Directional Dispersion and Assignment of Optical Phonons in $LiNbO_3$

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From the general polariton dispersion theory it can be shown that in an uniaxial crystal the frequencies of optical phonons * which are identical to those of the short wavelength polaritons depend on the angle Θ between the optic axis and the phonon wave vector. For $\Theta=0$ and $\Theta=\pi/2$ the phonons are exactly transversal or longitudinal so that they can be assigned to be of totally symmetric or twofold degenerate type. Careful measurements of the directional dispersion of all phonon modes of $LiNbO_3$ form a firm basis for a new complete assignment. 6 of the total number of 13 dispersion branches previously given in the literature had to be reassigned.

Introduction

$LiNbO_3$ has shown to be among the most interesting materials for investigations of optical properties in the solid state. The first Raman spectra were published by Schaufele and Weber [1]. Kaminow and Johnston [2] gave assignments of all phonon modes and determined absolute scattering efficiencies and electro-optic coefficients. Measurements of the infrared reflection and transmission spectra in combination with Raman scattering experiments allowed the determination of oscillator strengths [3]. Careful measurements of the refractive indices and dielectric constants have been presented [3, 4] and the observation of strong spontaneous Raman scattering by polaritons [5] lead to the first realisation of a tunable polariton laser in 1969 [6, 7].

Furthermore parametric luminescence has been reported by several authors [8–11] and polaritons associated with soft modes have been observed [12]. On the basis of the experimental results cited above directional dispersion branches, Eigen-vectors and Raman scattering cross sections have been calculated by Obukhovskii et al. [13] and Borstel and Merten [14]. However, experimental results by Claus and Schrötter [15] concerning the directional dispersion of the $A(T)$ **-phonon at 633 cm^{-1} did not agree with the calculated frequency shifts. This fact suggested that the assignments given earlier in the literature [2, 3] had to be corrected. In the present work all phonon dispersion branches have been recorded for angles Θ between the optic axis of the crystal and the phonon wave vectors in steps of 5° from $\Theta=\pi/2$ to $\Theta=0$. This allowed the determination of new assignments for the limiting cases $\Theta=0$ and $\Theta=\pi/2$. We believe that these assignments are of interest because $LiNbO_3$ is frequently used as a model crystal for calculations of different optical properties and because of technical applications of the crystal in nonlinear optical experiments as for instance second harmonic generation and parametric oscillators.

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* extraordinary optical phonons.

Theory

From electrodynamics and crystal optics the following relationships between the macroscopic electric field $\boldsymbol{E}$, the polarization $\boldsymbol{P}$ and electric diplacement $\boldsymbol{D}$ are known

$$\boldsymbol{D}=\boldsymbol{E}+4\pi\boldsymbol{P}, \tag{1}$$

$$\boldsymbol{D}=n^2(\boldsymbol{E}-\boldsymbol{s}(\boldsymbol{s}\cdot\boldsymbol{E})). \tag{2}$$

n denotes the refractive index and $\boldsymbol{s}=\boldsymbol{k}/|\boldsymbol{k}|$ a unit vector in direction of the wave vector $\boldsymbol{k}$. Since $\boldsymbol{s}$ is

** All totally symmetric modes simply indicated by A in the paper and in the figures belong to the factor group A_1.

perpendicular to $\boldsymbol{D}$ ($\operatorname{div}\boldsymbol{D}=0$) it follows from (1)

$$\boldsymbol{s}\cdot\boldsymbol{E}=-4\pi\,\boldsymbol{s}\cdot\boldsymbol{P} \tag{3}$$

and from (2) and (3) the following relation between $\boldsymbol{E}$ and $\boldsymbol{P}$ is obtained

$$\boldsymbol{E}=\frac{4\pi}{n^2-1}\left[\boldsymbol{P}-n^2\,\boldsymbol{s}(\boldsymbol{s}\cdot\boldsymbol{P})\right] \tag{4}$$

where $n^2=c^2k^2/\omega^2$. MERTEN [16] could show that the polariton region of IR-active long wave optical phonons can be completely described by Eq. (4) together with

$$-\omega^2\,\boldsymbol{Q}=B^{11}\,\boldsymbol{Q}+B^{12}\,\boldsymbol{E} \tag{5}$$

and

$$\boldsymbol{P}=(B^{12})^{+}\,\boldsymbol{Q}+B^{22}\,\boldsymbol{E}\,. \tag{6}$$

$$(\omega=c\,k/n)$$

Herein ω denotes the polariton frequency, c the velocity of light in vacuum and $\boldsymbol{Q}$ the r-dimensional vector of the quasi normal coordinates where r is the number of IR-active lattice vibrations. The term "quasi-normal coordinates" shall indicate that these coordinates don't diagonalize the total energy density matrix but only its mechanical part, i. e. only for $\boldsymbol{E}=0$ the Q_i become normal coordinates in the usual sense whereas in general they are coupled by the macroscopic electric field $\boldsymbol{E}$. In uniaxial crystals the elements of the tensors B^{11}, B^{12} and B^{22} can be obtained from the values $\omega_{\perp\mathrm{T}i}$; $\omega_{\perp\mathrm{L}i}$; $\omega_{\parallel\mathrm{T}j}$; $\omega_{\parallel\mathrm{L}j}$ of the transverse (T) and longitudinal (L) phonon frequencies for polaritons parallel ($\parallel$) and perpendicular ($\perp$) to the optic axis [14]. Using group theoretical notations this means that all frequencies of polar vibrational modes with the assignments $E(\mathrm{T})$, $E(\mathrm{L})$, $A(\mathrm{T})$ and $A(\mathrm{L})$, respectively, have to be determined. Finally the ordinary and extraordinary refractive indices $n_0=\sqrt{\varepsilon_{\infty\perp}}$ and $n_e=\sqrt{\varepsilon_{\infty\parallel}}$ are required. Taking into account the factorized form of the Lyddane-Sachs-Teller relation due to KUROSAWA [17]

$$\varepsilon_\perp(\omega)=\varepsilon_{\infty\perp}\prod_i\frac{\omega^2_{\perp\mathrm{L}i}-\omega^2}{\omega^2_{\perp\mathrm{T}i}-\omega^2} \tag{7}$$

and

$$\varepsilon_\parallel(\omega)=\varepsilon_{\infty\parallel}\prod_j\frac{\omega^2_{\parallel\mathrm{L}j}-\omega^2}{\omega^2_{\parallel\mathrm{T}j}-\omega^2} \tag{8}$$

no data concerning the mode strengths are required, however, the frequencies of all LO-modes have to be determined. The condition for a nontrivial solution of the system of Eqs. (4) – (6) leads to

$$n^2=c^2k^2/\omega^2=\varepsilon_\perp(\omega) \tag{9}$$

for ordinary polaritons which are directionally independent as the vector $\boldsymbol{s}$ does not appear in (9). For extraordinary polaritons a generalized Fresnel's equation for the wave normal vector is obtained

$$\frac{s_\perp^2}{\frac{1}{n^2}-\frac{1}{\varepsilon_\perp(\omega)}}+\frac{s_\parallel^2}{\frac{1}{n^2}-\frac{1}{\varepsilon_\parallel(\omega)}}=0\,. \tag{10}$$

In the limit $k\to\infty$ which is identical to $n^2\to\infty$ for finite ω Eq. (10) reduces to

$$s_\perp{}^2\,\varepsilon_\perp(\omega)+s_\parallel{}^2\,\varepsilon_\parallel(\omega)=0\,. \tag{11}$$

This means that the phonon frequencies do not depend on the magnitude of the wave vector any more but only on the direction of $\boldsymbol{k}$. Since $s_\perp=\sin\Theta$ and $s_\parallel=\cos\Theta$ the Θ-dependence of the phonon directional dispersion branches is determined by

$$\mathrm{tg}^2\,\Theta=-\varepsilon_\parallel(\omega)/\varepsilon_\perp(\omega) \tag{12}$$

where $\varepsilon_\perp(\omega)$ and $\varepsilon_\parallel(\omega)$ are given by Eqs. (7) and (8). For $LiNbO_3$ there are $4\,A(\mathrm{T})$ and $A(\mathrm{L})$ frequencies and $9\,E(\mathrm{T})$ and $E(\mathrm{L})$ frequencies. Thus in Eq. (7) $i=1,\ldots.\,9$ and in Eq. (8) $j=1,\ldots,4$. The polynom resulting from (11) is of power 13 in ω^2. Linear and quadratic approximations for $\omega^2=\omega^2(\Theta)$ have been discussed by MERTEN and LAMPRECHT [18].

In the present paper all dispersion branches of long optical phonons have been directly calculated from Eq. (11).

Experimental

All spectra have been recorded using the 647,1 nm exciting line of a Krypton laser with about 600 mW output power. The dimensions of the 10 crystal samples used were $(3\times5\times5)$ mm^3. In the first crystal of the series the optic axis (z) was perpendicular to two (3×5) mm^2 surfaces and in the following samples the z-axis was oriented away from this direction in steps of 5° for each crystal so that in crystal nn 10 the optic axis was oriented at 45° to the (3×5) mm^2 surface in question. The use of this series of samples allowed the recording of spectra in backward as well as right angle scattering for angles Θ between 0 and $\pi/2$ in steps of 5°. The geometrical scattering arrangement and all optical elements could thus be left unchanged for each series of spectra. The experimental set-up for the backward scattering experiments has been described earlier [19]. The crystal samples were attached on a glass prism with a suitable immersion liquid so that reflections on the second surface inside the specimen were reduced. It should however be pointed out that reflec-

tions of this kind will generate Raman scattering of phonons with $\Theta' = (\pi - \Theta)$ which show frequencies identical to those at $\Theta' = \Theta$ when using the backward scattering technique. To the contrary in right angle scattering experiments reflections will generate the $\Theta' = (\pi/2 - \Theta)$-spectrum which obviously shows different frequencies. Finally the glass prism was oriented in such a way that the main reflections on the second surface inside it did not reach the scattering volume that was projected onto the entrance slit of the double monochromator. All the samples were cut from the same boule grown from a congruent melt. Comparison with material grown from stoichiometric melts did not reveal any difference between the spectra [23].

Results and Discussion

The following 3 series of spectra have been recorded by backward scattering experiments

a) $z\ (x\,x)\ \bar{z}$ for $\Theta = 0$ to $x\,(z\,z)\ \bar{x}$ for $\Theta = \pi/2$.

Thus for $\Theta = \pi/2$ the spectra show the A(T) modes while for $\Theta = 0$ the A(L) and E(T) modes are recorded. In the intermediate region the phonons are of mixed type and the scattering geometries are

$$z \rightarrow x\,(x \rightarrow z\ \ x \rightarrow z)\ \bar{z} \rightarrow \bar{x}\,.$$

Figure 1 shows a selected number of spectra from this series. Because $LiNbO_3$ is not optically active the scattering geometries are well defined also for angles $\Theta + \pi/2$. The directional dispersion of 5 branches can easily be seen.

b) $z\,(y\,x)\ \bar{z}$ for $\Theta = 0$ to $x\,(y\,z)\ \bar{x}$ for $\Theta = \pi/2$

which represents the E(T) modes for $\Theta = 0$ and the E(T + L) modes for $\Theta = \pi/2$. The experiment showed that primarily all directionally independent ordinary branches could be beautifully observed by these scattering geometries. For arbitrary Θ-values the scattering geometries were

$$z \rightarrow x\,(y\,x \rightarrow z)\,\bar{z} \rightarrow \bar{x}\,.$$

c) $z(y\,y)\ \bar{z}$ for $\Theta = 0$ to $x(y\,y)\ \bar{x}$ for $\Theta = \pi/2$.

All spectra show A as well as E modes. For $\Theta = 0$ the A(L) and E(T) and for $\Theta = \pi/2$ A(T) and E(T + L) modes are observed. The scattering geometries for general directions of the wave vector correspondingly are $z \rightarrow x\,(y\,y)\ \bar{z} \rightarrow \bar{x}$.

Using right angle scattering the following two series of spectra which were also recorded at 130 K gave most information on the directional dependence of the extraordinary phonons

a) $x + z\,(y\,y)\ x + \bar{z}$ for $\Theta = 0$

to $\bar{x} + z\,(y\,y)\ x + z$ for $\Theta = \pi/2$

and

b) $x + z\,(y\ \ z + x)\ x + \bar{z}$ for $\Theta = 0$

to $\bar{x} + z\,(y\ \ z + x)\ x + z$ for $\Theta = \pi/2$.

In addition, a number of polariton spectra have been recorded in order to check the assignments [20].

On the basis of these experimental data the directional dispersion branches of the extraordinary phonons have been calculated using the refractive indices and dielectric constants given in [4] and [3] respectively. As can be seen from Figs. 2 a and b a very good agreement of theory and experiment is obtained. In general, data points of dispersion branches from those series of spectra have been plotted in the figures where these branches could best be observed. Only in a small number of cases the discrepancies of phonon wave numbers from different corresponding spectra were more than $\pm 2\ cm^{-1}$. A comparison of the new data with the assignments from Ref. [2] is presented in Figure 3. Dispersion branches assigned by Kaminow and Johnston which could not be experimentally observed are indicated by dashed arrows in brackets. The lowest frequency dispersion branch according to Ref. [2] was E(T) at 92 cm^{-1} coupled to E(L) at 117 cm^{-1}. This LO-TO-splitting requires a rather great oscillator strength which could not be experimentally observed by IR measurements. Therefore, the frequency of the E(L) phonon was later changed to 95 cm^{-1} (l. c. [21]). In the Raman spectra these phonons could however not unambiguously be observed. The experiment shows a very broad structure in the region ~ 80 to 120 cm^{-1} with several weak peaks appearing with different intensities at different scattering geometries. It seems to be most likely to interprete this structure as difference bands. As a matter of fact several difference frequencies can be obtained in this region. The TO wave numbers in Fig. 3 a of the lowest 3 A and E branches for instance, will suggest 79, 83, 87, 96, 100, 110 and 121 cm^{-1}.

The scattering intensity of the structure showed a drastic decrease at liquid nitrogen temperatures as can be seen from Figure 4. The spectra are recorded at $\Theta = \pi/2$ and without an analyzer so that phonons of symmetry A as well as E are observed. Whereas the half widths of all first order phonons at higher frequencies decreased so that narrow pairs

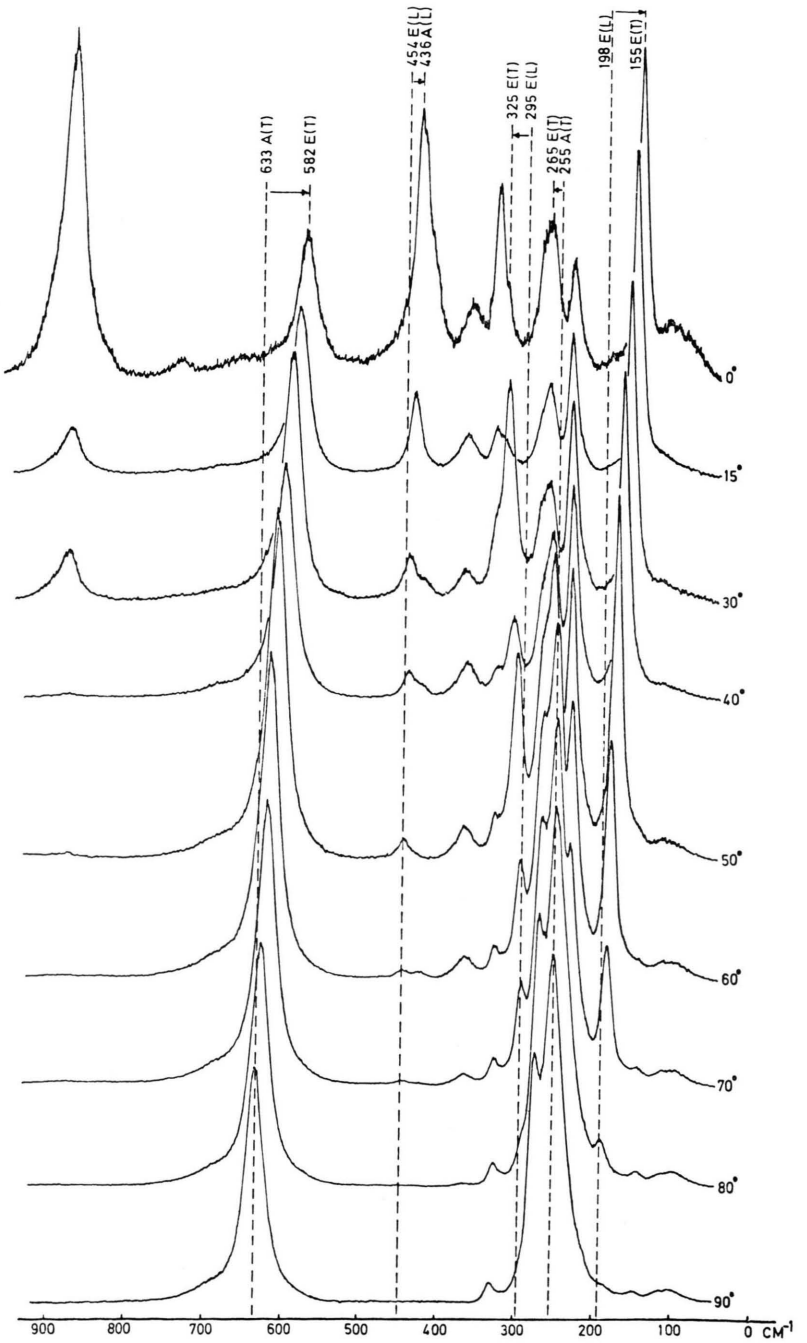

Fig. 1. Experimental data on the directional dispersion of extraordinary phonons in $LiNbO_3$. The angles to the right of the spectra refer to the angle Θ between the wave vector and the optic axis of the crystal. The experiments were carried out by backward scattering, $\Theta=0$ corresponding to $z(x\,x)\,\bar{z}$ and $\Theta=\pi/2$ corresponding to $x(z\,z)\,\bar{x}$ geometry.

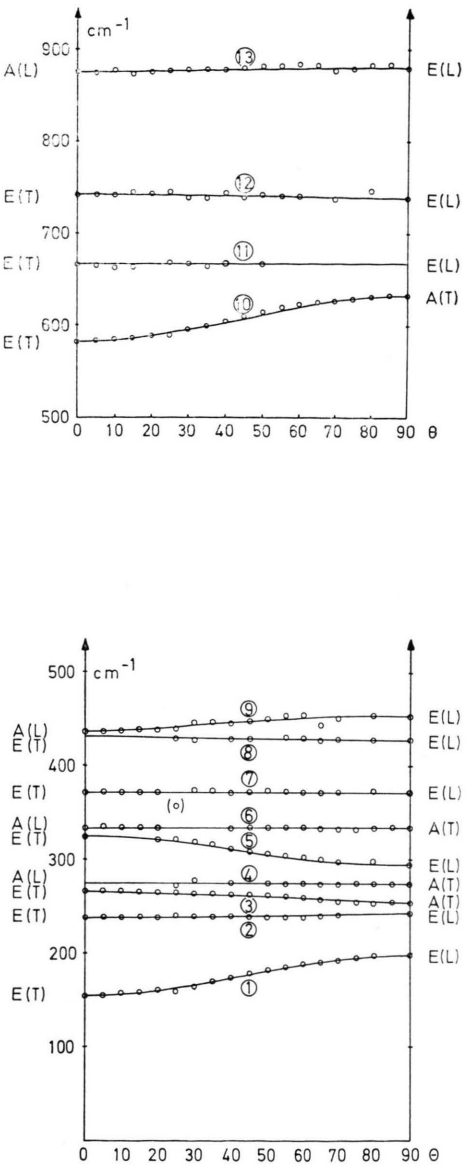

Fig. 2 a, b. Calculated dispersion branches and experimental data points on the directional dispersion of extraordinary phonons in $LiNbO_3$.

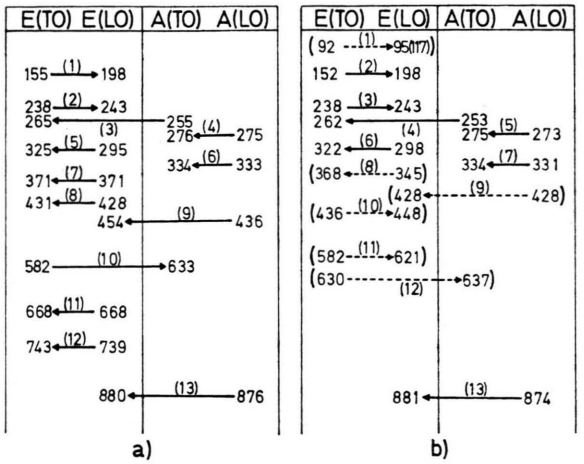

Fig. 3. a) Assignments and wave numbers of the dispersion branches according to the present investigations. b) Assignments according to Ref. [2]. Erroneous branches are given in brackets and indicated by dashed arrows.

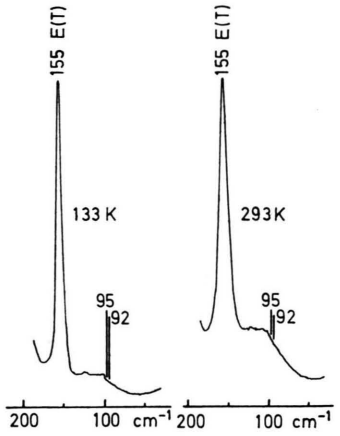

Fig. 4. On the assignment of the low frequency bandstructure, see text.

of Raman lines could be better resolved, the low frequency structure did not show a better resolution at lower temperatures. Finally, the positions of the wave numbers 92 and 95 cm^{-1} have been indicated in Fig. 4 which shows that the lowest frequency phonon branch will not be at that position in any case. The branch $E(T)$ at 155 to $E(L)$ at 198 cm^{-1} has thus been assigned as nr. 1, see Figure 3 a. The branches 1 to 6 of the new assignments, Fig. 3 a are in agreement and identical to the branches 2 to 7 of the assignments given by Ref. [2], Figure 3 b. The next error in Ref. [2] appears at branch 8, Figure 3b. As can be seen from Fig. 1 the Raman line at 371 cm^{-1} and $\Theta = 0$ does not couple to an LO-frequency more than 20 cm^{-1} lower for $\Theta = \pi/2$. The scattering intensity decreases because the $\Theta = \pi/2$-spectrum shows only the $A(T)$ modes. The branches 8 and 9, Fig. 3 a could both be observed separately in three of the series of spectra. Especially at lower temperatures the resolution was rather good, see Fig. 5 which shows a $\Theta = 40°$ spectrum at right angle scattering. Branch 9 can be seen in Figure 1. The most drastical discrepancy appears in the region 582 to

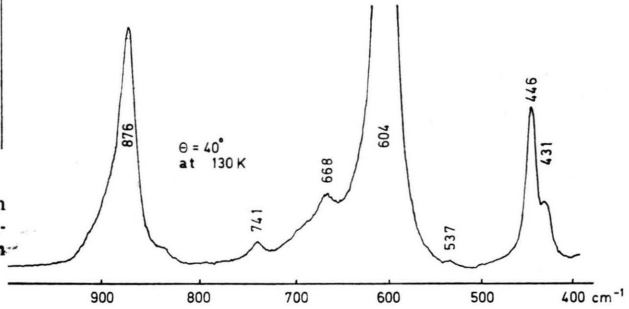

Fig. 5. A $\Theta = 40°$-spectrum recorded by right angle scattering at 130 K showing Raman lines corresponding to the branches 11, 12, Fig. 3 a and a two-phonon process at ~ 537 cm^{-1}.

~ 637 cm^{-1} where only one directional dispersion branch can be observed whereas there should be two according to [2]. This branch can beautifully be seen in Fig. 1 and has been reported earlier by CLAUS and SCHRÖTTER [15]. Finally, branch 13 is in agreement with the old assignment. Raman scattering by the upper ordinary polariton branch associated with photons has earlier been quantitatively analyzed in Ref. [22] using the assignments of Ref. [2]. It should be pointed out that this polariton branch is determined mainly by the value of the refractive index $n_0 = \sqrt{\varepsilon_{\infty\perp}}$ and the position of the highest $E(L)$ frequency. The contribution of the quasi normal coordinates of the lower branches is very small and, regarding the experiment, almost negligible. This fact caused that the error of the assignments in Ref. [2] could not be detected with those experiments.

So far, two directional dispersion branches are missing according to group theoretical calculation. The experiments showed the existence of three weaker branches at 537, 668 and 741 cm^{-1}. Furthermore, sporadically a very weak Raman line at ~ 840 cm^{-1} was observed in some of the spectra recorded at lower temperatures, see Figure 5. There seemed, however, to be too little evidence for an interpretation of this line as a first order branch.

Branch 12, Fig. 3 a was experimentally most evident, as it could be observed over the whole Θ-range with some directional dispersion. Less evidence seemed to exist for branch 11, Fig. 3 a, which disappeared near $\Theta = \pi/2$ in the strong A(T) phonon at 633 cm^{-1}, see Fig. 2 b. It might be interpreted as $2 \times A$(T) at 334 cm^{-1}. The introduction of a first order branch at ~ 537 cm^{-1} which could also be detected over the whole Θ-region, however, predicted a behaviour of the ordinary polariton dispersion which was not in agreement with the experiment [20]. Because of these facts the authors have chosen the assignments given in Figure 3 a. The wave number shifts due to directional dispersion of branch 7 and 11 obtained from the spectra were too small and accidental. Therefore these branches have been introduced with approximately constant frequencies.

Conclusion

The directional dispersion of all first order phonon branches in $LiNbO_3$ has been studied and new assignments of the corresponding modes for wave vectors parallel and perpendicular to the optic axis are given. In two cases the decision whether the branches are of first or second order was somewhat problematic. Arguments are given for the present assignments and the alternatives rejected are discussed. In any case the oscillator strengths of the two missing branches when branch 11 and 12 are omitted, have to be very small because the experimental data of all other branches fit the theoretical curves very well. This means that the two branches in question do not give an important contribution to the dielectric constants, see the LST relations Eqs. (7) and (8). It should be noted that the wave numbers of most phonons are to be regarded with an error of ± 2 cm^{-1} since only few Raman lines show distinct peaks and half widths less than 15 cm^{-1}. The wave numbers given in Fig. 3 a are those which determined the calculated dispersion branches best fitted to the experimental data over the whole Θ-range. Spectra have been reproduced in order to enable the reader to review the experimental data which form the basis for the new assignment.

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