

Eigenfrequencies and Eigenvectors of Polaritons with Application to  $\text{LiNbO}_3$ II. Polaritons of Small Wave Vectors  $\mathbf{k}$  ( $k \leq 10^4 \text{ cm}^{-1}$ )

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In this second paper the region of strong dispersion of extraordinary polaritons ( $k \approx 10^3 - 10^4 \text{ cm}^{-1}$ ) and the limiting case  $k \rightarrow 0$  is treated. The dependence on  $\mathbf{k}$  of the eigenfrequencies  $\omega$ , of the quasi-normal coordinates  $Q_i$ , of the electric field  $\mathbf{E}$  and of the electric polarization  $\mathbf{P}$  is discussed in detail for four branches of  $\text{LiNbO}_3$  as examples. The behaviour of eigenfrequencies and eigenvectors in the vicinity of the crossing points of the vibrational branches is of special interest. It is shown in the appendix that the *coupled harmonic oscillator formalism* due to Onstott and Lucovsky is equivalent to our theory in the special case  $k \rightarrow \infty$ ,  $\epsilon_{\perp}^{\infty} = \epsilon_{\parallel}^{\infty}$ .

## Polaritons of Small Wave Vectors

In the first part of this article<sup>1</sup> (in the following denoted as I) only the limiting case  $k \rightarrow \infty$  of polaritons (i.e. the long optical phonons) has been treated in detail<sup>2</sup>. Since the properties of polaritons of small wave vectors ( $k \lesssim 10^4 \text{ cm}^{-1}$ ) differ from that in many respects it seems reasonable to treat this range of polaritons separately in the following.

Since the general theory of polaritons, which follows from the three basic equations [Eqs. (1) of I]

$$-\omega^2 \mathbf{Q} = B^{11} \mathbf{Q} + B^{12} \mathbf{E}, \quad (12a)$$

$$\mathbf{P} = (B^{12})^+ \mathbf{Q} + B^{22} \mathbf{E}, \quad (12b)$$

$$\mathbf{E} = \frac{4\pi}{n^2 - 1} (\mathbf{P} - n^2 \mathbf{s} \mathbf{s} \cdot \mathbf{P}), \quad (12c)$$

$$\left( n^2 = \frac{c^2 k^2}{\omega^2} \right)$$

has already been discussed in Part I, in the following we may confine ourselves to point out from theory the special features of polaritons of small  $\mathbf{k}$ .

In the case of small wave vectors in addition to the longitudinal part  $\mathbf{P}_L$  also the transverse part  $\mathbf{P}_T$  of polarization  $\mathbf{P}$  contributes to the electric field  $\mathbf{E}$ , in contrast to the case of long optical phonons ( $k \rightarrow \infty$ ,  $n^2 \rightarrow \infty$ ). This is seen directly from Eq. (12c), written in the form

$$\mathbf{E} = \frac{4\pi}{n^2 - 1} \mathbf{P}_T - 4\pi \mathbf{P}_L. \quad (12c')$$

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Hence, in contrast to the limiting case  $k \rightarrow \infty$  the electric field for general directions of the wave vector is no longer exactly longitudinal but of mixed transverse-longitudinal character.

Concerning the dispersion of eigenfrequencies and eigenvectors two different ranges of  $k$  are to be distinguished. In the range  $10^3 \text{ cm}^{-1} \lesssim k \lesssim 10^4 \text{ cm}^{-1}$  the eigenfrequencies and eigenvectors show a relatively strong dispersion, whereas for wave vectors  $k \lesssim 10^3 \text{ cm}^{-1}$  the dispersion becomes negligible. For in the limiting case  $n^2 \rightarrow 0$  Eq. (12c) and (12c') reduce to

$$\mathbf{E} = -4\pi \mathbf{P}, \quad (12c'')$$

i.e. the wave vector is no longer contained in Eqs. (12). In other words, near the zone centre ( $k \lesssim 10^3 \text{ cm}^{-1}$ ) all polarization vectors become independent of the wave vector and are each directed parallel to one of the principal directions determined by crystal symmetry, i.e. for uniaxial crystals the eigenvectors  $\mathbf{Q}$ ,  $\mathbf{E}$ ,  $\mathbf{P}$  of polaritons are directed either parallel or perpendicular to the optic axis. In this region of  $k \lesssim 10^3 \text{ cm}^{-1}$  it is possible to decompose the system (12) into its irreducible components according to group theory for  $k = 0$ .

## T-Representation and L-Representation of Eigenvectors

The quasi-normal coordinates  $Q_i$  used in Eqs. (12) are normal coordinates in the usual sense only for vanishing electric field  $\mathbf{E}$ , i.e. for the exactly transverse vibrations along the principal directions in the limiting case  $k \rightarrow \infty$ . These normal coordinates are coupled for all other wave vectors by the electric field. We call these coordinates in the following



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quasi-normal coordinates in the T-representation. These coordinates diagonalize only the mechanical part of the total energy density and correspond to a decomposition of the vibrational equations according to irreducible representations for vanishing electric field ( $\mathbf{E} = 0$ ). As these quasi-normal coordinates remain coupled even for  $\mathbf{k} = 0$  they cannot correspond to the irreducible representations of the vibrations for  $\mathbf{k} = 0$  according to group theory. Nevertheless it must be possible to introduce a new set of normal coordinates  $\tilde{Q}_{0i}$ , which diagonalize the total energy density for  $\mathbf{k} = 0$  and therefore are normal coordinates in the usual sense. We call this new set of normal coordinates quasi-normal coordinates in the L-representation<sup>5</sup>.

L- and T-representation are connected by a linear transformation. To derive this relation we start from the basic equations (12) for  $\mathbf{k} = 0$  ( $n^2 = 0$ ). Let  $\mathbf{Q}_0$ ,  $\mathbf{E}_0$ ,  $\mathbf{P}_0$  be the eigenvectors of (12) for  $\mathbf{k} = 0$ , then we have

$$-\omega^2 \mathbf{Q}_0 = B^{11} \mathbf{Q}_0 + B^{12} \mathbf{E}_0, \quad (13a)$$

$$\mathbf{P}_0 = (B^{12})^+ \mathbf{Q}_0 + B^{22} \mathbf{E}_0, \quad (13b)$$

$$\mathbf{E}_0 = -4\pi \mathbf{P}_0. \quad (13c)$$

Eliminating  $\mathbf{E}_0$  and  $\mathbf{P}_0$  from (13) and defining

$$D^{11} = B^{11} - 4\pi B^{12}(I + 4\pi B^{22})^{-1}(B^{12})^+ \quad (14)$$

Eqs. (13) reduce to

$$-\omega^2 \mathbf{Q}_0 = D^{11} \mathbf{Q}_0. \quad (15)$$

The matrix  $D^{11}$  is not diagonal because the second term on the right of Eq. (14) is a nondiagonal matrix. But it may be transformed into a diagonal form by introducing new normal coordinates  $\tilde{Q}_{0i}$  ( $i = 1, \dots, r$ ), which correspond to the classification according to the irreducible representations  $\mathbf{k} = 0$ . They differ from the normal coordinates of the classification of optic vibrational modes only by the fact that in  $D^{11}$  — and therefore also in the eigenfrequencies  $\omega_{0i}$  of Eqs. (13) — the contribution of the macroscopic electric field for  $\mathbf{k} = 0$  is involved. To derive the connection between  $\tilde{\mathbf{Q}}_0$  and  $\mathbf{Q}_0$  let  $X$  be an orthonormal matrix whose columns are the eigenvectors  $\mathbf{Q}_{0i}$  ( $i = 1, \dots, r$ ) of (15). The set of solutions of the eigenvalue equation (15) may then be written as

$$-X\Lambda = D^{11}X, \quad (16)$$

where  $\Lambda$  is the diagonal matrix of the eigenfrequencies<sup>6</sup>  $\omega_{0i}^2$

$$\Lambda = \begin{pmatrix} \omega_{01}^2 & & & \\ & \ddots & & \\ & & \omega_{0i}^2 & \\ & & & \ddots \\ & & & & \omega_{0r}^2 \end{pmatrix}. \quad (17)$$

From (16)  $D^{11}$  and  $\Lambda$  are connected by means of a similarity transformation:

$$\Lambda = -X^{-1}D^{11}X. \quad (16')$$

Introducing the matrix  $X$  into (15) it results

$$-\omega^2(X^{-1}\mathbf{Q}_0) = (X^{-1}D^{11}X)(X^{-1}\mathbf{Q}_0), \quad (15')$$

or

$$-\omega^2 \tilde{\mathbf{Q}}_0 = \Lambda \tilde{\mathbf{Q}}_0, \quad (18)$$

where  $\Lambda$  is given by (17) and  $\tilde{\mathbf{Q}}_0 \equiv X^{-1}\mathbf{Q}_0 = X^+\mathbf{Q}_0$ .  $X^+$  is the transposed matrix of  $X$ . The  $r$  eigenvectors  $\tilde{\mathbf{Q}}_{01} = (1, 0, \dots, 0), \dots, \tilde{\mathbf{Q}}_{0r} = (0, \dots, 0, 1)$  build up a new basis of the  $r$ -dimensional vector space. Let  $\tilde{\mathbf{Q}}$  be a general vector of the latter. In the basic system (12)  $\mathbf{Q}$  may now be completely replaced by  $\tilde{\mathbf{Q}}$ :

$$-\omega^2 \tilde{\mathbf{Q}} = C^{11} \tilde{\mathbf{Q}} + C^{12} \mathbf{E}, \quad (19a)$$

$$\mathbf{P} = (C^{12})^+ \tilde{\mathbf{Q}} + C^{22} \mathbf{E}, \quad (19b)$$

$$\mathbf{E} = \frac{4\pi}{n^2 - 1} (\mathbf{P} - n^2 \mathbf{s} \cdot \mathbf{s} \cdot \mathbf{P}), \quad (19c)$$

where  $C^{11} \equiv X^{-1}B^{11}X$ ,  $C^{12} \equiv X^{-1}B^{12}$ ,  $C^{22} \equiv B^{22}$ ,  $\tilde{\mathbf{Q}} \equiv X^{-1}\mathbf{Q}$ . For  $\mathbf{k} = 0$  and eliminating  $\mathbf{E} = \mathbf{E}_0$  and  $\mathbf{P} = \mathbf{P}_0$  we yield from (19) the eigenvalue equation (15) again. Every vibrational mode here is characterized by only one normal coordinate. But for  $\mathbf{k} > 0$  these coordinates become coupled again, because the electric field changes according to  $\mathbf{E}_0$ .

### Crossing Points of Polariton Branches

Another point of interest is the question whether crossing points of polariton dispersion branches are possible. It has been shown<sup>7</sup> by a detailed analysis of the secular equation of (12), that for uniaxial crystals crossing points of polariton branches may exist only for extraordinary polaritons in a principal direction, namely crossing points of exactly longitudinal branches with exactly transverse ones. If the wave vector  $\mathbf{k}$  leaves the principal direction the crossing point is lifted. Together with the requirement of a continuous behaviour of all

dispersion branches, it follows that for all the quantities calculated from Eqs. (12) there is a discontinuous transition at the crossing point in the principal direction with respect to the first derivative from one type of vibration to another.

### Eigenfrequencies $\omega$ and Eigenvectors $Q, E, P$ of Polaritons in $\text{LiNbO}_3$

The details in the properties of polaritons, especially in the wave vector dependence of its frequencies and eigenvectors, may be illustrated very clearly by an example. As in Part I  $\text{LiNbO}_3$  has been chosen as an example of a complicated uniaxial crystal. But compared to Part I the input frequencies due to KAMINOW and JOHNSTON<sup>8</sup> have been changed. The reason for this is the fact that some of the assignments of long optical modes given by these authors are shown to be incorrect<sup>9</sup>. Our new assignment based on new measurements which differs in various aspects from those values in Table 1 of Part I is given in Table 1. For details cf. <sup>10</sup>.

Figures 1a—1e show the dispersion of all ordinary and extraordinary polariton branches in  $\text{LiNbO}_3$  for different orientations of wave vector  $k$  relative to

Table 1. Frequencies  $\omega_{||}$ ,  $\omega_{||}^i$ ,  $\omega_{\perp}$ ,  $\omega_{\perp}^i$  of  $\text{LiNbO}_3$ <sup>10</sup>.

	$\omega$ [ $\text{cm}^{-1}$ ]
$\omega_{  }$	255
	276
	334
	633
$\omega_{  }^i$	275
	333
	436
	876
$\omega_{\perp}$	155
	238
	265
	325
	371
	431
	582
	668
$\omega_{\perp}^i$	743
	198
	243
	295
	371
	428
	454
	668
	739
	880

the optic axis. As expected, the polariton branches are very similar to those of  $\alpha$ -quartz, which have been discussed already in <sup>11, 12</sup>. Concerning the details we may therefore refer to these papers. For the following, the existence of several crossing points for extraordinary polaritons in principal directions perpendicular to the optic axis ( $\vartheta = 90^\circ$ ) is of particular interest. As mentioned above, the transition which happens at every crossing point discontinuously from an exactly longitudinal mode to an exactly transverse one or vice versa, becomes continuous outside the principal direction (cf. Fig. 1d). A comparison of theoretical and experimental values for the dispersion branch 10 of the ordinary polariton is given in <sup>13</sup>. The agreement between theory and experiment is very satisfactory.

To discuss the behaviour of the eigenvectors  $Q, E, P$  of polaritons in  $\text{LiNbO}_3$ , we have chosen the extraordinary vibrational branches 2, 4, 10, 13, which shall be treated now: The branch 2 (Fig. 2a) is exactly transverse for  $\vartheta = 0^\circ$ , i.e. of type  $E(T)$ . For  $\vartheta = 90^\circ$  there exist two crossing points, namely at  $k \approx 8650 \text{ cm}^{-1}$  and  $k \approx 20600 \text{ cm}^{-1}$ . Because the type of vibration is changing discontinuously

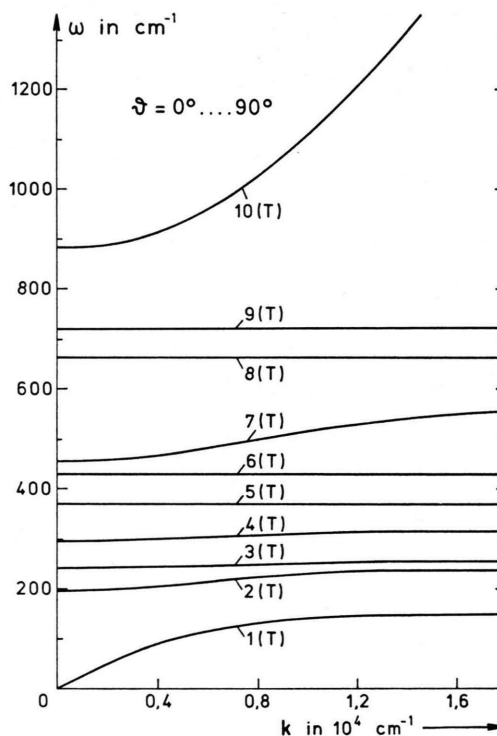


Fig. 1a. Dispersion of ordinary polariton branches in  $\text{LiNbO}_3$ .

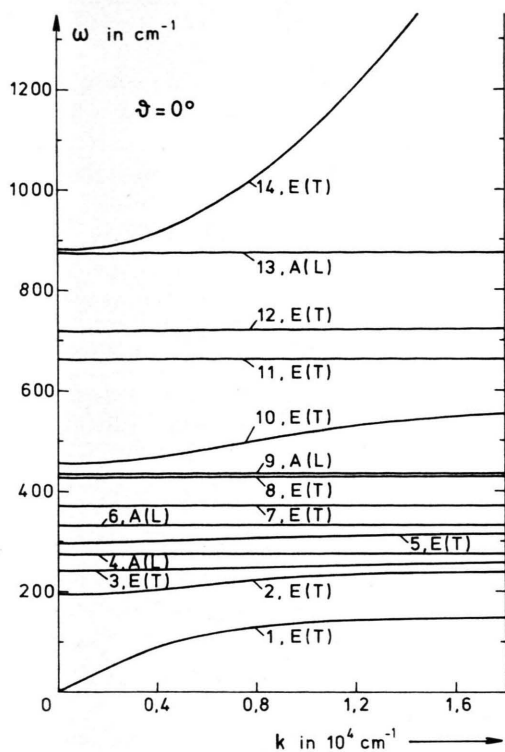


Fig. 1 b.

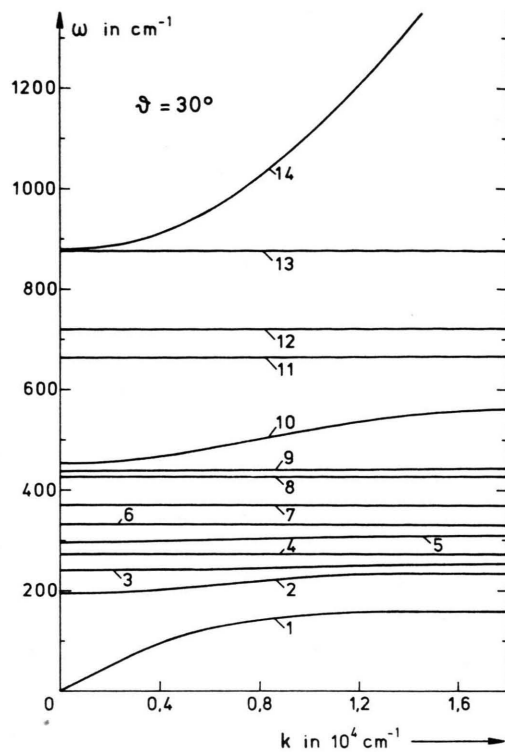


Fig. 1 c.

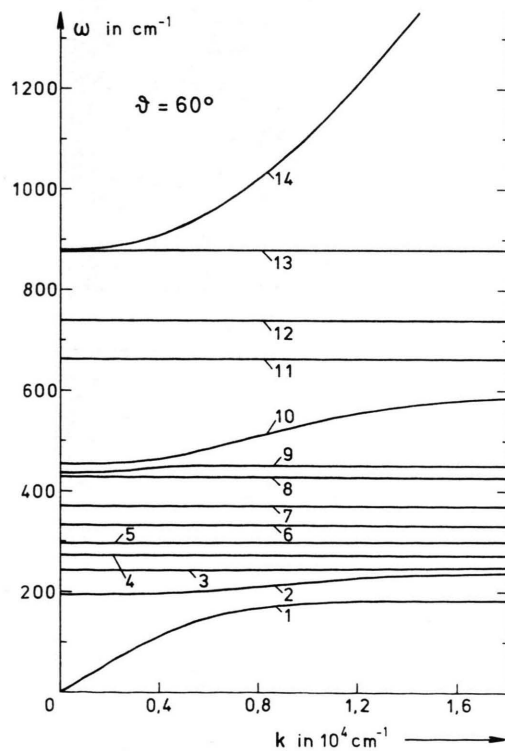


Fig. 1 d.

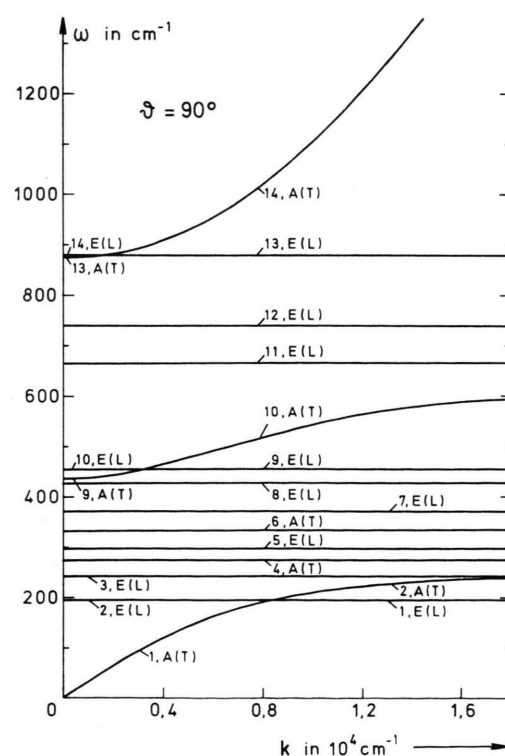


Fig. 1 e.

Fig. 1 b – 1 e. Dispersion of extraordinary polariton branches in  $\text{LiNbO}_3$ .

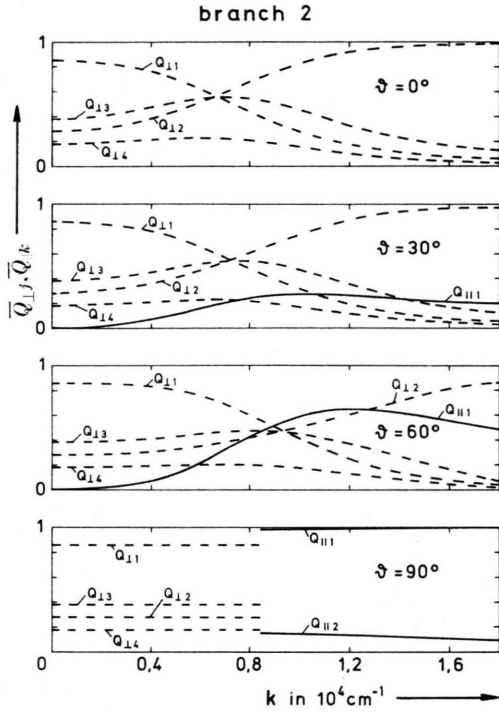


Fig. 2a. Quasi-normal coordinates  
 $\bar{Q}_{\perp j} = Q_{\perp j}/Q$ ,  $\bar{Q}_{\parallel k} = Q_{\parallel k}/Q$   
of the extraordinary polariton branch 2 in LiNbO<sub>3</sub>

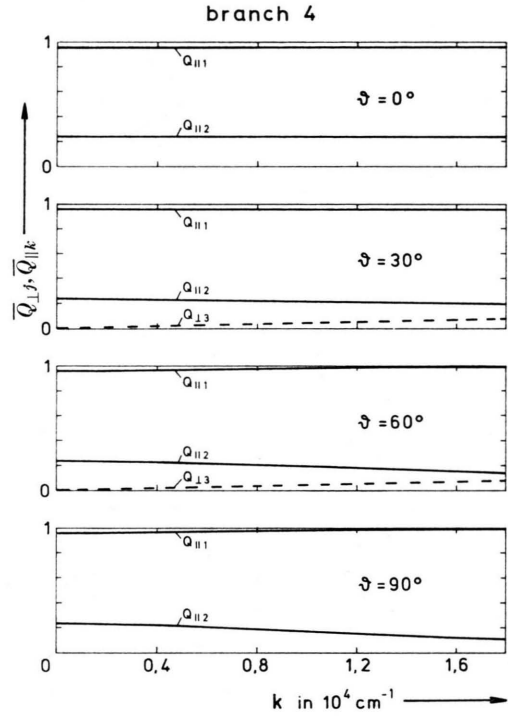


Fig. 2b. Quasi-normal coordinates  
 $\bar{Q}_{\perp j} = Q_{\perp j}/Q$ ,  $\bar{Q}_{\parallel k} = Q_{\parallel k}/Q$   
of the extraordinary polariton branch 4 in LiNbO<sub>3</sub>.

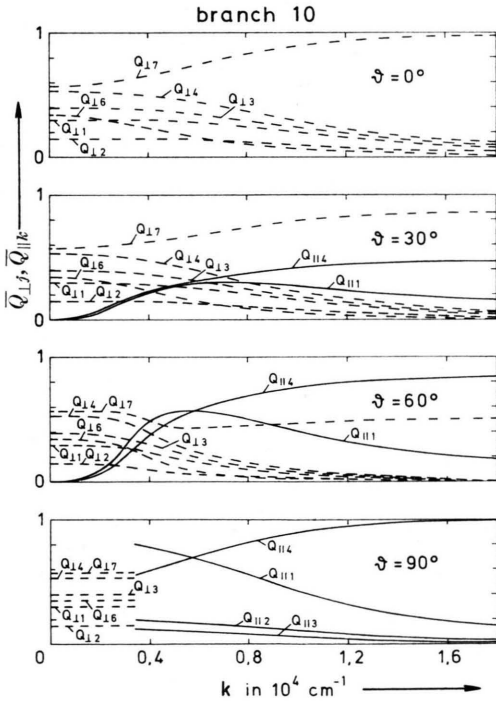


Fig. 2c. Quasi-normal coordinates  
 $\bar{Q}_{\perp j} = Q_{\perp j}/Q$ ,  $\bar{Q}_{\parallel k} = Q_{\parallel k}/Q$   
of the extraordinary polariton branch 10 in LiNbO<sub>3</sub>.

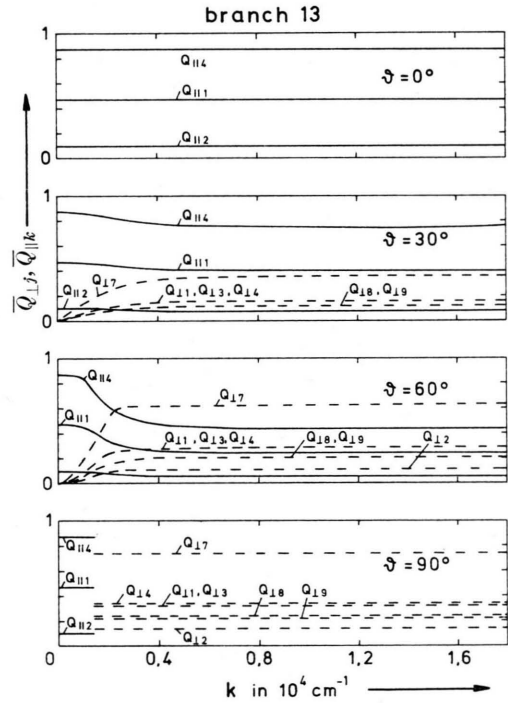


Fig. 2d. Quasi-normal coordinates  
 $\bar{Q}_{\perp j} = Q_{\perp j}/Q$ ,  $\bar{Q}_{\parallel k} = Q_{\parallel k}/Q$   
of the extraordinary polariton branch 13 in LiNbO<sub>3</sub>.

Fig. 2. The quasi-normal coordinates omitted in the figures are all smaller than the lowest given one. All  $Q_{\perp j}$ ,  $Q_k$  in Figs. 2a — 2d should be read as  $\bar{Q}_{\perp j}$ ,  $\bar{Q}_k$ , resp.



in these crossing points, the branch for  $\vartheta = 90^\circ$  consists of three parts: In the range  $0 \leq k \lesssim 8650 \text{ cm}^{-1}$  the mode is exactly longitudinal, i.e. of type  $E(L)$ , in the range  $8650 \text{ cm}^{-1} \lesssim k \lesssim 20600 \text{ cm}^{-1}$  it is exactly transverse, i.e. of type  $A(T)$ , and for  $k \gtrsim 20600 \text{ cm}^{-1}$  it is exactly longitudinal again, i.e. of type  $E(L)$ . For reason of symmetry for  $\vartheta = 0^\circ$  therefore all quasi-normal coordinates  $Q_{\parallel k}$  must vanish, for  $\vartheta = 90^\circ$  in the transverse part all  $Q_{\perp j}$ , and in the longitudinal parts all  $Q_{\parallel k}$  again.

The other branches 4, 10, 13 show analogous properties: Branch 4 (Fig. 2b) is exactly longitudinal for  $\vartheta = 0^\circ$ , i.e. of type  $A(L)$ , for  $\vartheta = 90^\circ$  in the whole range of  $k$  exactly transverse, i.e. of type  $A(T)$ . Clearly all  $Q_{\perp j}$  must vanish for both principal directions. Branch 10 (Fig. 2c) is exactly transverse for  $\vartheta = 0^\circ$ , i.e. of type  $E(T)$ . For  $\vartheta = 90^\circ$  it is exactly longitudinal of type  $E(L)$  for  $k \lesssim 3350 \text{ cm}^{-1}$ , above this value of  $k$  exactly transverse of type  $A(T)$ . Branch 13 (Fig. 2d) has the symmetry  $A(L)$  for  $\vartheta = 0^\circ$ , for  $\vartheta = 90^\circ$  and  $k \lesssim 1400 \text{ cm}^{-1}$  the symmetry  $A(T)$ , above this value of  $k$  it is of type  $E(L)$ .

For  $k = 0$  it is seen from the figures that all the quantities  $\omega$ ,  $Q$ ,  $E$ ,  $P$  are independent of angle  $\vartheta$  according to (12c''). Because of the polarization of the vibrations, these eigenvectors are either perpendicular to the optic axis (all  $Q_{\perp j} \neq 0$ , all  $Q_{\parallel k} = 0$ ), namely for the branches 2 and 10, or parallel to the optic axis (all  $Q_{\parallel k} \neq 0$ , all  $Q_{\perp j} = 0$ ), namely for the branches 4 and 13.

Starting with these  $\vartheta$ -independent values at  $k = 0$  the eigenfrequencies and eigenvectors show a relatively strong dispersion in the range  $10^3 \text{ cm}^{-1} \lesssim k \lesssim 10^4 \text{ cm}^{-1}$  and approach for  $k \gtrsim 2 \cdot 10^4 \text{ cm}^{-1}$  asymptotically the  $\vartheta$ -dependent values of long optical phonons ( $k \rightarrow \infty$ ).

In Figs. 3 and 4 the electric field  $E$  and the polarization  $P$  is plotted versus the wave number  $k$  once more. The crossing points at  $\vartheta = 90^\circ$  result in a discontinuous behaviour of all eigenvectors. To show the behaviour near a crossing point in Fig. 5  $E$  and  $P$  have been plotted versus  $k$  near  $\vartheta = 90^\circ$  for branch 2 as an example. It is seen very clearly how the crossing points at  $k \approx 8650 \text{ cm}^{-1}$  is lifted outside the principal direction and how the discontinuous behaviour is approached with increasing angle.

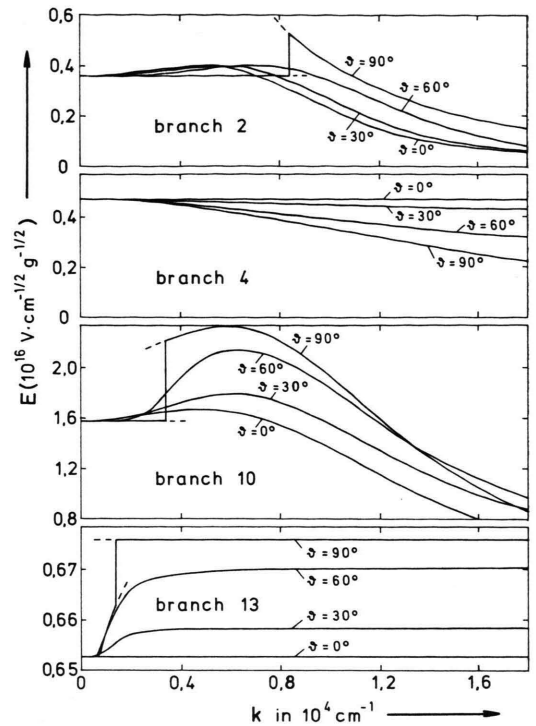


Fig. 3. Electric field  $E$  (relative values) of extraordinary polariton branches in  $\text{LiNbO}_3$ .

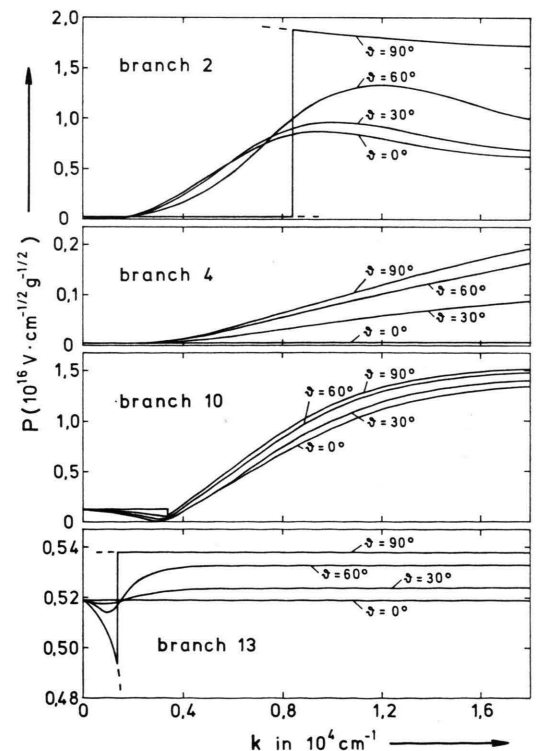


Fig. 4. Electric polarization  $P$  (relative values) of extraordinary polariton branches in  $\text{LiNbO}_3$ .

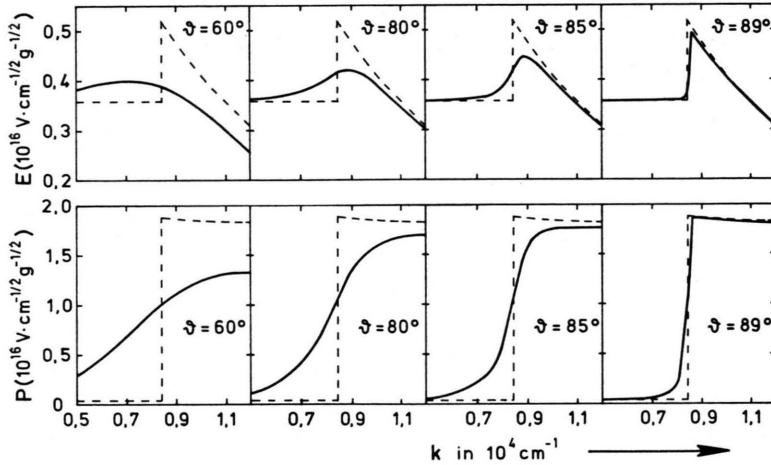


Fig. 5. Behaviour of electric field and polarization near crossing points in the principal direction of  $\vartheta = 90^\circ$ .

If  $k$  has such a value that  $n^2 = 1$  the denominator of the first term on the right hand side of Eq. (12c') vanishes. Because  $E$  is finite, the transverse part  $P_T$  of  $P$  must vanish at this point of  $k$ -space. For exact transverse polaritons in principal directions the complete polarization  $P$  clearly vanishes due to a compensation of displacement and electronic contributions. As an example, Fig. 6 shows the

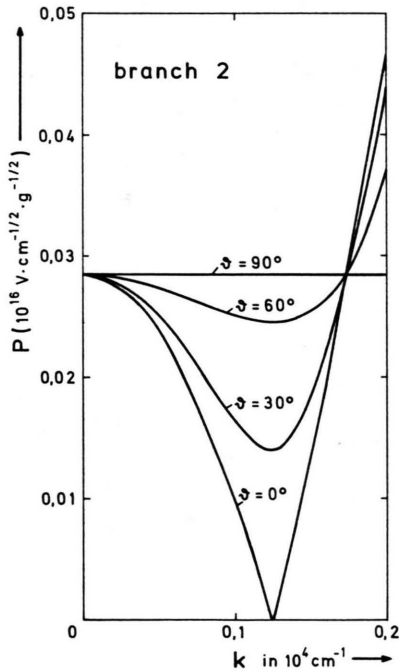


Fig. 6. Behaviour of polarization near a singular  $k$ -vector ( $n^2 = c^2 k^2 / \omega^2 = 1$ ). For exactly transverse modes in the principal direction ( $\vartheta = 0^\circ$ ) the displacement part and the electronic part cancel each other exactly for this  $k$ .

behaviour of  $P$  (branch 2) in the range  $0 \leq k \leq 2000 \text{ cm}^{-1}$ . Because of the exactly transverse character for  $\vartheta = 0^\circ$ , the polarization completely vanishes at  $k \approx 1250 \text{ cm}^{-1}$ , whereas in the longitudinal case at  $\vartheta = 90^\circ$  the vibration shows no dispersion because of  $P_T = 0$ .

All numerical calculations were carried out on the IBM computer 360/50 of the Universität Münster.

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## Appendix A

The *coupled harmonic oscillator formalism* for uniaxial crystals in the limiting case  $k \rightarrow \infty$  due to ONSTOTT and LUCOVSKY<sup>3</sup> and OLECHNA<sup>4</sup> is based on the following two equations of motion for the coupled system, given in the notation<sup>14</sup> of 3, 4:

$$\begin{aligned} & [\omega_E^2(i) + \Omega_E^2(i) \cos^2 \theta - \omega^2] u_E(i) \\ & + \sum_{k \neq i} \Omega_E(i) \Omega_E(k) u_E(k) \cos^2 \theta \\ & - \sum_j \Omega_E(i) \Omega_A(j) u_A(j) \sin \theta \cos \theta = 0, \end{aligned} \quad (\text{A } 1 \text{ a})$$

$$\begin{aligned} & [\omega_A^2(j) + \Omega_A^2(j) \sin^2 \theta - \omega^2] u_A(j) \\ & + \sum_{l \neq j} \Omega_A(j) \Omega_A(l) u_A(l) \sin^2 \theta \\ & - \sum_i \Omega_A(j) \Omega_E(i) u_E(i) \sin \theta \cos \theta = 0. \end{aligned} \quad (\text{A } 1 \text{ b})$$

Herein  $u_A(j)$ ,  $u_E(i)$  are the phonon coordinates with mode motion along the optic axis and perpendicular to the optic axis, resp.,  $\omega_A(j)$ ,  $\omega_E(i)$  the corresponding dispersion frequencies and  $\Omega_A(j)$ ,  $\Omega_E(i)$  the corresponding plasma frequencies given by

$$\begin{aligned}\Omega_A^2(j) &= (\omega_A^{1*}(j))^2 - \omega_A^2(j), \\ \Omega_E^2(i) &= (\omega_E^{1*}(i))^2 - \omega_E^2(i),\end{aligned}\quad (\text{A } 1\text{c})$$

where  $\omega_A^{1*}(j)$ ,  $\omega_E^{1*}(i)$  denote the corresponding uncoupled longitudinal phonon frequencies and  $\theta$  the angle between the electric field  $\mathbf{E}$  and the optic axis.

The experimental TO and LO phonon frequencies  $\omega_A(j)$ ,  $\omega_E(i)$ ,  $\omega_A^1(j)$ ,  $\omega_E^1(i)$  determine the input values  $\omega_A(j)$ ,  $\omega_E(i)$ ,  $\omega_A^{1*}(j)$ ,  $\omega_E^{1*}(i)$  of (A 1), and the system may be solved yielding the eigenfrequencies  $\omega$  and coordinates  $u_A(j)$ ,  $u_E(i)$  in dependence on the angle  $\theta$ . As known, for  $\theta = 0^\circ$  the frequencies  $\omega_A(j)$ ,  $\omega_E^1(i)$  and for  $\theta = 90^\circ$  the  $\omega_E(i)$ ,  $\omega_A^1(j)$  must be the solutions of (A 1). Taking the experimental LO phonon frequencies  $\omega_A^1(j)$ ,  $\omega_E^1(i)$  for the longitudinal input frequencies  $\omega_A^{1*}(j)$ ,  $\omega_E^{1*}(i)$  and substituting  $\omega$  by  $\omega_E^1(i)$ ,  $\omega_A^1(j)$  for  $\theta = 0^\circ$  and  $\theta = 90^\circ$ , resp., it is seen, that the system (A 1) is not consistent. Therefore the longitudinal input frequencies have been fitted in 3,4 via an interpolation scheme yielding new uncoupled frequencies  $\omega_A^{1*}(j)$ ,  $\omega_E^{1*}(i)$  as input data, which will now give the exact solutions  $\omega_E^1(i)$ ,  $\omega_A^1(j)$  from (A 1).

Compared with our general basic system (12) for  $k \rightarrow \infty$  the elimination of  $\mathbf{E}$  and  $\mathbf{P}$  in (12) yields

$$[-B^{11} - \omega^2 I - B^{12} S (I - B^{22} S)^{-1} (B^{12})^+] \mathbf{U} = 0, \quad (\text{A } 2)$$

where  $S \equiv -4\pi \mathbf{s} \mathbf{s}$ .

For uniaxial crystals the elements of the tensors  $B^{ik}$  are given by<sup>1</sup>

$$B_E^{11}(i) = -\omega_E^2(i), \quad B_A^{11}(j) = -\omega_A^2(j), \quad (\text{A } 3\text{a})$$

$$B_E^{22} = (\epsilon_\perp^\infty - 1)/4\pi, \quad B_A^{22} = (\epsilon_\parallel^\infty - 1)/4\pi, \quad (\text{A } 3\text{b})$$

$$(B_E^{12}(i))^2 = \frac{\epsilon_\perp^\infty}{4\pi} \frac{\prod_m ((\omega_E^1(m))^2 - \omega_E^2(i))}{\prod_{m \neq i} ((\omega_E^2(m) - \omega_E^2(i))}, \quad (\text{A } 3\text{c})$$

and the analogous equation for  $(B_A^{12}(j))^2$  by replacing  $\mathbf{E}$  by  $\mathbf{A}$ ,  $i$  by  $j$ ,  $\perp$  by  $\parallel$  in Eq. (A 3c).  $\epsilon_\perp^\infty$ ,  $\epsilon_\parallel^\infty$  herein denote the high frequency dielectric constants perpendicular and parallel to the optic axis, resp.

Taking into account the relation  $S(I - B^{22}S)^{-1} = S/D$  with  $D \equiv \epsilon_\perp^\infty s_\perp^2 + \epsilon_\parallel^\infty s_\parallel^2$ ,  $\mathbf{s} = (s_\perp, s_\parallel)$ , and splitting (A 2) into its components, we have

$$\begin{aligned}\left[ \omega_E^2(i) + \frac{4\pi}{D} (B_E^{12}(i))^2 s_\perp^2 - \omega^2 \right] u_E(i) \\ + \sum_{k \neq i} \frac{4\pi}{D} B_E^{12}(i) B_E^{12}(k) u_E(k) s_\perp^2 \\ + \sum_j \frac{4\pi}{D} B_E^{12}(i) B_A^{12}(j) u_A(j) s_\parallel s_\perp = 0,\end{aligned}\quad (\text{A } 4\text{a})$$

$$\begin{aligned}\left[ \omega_A^2(j) + \frac{4\pi}{D} (B_A^{12}(j))^2 s_\parallel^2 - \omega^2 \right] u_A(j) \\ + \sum_{l \neq j} \frac{4\pi}{D} B_A^{12}(j) B_A^{12}(l) u_A(l) s_\parallel^2 \\ + \sum_i \frac{4\pi}{D} B_A^{12}(j) B_E^{12}(i) u_E(i) s_\parallel s_\perp = 0.\end{aligned}\quad (\text{A } 4\text{b})$$

Defining

$$\begin{aligned}\Omega_E^2(i) &\equiv \frac{4\pi}{D} (B_E^{12}(i))^2, \quad \Omega_A^2(j) \equiv \frac{4\pi}{D} (B_A^{12}(j))^2, \\ s_\perp &\equiv -\cos \theta, \quad s_\parallel \equiv \sin \theta,\end{aligned}$$

it is seen directly, that

this system includes the system (A 1). The Eqs. (A 4) describe exactly the behaviour of IR-active long optical phonons. The difference between (A 4) and (A 1) is made only by the fact, that in (A 4) in contrast to (A 1) the plasma frequencies  $\Omega$  are orientation dependent via the wave normal vector  $\mathbf{s}$  in  $D$ .

With the restriction  $\epsilon_\perp^\infty/\epsilon_\parallel^\infty = 1$  we have from (A 3c)

$$\Omega_E^2(i) = \frac{\prod_m ((\omega_E^1(m))^2 - \omega_E^2(i))}{\prod_{m \neq i} ((\omega_E^2(m) - \omega_E^2(i))}, \quad (\text{A } 5)$$

and an analogous equation for  $\Omega_A^2(j)$ , replacing in (A 5)  $\mathbf{E}$  by  $\mathbf{A}$  and  $i$  by  $j$ . The plasma frequencies become now orientation independent and yield exactly the system (A 1). By comparison of relation (A 5) and (A 1c) it is seen that for a multimode uniaxial crystal the interpolation scheme used by 3, 4 to obtain fitted longitudinal input frequencies  $\omega_E^{1*}$ ,  $\omega_A^{1*}$  may be simply replaced by the formula

$$(\omega_E^{1*}(i))^2 = \omega_E^2(i) + \frac{\prod_m ((\omega_E^1(m))^2 - \omega_E^2(i))}{\prod_{m \neq i} ((\omega_E^2(m) - \omega_E^2(i))}, \quad (\text{A } 6)$$

and an analogous equation for  $(\omega_A^{1*}(j))^2$ .



Hence it follows from an analytical comparison of both theories that the coupled harmonic oscillator formalism (A1) is included as the special case  $k \rightarrow \infty$ ,  $\epsilon_{\perp}^{\infty} = \epsilon_{\parallel}^{\infty}$  in our general basic equations (12). Application of (A1) leads to satisfactory results for uniaxial crystals such as  $\alpha$ -quartz for example ( $\epsilon_{\perp}^{\infty} = 2.36$ ,  $\epsilon_{\parallel}^{\infty} = 2.38$ ). If, however,  $\epsilon_{\perp}^{\infty}$  and  $\epsilon_{\parallel}^{\infty}$  are very different, application of (A1) may lead to strong deviations from the exact results given by Eqs. (12). The interpolation scheme used to calculate uncoupled LO phonon frequencies may be replaced by a simple formula which yields directly the exact limiting frequencies of the iteration procedure.

Table B 1.  $45^\circ$ -extraordinary optical phonons in  $\text{LiNbO}_3$ .

branch	$\omega_{e0} (45^\circ) [\text{cm}^{-1}]$	
	theoretical	experimental due to BARKER JR. and LOUDON <sup>15</sup>
1	176.3	177
2	240.0	—
3	261.8	—
4	274.4	—
5	308.6	308
6	333.8	—
7	371.0	353
8	428.4	—
9	447.9	447
10	606.9	610
11	666.5	—
12	741.2	—
13	877.9	878

<sup>1</sup> G. BORSTEL and L. MERTEN, Z. Naturforsch. **26a**, 653 [1971]; Part I.

<sup>2</sup> ONSTOTT and LUCOVSKY<sup>3</sup> and OLECHNA<sup>4</sup> recently have developed a *coupled harmonic oscillator* formalism for the special case of long optical phonons in uniaxial crystals. It is shown in the appendix, that this formalism is contained in Eqs. (12) as the limiting case  $n^2 \rightarrow \infty$ ,  $\epsilon_{\perp}^{\infty} = \epsilon_{\parallel}^{\infty}$ .

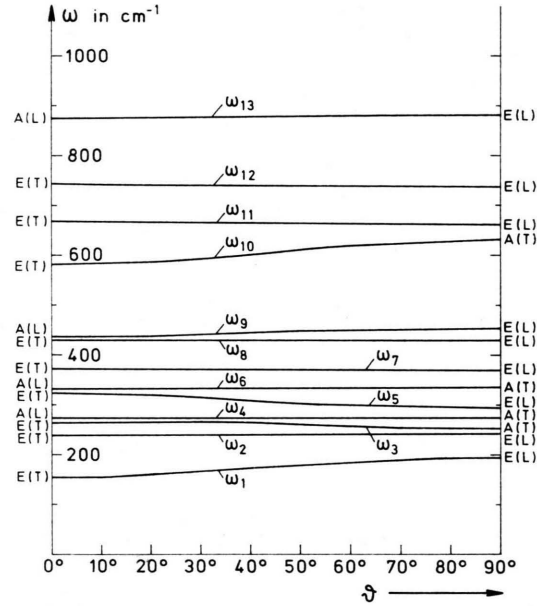
<sup>3</sup> J. ONSTOTT and G. LUCOVSKY, J. Phys. Chem. Sol. **31**, 2171 [1970].

<sup>4</sup> D. J. OLECHNA, J. Phys. Chem. Sol. **31**, 2755 [1970].

<sup>5</sup> The notation T-representation and L-representation refer to the fact that in the limiting case of long optical phonons ( $k \rightarrow \infty$ ) in the T-representation the normal coordinates of exactly transverse and in the L-representation of exactly longitudinal vibrations along a principal direction are decoupled. Because exactly longitudinal vibrations show no dispersion, the coordinates of each longitudinal vibration agree for all  $k$ -vectors of this principal direction. Hence, together with the statement that in the vicinity of  $k = 0$  all vibrations are directionally independent, it follows that the coordinates of the L-representation must be identical with the normal coordinates of the irreducible representations at  $k = 0$ .

## Appendix B

As mentioned above our input frequencies (cf. Table 1) in this second part differ from those of Part I in various aspects. Therefore as a completion to Fig 1 of I the directional dependence of frequencies of long optical phonons as it follows from our new assignment is shown in Fig. B 1. Table B 1 gives the corresponding values of frequencies of  $45^\circ$ -long optical phonons, cf. Table 3 of I.

Fig. B 1. Directional dependence of the extraordinary frequencies in  $\text{LiNbO}_3$ .

<sup>6</sup> The vibrations which are exactly longitudinal in some principal direction of the crystal show no dispersion in the whole range of  $k$ -space. Therefore for  $k = 0$  the eigenfrequencies  $\omega_{0i}$  agree with the frequencies  $\omega$  of long optical phonons.

<sup>7</sup> G. LAMPRECHT and L. MERTEN, Phys. Stat. Sol. **35**, 353 [1969].

<sup>8</sup> I. P. KAMINOW and W. D. JOHNSTON, Jr., Phys. Rev. **160**, 519 [1967].

<sup>9</sup> R. CLAUS and H. W. SCHRÖTTER, 2<sup>nd</sup> International Conference on Light Scattering in Solids, Paris 1971.

<sup>10</sup> R. CLAUS, G. BORSTEL et al., Z. Naturforsch. **27a**, Heft 8-9 [1972].

<sup>11</sup> L. MERTEN, Z. Naturforsch. **24a** 1878 [1969].

<sup>12</sup> R. LOUDON, Light Scattering Spectra of Solids, edit. G. B. WRIGHT, Springer-Verlag, New York 1969, p. 25.

<sup>13</sup> R. CLAUS, G. BORSTEL, and L. MERTEN, Opt. Comm. **3**, 17 [1971].

<sup>14</sup> The following correspondence of the notations due to ONSTOTT, LUCOVSKY and OLECHNA<sup>3,4</sup> and our notations is valid:

$$U = Q, \quad \omega_A(j) = \omega_{\parallel j}, \quad \omega_E(i) = \omega_{\perp i}, \\ \omega_A^t(j) = \omega_{\parallel j}^t, \quad \omega_E^t(i) = \omega_{\perp i}^t, \quad \theta = 90^\circ - \vartheta.$$

<sup>15</sup> A. S. BARKER, Jr., and R. LOUDON, Phys. Rev. **158**, 443 [1967].