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2000 J. Phys.: Condens. Matter 12 2317

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# Theoretical study of temperature dependence of spontaneous polarization, optical properties and linear electro-optic coefficients of tetragonal $\text{KNbO}_3$

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Received 14 July 1999

**Abstract.** The microscopic mechanisms of refractive indices, birefringence, spontaneous polarization and linear electro-optic effects are examined for  $\text{KNbO}_3$  using a microscopic model which takes into account a quantum method based upon the orbital approximation and the dipole–dipole interaction due to the local field acting on the constituent ions. It is found that the electronic polarizabilities play a major role in these calculations and that the birefringence  $\delta n$  and the linear electro-optic coefficients are in good agreement with the experimental data.

## 1. Introduction

Potassium niobate,  $\text{KNbO}_3$ , like barium titanate,  $\text{BaTiO}_3$ , is a crystal of the perovskite family and has been the object of many theoretical and practical investigations. This material exhibits a sequence of ferroelectric phase transitions. At high temperature,  $\text{KNbO}_3$  is para-electric with a cubic structure. Upon cooling, this material undergoes successive structural phase transitions [1]. All these phase transitions are strongly of first-order character and related to a large thermal hysteresis [2], a remarkable optical anisotropy [3] and large electro-optic effects [4–7].

In a previous work, Günter has measured the temperature dependence of the electro-optic coefficient  $r_c$ . It is found that this coefficient depends strongly on the temperature [4]; it increases when the temperature approaches the cubic–tetragonal transition. Previous works on ferroelectrics and optical properties of  $\text{KNbO}_3$  [8], and linear electro-optic coefficients  $r_{13}$  and  $r_{33}$  of pure and Fe-doped  $\text{BaTiO}_3$ , of the same family [9, 10], show that the electronic polarizabilities play an important role.

The aim of this paper is to study the temperature dependence of the refractive indices, the birefringence, the spontaneous polarization and the linear electro-optic coefficients  $r_c = R_{33} - (n_0/n_e)^3 r_{13}$  and  $r_{42}$  of  $\text{KNbO}_3$  in the tetragonal phase by using a microscopic model which takes account of the electronic polarizabilities of the constituent ions.

In this article we discuss, in section 2, the electronic polarizabilities of the ions of  $\text{KNbO}_3$  by using a quantum method based upon the orbital approximation, in section 3, the dipole–dipole interaction due to the local field acting on the constituent ions, in section 4, the electro-optic effects description. Finally, section 5 is devoted to some results and discussions.

## 2. Quantum method description

In order to compute the electronic polarizabilities of tetragonal KNbO<sub>3</sub>, we used a quantum method based upon the orbital approximation. In this approach, each ion is considered as a combination of a core (inner electrons and nucleus) and a shell (outer electron). The Hamiltonian of the core-shell system is written

$$H = H_0 + H_1 \quad (1)$$

with

$$H_0 = \frac{p^2}{2m} - \frac{Z}{R}e^2 \quad (2)$$

$$H_1 = e\mathbf{E} \cdot \mathbf{R} \quad (3)$$

where  $H_0$  represents the Hamiltonian in the absence of the local field and  $H_1$  the electrostatic energy under the electric field. For small values of the electric field, the energy  $H_1$  can be considered as a perturbation. In equation (2),  $Z$  is the effective charge of the core for the outer electron considered. In (3),  $\mathbf{E}$  is the local field acting on a given ion and  $\mathbf{R}$  is the distance from the core to any point of the wavefunction describing the shell of this ion.

Writing the wavefunction in  $\mathbf{E} = 0$  as  $\psi_0$ , we assume that the wavefunction of the core-shell system under the electric field can be expanded as a linear series of perturbations. In this case, it can be described by the variational parameter  $\lambda$  as [11]

$$\psi(\lambda) = (1 + \lambda\mathbf{E} \cdot \mathbf{R})\psi_0. \quad (4)$$

By using the variational principle, namely  $dI = 0$ , where  $I$  is the energy of the system we can express  $\lambda$  by the following equation (see the appendix)

$$\lambda = -\frac{2}{a_B e E^2} \sum_k E_k^2 \langle x_k^2 \rangle \left[ 1 - \frac{4}{a_B^2 e^2 E^4} \left( \sum_k E_k^2 \langle x_k^2 \rangle \right)^3 \right] \quad (5)$$

where  $a_B$  is the Bohr radius  $\hbar^2/m_e^2$ .

The dipole moment  $\mathbf{p}$  of the core-shell system described by the wavefunction  $\psi$  is expressed as

$$\mathbf{p} = \frac{(-e) \int \psi^* \mathbf{R} \psi \, dv}{\int \psi^* \psi \, dv}. \quad (6)$$

The component of  $\mathbf{p}$  in the  $l$ -direction ( $l = 1, 2, 3$ ) is written

$$p_l = \frac{(-e) \int \psi^*(\lambda) x_l \psi(\lambda) \, dv}{\int \psi^*(\lambda) \psi(\lambda) \, dv} = \frac{-2e\lambda E_l \langle x_l^2 \rangle}{1 + \lambda^2 \sum_l E_l^2 \langle x_l^2 \rangle}. \quad (7)$$

By replacing  $\lambda$  by its expression in the last equation, and by expanding in  $(\sum_k E_k^2 \langle x_k^2 \rangle)^3 / a_B^2 e^2 E^4$  which is much less than one (this assumption can be justified by using the values of the local field reported in table 5), we obtain

$$p_l = \frac{4 \sum_k E_k^2 \langle x_k^2 \rangle}{a_B E^2} \left[ 1 - \frac{8}{a_B^2 e^2 E^4} \left( \sum_k E_k^2 \langle x_k^2 \rangle \right)^3 \right] E_l \langle x_l^2 \rangle. \quad (8)$$

In the case of tetragonal KNbO<sub>3</sub>, the component of the local field in the direction of the spontaneous polarization, namely the 3-direction, is greater than those in the other directions. This implies that

$$\sum_k \frac{E_k^2}{E^2} \langle x_k^2 \rangle \cong \langle x_3^2 \rangle \quad (9)$$

then

$$p_l = \frac{4\langle x_3^2 \rangle \langle x_l^2 \rangle}{a_B} \left( 1 - \frac{8\langle x_3^2 \rangle^3}{a_B^2 e^2} E^2 \right) E_l. \quad (10)$$

The  $(k, l)$  element of the electronic polarizability tensor is determined as follows [12]:

$$\alpha_{kl} = \frac{\partial p_k}{\partial E_l}. \quad (11)$$

By using the equation (10), we can express  $\alpha_{kl}$  for a considered  $r$ -orbital as follows:

$$\alpha_{kl,r} = \alpha_{k,r}^* [\delta_{kl} - \theta_r^* (E^2 \delta_{kl} + 2E_k E_l)] \quad (12)$$

where

$$\alpha_{k,r}^* = \frac{4}{a_B} \langle x_3^2 \rangle_r \langle x_k^2 \rangle_r \quad (13)$$

and

$$\theta_r^* = \frac{8}{a_B^2 e^2} \langle x_3^2 \rangle_r^3. \quad (14)$$

In equation (12)  $\delta_{kl}$  represents the Kronecker symbol.

We assume the electronic polarizability of a considered  $j$ -ion in the  $k$ -direction ( $k = 1, 2, 3$ ) as the sum of the contribution of respective orbitals, namely that which can be represented by

$$\alpha_{kl}(j) = \sum_r \alpha_{kl,r}(j). \quad (15)$$

Equation (12) can then be rearranged as

$$\alpha_{kl}(j) = \alpha_k^*(j) [\delta_{kl} - \theta_k(j) (E^2(j) \delta_{kl} + 2E_k(j) E_l(j))] \quad (16)$$

where

$$\alpha_k^*(j) = \sum_r \alpha_{k,r}^*(j) \quad (17)$$

and

$$\theta_k(j) = \frac{\sum_r \alpha_{k,r}^*(j) \theta_r^*(j)}{\sum_r \alpha_{k,r}^*(j)}. \quad (18)$$

For the calculation of the electronic polarizabilities of the K<sup>+</sup>, Nb<sup>5+</sup> and O<sup>2-</sup> ions we have used the Slater-type orbitals [11]

$$\psi_{nim} = \mathfrak{R}_{nl}(R) Y_{lm}(\theta, \varphi) \quad (19)$$

where  $n$ ,  $l$  and  $m$  represent the principal, azimuthal and magnetic quantum numbers, respectively, and  $R$ ,  $\theta$  and  $\varphi$  are the spherical coordinates.

The radial part  $\mathfrak{R}_{nl}(R)$  of equation (19) can be written [13]

$$\mathfrak{R}_{nl}(R) = (2\Gamma_{nl})^{n'+(1/2)} (2n'!)^{-1/2} R^{n'-1} e^{-\Gamma_{nl}/R} \quad (20)$$

with

$$\Gamma_{nl} = \frac{Z_{nl}}{(n'a_B)} \quad (21)$$

where  $n'$  represents the effective quantum number and  $n$  represents the principal quantum number.

In equation (19),  $Y_{lm}(\theta, \varphi)$  are the spherical harmonics represented as [13]

$$Y_{lm}(\theta, \varphi) = (-1)^{(m+(|m|/2))} \left( \sqrt{\frac{2l+(l-|m|)!}{4\pi(l+|m|)!}} \right)^{1/2} P_l^{|m|}(\cos \theta) e^{im\varphi} \quad (22)$$

by the associated Legendre functions  $P_l^{|m|}(\cos \theta)$ .

In order to take into account the directional character of the chemical bond, one usually uses the real forms of the wavefunctions, obtained by linear combination [14].

By using the equations (13) and (14) and the following expressions of  $\langle x_k^2 \rangle_r$  ( $k = 1, 2, 3$ ), we can determine  $\alpha_{k,r}^*(j)$  and  $\theta_r^*(j)$  of a given  $r$  orbital of the  $j$ -ion:

$$\langle x_1^2 \rangle_r = \langle R^2 \rangle_{nl} \langle \sin^2 \theta \cos^2 \varphi \rangle_{lm} \quad (23)$$

$$\langle x_2^2 \rangle_r = \langle R^2 \rangle_{nl} \langle \sin^2 \theta \sin^2 \varphi \rangle_{lm} \quad (24)$$

$$\langle x_3^2 \rangle_r = \langle R^2 \rangle_{nl} \langle \cos^2 \theta \rangle_{lm} \quad (25)$$

with

$$\langle R^2 \rangle_{nl} = n'^2(n'+1) \left( n' + \frac{1}{2} \right) \frac{a_B^2}{Z_{nl}^2}. \quad (26)$$

The values of  $\langle \sin^2 \theta \cos^2 \varphi \rangle_{lm}$ ,  $\langle \sin^2 \theta \sin^2 \varphi \rangle_{lm}$  and  $\langle \cos^2 \theta \rangle_{lm}$  for the orbitals considered are reported in table 1.

**Table 1.** The values of  $\langle \sin^2 \theta \cos^2 \varphi \rangle_{lm}$ ,  $\langle \sin^2 \theta \sin^2 \varphi \rangle_{lm}$  and  $\langle \cos^2 \theta \rangle_{lm}$  for the orbitals considered.

Orbital	$\langle \sin^2 \theta \cos^2 \varphi \rangle_{lm}$	$\langle \sin^2 \theta \sin^2 \varphi \rangle_{lm}$	$\langle \cos^2 \theta \rangle_{lm}$
s	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$
p <sub>x</sub>	$\frac{3}{5}$	$\frac{1}{5}$	$\frac{1}{5}$
p <sub>y</sub>	$\frac{1}{5}$	$\frac{3}{5}$	$\frac{1}{5}$
p <sub>z</sub>	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{3}{5}$
d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	$\frac{3}{7}$	$\frac{3}{7}$	$\frac{1}{7}$
d <sub>xz</sub>	$\frac{3}{7}$	$\frac{1}{7}$	$\frac{3}{7}$
d <sub>z<sup>2</sup></sub>	$\frac{5}{21}$	$\frac{5}{21}$	$\frac{11}{21}$
d <sub>yz</sub>	$\frac{1}{7}$	$\frac{3}{7}$	$\frac{3}{7}$
d <sub>xy</sub>	$\frac{3}{7}$	$\frac{3}{7}$	$\frac{1}{7}$

In order to calculate the coefficients  $\theta_k(j)$  of a given  $j$ -ion, we used an anisotropic effective charge for the outer electronic layer of this ion, and fitted its components in such a way that the calculated values of the free electronic polarizabilities  $\alpha_1^*(j)$ ,  $\alpha_2^*(j)$  and  $\alpha_3^*(j)$  coincided with the measured value of the free electronic polarizability  $\alpha^{exp}(j)$  of the same ion. The free electronic polarizabilities are calculated in  $E = 0$ .

The effective charges of the outer layers are determined by the Slater rules [16], and their fitted values are reported in table 2. The values of the measured  $\alpha^{exp}(j)$  and the calculated  $\theta_k(j)$  are reported in table 3.

Finally, the elements of the electronic polarizabilities tensor of the  $j$ -ion, which are used in the following section, are deduced from table 3 and the next relation.

$$\alpha_{kl}(j) = \alpha^{exp}(j) [\delta_{kl} - \theta_k(j)(E^2(j)\delta_{kl} + 2E_k(j)E_l(j))] \quad (27)$$

In the following section, local field  $E$  is labelled  $E^{loc}$ .

**Table 2.** The fitted values of the effective ionic charges of the outer layers of the constituent ions of  $\text{KNbO}_3$ .

$j$ -ion	Effective ionic charges		
$\text{K}^+$	$Z_{3sp}^{(x)} = 7.202\ 94$	$Z_{3sp}^{(y)} = 7.202\ 94$	$Z_{3sp}^{(z)} = 8.558\ 01$
$\text{Nb}^{5+}$	$Z_{3d}^{(x)} = Z_{4sp}^{(x)} = 20.314\ 43$	$Z_{3d}^{(y)} = Z_{4sp}^{(y)} = 20.314\ 43$	$Z_{3d}^{(z)} = Z_{4sp}^{(z)} = 24.347\ 19$
$\text{O}^{2-}$	$Z_{2sp}^{(x)} = 3.335\ 11$	$Z_{2sp}^{(y)} = 3.335\ 11$	$Z_{2sp}^{(z)} = 3.95895$

**Table 3.** The measured free electronic polarizabilities  $\alpha^{exp}$  (in  $\text{\AA}^3$ ) and the calculated values of the coefficients  $\theta_k$  (in  $10^{-16}$  CGS esu) of the constituent ions of  $\text{KNbO}_3$ .

$j$ -ion	$\alpha^{exp}(j)$	$\theta_1(j)$	$\theta_2(j)$	$\theta_3(j)$
$\text{K}^+$	1.9458	110.520	110.520	206.290
$\text{Nb}^{5+}$	0.1859	1.582	1.582	2.881
$\text{O}^{2-}$	2.3940	152.860	152.860	285.850

### 3. Dipole–dipole interaction

Writing the strains parallel to the [100], [010] and [001] directions as  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$ , respectively and the shearings concerning the (100), (010) and (001) planes as  $\delta_1$ ,  $\delta_2$  and  $\delta_3$ , respectively, we can determine the distance  $r(i, j)$  between the  $i$ - and  $j$ -ions as follows:

$$r(i, j) = \begin{pmatrix} 1 + \Delta_1 & \delta_3 & \delta_2 \\ \delta_3 & 1 + \Delta_2 & \delta_1 \\ \delta_2 & \delta_1 & 1 + \Delta_3 \end{pmatrix} r(i, j)^0 + (s(i) - s(j)) \quad (28)$$

where  $r(i, j)^0$  represents the distance between the  $i$ - and  $j$ -ions in the cubic phase and  $s(i)$  and  $s(j)$  represent the shifts of the  $i$ - and  $j$ -ions respectively.

In order to study the electro-optic effects, we have taken account of the variation of the strains, shearings and the ionic shifts under the bias electric field  $E^{bias}$ . These variations are determined as follows:

$$\Delta_k = (\Delta_k)^0 + \sum_{l=1}^3 d_{lk} E_l^{bias} \quad (29)$$

$$\delta_k = (\delta_k)^0 + \sum_{l=1}^3 d_{l(k+3)} E_l^{bias} \quad (30)$$

$$s_k(j) = (s_k(j))^0 + \sum_{l=1}^3 h_{kl}(j) E_l^{bias} \quad (31)$$

where  $(\Delta_k)^0$ ,  $(\delta_k)^0$  and  $(s_k(j))^0$  represent the spontaneous strains, shearings and ionic shifts respectively,  $d_{lk}$  are the piezoelectric coefficients and  $h_{kl}(j)$  represents the induced shift of the  $j$ -ion per unit of field.

The volume of the unit cell can be written as

$$v = a_0^3 [(1 + \Delta_1)(1 + \Delta_2)(1 + \Delta_3) - (1 + \Delta_1)(\delta_1)^2 - (1 + \Delta_2)(\delta_2)^2 - (1 + \Delta_3)(\delta_3)^2 + 2\delta_1\delta_2\delta_3] \quad (32)$$

where  $a_0$  is the lattice constant in the cubic phase.

The local field acting on the  $i$ -ion in the  $k$ -direction is expressed as [16]

$$E_k^{loc}(i) = E_k^{ext} + \sum_{j=1}^5 \sum_{k'=1}^3 T_{kk'}(i, j) p_{k'}(i, j) \quad (33)$$

with

$$T_{kk'}(i, j) = \sum_{l,m,n} \frac{3\mathbf{r}_k(i, j)\mathbf{r}_{k'}(i, j) - \delta_{kk'}\|\mathbf{r}(i, j)\|^2}{\|\mathbf{r}(i, j)\|^5}. \quad (34)$$

In equation (33),  $\mathbf{E}^{ext}$  represents an external electric field, which is in general the sum of the bias field  $\mathbf{E}^{bias}$  and the optical electric field  $\mathbf{E}^{opt}$ :  $\mathbf{E}^{ext} = \mathbf{E}^{bias} + \mathbf{E}^{opt}$ . In equation (34) the indices  $(l, m, n)$  represent the coordinates of a unit cell in the whole lattice:  $\delta_{kk'}$  is the Kronecker symbol; the indices  $i$  and  $j$  represent the constituent ions of the unit cell. The dipole moment along the  $k'$ -direction,  $p_{k'}^i(i, j)$ , can be expressed as

$$p_{k'}(i, j) = p_{k'}^e(j) + p_{k'}^i(i, j) \quad (35)$$

where

$$p_{k'}^e(j) = \sum_{l=1}^3 \alpha_{k'l}(j) E_l^{loc}(j) \quad (36)$$

represents the electronic dipole moment and

$$p_{k'}^i(i, j) = Z_{k'}^*(j) e(s_{k'}(j) - s_{k'}(i)) \quad (37)$$

represents the ionic dipole moment in the  $k'$ -direction. In equation (36),  $\alpha_{k'l}(j)$  represents the  $(k'l)$  element of the electronic polarizability of the  $j$ -ion given by equation (27), and  $Z_{k'}^*(j)$  in equation (37) represents the effective ionic charge in the  $k'$ -direction of the  $j$ -ion. The local field acting on the  $i$ -ion on the  $k$ -direction can be written as

$$\sum_{j=1}^5 \sum_{l=1}^3 S_{kl}(i, j) E_l^{loc}(j) = Q_k(i) \quad (38)$$

with

$$S_{kl}(i, j) = \delta_{kl}\delta_{ij} - \sum_{k'=1}^3 T_{kk'}(i, j)\alpha_{k'l}(j) \quad (39)$$

and

$$Q_k(i) = E_k^{ext} + \sum_{j=1}^5 \sum_{k'=1}^3 T_{kk'}(i, j) p_{k'}^i(i, j). \quad (40)$$

By solving equation (38) we can determine the  $(l, j)$  component,  $E_l^{loc}(j)$ , of the local field. The total polarization is expressed as

$$P_k = \frac{1}{v} \sum_{j=1}^5 (p_k^e(j) + p_k^{ion}(j)) \quad (41)$$

with

$$p_k^{ion}(j) = Z_k^*(j) e s_k(j). \quad (42)$$

The relation between the dielectric constant  $\varepsilon_{k,l'}$ , polarization  $P_k$  and the bias electric field  $E_{l'}^{bias}$  is

$$\varepsilon_{kl'} = \delta_{kl'} + 4\pi \frac{\partial P_k}{\partial E_{l'}^{bias}}. \quad (43)$$

When the external field is of optical origin, the optical dielectric constant  $\varepsilon_{k,l'}^{opt}$  can be expressed as

$$\varepsilon_{kl'}^{opt} = \delta_{kl'} + 4\pi \frac{\partial P_k}{\partial E_{l'}^{opt}} \quad (44)$$

where

$$\frac{\partial P_k}{\partial E_{l'}^{opt}} = \frac{1}{v} \sum_{j=1}^5 \frac{\partial p_k(j)}{\partial E_{l'}^{opt}}. \tag{45}$$

By using equation (36), the  $\partial p_k(j)/\partial E_{l'}^{opt}$  term can be written as

$$\frac{\partial p_k(j)}{\partial E_{l'}^{opt}} = \sum_{l=1}^3 \alpha_{kl}(j) \frac{\partial E_l^{loc}(j)}{\partial E_{l'}^{opt}}. \tag{46}$$

Here the term  $\partial E_l^{loc}(j)/\partial E_{l'}^{opt}$  can be evaluated by solving the following equation:

$$\sum_{j=1}^5 \sum_{l=1}^3 S_{kl}(i, j) \frac{\partial E_l^{loc}(j)}{\partial E_{l'}^{opt}} = \delta_{kl'} \tag{47}$$

which is deduced from equation (38). In electromagnetism, one proves that in a dielectric medium characterized by the optical dielectric impermeability tensor  $\tilde{\eta}^{opt} = (\tilde{\epsilon}^{opt})^{-1}$ , the refractive index, when the light is polarized in the direction of the unit vector  $\mathbf{u}(u_1, u_2, u_3)$ , is expressed as

$$n = \left( \sum_{k=1}^3 \sum_{l=1}^3 \eta_{kl}^{opt} u_k u_l \right)^{-1/2}. \tag{48}$$

The refractive indices depend on the amplitude and the direction of the applied field (namely  $n = n(\mathbf{E}^{bias})$ ) because  $\tilde{\eta}^{opt} = \tilde{\eta}^{opt}(\mathbf{E}^{bias})$ .

We distinguish here three particular cases.

- The light is polarized in the 1-direction (namely  $u_1 = 1, u_2 = u_3 = 0$ ). The refractive index in this case is  $n_1(\mathbf{E}^{bias}) = (\eta_{11}^{opt})^{-1/2}$ . When  $\mathbf{E}^{bias} = 0$ , we obtain the ordinary refractive index  $n_0$ .
- The light is polarized in the 3-direction (namely  $u_1 = u_2 = 0, u_3 = 1$ ). The refractive index in this case is  $n_3(\mathbf{E}^{bias}) = (\eta_{33}^{opt})^{-1/2}$ . When  $\mathbf{E}^{bias} = 0$ , we obtain the extraordinary refractive index  $n_e$ .
- The light is polarized at 45° in the  $x_2x_3$  plane (namely  $u_1 = 0, u_2 = u_3 = 2^{-1/2}$ ). The refractive index in this case is  $n_4(\mathbf{E}^{bias}) = [(\eta_{22}^{opt} + \eta_{23}^{opt} + \eta_{32}^{opt} + \eta_{33}^{opt})/2]^{-1/2}$ . When  $\mathbf{E}^{bias} = 0$ , we obtain the refractive index  $n_{04}$ .

#### 4. Electro-optic effects description

In tetragonal KNbO<sub>3</sub> only the electro-optic coefficients  $r_{13} = r_{23}, r_{33}$  and  $r_{42} = r_{51}$  are non-null [17]. The optical indicatrix, under the applied electric field  $\mathbf{E}^{bias}$  can be written as

$$\left( \frac{1}{n_o^2} + r_{13} E_3^{bias} \right) (x_1^2 + x_2^2) + \left( \frac{1}{n_e^2} + r_{33} E_3^{bias} \right) x_3^2 + 2r_{42} E_1^{bias} x_1 x_3 + 2r_{42} E_2^{bias} x_2 x_3 = 1 \tag{49}$$

where  $x_1, x_2$  and  $x_3$  are the Cartesian coordinates.

In general, the change of the optical dielectric impermeability  $\Delta \eta_m^{opt}$  ( $m = 1, 2, 3, 4, 5, 6$  is the contracted Voigt notation) [17], the electro-optic coefficient  $r_{ml'}$  ( $l' = 1, 2, 3$ ), and the applied field  $E_{l'}^{bias}$  are connected by the following equation:

$$\Delta \eta_m^{opt} = \sum_{l'=1}^3 r_{ml'} E_{l'}^{bias}. \tag{50}$$



When the bias field is parallel to the 3-axis,  $\mathbf{E}^{bias} (0, 0, E_3^{bias})$ , the electro-optic coefficients  $r_{13}$  and  $r_{33}$  can be expressed as

$$r_{13} = -\frac{2[n_1(E_3^{bias}) - n_o]}{n_o^3 E_3^{bias}} \quad (51)$$

and

$$r_{33} = -\frac{2[n_3(E_3^{bias}) - n_e]}{n_e^3 E_3^{bias}}. \quad (52)$$

When the bias field is parallel to the 2-axis,  $\mathbf{E}^{bias} (0, E_2^{bias}, 0)$ , the electro-optic coefficient  $r_{42}$  can be expressed as

$$r_{42} = -\frac{2[n_4(E_2^{bias}) - n_{o4}]}{n_{o4}^3 E_2^{bias}}. \quad (53)$$

The lattice parameters, the effective ionic charges, the spontaneous ionic shifts, the piezoelectric coefficients and the dielectric constants are experimental data. The coefficients  $h_{kl}(j)$  can be evaluated by using a fit that takes into account the experimental data of the dielectric constants.

When the applied electric field is along the 3-direction, we obtain

$$h_{13}(j) = h_{23}(j) = 0 \quad \text{and} \quad h_{33}(j) \neq 0. \quad (54)$$

These induced ionic shifts are the results of the Coulomb interactions induced by the change of the local field under the bias electric field. We assume that

$$h_{33,j} = h_3 Z_3^*(j) \quad (55)$$

where  $h_3$  is a constant.

When the applied electric field is along the 2-direction, we obtain

$$h_{12}(j) = 0 \quad h_{22}(j) \neq 0 \quad \text{and} \quad h_{32}(j) \neq 0. \quad (56)$$

We assume that

$$h_{22}(j) = h_2 Z_2^*(j) \quad \text{and} \quad h_{32}(j) = h_2 Z_3^*(j) \quad (57)$$

where  $h_2$  is a constant. In order to compute the  $h_3$  and  $h_2$  constants, we assume that  $\varepsilon_{33}^{cal} = \varepsilon_{33}^{exp}$  and  $\varepsilon_{22}^{cal} = \varepsilon_{22}^{exp}$  respectively.

## 5. Results and discussion

The calculations of the spontaneous polarization, the ordinary and extraordinary refractive indices  $n_o$  and  $n_e$ , respectively, the birefringence  $\delta n = n_e n - n_o$ , and the linear electro-optic constants  $r_c = r_{33} - (n_o/n_e)^2 r_{13}$  [4] and  $r_{42}$ , are carried out at various temperatures in the tetragonal phase of KNbO<sub>3</sub>. For our calculations, we used the temperature dependence of the lattice parameters [18], the dielectric constants reported in table 4 and the effective ionic charges reported in table 5. The spontaneous ionic shifts used in this calculation (table 6) are calculated from a microscopic model based upon the mean field approximation [19–21].

The spontaneous local field  $\mathbf{E}^{spon}$  corresponds to the value of the local electric field  $\mathbf{E}^{loc}$  in the absence of any external electric field ( $\mathbf{E}^{ext} = 0$ ). The values of this field are calculated by solving the self-consistent equation (equation (38)) after having evaluated the elements of  $S_{kl}(i, j)$  (equation (39)) and  $Q_k(i)$  (equation (40)). The calculation shows that the values of the spontaneous local field acting on the constituent ions of KNbO<sub>3</sub> along the 1-direction and

**Table 4.** The temperature dependence of the dielectric permittivities  $\epsilon_{22}$  and  $\epsilon_{33}$  in tetragonal  $\text{KNbO}_3$  (relative errors:  $\pm 15\%$ ) from [4].

Temperature (°C)	Temperature		Temperature	
	$\epsilon_{22}$	$\epsilon_{33}$	(°C)	$\epsilon_{22}$ $\epsilon_{33}$
227	2089	269	362	741 524
255	1548	295	377	724 645
277	1258	316	407	691 1000
300	1000	354	417	691 1174
327	851	416	427	691 1412
342	776	457	430	691 1479

**Table 5.** The effective charges of the constituent ions of  $\text{KNbO}_3$  in the tetragonal phase from [3].

Parameter	Value	Parameter	Value
$Z_1^*(\text{K}^+) = Z_2^*(\text{K}^+)$	1.000	$Z_3^*(\text{K}^+)$	1.000
$Z_1^*(\text{Nb}^{5+}) = Z_2^*(\text{Nb}^{5+})$	4.129	$Z_3^*(\text{Nb}^{5+})$	3.459
$Z_1^*(\text{O}^{2-}) = Z_2^*(\text{O}^{2-})$	-1.71	$Z_3^*(\text{O}^{2-})$	-1.486

**Table 6.** Temperature dependence of the calculated spontaneous ionic shifts of the constituent ions  $\text{Nb}^{5+}$ ,  $\text{O}_x^{2-}$ ,  $\text{O}_y^{2-}$  and  $\text{O}_z^{2-}$  of  $\text{KNbO}_3$  in the tetragonal phase. The spontaneous ionic shift of  $\text{K}^+$  is null.

Temperature (°C)	$(s_3(\text{Nb}^{5+}))^0$	$(s_3(\text{O}_x^{2-}/\text{O}_y^{2-}))^0$	$(s_3(\text{O}_z^{2-}))^0$
227	0.0566	-0.0916	-0.1058
255	0.0525	-0.0902	-0.0991
277	0.0504	-0.0893	-0.0961
300	0.0488	-0.0883	-0.0939
327	0.0475	-0.0866	-0.0915
342	0.0469	-0.0854	-0.0896
362	0.0458	-0.0833	-0.0859
377	0.0448	-0.0812	-0.0818
407	0.0419	-0.0758	-0.0694
417	0.0406	-0.0734	-0.0637
427	0.0390	-0.0709	-0.0570
430	0.0384	-0.0700	-0.0548

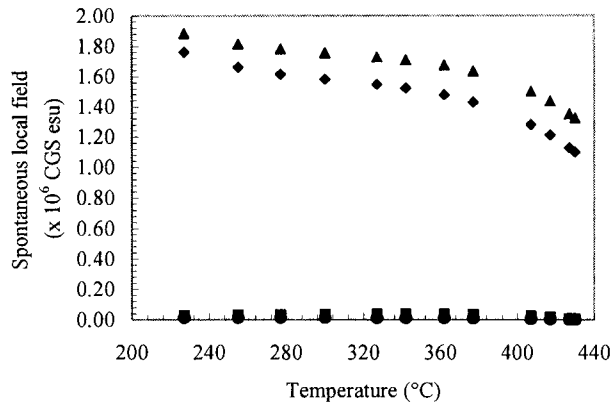
2-direction are null. In figure 1, we report the local field acting on the constituent ions along the 3-direction as a function of temperature.

Looking at table 6 and figure 1, it is found that the spontaneous ionic shifts and the spontaneous local field of the  $\text{Nb}^{5+}$  and  $\text{O}_z^{2-}$  ions are greater than those of the  $\text{K}^+$ ,  $\text{O}_x^{2-}$  and  $\text{O}_y^{2-}$  ions.

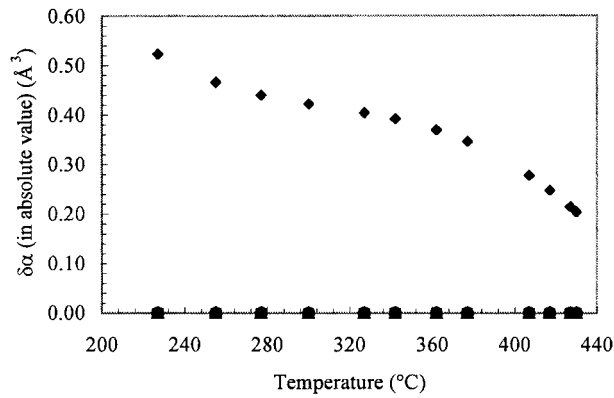
In the tetragonal phase, we can define the amplitude of the anisotropy of the electronic polarizability  $\delta\alpha(j)$  of the  $j$ -ion as follows:

$$\delta\alpha(j) = \alpha_{33}(j) - \alpha_{11}(j). \quad (58)$$

The elements of the electronic polarizability tensor in the spontaneous state ( $\mathbf{E}^{ext} = 0$ ) are evaluated by considering equation (27), table 3 and figure 1. The calculation shows that only the diagonal elements  $\alpha_{kk}(j)$  are non-null. The calculated values of the amplitude of the anisotropy of the electronic polarizability  $\delta\alpha(j)$  are reported in figure 2. The analysis of these results shows that the oxygen  $\text{O}_z^{2-}$  ion presents an anisotropic electronic polarizability



**Figure 1.** The temperature dependence of the 3-direction component of the spontaneous local field of the ions K<sup>+</sup> (full circles), Nb<sup>5+</sup> (full triangles), O<sub>x</sub><sup>2-</sup>/O<sub>y</sub><sup>2-</sup> (full squares) and O<sub>z</sub><sup>2-</sup> (full diamonds) of KNbO<sub>3</sub> in the tetragonal phase.

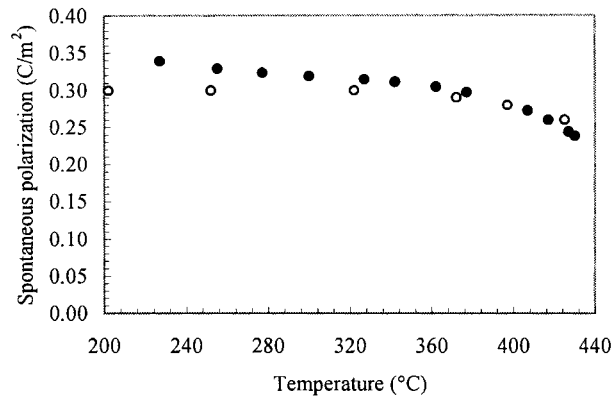


**Figure 2.** The temperature dependence of the amplitude of the anisotropy of the electronic polarizability (in absolute values) of the ions K<sup>+</sup> (full circles), Nb<sup>5+</sup> (full triangles), O<sub>x</sub><sup>2-</sup>/O<sub>y</sub><sup>2-</sup> (full squares) and O<sub>z</sub><sup>2-</sup> (full diamonds) of KNbO<sub>3</sub> in the tetragonal phase.

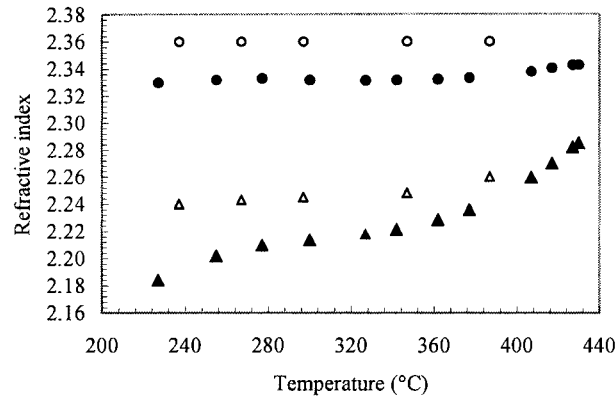
and that the calculated values of  $\delta\alpha(\text{O}_x^{2-})$  decrease, absolutely, from 0.5232 at 227°C to 0.2038 at 430°C. These results are in good agreement with some previous studies [22, 23].

The spontaneous polarization,  $\mathbf{P}^{spon}$ , of KNbO<sub>3</sub> in the tetragonal phase is defined as the total polarization of the crystal, whose components  $P_k$  are deduced from equation (41), in the absence of any external field. The calculations show that only the third component,  $P_3^{spon}$ , of the spontaneous polarization is non-null. Its values are reported in figure 3 and show that  $\mathbf{P}^{spon}$  increases on cooling.

By using equation (47) we determine the elements  $\partial E_l^{loc}(j)/\partial E_l^{opt}$  and therefore the elements of the optical dielectric constant tensor  $\varepsilon_{kl}^{opt}$  (equations (44)–(46)). However, the refractive indices are deduced from equation (48). The calculated values of the refractive indices  $n_o$  and  $n_e$  are reported in figure 4. In figure 5, we report the values of the birefringence  $\delta n$  as a function of the temperature in the tetragonal phase of KNbO<sub>3</sub>.



**Figure 3.** The temperature dependence of the calculated values of the spontaneous polarization (full circles) and the measured values (open circle), according to [24], of  $\text{KNbO}_3$  in the tetragonal phase.



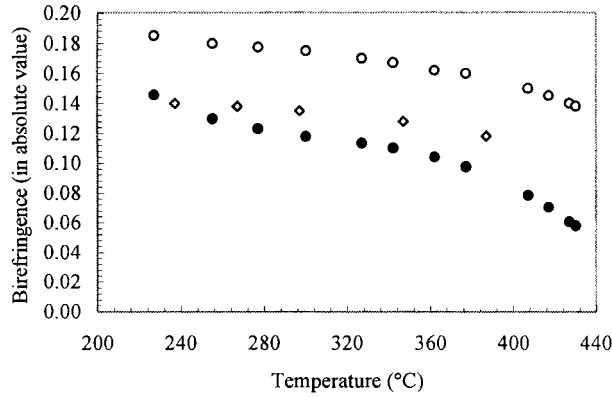
**Figure 4.** The temperature dependence of the calculated values of the ordinary (full circles) and the extraordinary (full triangles) refractive indices of  $\text{KNbO}_3$  in the tetragonal phase. The open circles and the open triangles represent, respectively, the measured values of the ordinary and the extraordinary refractive indices from [25].

The results in figure 4 show that the ordinary refractive index increases when the temperature increases, while the extraordinary refractive index remains constant when the temperature changes in the tetragonal phase.

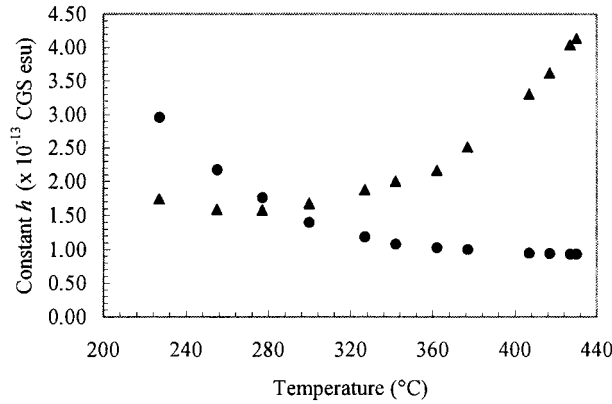
Thereafter, we introduce a much smaller bias field in the 2-direction ( $E_2^{bias} = 10^{-6}$  in CGS esu), and we recalculate the components of the local field and that of the total polarization by taking account now of the equations (29)–(31). For the values of the elements  $h_{k2}(j)$  we use the procedure of fit described in the previous section and we fit the constant  $h_2$  in such a way that the calculated value of  $\varepsilon_{22}$  coincides with the measured value, where the static dielectric constant  $\varepsilon_{22}$  is calculated by using the following expression:

$$\varepsilon_{22} = 1 + 4\pi \frac{P_2(E_2^{bias})}{E_2^{bias}}. \quad (59)$$

Then we again calculate the elements of the optical dielectric constant tensor  $\varepsilon_{kl}^{opt}(E_2^{bias})$  and



**Figure 5.** The temperature dependence of the calculated (full circles) and the measured (open circles from [3] and open squares from [25]) values of the birefringence of KNbO<sub>3</sub>.



**Figure 6.** The temperature dependence of the fitted values of the constants  $h_2$  (full circles) and  $h_3$  (full triangles) in KNbO<sub>3</sub>.

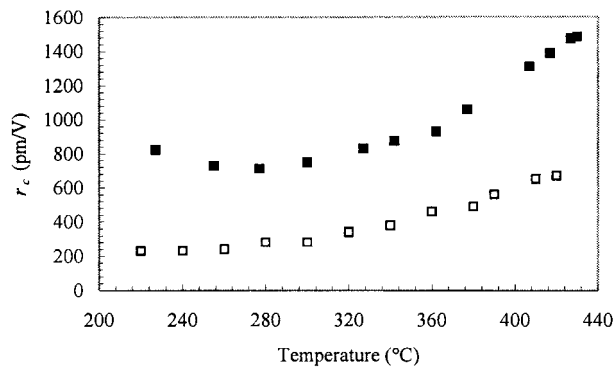
consequently the refractive index  $n_4(E_2^{bias})$ . The linear electro-optic coefficient  $r_{42}$  is then deduced from equation (53).

We now consider a much smaller bias field in the 3-direction ( $E_3^{bias} = 10^{-6}$  in CGS esu), and we recalculate the components of the local field and that of the total polarization. For the values of the elements  $h_{k3}(j)$  we use the procedure of fit described in the previous section, and we fit the constant  $h_3$  in such a way that the calculated value of  $\varepsilon_{33}$  coincides with the measured value, where the static dielectric constant  $\varepsilon_{33}$  is calculated using the following expression:

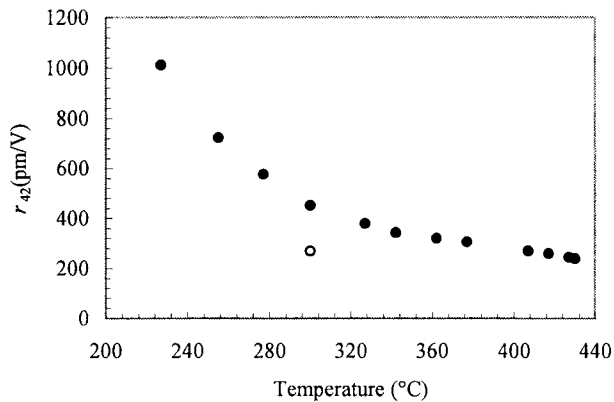
$$\varepsilon_{33} = 1 + 4\pi \frac{P_3(E_3^{bias}) - P_3^{spon}}{E_3^{bias}}. \quad (60)$$

We then calculate the elements of the optical dielectric constant tensor  $\varepsilon_{kl}^{opt}(E_3^{bias})$  and consequently the refractive indices  $n_1(E_3^{bias})$  and  $n_3(E_3^{bias})$ . The linear electro-optic coefficient  $r_c$  (defined above) is calculated from the linear electro-optic coefficients  $r_{13}$  (equation (51)) and  $r_{33}$  (equation (52)).

In figure 6, we report the fitted values of  $h_2$  and  $h_3$  as a function of the temperature.



**Figure 7.** The linear electro-optic coefficient  $r_c$  (full squares) in the tetragonal phase of  $\text{KNbO}_3$  as a function of the temperature. The open squares represent the measured values from [4].



**Figure 8.** The linear electro-optic coefficient  $r_{42}$  in the tetragonal phase of  $\text{KNbO}_3$  as a function of the temperature. The open circle represents the measured value from [4].

Looking at table 4 and figure 6, it is found that  $\epsilon_{22}$  decreases as the constant  $h_2$  decreases on cooling, whereas  $\epsilon_{33}$  increases as the constant  $h_3$  increases. Figure 7 corresponds to the temperature dependence of the linear electro-optic coefficient  $r_c$  and figure 8 represents the temperature dependence of the coefficient  $r_{42}$ .

Looking at figure 7 it is found that the linear electro-optic coefficient  $r_c$ , along with the dielectric permittivity  $\epsilon_{33}$  (table 4) and the constant  $h_3$  (figure 6), increases on cooling. On the other hand, figure 8 shows that  $r_{42}$ , along with the dielectric permittivity  $\epsilon_{22}$  (table 4) and the constant  $h_2$  (figure 6), decreases when the temperature increases.

The theoretical results of the refractive indices, the birefringence and the linear electro-optic coefficients are in good agreement with the results obtained by Bernasconi *et al* [5] and are in accordance with the 'Bond anharmonic polarizability model' [2] usually used to explain the linear and nonlinear optical properties of some oxygen-octahedra ferroelectrics such as  $\text{KNbO}_3$  [26,27].

These calculations show that the experimental data of the physical properties above mentioned can be mainly explained by considering nonlinear and anisotropic electronic polarizabilities, particularly the contribution of the oxygen ion  $\text{O}_z^{2-}$ .

### Acknowledgments

The authors would like to thank S Zhang and P Günter for private communications.

### Appendix

The energy  $I$  of the system can be written as

$$I = \frac{\int \psi^* H \psi \, dv}{\int \psi^* \psi \, dv}. \quad (\text{A1})$$

By using the equations (4) and (A1), the energy  $I$  can be expressed as

$$I = \frac{I_0 + 2\lambda e \sum_k E_k^2 \langle x_k^2 \rangle + \lambda^2 \sum_k E_k^2 \langle x_k H_0 x_k \rangle}{1 + \lambda^2 \sum_k E_k^2 \langle x_k^2 \rangle}. \quad (\text{A2})$$

The terms with odd powers of  $x_k$  are omitted because they are nulls when the wavefunction  $\psi_0$  is replaced by the real form of the wavefunction  $\psi_{nlm}$  used in this work (equation (19)). This assumption can be shown by considering the parity of the real form of the wavefunctions,  $\psi_{nlm}$ , and that of the odd powers of  $x_k$ .

In the equation (A2),  $I_0$  is the energy in  $E = 0$ . By assuming that the wavefunction  $\psi_0$  is normalized to unity, namely  $\langle \psi_0 | \psi_0 \rangle = 1$ ,  $I_0$  can be expressed as

$$I_0 = \int \psi_0^* H_0 \psi_0 \, dv. \quad (\text{A3})$$

In the equation (A2), the index  $k$  ( $k = 1, 2, 3$ ) represents the directions  $x$ ,  $y$  and  $z$ . The terms  $\langle x_k^2 \rangle$  and  $\langle x_k H_0 x_k \rangle$  are written as

$$\langle x_k^2 \rangle = \int \psi_0^* x_k^2 \psi_0 \, dv \quad (\text{A4})$$

$$\langle x_k H_0 x_k \rangle = \int \psi_0^* x_k H_0 x_k \psi_0 \, dv. \quad (\text{A5})$$

By using the variational principle, namely  $dI = 0$ , we can calculate the value of  $\lambda$  and determine the wavefunction  $\psi(\lambda)$  under the electric field by the condition

$$\frac{\partial I}{\partial \lambda} = \lambda^2 e \left( \sum_k E_k^2 \langle x_k^2 \rangle \right)^2 + \lambda \left( I_0 \sum_k E_k^2 \langle x_k^2 \rangle - \sum_k E_k^2 \langle x_k H_0 x_k \rangle \right) - e \sum_k E_k^2 \langle x_k^2 \rangle = 0. \quad (\text{A6})$$

In quantum mechanics, one can show that

$$\langle x_k H_0 x_k \rangle = \langle x_k^2 \rangle I_0 + \frac{\hbar^2}{2m}. \quad (\text{A7})$$

By using the equations (A6) and (A7) and by replacing  $\sum_k E_k^2$  and  $E^2$ , we get

$$\lambda = \frac{E^2 \hbar^2}{2m} \pm \left[ \frac{E^4 \hbar^4}{4m^2} + 4e^2 \left( \sum_k E_k \langle x_k^2 \rangle \right)^3 \right]^{1/2} 2e \left( \sum_k E_k^2 \langle x_k^2 \rangle \right)^{-2}. \quad (\text{A8})$$

Since only the smaller solution of  $\lambda$  is meaningful in equation (A8) under the minimum condition of the energy, we adopt now the solution having the minus sign.

Expanding the equation (A8) until the square of  $E$ , we can express  $\lambda$  by the following equation:

$$\lambda = -\frac{2}{a_B e E^2} \sum_k E_k^2 \langle x_k^2 \rangle \left[ 1 - \frac{4}{a_B^2 e^2 E^4} \left( \sum_k E_k^2 \langle x_k^2 \rangle \right)^3 \right] \quad (\text{A9})$$

where  $a_B$  means the Bohr radius  $\hbar^2/m e^2$ .

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