

## **Unique Cuspidal Features in the Group-Velocity Surface of Barium Sodium Niobate and Rochelle Salt<sup>1</sup>**

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Crystals that have sufficient elastic anisotropy can exhibit cuspidal features in the group-velocity surface so that the group velocity is double- or triple-valued. In nonpiezoelectric crystals such cuspidal features occur only in the quasi-transverse (QT) modes when the wave vectors are restricted to the symmetry planes of the crystal. Sufficient piezoelectric stiffening of the elastic constants, however, can generate cuspidal features in other modes when the wave vectors are restricted to these same symmetry planes. In barium sodium niobate (BSN) there is insufficient elastic anisotropy to generate cuspidal features when piezoelectric stiffening is neglected. The addition of piezoelectric stiffening changes only the quasi-longitudinal (QL) and QT modes in the (100) and (010) planes, and changes only the pure transverse (T) mode in the (001) plane. There is sufficient piezoelectric stiffening, however, to generate small cuspidal features in the QL mode about the [001] and [00 $\bar{1}$ ] axes in the (100) and (010) planes. In Rochelle salt, however, there is sufficient elastic anisotropy to generate cuspidal features in the QT modes about collinear axes along nonsymmetry directions in the (100) and (010) planes. The addition of piezoelectric stiffening changes only the T mode in the (100), (010) and (001) symmetry planes. This piezoelectric stiffening is large enough, however, to generate large cuspidal features in the T mode about new collinear axes along nonsymmetry directions in the (010) and (001) planes.

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**KEY WORDS:** anisotropy factors; elastic anisotropy; elastic constants; group velocities; hexagonal crystals; orthorhombic crystals; phonon focusing; tetragonal crystals.

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<sup>1</sup> Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.

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## 1. INTRODUCTION

Phonon focusing in the long-wavelength limit depends upon the second-order elastic constants [1]. The ratios between these constant determine the shape of the phase- and group-velocity surfaces. If there is sufficient anisotropy the group-velocity surface can exhibit cuspidal features where this surface can be double- or triple-valued [2, 3]. In nonpiezoelectric crystals such cuspidal features are restricted to the quasi-transverse (QT) modes. If the wave vectors are further restricted to the symmetry planes of the crystal (i.e., in-plane wave vectors), then one of the transverse modes becomes polarized perpendicular to the wave vector thus becoming purely transverse (T). Such pure or (T) modes are characterized by the absence of any in-plane cuspidal features [3].

In piezoelectric crystals, however, the coupling between the stress field and the accompanying electric field stiffens the elastic constants. The amount of elastic stiffening depends not only upon the piezoelectric and permittivity constants, but also upon the direction of the wave vector for the propagating elastic wave [4]. By changing the ratios between the elastic constants, elastic stiffening modifies the shape of phase- and group-velocity surfaces and, thus, modifies the phonon-focusing properties of single crystals [5]. In strongly piezoelectric materials this coupling between the elastic and the electric variables is strong enough to change dramatically phonon-focusing scatter plots [6, 7] and predictions of boundary-scattered phonon conductivity [8].

This paper discusses two strongly piezoelectric orthorhombic crystals, barium sodium niobate and Rochelle salt. Piezoelectric stiffening in both of these crystals is strong enough to create in-plane cuspidal features in the group-velocity plots for modes that are cusp-free when effects of piezoelectric stiffening are ignored. In barium sodium niobate, unique cuspidal features appear in the QL mode. In Rochelle salt, unique in-plane cuspidal features appear in the pure T mode.

## 2. THEORY

In piezoelectric media the elastic and electric variables are coupled affecting the dynamics of the system. The elastic stress tensor  $\sigma_{ij}$  and the electric displacement  $D_r$  are given by [4, 6]

$$\sigma_{ij} = C_{ijlm}^E S_{lm} - e_{ijr} E_r \quad (1)$$

$$D_r = e_{ijr} S_{ij} + \epsilon_{rl}^S E_l \quad (2)$$

where  $\mathbf{E}$  is the electric field,  $S_{lm}$  is the elastic strain tensor,

$$S_{lm} = \frac{1}{2} \left[ \frac{\partial u_l}{\partial x_m} + \frac{\partial u_m}{\partial x_l} \right] \quad (3)$$

$\mathbf{u}(x, t)$  is the deformation or displacement field of the medium,  $C_{ijlm}^E$  is the elastic constant tensor at constant electric field,  $e_{ijr}$  is the piezoelectric stress tensor, and  $\epsilon_{rl}^S$  is the permittivity tensor at constant strain. Note that the Einstein convention is used (i.e., summation over repeated subscripts). Contracted Voigt notation is generally used to represent the elastic, piezoelectric, and permittivity tensors as matrices  $C_{IJ}$ ,  $e_{rI}$ , and  $\epsilon_{pq}$ , respectively.

The local force on the medium is

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial \sigma_{ij}}{\partial x_j} \quad (4)$$

where  $\rho$  is the density. This allows plane wave solutions

$$\mathbf{u} = \mathbf{U} e^{i(\omega t - \mathbf{k} \cdot \mathbf{x})} \quad (5)$$

Since acoustic phase velocities are five orders of magnitude smaller than the velocity of light, one can make the quasistatic approximation [4] for the electric field so that  $\mathbf{E}$  is constrained to be parallel to the wave vector  $\mathbf{k}$ . Assuming that there are no free charges,

$$\nabla \cdot \mathbf{D} = 0 \quad (6)$$

The above equations can be combined to give the stiffened Christoffel equations:

$$(A_{il} - \rho s^2 \delta_{il}) U_i = 0 \quad (7)$$

where  $s$  is the phase velocity  $\omega/k$ , and  $\delta_{il}$  is the Kronecker delta. The Christoffel coefficients are given by

$$A_{il} = C_{ijlm} n_j n_m \quad (8)$$

where  $n_j$  are the direction cosines of the wave vector  $\mathbf{k}$  and  $C_{ijlm}$  are the piezoelectrically stiffened elastic constants [4, 6]:

$$C_{ijlm} = C_{ijlm}^E + \frac{e_{ijr} n_r e_{lms} n_s}{\epsilon_{pq}^S n_p n_q} \quad (9)$$

Solutions for the phase velocity  $s$  is obtained by equating the secular determinant to zero:

$$|A_{ij} - \rho s^2 \delta_{ij}| = 0 \quad (10)$$

If the wave vectors are confined to a symmetry plane the solution factors into a pure transverse mode  $s_T$  polarized perpendicular to that symmetry plane, and two mixed, i.e., impure, modes  $s_+$  and  $s_-$  orthogonally polarized in that symmetry plane. When the (100) plane, for example, is a symmetry plane, then  $n_1 = 0$  and  $A_{12} = A_{13} = 0$ . The solutions for the phase velocity then factor to

$$\rho s_T^2 = A_{11} \quad (11)$$

and

$$2\rho s_{\pm}^2 = A_{22} + A_{33} \pm [(A_{22} - A_{33})^2 + 4A_{23}^2]^{1/2} \quad (12)$$

Solutions for the (100), (010), and (001) planes of orthorhombic crystals are given in terms of generalized elastic constants in Table I of Ref. 3.

The group velocity is defined as  $\mathbf{v} = \partial\omega/\partial\mathbf{k}$ . In the absence of dispersion this becomes

$$\mathbf{v} = \frac{\partial s}{\partial \mathbf{n}} \quad (13)$$

Differentiating the Christoffel equation with respect to  $n_\alpha$  and multiplying this result by  $U_i$  using the normalizing condition  $U_i U_i = 1$ , one obtains the useful result [6]

$$v_\alpha = \frac{1}{2\rho s} \frac{\partial A_{ij}}{\partial n_\alpha} U_i U_j \quad (14)$$

Piezoelectric stiffening of the Christoffel coefficients gives, from Eqs. (8) and (14) [6],

$$v_\alpha = \left[ 2C_{ialm}^E n_m + \frac{\partial}{\partial n_\alpha} \left[ \frac{e_{ijr} n_j n_r e_{lms} n_m n_s}{\epsilon_{pq}^S n_p n_q} \right] \right] \frac{U_i U_l}{2\rho s} \quad (15)$$

Orthorhombic crystals exist in three crystal classes: 222,  $mm2$ , and  $mmm$ . Only classes 222 and  $mm2$ , however, can exhibit piezoelectricity. Rochelle salt (potassium sodium tartrate  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ) is 222 [6, 9], whereas barium sodium niobate ( $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ ) is  $mm2$  [6, 9]. Both of these crystals have large piezoelectric stress constants [6, 10].

### 2.1. Orthorhombic 222

If the crystal symmetry is orthorhombic 222, then each of the three symmetry planes is perpendicular to a two-fold axis, and the only nonzero piezoelectric stress constants  $e_{rI}$  are [4, 6]  $e_{14}$ ,  $e_{25}$ , and  $e_{36}$ . As a result, the only stiffened elastic constants are

$$C_{44} = C_{44}^E + (e_{14}n_1)^2/\varepsilon$$

$$C_{55} = C_{55}^E + (e_{25}n_2)^2/\varepsilon$$

$$C_{66} = C_{66}^E + (e_{36}n_3)^2/\varepsilon$$

where

$$\varepsilon = \varepsilon_{11}n_1^2 + \varepsilon_{22}n_2^2 + \varepsilon_{33}n_3^2$$

For the (100) plane, for example,  $n_1 = 0$  and only  $C_{55}$  and  $C_{66}$  are stiffened, so only the pure transverse (T) mode is stiffened [6]. The two mixed modes remain unstiffened in this plane. Similar arguments for the (010) and (001) planes show that only the T mode stiffens in each of these planes whereas the two mixed modes remain unstiffened [6].

### 2.2. Orthorhombic $mm2$

If, however, the crystal symmetry is orthorhombic  $mm2$ , then the (100) and (010) planes exhibit mirror symmetry, whereas the (001) plane is perpendicular to the two-fold [001] axis. The only nonzero values  $e_{rI}$  for  $mm2$  symmetry are [4, 6]  $e_{15}$ ,  $e_{24}$ ,  $e_{31}$ ,  $e_{32}$ , and  $e_{33}$ . In this case the only unstiffened elastic constant is  $C_{66}$ . The remaining eight stiffened elastic constants are

$$C_{11} = C_{11}^E + (e_{31}n_3)^2/\varepsilon$$

$$C_{22} = C_{22}^E + (e_{32}n_3)^2/\varepsilon$$

$$C_{33} = C_{33}^E + (e_{33}n_3)^2/\varepsilon$$

$$C_{44} = C_{44}^E + (e_{24}n_2)^2/\varepsilon$$

$$C_{55} = C_{55}^E + (e_{15}n_1)^2/\varepsilon$$

$$C_{12} = C_{12}^E + e_{31}e_{32}n_3^2/\varepsilon$$

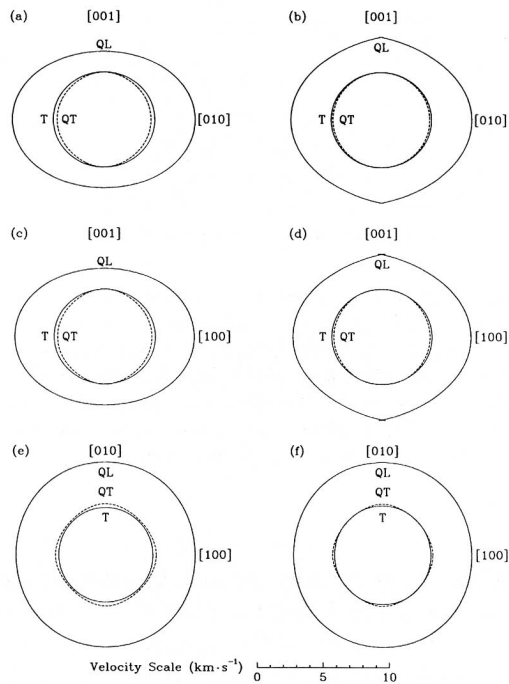
$$C_{23} = C_{23}^E + e_{32}e_{33}n_3^2/\varepsilon$$

$$C_{13} = C_{13}^E + e_{31}e_{33}n_3^2/\varepsilon$$

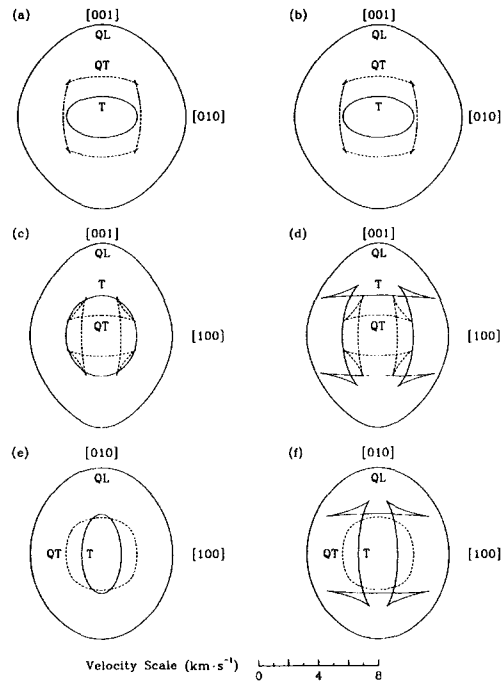
where

$$v = \varepsilon_{11}n_1^2 + \varepsilon_{22}n_2^2 + \varepsilon_{33}n_3^2$$

For the (100) plane, for example,  $n_1 = 0$  so that  $C_{55}$  is no longer stiffened. As a result only the T mode is unstiffened in the (100) plane, whereas both mixed modes are stiffened [6]. For the (010) plane,  $n_2 = 0$  so that  $C_{44}$  is no longer stiffened, making the T mode the only unstiffened mode in the (010) plane [6]. For the (001) plane, however,  $n_3 = 0$  so that the only stiffened elastic constants are  $C_{44}$  and  $C_{55}$ . As a result, the T mode is the only stiffened mode [6]; the two mixed modes remain unstiffened in the (001) plane.



**Fig. 1.** Polar plots of the group velocity for barium sodium niobate (BSN) for each symmetry plane. Curve a, (100) plane with piezoelectric stiffening ignored; b, (100) plane with piezoelectric stiffening; c, (010) plane with piezoelectric stiffening ignored; d, (010) plane with piezoelectric stiffening; e, (001) plane with piezoelectric stiffening ignored; f, (001) plane with piezoelectric stiffening.



**Fig. 2.** Polar plots of the group velocity for Rochelle salt for each symmetry plane. Curve a, (100) plane with piezoelectric stiffening ignored; b, (100) plane with piezoelectric stiffening; c, (010) plane with piezoelectric stiffening ignored; d, (010) plane with piezoelectric stiffening; e, (001) plane with piezoelectric stiffening ignored; f, (001) plane with piezoelectric stiffening.

### 3. RESULTS

Polar plots of the group velocity for each symmetry plane are given for barium sodium niobate in Fig. 1 and for Rochelle salt in Fig. 2. Plots a, c, and e are results with piezoelectric stiffening ignored. These results are contrasted with piezoelectric stiffened results in plots b, d, and f.

### 4. DISCUSSION

Results are in agreement with predictions [6] based upon the 222 and  $mm2$  classes of orthorhombic crystals. Wave vectors that lie in a plane which is normal to a two-fold axis of symmetry give piezoelectric stiffening to the pure (T) mode, whereas the two mixed modes remain unstiffened.

Wave vectors, however, that lie in a mirror plane give piezoelectric stiffening to both mixed modes, whereas the pure (T) mode remains unstiffened. Note that in the absence of piezoelectricity, in-plane cuspidal features (resulting from constraining the wave vectors to a symmetry plane) are permitted only for the QT mixed mode.

The large value of the piezoelectric stress constant  $e_{33}$  in barium sodium niobate significantly stiffens  $C_{33}$ , resulting in small cuspidal features in the QL mode about the  $[001]$  and  $[00\bar{1}]$  axes in the (100) and (010) planes. Stiffening for the QT mode in the (100) and (010) planes and for the T mode in the (001) plane, however, gives only minor changes to the group velocities. The large value of  $e_{14}$  in Rochelle salt significantly stiffens  $C_{44}$ , giving large prominent cuspidal features to the T mode in the (010) and (001) planes. The small values of  $e_{25}$  and  $e_{36}$ , in contrast, however, give very little stiffening to  $C_{55}$  and  $C_{66}$ , respectively and, thus, no significant changes to the group velocities for the (100) plane.

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