Superposition Model for the Zero-field Splitting b_2^0 of Gd^{3+} Ions in α-$LiIO_3$ and $LiNbO_3$ Crystals

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The zero-field splitting of Gd^{3+} ions in α-$LiIO_3$ and $LiNbO_3$ crystals are studied by the superposition model. The zero-field splittings b_2^0 for the trigonal Gd^{3+} centers in both crystals are reasonably explained and the defect structures of these Gd^{3+} centers are obtained. These defect structures are consistent with the expectation based on the electrostatic interaction models and agree qualitatively with the corresponding results obtained for similar trivalent paramagnetic (rare-earth and transition-metal) ions in α-$LiIO_3$ and $LiNbO_3$ crystals.

Keywords: Electron Paramagnetic Resonance (EPR); Defect Structure; Superposition Model; Gd^{3+}; α-$LiIO_3$; $LiNbO_3$.

1. Introduction

Crystals of $LiNbO_3$ and α-$LiIO_3$, activated with transition metal and rare-earth ions, are of considerable interest because they can be used for optical devices (solid state lasers, holographic data storage, amplifiers, optical waveguides, etc.). Many methods have been used to study these active or impurity centers in the two crystals [1 – 12]. The EPR zero-field splittings b_2^0 for Gd^{3+} ions (or the trigonal Gd^{3+} centers) in α-$LiIO_3$ [13] and $LiNbO_3$ [14] crystals were reported, however no theoretical investigations for these EPR data have been made. Since the zero-field splittings b_2^0 of paramagnetic impurities are sensitive to the local geometry of these impurity ions in crystals, useful information on the defect structures of the trigonal Gd^{3+} centers in α-$LiIO_3$ and $LiNbO_3$ crystals can be obtained by studying these EPR data. So the theoretical investigations of zero-field splittings b_2^0 for Gd^{3+} ions in both crystals are of interest and intriguing. In this paper, we explain the zero-field splittings b_2^0 and study the defect structures for the trigonal Gd^{3+} centers in α-$LiIO_3$ and $LiNbO_3$ crystals with the superposition model. The results are discussed.

2. Superposition Model

The empirical superposition model [15, 16] has been successfully used to explain the zero-field splittings of S-state ($4f^7$, $3d^5$)-ions in crystals. The model assumes that the zero-field splitting b_2^m is given by a sum of axially symmetry contributions of the n ligands of the MX_n cluster only, i.e. [15, 16]

$$b_2^m = \sum_i \bar{b}_2(R_0)\left(\frac{R_0}{R_i}\right)^{t_2} K_2^m(\theta_i, \phi_i), \qquad (1)$$

where $K_2^m(\theta_i, \phi_i)$ are the coordination factors [15, 16]. Thus, for S-state ions in the trigonal MX_6 cluster, we have

$$b_2^0 = \left(3/2\right)\bar{b}_2(R_0)\left[\left(\frac{R_0}{R_1}\right)^{t_2}\left(3\cos^2\theta_1 - 1\right) + \left(\frac{R_0}{R_2}\right)^{t_2}\left(3\cos^2\theta_2 - 1\right)\right], \qquad (2)$$

where R_i ($i = 1, 2$) is the metal-ligand distance and θ_i is the angle between R_i and the C_3 axis of the studied trigonal MX_6 cluster in the crystal. t_2 is the power-law exponent and $\bar{b}_2(R_0)$ is the intrinsic parameter with the reference distance R_0. For the Gd^{3+}-O^{2-}-combination [17] we have $t_2 \approx 2.5 \pm 1.5$

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and $\bar{b}_2(R_0) \approx -(2000 \pm 500) \cdot 10^{-4}\mathrm{cm}^{-1}$ with $R_0 \approx 2.699$ Å.

3. Calculation for α-$LiIO_3$: Gd^{3+}

Similar to trigonal iron-group ions (e.g. Cr^{3+} and Fe^{3+} [10, 11, 18]) and Er^{3+} [19] in α-$LiIO_3$ crystals, Gd^{3+} substitutes for Li^+ in this lattice, and the excess charge compensation is performed by two nearest Li^+ vacancy (V_{Li}) along the C_3-axis. Since the effective charge of the cation vacancy V_{Li} is negative, the Li^+ and O^{2-} in the vicinity of V_{Li} should be displaced from their equilibrium positions because of the electrostatic interactions between V_{Li} and these ions. The radiofrequency discrete saturation (RFDS) studies [13] are suggested that for the Gd^{3+} center in α-$LiIO_3$ the two next-nearest Li^+ ions along the C_3-axis are shifted towards the neighbouring vacancy V_{Li} by 0.57 and 0.25 Å, respectively, from the equilibrium position owing to the electrostatic attraction between Li^+ and V_{Li}. However, the displacement ΔX away from the V_{Li} for the six nearest O^{2-} ions (i.e., the ions in the planes between Gd^{3+} and V_{Li}), and hence the defect structure of the trigonal Gd^{3+} center in α-$LiIO_3$ were not reported. Considering the O^{2-} displacement ΔX caused by the electrostatic repulsion between O^{2-} and V_{Li}, the structural parameters R_i and θ_i for the trigonal Gd^{3+} center in α-$LiIO_3$ can be calculated from the structural data R_1^0 (≈ 2.13 Å), R_2^0 (≈ 2.11 Å), θ_1^0 ($\approx 52.05°$) and θ_2^0 ($\approx 52.90°$) of the host LiO_6 cluster in α-$LiIO_3$ [20] and the displacement ΔX. By fitting the calculated zero-field splitting b_2^0 from the superposition model to the observed value, we obtain the displacement

$$\Delta X \approx 0.098\ (29)\ \text{Å}. \qquad (3)$$

The displacement direction agrees with those obtained for the trigonal Cr^{3+} and Fe^{3+} centers in α-$LiIO_3$ [10, 18]. The comparison of b_2^0 between calculation and experiment is shown in Table 1.

Table 1. Zero-field splittings b_2^0 (in unit of 10^{-4} cm^{-1}) for the trigonal Gd^{3+} centers in α-$LiIO_3$ and $LiNbO_3$ crystals.

	Calculation[a]	Calculation[b]	Experiment	
α-$LiIO_3$	141.2	141.3	141.6	[23]
$LiNbO_3$	1188	1183	1185 (13)	[14]

[a] Calculated by considering the ligand- or Gd^{3+}-displacement but neglecting the radial extension of the impurity-ligand distances

[b] Calculated by considering the ligand- or Gd^{3+}-displacement and the radial extension of the impurity-ligand distances.

4. Calculation for $LiNbO_3$: Gd^{3+}

The structure of $LiNbO_3$ is made up of irregular oxygen octahedra piled along the C_3-axis and sharing faces. The centers of the octahedra are occupied by cations in the following sequence: Nb^{5+}, vacancy, Li^+, Nb^{5+}, vacancy, Li^+ etc. [21]. So, the impurity ions, such as rare-earth and transition-metal ions, max occupy different sites. Since the impurity ions can influence strongly the properties of $LiNbO_3$ crystals, knowledge of the location of the impurity and the defect structure of the impurity center are of importance. Rutherford backscattering spectrometry (RBS)/channeling, x-ray standing wave (XSW), proton-induced x-ray emission (PIXE), extended x-ray absorption fine structure (EXAFS), electron nuclear double resonance (ENDOR) and EPR measurements [1 – 7, 11] were used to study the lattice locations and defect structures for many rare-earth and transition-metal ions in $LiNbO_3$. It is found that all these divalent, trivalent and tetravalent paramagnetic impurity ions occpuy Li^+ octahedral sites. So, although the lattice location of Gd^{3+} in $LiNbO_3$ was not reported, we can suggest reasonably that Gd^{3+}, like the other paramagnetic ions, occupies the Li^+ octahedral sites. In the $LiNbO_3$ structure, since the electrostatic repulsive forces between Li^+ and Nb^{5+} pair displace the cations from the centers of symmetry of their oxygen octahedra, the positions of Li^+ and Nb^{5+} are eccentric and closer to the distinctive neighbouring vacant octahedra [11, 21]. If Li^+ is replaced by the impurity ion carrying extra charge, the impurity ion should not occupy exactly the site of Li^+, but is further displaced by ΔZ away from the center of octahedron along the C_3-axis because the electrostatic repulsive force acting on the impurity is greater. This has been confirmed by RBS/channeling, XSW, EXAFS and EPR studies for many rare-earth and transition-metal ions in $LiNbO_3$ crystals [1 – 4, 11]. For rare-earth impurity ions in $LiNbO_3$ the displacement of the impurity from the Li^+ position is also strongly dependent upon the ionic radius of the impurity [1, 2]. For Gd^{3+} in $LiNbO_3$ the off-center displacement ΔZ was not reported. According to the RBS/

channeling measurements [1], the displacement of the trivalent rare-earth impurity ion from the Li^+ position can be approximately regarded as a function of the ionic radius of the impurity. Thus, from the ionic radius of Gd^{3+} [22], we can estimate the displacement to be $\Delta Z \approx 0.4$ Å. The local structural data R_i and θ_l of a trigonal Gd^{3+} center in $LiNbO_3$ can also be calculated from the structural parameters R_1^0 ($\approx$2.238 Å), R_2^0 ($\approx$2.068 Å), θ_1^0 ($\approx$44.57°) and θ_2^0 ($\approx$69.74°) of the LiO_6 octahedron in the host $LiNbO_3$ [21] and the displacement $\mathit{\Delta} Z$. If we apply the parameter $\bar{b}_2(R_0) \approx -2000 \times 10^{-4}\text{cm}^{-1}$ and $t_2 \approx 1$ (which are within the errors), the zero-field splitting b_2^0 for the trigonal Gd^{3+} center in $LiNbO_3$ can be reasonably explained. The comparison of b_2^0 between calculation and experiment is also shown in Table 1.

5. Discussions

We have shown that the zero-field splittings b_2^0 for the trigonal Gd^{3+} centers in α-$LiIO_3$ and $LiNbO_3$ crystals can be explained by taking into account suitable ligand (O^{2-} ions) displacements for α-$LiIO_3$:Gd^{3+} and Gd^{3+} displacements for $LiNbO_3$:Gd^{3+}. These displacements are consistent with expectations based on electrostatic interaction models and results obtained for similar trivalent paramagnetic impurities in the corresponding centers of both crystals [1 – 4, 10, 11, 18]. So, the above displacements and the superposition model parameters $\bar{b}_2(R_0)$ and t_2 obtained in [17] can be regarded as reasonable.

It should be pointed out that the radial extension of the metal-ligand distances R_i caused by the larger ionic radius ($\approx$0.938 Å [22]) of Gd^{3+} than that ($\approx$0.68 Å [22]) of the replaced Li^+ ion for the Gd^{3+} centers in both crystals are not considered in the above studies. In the previous papers, an approximate relationship [18, 23]

$$R \approx R_{\mathrm{H}} + (r_{\mathrm{i}} - r_{\mathrm{h}})/2 \tag{4}$$

was often used to estimate the impurity-ligand distance R in the doped crystals (R_{H} is the metal-ligand distance in the host crystal, and r_i and r_h are the ionic radius of the impurity and the replaced host ion, respectively). From this relationship, for α-$LiIO_3$:Gd^{3+}, we obtain $R_1^0 \approx 2.259$ Å and $R_2^0 \approx 2.239$ Å by considering the above radial extension. Thus, by fitting the calculated zero-field splitting b_2^0 to the observed value, we obtain

$$\Delta X \approx 0.106\ (35)\ \text{Å}. \tag{5}$$

The results is very close to the above value obtained by neglecting the radial extension of the distances R_i. Calculated and experimental values of b_2^0 are given in Table 1.

For $LiNbO_3$: Gd^3, we have $R_1^0 \approx 2.367$ Å and $R_2^0 \approx 2.197$ Å from (4). By slightly changing the power-law exponent t_2 from 1 to 1.2 (the latter is within the error of t_2), the calculated splitting b_2^0 agrees well with the observed value (see Table 1). Obviously, the consideration of the radial extensions of the metal-ligand distances does not change the above conclusions, and so these conclusions are suitable and rational.

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