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Substitution position of the impurity ion Mn^{2+} in $LiNbO_3$

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The complete crystal-field spin-orbit interaction matrices of point group C_{3v} for the d^5 configuration have been derived. It is shown by investigating the EPR parameter that the impurity ion Mn^{2+} replaces the Li^+ ion in $LiNbO_3$. The argument is presented that both the spin-orbit-coupling mechanism and the superposition model are good approaches to accurate calculations.

I. INTRODUCTION

Since the Li and Nb ions of $LiNbO_3$ lie in octahedral sites of C_3 (nearly C_{3V}) symmetry about the [111] axis[1-4] and they have similar ionic radii, Li^+, 0.68 Å and Nb^{5+}, 0.69 Å,[5] impurity ions can go to the Li and Nb sites.[6-11] Therefore, a conclusion about the position of substitutional impurities in $LiNbO_3$ has not been drawn as yet.[12] Some persons have assumed that the impurities go to Li^+ sites,[13-17] whereas others have suggested from other studies it is the Nb^{5+} sites.[16-20] In this paper, the complete crystal-field spin-orbit interaction matrices have been derived for the point group C_{3V} of d^5 configuration, and the EPR zero-field splitting parameter D in $LiNbO_3$:Mn^{2+} has been calculated separately for Mn^{2+} at the Li^+ and Nb^{5+} sites by diagonalizing the complete matrices (DM) and, for comparison, by using the spin-orbit coupling mechanism (SO) and the superposition model (SM). The results indicate that the impurities Mn^{2+} replace the Li^+ rather than the Nb^{5+} ions and that both the SO and SM are good approaches to accurate calculations (DM).

II. PERTURBATION HAMILTONIAN MATRIX

For interpretation of the experimental data accumulated by the more sophisticated experimental techniques, it is necessary to use a more complete calculational method which allows for the investigation of small perturbations such as the low-symmetry crystal-field and spin-orbit interactions. In fact, the spin-orbit crystal-field matrices of point group C_{3v} for $d^{9,1}$, $d^{8,2}$, $d^{7,3}$ and $d^{6,4}$ configurations have been published.[21,22] Here we deal with the d^5 configuration in C_{3V} symmetry. The Hamiltonian is taken as

$$H = H_0 + H_{SO} + V(C_{3V}) , \tag{1}$$

where H_0 is the free-ion Hamiltonian and the perturbation terms represent both the spin-orbit coupling

$$H_{SO} = \zeta \sum_i l_i S_i , \tag{2}$$

and the crystal-field interaction of C_{3V} symmetry,

$$V(C_{3V}) = \sum_i (C_0^2 r_i^2 A_0^2 + c_0^4 r_i^4 A_0^4 + C_3^4 r_i^4 A_3^4) , \tag{3}$$

with

$$C_m^n = \left[\frac{4\pi}{2n+1} \right]^{1/2} Y_{mn}(\theta_i, \varphi_i) , \tag{4}$$

where $(r_i, \theta_i, \varphi_i)$ are the coordinates of the nth d electron of central ion. Clearly, the derived Hamiltonian matrices (having dimensions of 64×64 for the irreducible representations Γ_4 and Γ_5 of point group C_{3V}) include the spin-orbit coupling and the electrostatic and the crystal-field interactions, and are so-called spin-orbit crystal-field matrices. The matrix elements are functions of the Racah parameters B and C,[23] Trees' and Racah's correction parameters α (Ref. 24) and β,[25] the spin-orbit coupling parameter ζ,[23] and the crystal-field parameters

$$\begin{aligned} A_0^2\langle r^2 \rangle &= -\tfrac{1}{2}\langle r^2 \rangle \sum_i eQ_i(3\cos^2\Theta_i - 1)/R_i^3 , \\ A_0^4\langle r^4 \rangle &= -\tfrac{1}{8}\langle r^4 \rangle \sum_i eQ_i(35\cos^4\Theta_i - 30\cos^2\Theta_i + 3)/R_i^5 , \\ A_3^4\langle r^4 \rangle &= -\frac{\sqrt{35}}{4}\langle r^4 \rangle \sum_i eQ_i \cos\Theta_i \sin^3\Theta_i / R_i^5 , \end{aligned} \tag{5}$$

where Q_i and (R_i, Θ_i, Φ_i) are the charge and coordinates of the ith ligand, while $\langle r^2 \rangle$ and $\langle r^4 \rangle$ are expectation values. By diagonalizing the spin-orbit crystal-field matrices (DM), we can obtain the zero-field splitting D provided the values of these parameters are known. In the following calculation, the values of $B = 911$ cm^{-1}, $C = 3273$ cm^{-1}, $\zeta = 337$ cm^{-1}, $\langle r^2 \rangle = 2.7755$ a.u., $\langle r^4 \rangle = 23.2594$ a.u.,[26] $\alpha = 65$ cm^{-1},[24] and $\beta = -131$ cm^{-1} (Ref. 25) are taken.

III. TWO APPROXIMATE PERTURBATION PROCEDURES FOR EPR

In the past few years, two successful methods have been used to study the EPR parameters of the d^5 ion in crystals. One is the usual Blume-Orbach[27] method based on crystal-field and spin-orbit interactions, and the other is the Newman superposition model.[28-31] The SO mechanism has been remarkably successful in explaining many of the features of spectra in crystals[32–36] and has been studied in detail and applied to rhombic and trigonal symmetries by Sharma, Das, and Orbach.[37–41] In trigonal symmetry the axial EPR term D has been given as

$$D_{\mathrm{SO}}=\frac{\sqrt{5}}{63}\langle r^4\rangle\zeta^2(7P_{\alpha\alpha}+4P_{\alpha\beta})P_{\alpha\gamma}\left[A_0^4+\left[\frac{7}{10}\right]^{1/2}A_3^4\right]-\frac{3\sqrt{5}}{14}\langle r^2\rangle\zeta^2P_{\alpha\beta}P_{\alpha\gamma}A_0^2\ , \tag{6}$$

where $P_{\alpha\alpha}$, $P_{\alpha\beta}$, and $P_{\alpha\gamma}$ are the constants depending on the crystal-field strength and, in the following calculation, are taken to be 3.921×10^{-5}, -0.169×10^{-5}, and 1.466×10^{-5} cm obtained from Ref. 37. The Newman superposition model,[28–31] which leads to a treatment identical with that for the $4f^7$ ground-state splitting, has been successfully applied to the $3d^5$ ions.[42–45]. The parameter D can be expressed as

$$D_{\mathrm{SM}}=\tfrac{1}{2}\sum_i\bar{b}_2(3\cos^2\Theta_i-1)\left[\frac{R_0}{R_i}\right]^{t_2}\ . \tag{7}$$

In the following calculation the intrinsic parameter $\bar{b}_2=0.0996\ \mathrm{cm}^{-1}$,[46] the power-law exponent $t_2=7$,[31] and the reference distances $R_0=2.153$ and 2.001 Å (just as the average bond lengths of Li^+-O^{2-} in the Li site and N_6^{5+}-O^{2-} in the Nb site,[1–4] respectively) are taken.

IV. RESULTS AND DISCUSSION

From the above, it is easy to see that the EPR parameter D can be obtained by the DM method and by both the approximate perturbation methods SO and SM as long as the location of Mn^{2+} in $\mathrm{LiNbO_3}$ [i.e., its coordinates $(R_i,\ \Theta_i,\ \Phi_i)$] is known. According to the crystal-structure analyses on single-crystal $\mathrm{LiNbO_3}$,[1–4] there are two different sets of coordinates (R_i,Θ_i,Φ_i) for the Li^+ and Nb^{5+} sites and, further, two sets of parameter D, as listed in Table I.

TABLE I. EPS zero-field splitting parameter D in $\mathrm{LiNbO_3{:}Mn^{2+}}$ (in $10^{-4}\ \mathrm{cm}^{-1}$).

	SM	SO	DM
Li site	673	732	725
Nb site	403	408	413
expt.		730±20 (Ref. 11)	

From Table I it can easily be seen that the Mn^{2+} ion substitutes for Li^+ rather than for the Nb^{5+} ion. Here the weak Mn^{2+}-V_{Li} vacancy reported at present[11] is not considered because the Li vacancies cause a reduced defect symmetry with point group C_1 symmetry. Present results on the most strongly axial EPR symmetry are clearcut; that is, consistent with a recent electron-nuclear double-resonance analysis in $\mathrm{LiTaO_3}$: Fe^{3+}.[12]

Recently, for the SO and SM methods, discussion as to which method is appropriate for producing reasonable results for $3d^5$ ground-state splitting has been seen frequently in the literature.[47–49] In this work, for the Mn^{2+} at both the Li and Nb sites, the results calculated by using the DM, SM, and SO methods show that both the spin-orbit interaction mechanism and the superposition model are good approaches to accurate calculations, and all the methods lead to results almost identical with that for the $3d^5$ ground-state splitting of the Mn^{2+} ion. This conclusion is the same as that of recent theoretical analyses for the spin Hamiltonian parameter of $3d^5$ ions.[46,50]

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