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Effective Ionic Charges of Lithium Niobate Crystal Obtained from the TO–LO Splittings of Infrared Active Lattice Vibrations

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In ionic crystals, the frequency splittings of the transverse (TO) and the longitudinal (LO) modes are observed for the infrared active vibrations due to long range electrostatic interaction. The values of effective ionic charges of cubic crystals such as sodium chloride, caesium chloride or zinc blende type have been obtained by using the TO–LO splittings.[1] In a previous paper[2] a simple equation useful for obtaining the effective ionic charges of cubic and non-cubic crystals was derived and applied to wurtzite and rutile type crystals. In the present paper the equation is applied to the $LiNbO_3$ crystal.

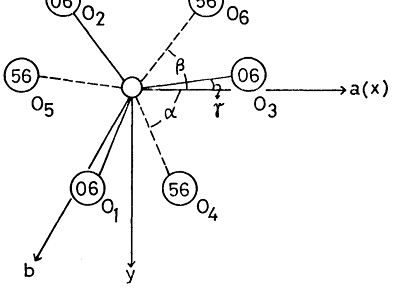

Fig. 1. Atoms in the Bravais lattice of $LiNbO_3$. The larger circles represent the oxygen atoms and the smaller circles the niobium and lithium atoms. The niobium atoms occupy the positions (0, 0, 0) and (0, 0, 1/2), and the lithium atoms the positions (0, 0, 0.2829) and (0, 0, 0.7829). The hexagonal axes are shown in the figure. The numbers in the circles represent the height along c axis.

The space group of the $LiNbO_3$ crystal at room temperature is $R3c–C_{3v}^6$, two formula units being in a unit cell.[3] The structure is shown in Fig. 1. By factor group analysis the lattice vibrations are classified into $5a_1+5a_2+10e$. Acoustic modes belong to the a_1 and e species. The vibrations of a_1 and e are active in both infrared and Raman spectra. The infrared reflection and polarized Raman spectra for the crystal were measured and assignments of the transverse and longitudinal modes of a_1 and e were made by several investigators.[4–8] In the present paper the assignments by Claus *et al.*[8] are used in the calculation of the values of the effective ionic charges.

The effective ionic charges Z_{Li}, Z_{Nb}, and Z_O are connected to the TO–LO splittings by the equation

$$\sum_i\omega_i^2(\mathrm{L}) - \sum_i\omega_i^2(\mathrm{T}) = 8\pi(Z_{Nb}^2/m_{Nb}+Z_{Li}^2/m_{Li} + 3Z_O^2/m_O)e^2/v_a \qquad (1)$$

where $\omega(\mathrm{L})$ and $\omega(\mathrm{T})$ represent the frequencies of the longitudinal and transverse modes, respectively. The summation is carried out for all vibrations of either the a_1 or e species. Equation (1) was derived according to the procedure described previously.[2] The Cartesian symmetry coordinates are given in Table 1. It is noteworthy that $\sum_i\omega_i^2(\mathrm{L})—\sum_i\omega_i^2(\mathrm{T})$ for the wurtzite, rutile and $LiNbO_3$ type crystal structures is given by

$$\sum_i\omega_i^2(\mathrm{L}) - \sum_i\omega_i^2(\mathrm{T}) = (4\pi e^2/v_a)\, z_a\sum_k n_k Z_k^2/m_k \qquad (2)$$

where z_a and v_a represent the number of the formula unit in the unit cell and the volume of the unit cell, respectively, Z_k and m_k the effective ionic charge and the mass of particle k, respectively, and n_k is the number of particle k in the formula unit. Since the crystal should be electrically neutral, we have

$$Z_{Li} + Z_{Nb} + 3Z_O = 0 \qquad (3)$$

However, the values of Z_{Li}, Z_{Nb}, and Z_O can not be definitely determined from Eqs. (1) and (3), and a third equation is introduced by taking into account the spontaneous polarization of the crystal. Spontaneous polarization P_s can be calculated by

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TABLE 1. CARTESIAN SYMMETRY COORDINATES OF $LiNbO_3$ CRYSTAL[a)]

a_1 species

$s_1 = [z(Li)+z(Li)]/\sqrt{2}$ $\quad$ $s_2 = [z(Nb_1)+z(Nb_2)]/\sqrt{2}$

$s_3 = [z(O_1)+z(O_2)+z(O_3)+z(O_4)+z(O_5)+z(O_6)]/\sqrt{6}$

$s_4 = [ac\cdot x(O_1)-as\cdot y(O_1)+bc\cdot x(O_2)+bs\cdot y(O_2)-cc\cdot x(O_3)+cs\cdot y(O_3)-ac\cdot x(O_4)-as\cdot y(O_4)+cc\cdot x(O_5)+cs\cdot y(O_5)-bc\cdot x(O_6)+bs\cdot y(O_6)]/\sqrt{6}$

$s_5 = [as\cdot x(O_1)+ac\cdot y(O_1)-bs\cdot x(O_2)+bc\cdot y(O_2)-cs\cdot x(O_3)-cc\cdot y(O_3)-as\cdot x(O_4)+ac\cdot y(O_4)+cs\cdot x(O_5)-cc\cdot y(O_5)+bs\cdot x(O_6)+bc\cdot y(O_6)]/\sqrt{6}$

e species

$s_1 = [x(Li_1)+x(Li)_2]/\sqrt{2}$ $\quad$ $s_2 = [y(Li_1)-y(Li_2)]/\sqrt{2}$

$s_3 = [x(Nb_1)+x(Nb_2)]/\sqrt{2}$ $\quad$ $s_4 = [y(Nb_1)-y(Nb_2)]/\sqrt{2}$

$s_5 = [2z(O_1)-z(O_2)-z(O_3)-2z(O_4)+z(O_5)+z(O_6)]/2\sqrt{3}$

$s_6 = [z(O_2)-z(O_3)+z(O_5)-z(O_6)]/2$

$s_7 = [2ac\cdot x(O_1)-2as\cdot y(O_1)-bc\cdot x(O_2)-bs\cdot y(O_2)+cc\cdot x(O_3)-cs\cdot y(O_3)+2ac\cdot x(O_4)+2as\cdot y(O_4)-bc\cdot x(O_6)+bs\cdot y(O_6)+cc\cdot x(O_5)+cs\cdot y(O_5)]/2\sqrt{3}$

$s_8 = [cc\cdot x(O_3)-cs\cdot y(O_3)+bc\cdot x(O_2)+bs\cdot y(O_2)+cc\cdot x(O_5)+cs\cdot y(O_5)+bc\cdot x(O_6)-bs\cdot y(O_6)]/2$

$s_9 = [bs\cdot x(O_2)-bc\cdot y(O_2)-cs\cdot x(O_3)-cc\cdot y(O_3)+bs\cdot x(O_6)+bc\cdot y(O_6)-cs\cdot x(O_5)+cc\cdot y(O_5)]/2$

$s_{10} = [2as\cdot x(O_1)+2ac\cdot y(O_1)+bs\cdot x(O_2)-bc\cdot y(O_2)+cs\cdot x(O_3)+cc\cdot y(O_3)+2as\cdot x(O_4)-2ac\cdot y(O_4)+cs\cdot x(O_5)-cc\cdot y(O_5)+bs\cdot x(O_6)+bc\cdot y(O_6)]/2\sqrt{3}$

a) as=sinα, ac=cosα, bs=sinβ, bc=cosβ, cs=sinγ and cc=cosγ. α, β, and γ are shown in Fig. 1. The coordinates of a_2 species and those of y-components of e species are not given in this table.

$$P_s = \underset{\substack{\text{whole}\\\text{crystal}}}{\iiint}\rho(\boldsymbol{r})\boldsymbol{r}dv/V = \underset{\substack{\text{unit}\\\text{cell}}}{\iiint}\rho(\boldsymbol{r})\boldsymbol{r}dv/v_a \tag{4}$$

where $\rho(\boldsymbol{r})$ represents the charge density at $\boldsymbol{r}$ in the crystal and V the volume of the crystal. On the basis of the point charge model, P_S for $LiNbO_3$ is written as

$$P_s = \{Z_{Li}(1/2+2x_{Li})c_0+Z_{Nb}c_0/2+Z_O(3/2+6x_O)c_0\}e/v_a \tag{5}$$

where c_O, x_{Li}, and x_O are 13.8631, 0.2829 and 0.0647 Å, respectively. The values of Z can be obtained by using the three Eqs. (1), (3), and (5).

Although spontaneous polarization is temperature dependent, that of $LiNbO_3$ can be reasonably assumed to be temperature independent near room temperature, since the ferroelectric phase transition temperature is 1210 °C,[9)] which is very much higher than room temperature. In the present calculation the value of P_S 0.71 C/m^2 measured by Camlibel[10)] at room temperature was used. The assignments by Claus *et al.*[8)] for the TO and LO frequencies slightly differ from those by Kaminow and Johnston.[6)] The values from the two assignments do not differ so much since the effective ionic charges depend on the difference of TO and LO frequencies as shown in Eq. (1).

As Eq. (1) is the second order with respect to Z and the sign of spontaneous polarization has not been determined, four sets of solutions were obtained as shown in Table 2. The solution of set 1 is most reasonable since abnormal signs of Z in set 2 and set 3 are given and the value of Z_{Li} is greater than $+1.0$ in set 4. These values were obtained on the basis of the TO–LO splittings of the a_1 species. The values determined from the splittings of the e species, which are close to those obtained from the a_1 species, are also given in Table 2. The results indicate that the spontaneous polarization of $LiNbO_3$ defined by Eq. (5) is -0.71 C/m^2. The value (0.347) of Z_{Li} in set 1 suggests the covalent character of Li–O bonds.

TABLE 2. THE VALUES OF EFFECTIVE IONIC CHARGES AND EXPERIMENTAL VALUES USED IN THE CALCULATION

(1) The frequencies of TO and LO modes[8)] (in cm^{-1})

a_1(L)	876	e(L)	880	e(T)	743
	436		739		668
	333		668		582
	275		454		431
			428		371
a_1(T)	633		371		325
	334		295		265
	276		243		238
	255		198		155

(2) Values of effective ionic charges (in unit of e)

	a_1 species				e species
S (C/m^2)[9)]	-0.71		$+0.71$		-0.71
	set 1	set 2	set 3	set 4	set 1
Z_{Li}	0.347	-1.354	-0.347	1.354	0.413
Z_{Nb}	3.791	-1.945	-3.791	1.945	4.013
Z_O	-1.379	1.100	1.379	-1.100	-1.475

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