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Substitution site of the Fe^{3+} impurity in crystalline $LiNbO_3$

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It is shown, by investigating the ESR parameters, that the impurity Fe^{3+} ion substitutes the Nb^{5+} ion rather than the Li^+, with use of the generalized crystal-field theory and a complete diagonalization procedure.

I. INTRODUCTION

$LiNbO_3$ and $LiTaO_3$ are dielectric crystals that are of particular interest because of the photorefractive effects observed in these materials. The photorefractive effect,[1–5] 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. For an understanding of the role of impurities in the photorefractive effect on a microscopic scale, it is necessary to know the location of those impurities in the lattice. The largest influence on the photorefractive effect is reported for iron.[2] In spite of many efforts both by optical and electron-spin-resonance (ESR) spectroscopy[4–6] as well as theory[7] to determine the site of Fe^{3+} in $LiNbO_3$, no safe conclusion could be drawn. A Li^+ substitutional site with C_3 symmetry is also discussed as a substitutional Nb^{5+} site, which seems to be favored from the analysis of Mössbaseur spectra.[8,9]

"The site of a paramagnetic impurity could in principle be determined from electron nuclear double resonance (ENDOR) by resolving the superhyperfine (SHF) interactions between the magnetic moments of the unpaired electrons and the magnetic moments of the lattice nuclei. All attempts to do so in congruent $LiNbO_3$:Fe^{3+} have so far failed."[10]

As either Fe^{3+} or Mn^{2+} is in $3d^5$ configuration with the ground state ^6S, one may expect that the electron-paramagnetic-resonance (EPR) zero-field splitting (ZFS) of Fe^{3+} does not differ in magnitude remarkably from that of Mn^{2+} when they are substituted into the same host crystal. However, this is not the case. A large amount of experimental observations have shown that the ZFS of Fe^{3+} is much larger than that of Mn^{2+} and even for many crystals the ZFS parameters of Fe^{3+} are found to be one order of magnitude larger than those of Mn^{2+}.[11–14] This behavior is difficult to understand, and so Low and Rosengarten[14] reached the conclusion that crystal-field theory is not capable of providing a unified explanation for the ZFS parameters of $d^5(S)$ ions. Such a difficulty with the S-state ZFS continued until 1985, although many works have been published which arrive at good numerical estimates for the Mn^{2+} ion in crystals. In 1986, this difficulty was analyzed in some detail by Zhao *et al.*[15,16] They have calculated the ZFS of Fe^3 doped into a corundum and four garnets (YAG, YGG, LuAG, and LuGG) together with that of Mn^{2+}:Al_2O_3, considering various mechanisms and using a semi-self-consistent-field (semi-SCF) d-orbit and average covalency model proposed by Zhao *et al.*[15–20] The calculation results agree well with the experimental findings. Obviously, this method has achieved success in the calculations of the optical-absorption bands and ZFS for $3d^n$ ions in crystals. We expect it to also work well in the case of the substitution puzzle in crystals doped with transition-metal ions, e.g., Fe^{3+} or Mn^{2+}. In 1990–1991, Zhou[21,22] and Zheng[23,24] found that the Mn^{2+} ion replaces the Li^+ ion in $LiNbO_3$, the Mg^{2+} ion in $KMgF_3$, and the Fe^{3+} ion replaces the Cd^{2+} ion in $CdNb_2O_7$, the Al^{3+} ion in $AlCl_3 \cdot 6H_2O$, on the basis of the semi-SCF d-orbit and average covalency model[15–20] and the experimental ZFS data.

In this work, the EPR ZFS parameters D and $a-F$ in Fe^{3+}:$LiNbO_3$ have been calculated separately for Fe^{3+} at the Li^+ and Nb^{5+} sites by diagonalizing the complete crystal-field spin-orbit interaction matrices based on both the semi-SCF d-orbit and average covalency model[15–20] and the experimental ZFS parameters. The results show that the impurity ion Fe^{3+} substituted the Nb^{5+} ion rather than the Li^+ ion.

II. COMPLETE CRYSTAL-FIELD SPIN-ORBIT MATRICES

For interpretation of the experimental data accumulated by the more sophisticated experimental technique, it is necessary to use a more complete calculation method which allows for the investigation of small perturbations such as the low-symmetry crystal-field and spin-orbit interactions. The complete d^5 diagonalization procedure (CDP) was successfully employed for the calculation of the Mn^{2+} ZFS in ZnF_2 and MnF_2 (Refs. 25 and 26) in D_{2h} symmetry. In 1987–1988, Febbraro[27,28] reexamined the theoretical framework and the general results of the complete d^5 diagonalization procedure in order to investigate the properties of $3d^5$ ions in crystals.

The irreducible representations of the double group C_3' arising for the d^5 configuration are Γ_4, Γ_5, and Γ_6, $\Gamma_5 = \Gamma_4^*$.

The irreducible representation basis functions of the C_3' group and the complete crystal-field spin-orbit matrices are listed in an unpublished work. The matrices are functions of B, C, α, β, and crystal-field parameters B_2^0, B_4^0, B_4^3, and B_4^{-3}.

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III. CALCULATION MODEL AND RESULTS

Following the work by Abragam and Bleaney,[29] the ZFS parameters are given by

$$E(\pm\tfrac{1}{2})\simeq-\tfrac{2}{3}(a-F)-\tfrac{8}{3}D\ , \tag{1}$$

$$E(\pm\tfrac{3}{2})\simeq a-F-\tfrac{2}{3}D\ , \tag{2}$$

$$E(\pm\tfrac{5}{2})\simeq-\tfrac{1}{3}(a-F)+\tfrac{10}{3}D\ ; \tag{3}$$

hence, we have

$$D\cong\tfrac{1}{28}[4(E_2-E_1)+5(E_3-E_2)]\ , \tag{4}$$

$$a-F\cong-\tfrac{3}{14}[(E_3-E_2)-2(E_2-E_1)]\ , \tag{5}$$

$$(|D|\gg|a-F|,|a|)\ ,$$

where E_1, E_2, and E_3 represent the zero-field energy eigenvalues of the ground state $|\pm\frac{1}{2}\rangle$, $|\pm\frac{3}{2}\rangle$, and $|\pm\frac{5}{2}\rangle$, respectively.

It can be seen from Eqs. (4) and (5) that we can yield the ZFS parameters D and $a-F$ provided the values of the energies E_2-E_1 and E_3-E_2 are known by means of the CDP method.

In the generalized crystal-field model, the C_3' crystal-field parameters B_q^k are given by

$$B_2^0=[-3eq\langle r^2\rangle/2]\sum_{i=1}^{2}(3\cos^2\theta_i-1)/R_i^3, \tag{6}$$

$$B_4^0=[-3eq\langle r^4\rangle/8]\sum_{i=1}^{2}(35\cos^4\theta_i-30\cos^2\theta_i+3)/R_i^5\ , \tag{7}$$

$$\begin{aligned}B_4^3=-(B_4^{-3})^*=&[(\sqrt{35})3eq\langle r^4\rangle/4]\\&\times[(\cos\theta_2\sin^3\theta_2/R_2^5)\\&-(\cos\theta_1\sin^3\theta_1e^{-i3\psi}/R_1^5)]\ .\end{aligned} \tag{8}$$

The crystal-field parameters B_q^k can be calculated from the crystalline structure data provided that the expectation values $\langle r^n\rangle$ and the effective charge q are known. In a general view, $\langle r^n\rangle$ in crystals are smaller in magnitude than the free-ion values $\langle r^n\rangle_0$ as Racah parameters B and C, Trees parameter α, and spin-orbit coupling constant ξ_d in crystals. This is mainly because of the overlap between the central ion and the ligand orbits; such a covalency effect results in a reduction of the free-ion values. A reasonable approximation is made that[15-20]

$$\begin{gathered}B=N^4B_0\ ,\quad C=N^4C_0\ ,\quad \alpha=N^4\alpha_0\ ,\quad \beta=N^4\beta_0\ ,\\ \xi=N^2\xi_0\ ,\quad \langle r^k\rangle=N^2\langle r^k\rangle_0\ ,\end{gathered} \tag{9}$$

where N measures the average reduction factor due to the covalency. As one sees, this model leaves at most two adjustable parameters N and q, which remain to be determined from the experimental optical-absorption bands.

For the Fe^{3+} ion, the semi-SCF d orbit is given by[15,16]

$$\begin{aligned}R_d(r)=0.677&\left[\frac{11.2^7}{6!}\right]^{1/2}r^2\exp(-5.6r)\\&+0.552\,37\left[\frac{3.446^7}{6!}\right]^{1/2}r^2\exp(-1.732r)\ .\end{aligned} \tag{10}$$

From this orbit the Racah parameters B_0 and C_0, the spin-orbit coupling constant ξ_0, and the expectation values $\langle r^k\rangle_0$ are calculated for the free ion as follows:

$$\begin{gathered}B_0=1130.22\ \text{cm}^{-1}\ ,\quad C_0=4111.45\ ,\\ \xi_0=588.946\ \text{cm}^{-1}\ ,\\ \langle r^2\rangle_0=1.890\,39\ \text{a.u.}\ ,\\ \langle r^4\rangle_0=11.464\,85\ \text{a.u.}\end{gathered} \tag{11}$$

The Trees correction constant $\alpha_0=40\ \text{cm}^{-1}$ and Racah seniority correction β_0 are fitted from the free-ion spectra. The comparison between the theory and experiment is shown in Table I. It can be seen from Table I that the agreement between the calculated and observed bands is always better than 3%. In the calculation, Tree's and Racah's corrections result from a mean-square fit. However, the discrepancy reaches 15% by neglecting α_0 and β_0.

TABLE I. Energy levels of free Fe^{3+} ion ($\alpha_0=40\ \text{cm}^{-1}$, $\beta_0=-131\ \text{cm}^{-1}$) (in cm^{-1}).

Terms	J	Calc.	Obs.[a]
^6S	$\frac{5}{2}$	0	0
^4G	$\frac{5}{2}$	32 558	32 246
	$\frac{7}{2}$	32 603	32 293
	$\frac{11}{2}$	32 616	32 300
	$\frac{9}{2}$	32 630	32 305
^4P	$\frac{5}{2}$	36 203	35 256
	$\frac{3}{2}$	36 315	35 325
	$\frac{1}{2}$	36 428	35 404
^4D	$\frac{7}{2}$	39 938	38 776
	$\frac{1}{2}$	40 063	38 893
	$\frac{3}{2}$	40 147	38 932
	$\frac{5}{2}$	40 161	38 935
^2I	$\frac{11}{2}$	46 893	47 033
	$\frac{13}{2}$	47 004	47 090
$^2D_3$	$\frac{5}{2}$	50 832	49 540
	$\frac{3}{2}$	51 582	50 049
$^2F_1$	$\frac{7}{2}$	52 895	51 396
	$\frac{5}{2}$	53 672	52 166
^4F	$\frac{5}{2}$	53 742	52 620
	$\frac{7}{2}$	53 832	52 694
	$\frac{9}{2}$	54 093	52 693
	$\frac{3}{2}$	54 228	52 837
^2H	$\frac{9}{2}$	56 742	56 012
	$\frac{11}{2}$	57 160	56 368
$^2G_2$	$\frac{7}{2}$	58 615	57 594
	$\frac{9}{2}$	58 958	57 720
$^2F_2$	$\frac{5}{2}$	62 775	61 156
	$\frac{7}{2}$	62 814	61 253
$^2D_2$	$\frac{3}{2}$	76 388	?
	$\frac{5}{2}$	76 467	73 842
$^2G_1$	$\frac{9}{2}$	84 874	82 851
	$\frac{7}{2}$	84 906	82 893

[a] Reference 30.

For the corundum and garnets, we found $N=0.863$ for Fe^{3+}: Al_2O_3 and $N=0.850$ for Fe^{3+}:YAG, YGG, LuAG, and LuGG from the optical-absorption spectra in crystals.[15,16] In the calculation, q = valent charge $=-2e$. The good agreement between theory and experiments shows that $q=-2e$ is a reasonable value. The absorption spectrum of Fe^{3+}:$LiNbO_3$ has been observed by Dischler, Herrington, and Rauber.[31] They found that there are two bands at 20 747 and 23 500 cm^{-1}. We have remeasured the absorption spectrum and found that 20 747 cm^{-1} band is a sharp one, which agrees with the characteristics for $^6A_1 \rightarrow {}^4A_1(G)$, $^4E(G)$. Thus we have reason to assign

$$20\,747=\Delta E[{}^4E(G),{}^4A_1(G)]$$
$$=10B+5C+20\alpha \sim 32\,480N^4\ ,$$

which leads to $N \sim 0.891$.

From the 84×84 matrices deduced and Eqs. (4)–(11), it is easy to see that the ZFS parameters D and $a-F$ can be obtained by the CDP method as long as the location of Fe^{3+} in $LiNbO_3$ [i.e., its coordinates (R_i,θ_i,ϕ_i)] is known. According to an x-ray-diffraction analysis on single-crystal $LiNbO_3$,[32–39] there are two different sets of coordinates (R_i,θ_i,ϕ_i) for the Li^+ and Nb^{5+} and, further, two sets of parameters D and $a-F$, as listed in Table II.

TABLE II. Zero-field splitting parameters D and $a-F$ in Fe^{5+}:$LiNbO_3$: (in 10^{-4} cm^{-1}).

Site	Li^+ site		Nb^{5+} site
	$R_1=2.238$ Å		$R_1=1.889$ Å
	$R_2=2.068$ Å		$R_2=2.112$ Å
	$\theta_1=44.57°$		$\theta_1=61.65°$
	$\theta_2=110.26°$		$\theta_2=132.01°$
	$\lvert\phi\rvert=3.81°$		$\lvert\phi\rvert=0.68°$
D_{calc}	860		1054
D_{obs}		1106[a]	
$(a-F)_{calc}$	30		114
$(a-F)_{obs}$		128[a]	

[a] Reference 35.

From Table II it can be seen that the Fe^{5+} ion is on a substitutional Nb^{5+} site rather than for the Li^{5+} site, because of $(a-F)(\mathrm{Nb})\approx(a-F)(\mathrm{obs})$ and $(a-F)(\mathrm{Li})\ll(a-F)(\mathrm{obs})$. Calculation indicates that if $|q|<2|e|$, then $(a-F)(\mathrm{Li})<30$ and $D(\mathrm{Li})<860$. Hence the Nb-substitution conclusion is reasonable. It must be pointed out that the coordination of Fe^{3+} ions in $LiNbO_3$ has been investigated by the extended x-ray-absorption fine-structure (EXAFS) technique.[36] From the analysis of the data, it was found that the Fe^{3+} site is in the Li site. Because of the low sensitivity of EXAFS to diluted concentrations of atoms, from their results other lattice positions of Fe^{3+} ions present in minor concentrations cannot be excluded.[36] Of course, our results remain to be verified by further experiments.

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