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_{3v} 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 $g_{\parallel}$, $g_{\perp}$) 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 only takes into account the undoped structural data in his calculation. Moreover, 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. The Theoretical Model of C_{3v}/D_{3d} Symmetry

According to the detection by EPR spectroscopy, the local structure of the $[MgF_6]^{4-}$ 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 ΔZ 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 $[NiF_6]^{4-}$ group are

$$\begin{aligned} R_i &= (\Delta Z^2 + R_{Hi}^2 \mp 2\Delta Z \cdot R_{Hi} \cos\theta_{Hi})^{1/2}, \\ \cos\theta_i &= \frac{R_{Hi}\cos\theta_{Hi} \mp \Delta Z}{R_i}, \end{aligned} \tag{1}$$

where $i = 1, 2$ and $-, +$ denote the upper and lower ligand of the $[NiF_6]^{4-}$ group, $R_{H1} = 0.2027$ nm, $R_{H2} =$

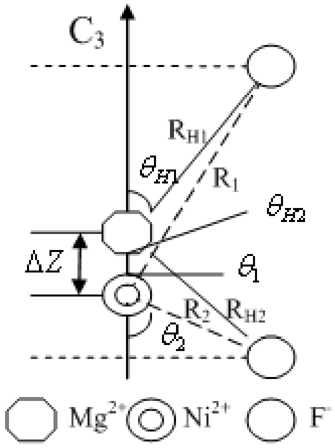

Fig. 1. The displaced model of the C_{3v} symmetry.

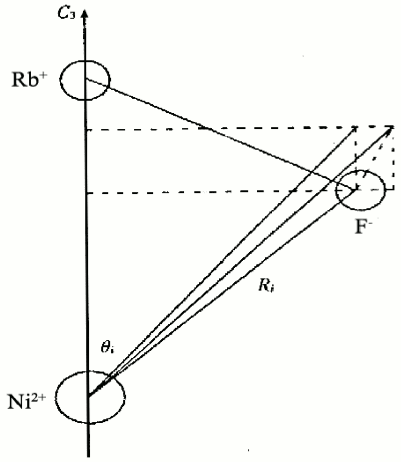

Fig. 2. The elongated model of the D_{3d} symmetry.

0.1987 nm and $\theta_{H1} = 48.15°$, $\theta_{H2} = 57.65°$ [4] denote the bond lengths and bond angles of the host crystal $[NiF_6]^{4-}$ group, respectively. ΔZ denotes that the impurity ion moves by ΔZ 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 $r_h(Mg^{2+})$ (= 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 $\theta_H = 56.16°$ [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]

$$H = H_f(B,C) + H_{so}(\zeta) + H_{CF}(Dq, D\sigma, D\tau), \quad (2)$$

where H_f denotes the electrostatic interactions, H_{so} stands for the spin-orbit interaction and H_{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]

$$\begin{aligned} H_S = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + \mu_B g_\parallel B_z S_z \\ + \mu_B g_\perp (B_x S_x + B_y S_y). \end{aligned} \quad (3)$$

Using the microscopic SH theory [3, 12], the general expressions for the SH parameters D, $g_\parallel$, $g_\perp$ 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 Dq, $D\sigma$ and $D\tau$ in the superposition model are given as [6]

$$\begin{aligned} Dq &= -3/\sqrt{2}\bar{A}_4(R)\sum_{i=1}^{2}[(R_0/R_i)^{t4}(\sin^3\theta_i\cos\theta_i)], \\ D\sigma &= \frac{3}{7}\bar{A}_2(R)\sum_{i=1}^{2}[(R_0/R_i)^{t2}(3\cos^2\theta_i - 1)], \\ D\tau &= \frac{1}{7}\bar{A}_4(R)\sum_{i=1}^{2}[(R_0/R_i)^{t4}(35\cos^4\theta_i \\ &\quad - 30\cos^2\theta_i + 3) + 7\sqrt{2}\sin^3\theta_i\cos\theta_i], \end{aligned} \quad (4)$$

where $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters. $\bar{A}_4(R)$ (≈ 550 cm^{-1}) is related to the cubic CF parameter Dq as $\bar{A}_4(R) = 3Dq/4$ [6, 12]. The ratio

Table 1. The EPR parameters of $RbMgF_3$:Ni^{2+} with C_{3v} symmetry.

	$g_\parallel$	$g_\perp$	D/cm^{-1}
Observed [4]	2.289	?	2.372
This work	2.2895	2.3062	2.3723
[5]	2.276	2.296	2.379

Table 2. The EPR parameters of $RbMgF_3$:Ni^{2+} with D_{3d} symmetry.

	$g_\parallel$	$g_\perp$	D/cm^{-1}
Observed [4]	2.259	2.278	?
This work	2.2588	2.2784	2.6113
[5]	2.254	2.272	2.405

$\bar{A}_2(R)/\bar{A}_4(R) = 8 \sim 12$ was found for $3d^n$ ions in many crystals [7, 10, 12], and we take $\bar{A}_2(R) = 9\bar{A}_4(R)$ here. The angle θ between the direction of the metal-ligand distance R and C_3 axis denotes the trigonal distortion angle in the $[NiF_6]^{4-}$ octahedron.

In the calculation, the Racah electrostatic parameters and the spin-orbit coupling constant of the free Ni^{2+} ion are given as [15]

$$B_0 = 1208\ \text{cm}^{-1}, \quad C_0 = 4459\ \text{cm}^{-1}, \\ \zeta_\text{d}^0 = 636\ \text{cm}^{-1}. \tag{5}$$

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

$$B = k^2 B_0, \quad C = k^2 C_0, \quad \zeta_\text{d} = k\zeta_\text{d}^0, \tag{6}$$

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 (≈ 0.9274) and the displacement ΔZ (≈ -0.015274 nm) for the C_{3v} symmetry, and $\Delta\theta$ ($\approx -2.0626°$) and k (≈ 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 Ni^{2+} in $RbMgF_3$ crystal can be satisfactorily explained, and the defect structure of the paramagnetic impurity center can be estimated.

b) (i) Owing to $\Delta Z \approx -0.015274\ \text{nm} < 0$ for the C_{3v} symmetry, it illustrates that the displacement of the Ni^{2+} ions moves towards the bigger oxygen triangle. This conclusion is consistent with that of the Al_2O_3:Fe^{3+} crystal and can be understood [9].

b) (ii) Owing to $\Delta\theta \approx -2.0626°$ and R (≈ 0.2049 nm) $> R_\text{H}$ 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 Dq (< 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 Dq is bigger than 700 cm^{-1}, which is consistent with Ni^{2+} ions in many other crystals [3, 12, 15]. Thus, the present Dq value may be more reasonable.

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