Theoretical Calculation of Zero Field Splitting of Mn^{2+} Ion in $LiTaO_3$ Crystal

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The semi-empirical superposition model has been applied to calculate the zero field splitting parameters of Mn^{2+} ion in $LiTaO_3$ single crystal, assuming that Mn^{2+} ion occupies one of two possible sites: Li^{1+} or Ta^{5+} site, respectively. The 2nd-order axial zero field splitting parameters are 958×10^{-4} cm^{-1} at Li^{1+} site and 193×10^{-4} cm^{-1} at Ta^{5+} site for Mn^{2+} ions. The 4th-order zero field splitting parameters at Li^{1+} and Ta^{5+} sites are also determined. These calculated zero field splitting parameters are very important to determine the substitutional sites of doped impurity ions in $LiTaO_3$ crystal.

Key words : Mn^{2+} ion, $LiTaO_3$ single crystal, zero field splitting, superposition model, substitutional sites

1. Introduction

Lithium tantalate ($LiTaO_3$) and lithium niobate ($LiNbO_3$) are interesting and useful materials which have found many applications in the fields of optics and acoustics because they are useful for electro-optic devices [1-2], holography [3], and low-loss wave guides [4]. The structure of $LiTaO_3$ has been investigated by Abrahams *et al.* [5-6]. The material was found to be ferroelectric by Matthias and Remeika [7]. They possess identical crystal structures and also exhibit similar physical properties. However, significant differences occur in the Curie (T_c) and melting (T_m) temperatures for these materials. Values of T_c and T_m are 893 K and 1833 K for $LiTaO_3$ and 1470 K and 1533 K for $LiNbO_3$ [8]. The transition of $LiTaO_3$ is well known as a displacive type with some order-disorder nature admixed [9]. There are six molecules per hexagonal (two per rhombohedral) unit cell. The Li^{1+} and Ta^{5+} ions in $LiTaO_3$ lie along the c-axis with C_3 site symmetry and are located in a slightly distorted oxygen octahedron [9, 10], while the O^{2-} ions lie on planes normal to this axis, having the site symmetry 1 [5, 6, 11].

The information about the impurity sites in $LiNbO_3$ and $LiTaO_3$ has come to be of great importance in understanding the nonlinear properties of these ferroelectric crystals. In view of these results, in particular, the site location of paramagnetic ions has been the subject of special interest in order to understand the role played by these defects. Electron paramagnetic resonance (EPR) is powerful tool to investigate the site location of impurity center.

The zero field splitting parameters of Mn^{2+} [12] and Fe^{3+} [13] ions have been calculated at the Li and Nb sites to

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determine the substitutional sites in $LiNbO_3$ crystals using the superposition model and experimental results, respectively. They suggested that both Mn^{2+} and Fe^{3+} ions substitute for Nb site rather than Li site from the comparison of experimental and theoretical calculation. However, it has not yet been discussed whether Mn^{2+} ion replaces Li^{1+} or Ta^{5+} ions in $LiTaO_3$. It is difficult to answer whether paramagnetic impurities substitute for Li^{1+} or Ta^{5+} sites in $LiTaO_3$ because of the similarity of cation sites. Superposition model also give very detailed information on the lattice site. In this paper, we apply the superposition model to calculate the zero field splitting parameters of the Mn^{2+} ion in $LiTaO_3$ crystals. The ZFS parameters calculated at each site can be used to determine the actual site location of Mn^{2+} ion after comparison with experimental electron paramagnetic resonance data.

2. Superposition Model

The main assumption underlying this model is that the spin-Hamiltonian parameters for a paramagnetic ion can be built up from individual contributions due to neighboring ligands. The contribution of next nearest neighbors as well as interaction between ligands is ignored. The zero field splitting parameters b_k^q can be expressed [14] as

$$b_k^q = \sum_i K_k^q(\theta_i, \phi_i)\bar{b}_k(R_i), \tag{1}$$

where $K_k^q(\theta_i, \phi_i)$ are the "coordination factors" depending on the angular positions of all ions at a given distance R_i from the paramagnetic ion. The $\bar{b}_k(R_i)$ are the "intrinsic parameters" depending on the nature of ligand and the covalency of the bonding. It has been assumed that the

functional form of $\overline{b}_k(R_i)$ obeys a simple potential law

$$\overline{b}_k(R_i)=\overline{b}_k(R_0)\left(\frac{R_0}{R_i}\right)^{t_k}, \tag{2}$$

where t_k is the power-law exponent typical for a particular ion/ligands complex, R_0 is the reference distance and R_i is the distance of the i-th ligand.

3. Calculation and Discussion

Structure of LiTaO₃ at room temperature which is below the ferroelectric Curie temperature consists of planar sheets of oxygen atoms in a distorted hexagonal closed-packed configuration. The octahedral interstices formed in this structure are one-third each filled by lithium atoms and tantalum atoms, while another one-third remains vacant. In the [111] direction, the cations are distributed in the octahedra in the following sequence: Ta, vacancy, Li, Ta, vacancy, Li, etc. In the ferroelectric phase, the Li and Ta ions are surrounded by six oxygens in a distorted octahedron and lie along the C_3 axis but away from the center of the octahedron. The size of the Li (0.68 Å) and Ta (0.68 Å) octahedron is nearly the same, whereas the major difference is in the extent of distortion. The rotation angle (α) between the upper and lower oxygen triangle is 3° 56' for the Li and 0° 38' for the Ta octahedron [15]. Crystal structural data [6] of LiTaO₃ crystal used in our calculation are summarized in Table 1.

The axis system in Fig. 1 in ref [12], namely (x,y,z) axis system for Li-site and (x',y',z') axis system for Ta-site, is used to calculate the zero field splitting parameters of Mn²⁺ ion in LiTaO₃ single crystals. The zero field splitting parameters calculated in each axis system were transformed to laboratory axis system (X,Y,Z) for comparison of the values b_4^3. Using the general formulae for the transformations of the zero field splitting parameters b_k^q due to an arbitrary rotation φ about the z-axis [16]

$$[b_k^q]=\sin(q\varphi)\{b_k^{-q}\}+\cos(q\varphi)\{b_k^q\}, \tag{3}$$

one can obtain an infinite number of sets of values (b_4^3, b_4^{-3}). Moreover, in most cases no definition of the x- and y-axes is provided. A proper measure of the strength of these terms is given by the length of the "vector" [17], $|v_4^3| = [(b_4^3)^2 + (b_4^{-3})^2]^{1/2}$, which is invariant with respect to the transformation in Eq. 3.

Table 1. Crystal structural data of LiTaO₃

	Li	Ta
R_1	2.3110 Å	1.9082 Å
R_2	2.0455 Å	2.0740 Å
θ_1	42.87°	60.25°
θ_2	107.15°	130.61°
α	3°56'	0°38'

Table 2. The zero field splitting parameter b_2^0 calculated using the superposition model for Mn²⁺ ion at the Li- and Ta- sites in LiTaO₃ crystal. All units are in $10^{-4}\,cm^{-1}$

SPM parameters	ZFS parameters b_2^0	
	Li-site	Ta-site
$\overline{b}_2 =-996$ $t_2=7.$	1111	221
$\overline{b}_2 =-637$ $t_2=8$	804	164
average	958	193

Table 3. The zero field splitting parameters b_4^q calculated using the superposition model for Mn²⁺ ion at the Li- and Ta-sites in LiTaO₃ crystal. All b_4^q values are transformed to the laboratory axis system. All units are in $10^{-4}\,cm^{-1}$

SPM parameters	ZFS parameters	
	Li-site	Ta-site
$\overline{b}_4 =2.61$ $t_4=14$	$b_4^0 =0.3$	$b_4^0 =-5.9$
	$b_4^3 =-122.0$	$b_4^3 =-3.9$
	$b_4^{-3} =-182.9$	$b_4^{-3} =-205.4$
	$|v_4^3| =219.9$	$|v_4^3| =205.4$

The coordination factors' $K_k^q(\theta_i, \phi_i)$ are calculated using the structural data in Table 1. The intrinsic parameter $\overline{b}_2 = -0.0996\ cm^{-1}$, the power-law exponent $t_2=7$ [18] and $\overline{b}_2 = -0.0637\ cm^{-1}$, $t_2=8$ [19] are used to calculated the ZFS of Mn²⁺ ion. The reference distances are $R_0=2.1783$ Å for Li site and $R_0=1.9911$ Å for Ta site, respectively.

We consider here two possible sites for a paramagnetic impurity in LiTaO₃, namely, the Li and Ta site. The values of b_2^0 predicted by the superposition model for Mn²⁺ center at the Li and Ta site are shown in Table 2. The average value of 2nd order zero field splitting parameter $b_2^0 = 958 \times 10^{-4}\ cm^{-1}$ at Li site is about five times larger than that ($\overline{b}_2 =193 \times 10^{-4}\ cm^{-1}$) at Ta site. These values can be compared with experimental zero field splitting parameters obtained from electron paramagnetic resonance and then determine the actual site location of Mn²⁺ ion in LiTaO₃ single crystal.

The parameters $\overline{b}_4$ and t_4 for Mn²⁺ in LiTaO₃ have not been determined yet, however, they may be obtained from other crystals having similar Mn²⁺-O²⁻ bonds. The following values $\overline{b}_4 =2.61 \times 10^{-4}\ cm^{-1}$ and $t_4=14$ deduced for Mn²⁺ : MgO [20], where Mn²⁺ ions reside in octahedral oxygen coordination similar to that for Mn²⁺ in LiTaO₃, have been adopted. The reference distances are $R_0=2.1783$ Å at Li¹⁺ site and $R_0=1.9911$ Å at Ta⁵⁺ site. The fourth order zero field splitting parameters calculated on the basis of superposition model for the Mn²⁺ at the Li¹⁺ and Ta⁵⁺ sites, respectively, are summarized in Table 3.

In summary, the second and fourth order zero field splitting parameter of Mn²⁺ ion at Li and Ta sites in LiTaO₃

crystals are calculated using superposition model, respectively. From the comparison of experimental electron paramagnetic resonance data and the superposition model calculation results, the actual site locations of Mn^{2+} ion in $LiTaO_3$ single crystals can be determined.

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