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Superposition model calculation of zero-field splitting of Fe^{3+} in LiTaO_3 crystal

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Abstract

The second-order zero-field splitting (ZFS) parameter b_2^0 of the Fe^{3+} ion centre at the Li site, the Ta site and the structural vacancy site in the LiTaO_3 crystal are calculated using the empirical superposition model. The fourth-order ZFS parameters b_4^0 , b_4^3 and b_4^{-3} are also calculated at the Li and Ta site, respectively. The calculated b_2^0 of Fe^{3+} ion at the Li site agrees well with the experimental one. It is concluded that the Fe^{3+} replaces the Li^+ ion rather than the Ta^{5+} ion in the LiTaO_3 crystal. This conclusion confirms the site assignment from the electron nuclear double resonance experiments.

1. Introduction

LiTaO_3 and LiNbO_3 crystals are attractive for the application of their ferroelectric, piezoelectric and electro-optic properties. The photo-refractive effect, which can be used for the storage of volume phase holograms, seems to be correlated to the presence of defects such as transition-metal impurities [1–5]. The information about the impurity sites in LiTaO_3 and LiNbO_3 has come to be important in understanding the nonlinear properties of these ferroelectric crystals. In particular, Fe^{3+} dopants play a key role for the photo-refractive effect [2]. For a better understanding of the photorefractive effect a precise knowledge of the defect structure of Fe^{3+} impurities in LiTaO_3 and LiNbO_3 is needed. It is necessary to know the location of those impurities in the lattice for an understanding of the role of impurities in the photo-refractive effect on a microscopic scale.

LiTaO_3 has the same trigonal structure as LiNbO_3 and also exhibits similar physical properties. In spite of many attempts to determine the site location of Fe^{3+} in LiNbO_3 by experiments [4, 6] applying optical and electron paramagnetic resonance (EPR) spectroscopy as well as by theory [7], the results were not clear beyond doubt. The site location of Fe^{3+} ion has been a subject of special interest in order to comprehend the role played by the defect. It was suggested that the most probable site of Fe^{3+} in LiNbO_3 was the Nb site [8–14] or Li site [15–17], though there are still many controversies over the actual site designations of

the Fe^{3+} impurity in LiNbO_3 . These ambiguous site assignments may arise from the similar environment for the cation sites.

The Newman superposition model (SPM) has proved to be a very powerful tool in probing the local structure of the singlet ground state ion in a variety of crystals [18,19]. In particular this method has been successfully applied to gain very detailed information on the lattice site and crystalline environment of Cr^{3+} , Mn^{2+} and Fe^{3+} ions in a number of single crystal [12,20–23]. In contrast to LiNbO_3 where Fe^{3+} replaces the Li^+ or the Nb^{5+} ion, no theoretical calculation of zero-field splitting (ZFS) parameters for the Fe^{3+} ion in the LiTaO_3 crystal has studied yet whether Fe^{3+} replaces Li^+ or Ta^{5+} in LiTaO_3 .

In this paper, we report the theoretical ZFS analysis of the Fe^{3+} ion located at the Li and the Ta sites in LiTaO_3 with C_3 symmetry, respectively, using by the Newman SPM. The ZFS parameters at the structural vacancy (SV) site are also calculated as a function of the displacement of the Fe^{3+} ion from the centre of the oxygen octahedron along the [111] direction. The actual substitutional site of the Fe^{3+} impurity ion in the LiTaO_3 crystal was determined.

2. Crystal structure

The ferroelectric phase transition in LiTaO_3 occurs at 893 K, and its melting temperature is 1833 K [24]. The transition of this material is well known as a displacive type with some order-disorder nature admixed [25]. There are six molecules per hexagonal (two per rhombohedral) unit cell. The Li^+ and Ta^{5+} ions in LiTaO_3 lie along the c -axis with C_3 (nearly C_{3v}) site symmetry and are located in a slightly distorted oxygen octahedron, while the O^{2-} ions lie on planes normal to this axis, having the site symmetry C_1 [26,27].

The atomic positions and lattice dimensions in the two phases have been studied by x-ray [26] and neutron [27,28] diffraction. At room temperature the Ta ion is displaced along the threefold axis away from a position midway between two planes of oxygen. The Li ion is displaced out of an oxygen plane, in the same direction. As the temperature is raised to T_c , both Ta and Li move along the threefold axis relative to the oxygen planes while keeping the Li–Ta distance approximately constant. These movements bring the Ta ion into a position midway between two oxygen planes, and the Li ion closer to a plane of oxygen ions. Some movements also occur among the oxygen ions within each oxygen plane. Above T_c the neutron diffraction data indicate that the Li atom is distributed on two positions, displaced along the threefold axis ± 0.037 nm from the centro-symmetric position in the oxygen plane.

The structure of LiTaO_3 at room temperature below the ferroelectric Curie temperature consists of planar sheets of oxygen atoms in a distorted hexagonal close-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. The rotation angle (α) between upper and lower oxygen triangles is $3^\circ 56'$ for the Li and $0^\circ 38'$ for the Ta octahedron [29]. Crystal structural data [28] of LiTaO_3 crystal used in our calculation are summarized in table 1.

3. Superposition model analysis

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 neighbouring ligands [30]. The contribution of next nearest neighbours as well as interaction between

Table 1. Crystal structural data of LiTaO₃.

	Li	Ta
R_1 (nm)	0.231 10	0.190 82
R_2 (nm)	0.204 55	0.207 40
θ_1 (°)	42.87	60.25
θ_2 (°)	107.15	130.61
α	3°56′	0°38′

ligands are ignored. The zero field splitting parameters b_k^q can be expressed [31] as

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

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 and tabulated by Newman and Ng [31]. The $\overline{b}_k(R_i)$ 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

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

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

4. Calculation and discussion

The identification of the site location of Fe³⁺ in LiTaO₃ is very difficult because of the very similar environment of the cation sites. The EPR spectra of Fe³⁺ in LiTaO₃ [32] show strong axial symmetry about the c -axis, suggesting that Fe³⁺ substitute at the C_3 symmetry, leading to three possible site assignments, namely, Li, Ta and SV sites. For Li⁺, Ta⁵⁺ and Fe³⁺ the ionic radius is 0.068, 0.068 and 0.064 nm, respectively.

The departure from C_{3v} symmetry is measured by the angle α of the rotation of the upper (or equivalently the lower) oxygen triangle measured from one of the σ_v planes [29]. The ZFS z -axis has been chosen along the [111] axis. For C_{3v} symmetry, the ZFS x -axis is defined along the line joining the centre of the upper oxygen triangle to one of its vertices. After x - and z -axes have been selected, the y -axis is chosen such that the axis system is right handed. The positions in LiTaO₃ as well as the distortion angle α in this coordinate system are given in table 1.

The ZFS parameters calculated in each axis system were transformed to the laboratory axis system (X, Y, Z) for the comparison of the values b_4^3 . Using the general formulae for the transformations of the ZFS parameters b_k^q due to an arbitrary rotation φ about the z -axis [33,34]

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

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’ [35] $|v_4^3| = [(b_4^3)^2 + (b_4^{-3})^2]^{1/2}$, which is invariant with respect to the transformation in equation (3).

The coordination factors $K_k^q(\theta_i, \phi_i)$ are also calculated using the structural data in table 1. The SPM parameters t_k and $\overline{b}_k(R_0)$ for Fe³⁺ in LiTaO₃ have not been determined; however,

Table 2. The ZFS parameter b_2^0 calculated using the SPM for the Fe^{3+} ion at the Li and Ta sites in the LiTaO_3 crystal. All units except t_2 and R_0 are in 10^{-4} cm^{-1} .

SPM parameters	ZFS parameters b_2^0		
	Calculation		Experimental data [32]
	Li site	Ta site	
$\bar{b}_2 = -4120$			
$t_2 = 8$	3896	1630	
$R_0 = 0.2101 \text{ nm}$			
$\bar{b}_2 = -5400$			
$t_2 = 7$	3541	1323	3302
$R_0 = 0.2019 \text{ nm}$			
$\bar{b}_2 = -5400$			
$t_2 = 8$	3712	1554	
$R_0 = 0.2019 \text{ nm}$			

they may be adopted from other crystals having similar $\text{Fe}^{3+}\text{-O}^{2-}$ bonds in octahedral oxygen coordination. Fe^{3+} ions in MgO reside in octahedral oxygen coordination similar to that for Fe^{3+} in LiTaO_3 . We consider here three possible sites for an Fe^{3+} impurity in LiTaO_3 , namely, the Li site, the Ta site and the SV site. The displacement of the Li and Ta ions from the centres of the respective oxygen octahedra used in the calculation of b_k^q for the Fe^{3+} centre are 0.055 97 and 0.020 16 nm, respectively [29].

The second-order ZFS parameters b_2^0 predicted by the SPM for the Fe^{3+} ion in LiTaO_3 either at the Li or Ta site are listed together with experimental data [32] in table 2. Note that confusion exists in [32]—the actual ZFS terms are confusingly referred to as ‘crystal field terms’ (for a detailed discussion see [36]). The parameter b_2^0 is calculated using $\bar{b}_2 = -0.412 \text{ cm}^{-1}$, $t_2 = 8$ and $R_0 = 0.2101 \text{ nm}$ adopted from the data for Fe^{3+} at the cubic site of MgO [37] and $\bar{b}_2 = -0.540 \text{ cm}^{-1}$, $t_2 = 7\text{--}8$, and $R_0 = 0.2019 \text{ nm}$ [38]. The calculated value of b_2^0 ($= 3541\text{--}3896 \times 10^{-4} \text{ cm}^{-1}$) for the Fe^{3+} ion at the Li site is about two or three times larger than that ($1323\text{--}1630 \times 10^{-4} \text{ cm}^{-1}$) at the Ta site as shown in table 2. The experimental b_2^0 ($= 3302 \times 10^{-4} \text{ cm}^{-1}$) of the Fe^{3+} ion agrees well with the calculated one at the Li^+ site. This implies that the Fe^{3+} ion substitutes for the Li^+ ion rather than the Ta^{5+} ion in the LiTaO_3 crystal.

We have calculated the b_2^0 value of the Fe^{3+} located at the SV sites versus the Fe^{3+} displacement from the centre of the oxygen octahedron in the range of $\pm 0.1 \text{ nm}$ using by SPM as shown in the figure 1. The b_2^0 denoted by open rectangles and circles are calculated with $\bar{b}_2 = -0.412 \text{ cm}^{-1}$, $t_2 = 8$ and $R_0 = 0.2101 \text{ nm}$ [37] and $\bar{b}_2 = -0.5400 \text{ cm}^{-1}$, $t_2 = 7$ and $R_0 = 0.2019 \text{ nm}$ [38], respectively. The calculated b_2^0 values at the centre of the oxygen octahedron of the SV site are $960\text{--}1023 \times 10^{-4} \text{ cm}^{-1}$. These calculated values are about three times smaller than experimental b_2^0 ($= 3302 \times 10^{-4} \text{ cm}^{-1}$). If the Fe^{3+} ion occupies the SV site, it should be displaced more than -0.02 nm toward the Ta^{5+} ion or $+0.05 \text{ nm}$ toward the Li^+ ion from the centre of the oxygen octahedron to satisfy the experimental b_2^0 value, as can be seen in figure 1. In that case, the deviation (-0.02 nm) of Fe^{3+} in the SV site is at least more than 18%, compared with its central position in an oxygen octahedron in LiTaO_3 . It seems to be unlikely that the Fe^{3+} ion enters the SV site in a LiTaO_3 crystal.

The site of a paramagnetic impurity could in principle be determined from electron nuclear double resonance (ENDOR) by resolving the super hyperfine interactions between the magnetic moments for the unpaired electrons and the magnetic moments of the lattice nuclei. It was

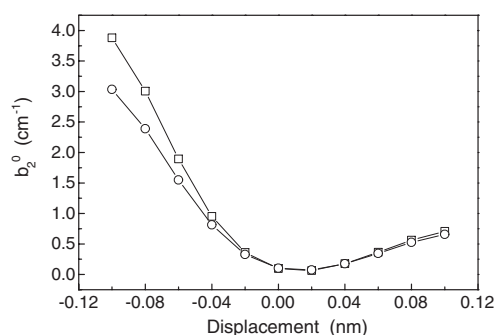


Figure 1. The second-order ZFS parameter b_2^0 at SV sites as a function of displacement of the Fe³⁺ ion from the centre of the oxygen octahedron in the LiTaO₃ crystal.

Table 3. The ZFS parameters b_4^q calculated using the SPM for the Fe³⁺ ion at the Li and Ta sites in the LiTaO₃ crystal. All b_4^q values are transformed to the laboratory axis system. All units except t_4 are in 10^{-4} cm^{-1} .

SPM parameters	ZFS parameters b_4^q	
	Li site	Ta site
	$b_4^0 = 2.9$	$b_4^0 = -66.0$
$\bar{b}_4 = 29.1$	$b_4^3 = 2153.7$	$b_4^3 = 2289.9$
$t_4 = 14$	$b_4^{-3} = -324.2$	$b_4^{-3} = 43.4$
	$ v_4^3 = 2178.0$	$ v_4^3 = 2290.3$

found that Fe³⁺ is on a substitutional Li⁺ site on the C_3 symmetry axis of the crystal from the analysis of the ENDOR spectra [32]. From the experimental and theoretical second-order ZFS parameter (see table 2) and ENDOR data, one may conclude that the Fe³⁺ ion substitutes for the Li⁺ ion in the LiTaO₃ crystal.

Though the ZFS parameters b_4^q have not been determined by experiments yet, the b_4^q s are also calculated with $\bar{b}_4 = 29.1(10^{-4} \text{ cm}^{-1})$ and $t_4 = 14$ for Fe³⁺ ions in MgO [39] using SPM. The reference distance R_0 of Li⁺-O²⁻ and Ta⁵⁺-O²⁻ bonds is taken as 2.178 and 1.199 11 nm, respectively. The fourth-order ZFS parameters b_4^0 , b_4^3 and b_4^{-3} at Li⁺ and Ta⁵⁺ sites are expressed in the laboratory axis system and given in table 3. The C_3 symmetry effect in the LiTaO₃ crystal should not be ignored from the calculated ZFS parameters in table 3.

Summarizing, the second-order ZFS parameters b_2^0 of Fe³⁺ ion in the LiTaO₃ single crystal have been calculated separately for Fe³⁺ at the Li⁺, Ta⁵⁺ and SV sites by the SPM. The fourth-order ZFS parameters b_4^0 , b_4^3 and b_4^{-3} are also calculated at the Li⁺ and Ta⁵⁺ sites. From the experimental ZFS parameters found by EPR study and the ZFS parameters calculated by SPM calculation, it can be concluded that the Fe³⁺ ion substitutes for the Li⁺ ion rather than the Ta⁵⁺ ion. This conclusion is consistent with the previous ENDOR experimental data [32].

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