \(-, +\) denote the upper and lower ligands of the \([\text{NiF}_6]^{4–}\) group, \(R_{H1} = 0.2027\) nm, \(R_{H2} = 0.2018\) nm.
Note

0.1987 nm and $\theta_{\text{H1}} = 48.15^\circ$, $\theta_{\text{H2}} = 57.65^\circ$ [4] denote the bond lengths and bond angles of the host crystal [NiF$_6$]$^{2-}$ group, respectively. $\Delta Z$ denotes that the impurity ion moves by $\Delta Z$ along the $C_3$ axis.

2.2. The Elongated Model of the $D_{3d}$ Symmetry

As the radius $r_i$(Ni$^{2+}$) (= 0.069 nm) of the impurity is larger than $r_i$(Mg$^{2+}$) (= 0.066 nm) [10] of the host ion, there will be a repulsive force on the upper and lower F$^-$ triangle plane, which increases the bond length $R$ (Ni-F) (note: we assume that the center ion is fixed and the symmetry is still $D_{3d}$). The two pyramids of the lattice are elongated outside along the $C_3$ axis (see Fig. 2). The value of the bond length $R$ in the doped crystal can be estimated from the approximate formula $R \approx R_H + (r_i - r_H)/2$ [11], where the bond length of the host crystal with $D_{3d}$ symmetry is $R_H = 0.2034$ nm [4]. Considering the contribution of the defect structure, we take $\Delta \theta$ as a fitting parameter, so $\theta = \theta_H + \Delta \theta$, where the bond angle of the host crystal is $\theta_H = 56.16^\circ$ [4]. There are $R_1 = R_2 = R$ and $\theta_1 = \theta_2 = \theta$ on the basis of the $D_{3d}$ symmetry.

3. The Method of Calculation

Ni$^{2+}$ ions in RbMgF$_3$ crystal occupy octahedral Mg$^{2+}$ sites [4]. The Hamiltonian of Ni$^{2+}(3d^8)$ in this system can be expressed as [12]

$$H = H_f(B, C) + H_{so}(\zeta) + H_{\text{CF}}(D_q, D_\sigma, D_\tau),$$

(2)

where $H_f$ denotes the electrostatic interactions, $H_{so}$ stands for the spin-orbit interaction and $H_{\text{CF}}$ denotes the crystal-field Hamiltonian. From (2), we have established the complete energy matrix using the strong-field basis functions [13] and the Matlab 6.5 computer program for 3d$^2$(3d$^8$) ions in trigonal ($C_{3v}$, $D_{3d}$) symmetry.

The effective spin Hamiltonian (SH), including the zero-field splitting and Zeeman terms, can be written as [3, 12]

$$H_S = D \left[ S_z^2 - \frac{1}{3} S(S + 1) \right] + \mu g_\| B_z S_z$$

$$+ \mu g_\perp (B_x S_x + B_y S_y).$$

(3)

Using the microscopic SH theory [3, 12], the general expressions for the SH parameters $D$, $g_\|$, $g_\perp$ in (3) are obtained as given in [3]. They can be calculated by the diagonalization of the complete energy matrix.

The trigonal crystal-field parameters $D_q$, $D_\sigma$ and $D_\tau$ in the superposition model are given as [6]

$$D_q = -3/\sqrt{2} \tilde{A}_4(R) \sum_{i=1}^2 [(R_0/R_i)^4 (\sin^3 \theta_i \cos \theta_i)],$$

$$D_\sigma = 3/7 \tilde{A}_2(R) \sum_{i=1}^2 [(R_0/R_i)^2 (3 \cos^2 \theta_i - 1)],$$

$$D_\tau = 1/7 \tilde{A}_4(R) \sum_{i=1}^2 [(R_0/R_i)^4 (35 \cos^4 \theta_i - 30 \cos^2 \theta_i + 3) + 7 \sqrt{2} \sin^3 \theta_i \cos \theta_i],$$

(4)

where $\tilde{A}_2(R)$ and $\tilde{A}_4(R)$ are the intrinsic parameters. $\tilde{A}_4(R)$ ($\approx 550$ cm$^{-1}$) is related to the cubic CF parameter $D_q$ as $\tilde{A}_4(R) = 3D_q/4$ [6, 12]. The ratio
Table 1. The EPR parameters of RbMgF₃:Ni²⁺ with C₃ᵥ symmetry.

<table>
<thead>
<tr>
<th></th>
<th>g₁</th>
<th>g₂</th>
<th>D(10⁻⁴ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed [4]</td>
<td>2.289</td>
<td>2.278</td>
<td>2.372</td>
</tr>
<tr>
<td>This work</td>
<td>2.2905</td>
<td>2.3062</td>
<td>2.3723</td>
</tr>
</tbody>
</table>

Table 2. The EPR parameters of RbMgF₃:Ni²⁺ with D₃d symmetry.

<table>
<thead>
<tr>
<th></th>
<th>g₁</th>
<th>g₂</th>
<th>D(10⁻⁴ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed [4]</td>
<td>2.259</td>
<td>2.278</td>
<td>2.405</td>
</tr>
<tr>
<td>This work</td>
<td>2.2588</td>
<td>2.2784</td>
<td>2.6113</td>
</tr>
<tr>
<td>[5]</td>
<td>2.254</td>
<td>2.272</td>
<td>2.405</td>
</tr>
</tbody>
</table>

$\tilde{A}_2(R)/\tilde{A}_4(R) = 8 \sim 12$ was found for 3d⁹ ions in many crystals [7, 10, 12], and we take $\tilde{A}_2(R) = 9\tilde{A}_4(R)$ here. The angle $\theta$ between the direction of the metal-ligand distance $R$ and $C_3$ axis denotes the trigonal distortion angle in the [NiF₆]³⁻ octahedron.

In the calculation, the Racah electrostatic parameters and the spin-orbit coupling constant of the free Ni²⁺ ion are given as [15]

$$B_0 = 1208 \text{ cm}^{-1}, \quad C_0 = 4459 \text{ cm}^{-1}, \quad \epsilon_0^0 = 636 \text{ cm}^{-1}.$$  (5)

Furthermore, as a reasonable approximation, we take [3, 11, 12]

$$B = k^2B_0, \quad C = k^2C_0, \quad \zeta_d = k\epsilon_d^0,$$  (6)

where $k$ is the orbital reduction factor.

4. Conclusion and Discussion

From the above studies, it is seen that the EPR parameters can be obtained as long as by fitting the orbital reduction factor $k$ ($\approx 0.9274$) and the displacement $\Delta Z$ ($\approx -0.015274$ nm) for the C₃ᵥ symmetry, and $\Delta \theta$ ($\approx -2.0626^\circ$) and $k$ ($\approx 0.9025$) for the $D_{3d}$ symmetry. The calculated results are shown in Tables 1 and 2.

a) From Table 1 and 2 one can find that by considering suitable local structural distortions, all the EPR parameters $D$, $g_\parallel$ and $g_\perp$ for Ni²⁺ in RbMgF₃ crystal can be satisfactorily explained, and the defect structure of the paramagnetic impurity center can be estimated.

b) (i) Owing to $\Delta Z \approx -0.015274$ nm $< 0$ for the $C_3$ symmetry, it illustrates that the displacement of the Ni²⁺ ions moves towards the bigger oxygen triangle. This conclusion is consistent with that of the Al₂O₃:Fe³⁺ crystal and can be understood [9].

b) (ii) Owing to $\Delta \theta \approx -2.0626^\circ$ and $R (= 0.2049$ nm $> R_H$ for the $D_{3d}$ symmetry, there has been an elongated trigonal distortion upper and lower F⁻ triangle.

c) Considering the theoretical calculation, we find that the CF parameter $D_q$ ($< 300$ cm⁻¹), caused by Xu neglecting the factual effect of the defect structure in his paper [5], is rather small. However, in our calculation the value of $D_q$ is bigger than 700 cm⁻¹, which is consistent with Ni²⁺ ions in many other crystals [3, 12, 15]. Thus, the present $D_q$ value may be more reasonable.

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