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LETTER TO THE EDITOR

Mössbauer isomer shifts and the nephelauxetic effect in LiNbO_3 crystals

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Abstract

The nature of the impurity centre in LiNbO_3 has been a subject of intense discussion in recent years. A semi-empirical model, based on the Phillips theory of bonding, has been developed to provide a quantitative explanation of the nephelauxetic effect of Cr^{3+} ions and Mössbauer isomer shifts of Fe ions in LiNbO_3 crystals. The results show quantitatively that the impurity Cr^{3+} substitutes for the Nb^{5+} ions rather than the Li^+ ions in stoichiometric LiNbO_3 crystals, and it is verified that Fe ions substitute at Li sites in LiNbO_3 .

In the last few years there has been great interest in developing lithium niobate crystals doped with transition metals ions for use in laser and non-linear optics devices. The Cr^{3+} ion is a good candidate for doping lithium niobate in order to obtain broad-spectrum tunable lasers. Several different Cr^{3+} defect centres were identified. However, two of them are dominant in such crystals [1]: one centre that corresponds to undisturbed Cr^{3+} in the Li^+ lattice site, and another centre that is related to Cr^{3+} at the Nb^{5+} site. In the past, it has been proposed that these centres consist of single Cr^{3+} ions on Li sites [2], single Cr^{3+} ions on Nb sites [3], and two Cr^{3+} ions substituted simultaneously for a pair of Li and Nb sites [4]. Since both Li^+ and Nb^{5+} lie on the threefold axis, it will be difficult to experimentally determine the site of the Cr^{3+} ions. There are still controversies concerning the Cr^{3+} sites and the interpretations conflict. In the final analysis, this is because our knowledge of the local environment of specific ions is still insufficient. On the other hand, photorefractive materials such as Fe-doped LiNbO_3 can be used to record holograms with modest laser power [5]. In the LiNbO_3 structure, it is generally believed that Fe impurities substitute for Li cations, based on Mössbauer spectroscopy studies [6, 7]. But a quantitative description is far from complete or clear.

For an understanding of the role of impurities in the photorefractive effect on a microscopic scale, it is necessary to know the location of impurities in the lattice. From optical absorption spectra [8], it has been found that the nephelauxetic effect in Cr^{3+} -doped LiNbO_3 crystal is relatively strong in comparison with those in other oxide crystals. This is due to the covalency

of bonds between the central ion and the ligands. It is also well known that, within each oxidation state, the ranges of Mössbauer isomer shifts reflect the sums of covalency and bonding effects. More recently, an acoustic memory in LiNbO₃ crystal has been observed, and the strength of this memory signal has been shown to be tied directly to the dielectric properties of the ferroelectric medium [9]. We think that the macroscopic physical properties of crystals must have a direct relationship with their constituent chemical bonds. Therefore, for LiNbO₃ crystal, it is reasonable to investigate the impurity properties by starting from the chemical bond viewpoint. In this letter we employed the Phillips [10] dielectric theory of ionic-covalent bonding to study the bonding, polarization, and spectrum properties of LiNbO₃ crystal.

At room temperature, the crystal structure of LiNbO₃ [11] is rhombohedral with space group *R3c*, *Z* = 2, *a* = 5.4944 Å, $\alpha = 55^\circ 52'$. Oxygen atoms are arranged octahedrally with the threefold axis along the *z* direction. Two lithium ions and two niobium ions occupy four out of six octahedral sites in a unit cell. The positions of the lithium and niobium ions are distorted from the centre of the octahedron due to the occurrence of an empty site for every three octahedral structures. According to theory [12, 13], the crystal formula of LiNbO₃ can be converted into a subformula equation (a bond-valence equation [14]) as below:

$$\text{LiNbO}_3 = (1/2)\text{LiO}(s)_{3/2} + (1/2)\text{LiO}(l)_{3/2} + (1/2)\text{NbO}(l)_{3/2} + (1/2)\text{NbO}(s)_{3/2}. \quad (1)$$

The properties of all constituent chemical bonds can then be obtained by using the theory of complex crystals [14]. The macroscopic linear susceptibility χ can be resolved into contributions χ^μ from the various types of bond or from the various binary crystals:

$$\chi = \varepsilon - 1 = \sum_{\mu} F^{\mu} \chi^{\mu} = \sum_{\mu} N_{\text{b}}^{\mu} \chi_{\text{b}}^{\mu} \quad (2)$$

where ε is dielectric constant, χ^μ is the total macroscopic susceptibility of a binary crystal composed of only one type of μ bond. F^μ is the fraction of the binary crystal composing the actual complex crystal. χ_{b}^μ is the susceptibility of a single bond of type μ in the corresponding binary crystal, and N_{b}^μ is the number of bonds per cubic centimetre:

$$\chi^\mu = (4\pi)^{-1} [(\hbar\Omega_{\text{p}}^\mu)^2 / (E_{\text{g}}^\mu)^2] \quad (3)$$

where E_{g}^μ is the average energy gap for the type μ bond. Ω_{p}^μ is the plasma frequency obtained from the numbers of valence electrons of type μ per cubic centimetre, N_{e}^μ , using

$$(\hbar\Omega_{\text{p}}^\mu)^2 = (4\pi N_{\text{e}}^\mu e^2 / m). \quad (4)$$

N_{e}^μ is expressed as follows:

$$N_{\text{e}}^\mu = (n_{\text{e}}^\mu)^* / v_{\text{b}}^\mu \quad (n_{\text{e}}^\mu)^* = [(Z_{\text{A}}^\mu)^* / N_{\text{CA}}^\mu + (Z_{\text{B}}^\mu)^* / N_{\text{CB}}^\mu] \quad (5)$$

$$(k_{\text{F}}^\mu)^3 = 3\pi^2 N_{\text{e}}^\mu \quad (6)$$

where $(n_{\text{e}}^\mu)^*$ is the number of effective valence electrons per μ bond, k_{F}^μ is the Fermi wavenumber of the valence electron, v_{b}^μ is the bond volume:

$$v_{\text{b}}^\mu = (d^\mu)^3 / \sum_{\nu} [(d^\nu)^3 N_{\text{b}}^\nu] \quad (7)$$

where d^μ is the bond length. The average energy gap E_{g}^μ for every μ bond can be separated into homopolar E_{h}^μ and heteropolar C^μ parts:

$$(E_{\text{g}}^\mu)^2 = (E_{\text{h}}^\mu)^2 + (C^\mu)^2. \quad (8)$$

The ionicity and covalency of any type of chemical bond are defined as follows:

$$f_{\text{i}}^\mu = (C^\mu)^2 / (E_{\text{g}}^\mu)^2 \quad f_{\text{c}}^\mu = (E_{\text{h}}^\mu)^2 / (E_{\text{g}}^\mu)^2 \quad (9)$$

where

$$E_h^\mu = 39.74/(d^\mu)^{2.48} \text{ (eV)}. \quad (10)$$

For any binary crystal AB_n type compounds the heteropolar C^μ part is defined as

$$C^\mu = 14.4b^\mu[(Z_A^\mu)^* + \Delta Z_A^\mu - n(Z_B^\mu)^*]e^{-k_s^\mu r_0^\mu}/r_0^\mu \text{ (eV)} \quad r_0^\mu = d^\mu/2 \quad (11)$$

$$k_s^\mu = (4k_F^\mu/\pi a_B)^{1/2} \quad (12)$$

where a_B is the Bohr radius and n is the ratio of element B to A in the subformula. ΔZ_A^μ are correction factors for d electron effects such as the crystal field stable energy and Jahn–Teller effect [12]. b^μ is proportional to the square of the average coordination number N_c^μ :

$$b^\mu = \beta(N_c^\mu)^2 \quad N_c^\mu = N_{CA}^\mu/(1+n) + nN_{CB}^\mu/(1+n) \quad (13)$$

where b^μ depends on a given crystal structure. If the dielectric constant of the crystal is known, the value of β can be deduced from the above equations.

In order to describe the local properties of impurities, we introduce the chemical environmental factor, h_e , written as

$$h_e = \left(\sum \alpha_L^v f_c^v \right)^{1/2} \quad (14)$$

where α_L^v is the polarizability of the ligand bond volume in the v th bond. the sum over v runs all the different types of the ligand bonds. For the μ th bond, the polarizable coefficient α_0^μ can be obtained from the Lorentz–Lorenz equation

$$(\varepsilon^\mu - 1)/(\varepsilon^\mu + 2) = (4\pi/3)\alpha_0^\mu \quad (15)$$

where ε^μ is the low-frequency dielectric constant of a binary crystal composed of only one type of μ bond; the polarizabilities of the bond volume are

$$\alpha_b^\mu = \alpha_0^\mu v_b^\mu \quad (16)$$

and the electron polarizabilities of the ion volume in the μ th bond are

$$\alpha_A^\mu = [(r_A^\mu)^3 / [(r_A^\mu)^3 + (r_B^\mu)^3]]\alpha_0^\mu \quad (17)$$

$$\alpha_B^\mu = [(r_B^\mu)^3 / [(r_A^\mu)^3 + (r_B^\mu)^3]]\alpha_0^\mu \quad (18)$$

where r_A^μ, r_B^μ are the radii [15] of the A, B atoms in the μ th bond, respectively.

What is meant by the nephelauxetic effect is that the parameter values of the interelectron repulsion are smaller in the solid than in the corresponding free ion. Jørgensen [16] found that the nephelauxetic effect can be factored into a function of just a ligand and the centre metal:

$$B/B_0 = 1 - k \text{ (centre ion)} h_e \text{ (ligand)} \quad (19)$$

where B and B_0 are the Racah parameters of free ions and the ions in crystals, respectively. It is known that the nephelauxetic effect depends on covalency and the polarizabilities of ligands. When the effect of a ligand is described with the chemical environmental factor, h_e , defined in equation (14), the effect of the centre ion is expressed as [17]

$$k = [(Z + 2 - S)/5]^2 \quad (20)$$

where Z is valence of the ion, S is the spin of the electron configuration of the ion.

A significant aspect of Mössbauer spectroscopy is the discovery of the isomer shift. It is known that the ^{57}Fe isomer shift can provide extensive and valuable information about the local chemical environment of iron. It is worthwhile noting that the experimentally derived isomer shift, δ , is known to be the sum of a term depending on the electron density at the ^{57}Fe nucleus and the temperature dependent second-order Doppler shift. The second-order Doppler shift

Table 1. Chemical bond parameters of LiNbO₃.

	Nb(s)O _{3/2}	Nb(l)O _{3/2}	Li(s)O _{3/2}	Li(l)O _{3/2}
d^μ (Å)	1.889	2.112	2.068	2.238
v_b^μ	3.290	4.598	4.317	5.471
N_c^μ	4.8	4.8	4.8	4.8
E_h^μ (eV)	8.207	6.223	6.556	5.390
C^μ (eV)	16.163	12.453	7.505	6.371
f_c^μ	0.205	0.2	0.433	0.417
χ^μ	4.521	5.515	1.672	1.899
β	0.0922	0.0922	0.0922	0.0922

Table 2. Mössbauer isomer shifts of Feⁿ⁺:LiNbO₃ in Li sites.

Fe ⁿ⁺	Bond	f_c^μ	h_e	δ_{calc}	δ_{expt} [7]
Fe ²⁺	Li(s)O _{3/2}	0.433	0.978	1.00	1.05
	Li(l)O _{3/2}	0.417			
Fe ³⁺	Li(s)O _{3/2}	0.433	0.978	0.19	0.20
	Li(l)O _{3/2}	0.417			

depends on the phonon spectrum (usually unknown), but not directly on the chemical bonding. According to [18], the second-order Doppler shift may be neglected, especially when the isomer shifts of various compounds are compared at room temperature. Therefore, in the following, the isomer shift δ is the experimentally derived shift including the second-order Doppler shift at room temperature. For a given oxidation state, a correlation between the isomer shift δ and the chemical environmental factor, h_e , is found [12]. It can be written as

$$\delta(^{57}\text{Fe}) = \delta_0 + bh_e \text{ (mm s}^{-1}\text{, relative to } \alpha\text{-Fe at room temperature)} \quad (21)$$

where for isolated ions Fe^{m+}, $b = -0.7$, it contains nuclear parameters. When h_e is equal to zero, $\delta = \delta_0$, which is the isomer shift of the free-ion state. For isolated high-spin Fe²⁺ (d⁶) and Fe³⁺ (d⁵), δ_0 is 1.68 and 0.87 mm s⁻¹, respectively.

For LiNbO₃, in the Li–O bond, $Z_{\text{Li}} = 1$, $Z_{\text{O}} = 2$, and in the Nb–O bond, $Z_{\text{Nb}} = 5$, $Z_{\text{O}} = 10$. Using the dielectric constant of LiNbO₃, $\epsilon = 4.4$ [19], we can calculate detailed bond parameters and linear optical susceptibilities of individual bonds; these are listed in table 1. From table 1, it can be seen that for each kind of bond there are two different bond lengths. Naturally, different bond lengths result in different bond susceptibilities. Strictly speaking, there are four types of chemical bond with different properties in a unit cell.

⁵⁷Fe-doped LiNbO₃ has been studied by Mössbauer spectroscopy [7]. Its Mössbauer spectra could be decomposed into a singlet by Fe³⁺ with the isomer shift $\delta = 0.2$ mm s⁻¹ and a doublet by Fe²⁺ with $\delta = 1.05$ mm s⁻¹ [7]. Using the above theoretical method, the isomer shifts of Fe²⁺ and Fe³⁺ occupying Li sites have been calculated and the results are listed in table 2. From table 2, it is clearly seen that the calculated results of the isomer shifts of Fe ions are in agreement with those given in [7]. Our calculated results support the viewpoint that Fe impurities substitute for Li cations. This also shows that the chemical bond parameters calculated by us are reasonable.

We assume that the Cr³⁺ substitutes for Li⁺ and for Nb⁵⁺ in order to investigate the site dependence of the interelectronic crystal field Racah repulsion parameters B . The Racah parameters of Cr³⁺ in LiNbO₃ crystal have been calculated according to the above theory, and

Table 3. Racah parameters of Cr:LiNbO₃.

Site	Bond	f_c^{μ}	h_e	k	B (cm ⁻¹)	B_{expt} (cm ⁻¹)
Nb	Nb(s)O _{3/2}	0.205	0.805	0.49	548	550 [8], 554 [20]
	Nb(l)O _{3/2}	0.2				
Li	LiO(s) _{3/2}	0.433	0.978	0.49	478	
	LiO(l) _{3/2}	0.417				

they are listed in table 3. It is seen from the table 3 that Racah parameters depend on the site very sensitively. A value $B = 556 \text{ cm}^{-1}$ has been obtained by assuming Cr³⁺ to be located at the Nb⁵⁺ site. It agrees well with the experimental values [8, 20]. In contrast, assuming a Li⁺ site, we have obtained $B = 478 \text{ cm}^{-1}$, which is remarkably lower in magnitude than the experimental results. These results indicate the Cr³⁺ ions substitute for Nb⁵⁺ ions rather than Li⁺ ions in stoichiometric LiNbO₃ crystals.

In conclusion, a semi-empirical model based on the Phillips theory of bonding is presented; it explains very well the nephelauxetic effect for Cr³⁺ ions and Mössbauer isomer shifts of Fe ions in LiNbO₃ crystals. The results show quantitatively that the impurities Cr³⁺ replace the Nb⁵⁺ ions rather than the Li⁺ ions in stoichiometric LiNbO₃ crystals, and it is verified quantitatively that Fe ions substitute at Li sites in LiNbO₃. The same model can be easily applied to other systems.

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