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Lattice modes in ferroelectric perovskites. III. Soft modes in $BaTiO_3$

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We report careful right-angle Raman measurements, in the tetragonal phase of $BaTiO_3$, of the lowest overdamped "soft" E(TO) mode. The measurements are from 22°C to the tetragonal-to-cubic phase transition, which occurs at $T_c = 135$°C. We fit the data to the usual damped-harmonic-oscillator form, and obtain the harmonic frequency ω_o and the damping constant γ. The results are in reasonable agreement with other measurements (which, however, have not gone as high in temperature). Unexpectedly, we find that ω_0 increases up to T_c, which means that the dielectric constant perpendicular to the ferroelectric axis, ϵ_a, decreases right up to T_c. However, this result agrees with capacitance measurements of ϵ_a to $T = T_c - 8$°C. We also comment on the results of the A_1 modes and reemphasize that all the A_1 and E modes disappear abruptly above T_c and thus obey the appropriate selection rules. There are, however, broad features at about 270 and 520 cm^{-1} that can be observed above as well as below T_c. These broad features are not any of the $3n-3 = 12$ optical modes at the center of the Brillouin zone.

I. INTRODUCTION

$BaTiO_3$ is in a certain sense a prototype ferroelectric material. Its discovery in the 1940s[1-7] showed that materials with a simple crystal structure could be ferroelectric.[1-7] Further, $BaTiO_3$ proved to be just one member of a very large class of ABO_3 perovskite materials that showed other types of structural phase transitions as well as ferroelectric transitions. The understanding of these materials was given a firm theoretical basis by Cochran[8] in 1959. He proposed that lattice-mode instabilities in the high-temperature phase could cause these transitions, so that the cubic structure below a transition temperature T_c would take on some other structure with a lower symmetry. These temperature-dependent lattice modes are usually called "soft modes" and for the ferroelectric case are the lowest transverse-optical (TO) modes at the Brillouin-zone center ($k=0$).[8] Kwok, Miller,[9] and Cowley[4] later showed that the structure below T_c could be the frozen-in displacements of the soft-mode eigenvector of the high-temperature phase.

Early infrared and neutron-scattering experiments, above T_c, showed that Cochran's ideas indeed predicted the softing of the correct lattice vibrational modes.[4-7] Thus, the "soft-mode" theory seems to be fairly well established.

One might thus conclude that $BaTiO_3$ is well understood. This is certainly not so. It has turned out that, from a lattice-dynamical point of view, it behaves rather strangely and other perovskite materials such as $KTaO_3$ and $SrTiO_3$ behave more understandably.[4-7] Although neither $KaTaO_3$ nor $SrTiO_3$ are actually ferroelectric, they do have zone-center modes that decrease considerably as the temperature is lowered and such decreases agree with the clamped dielectric measurements as proposed by Cochran. Further, $SrTiO_3$ has a soft mode at $k \neq 0$ which causes a nonferroelectric phase transition and the results fit nicely into the soft-mode picture. Perhaps $PbTiO_3$, which has been measured by Raman and neutron techniques, is the cleanest-behaving ferroelectric material.[4-6] The $k=0$ modes are well defined (i.e., underdamped) to T_c and behave according to the selection rules.

In this paper we report right-angle Raman measurements on the overdamped E mode in the ferroelectric phase from room temperature to T_c. We fit this mode to a damped-harmonic-oscillator response and carefully examine background corrections. The fits are excellent. However the temperature dependence of the results is unexpected. These results are compared to other results. Last, it is shown that the $k=0$ optical modes do, indeed, obey the proper selection rules at T_c although there are other broad features that can be observed above and below T_c.

II. MODES

$BaTiO_3$ has a phase transition at $T_c = 135$ °C, where it goes from a cubic high-temperature phase $[Pm3m - (O_h^1)]$ to a ferroelectric tetragonal phase $[P4mm - (C_{4v}^1)]$.[1] There are other phase transitions below 5 °C but these will not be discussed in this paper. Before describing earlier experimental results it is useful to describe how the modes are classified. In the high-temperature phase there are $3n-3 = 12$ optical modes at $k=0$. n is the number of atoms in the unit cell, which in this crystal is 5, or one formula unit per unit cell. These modes transform as the $3T_{1u}+T_{2u}$ irreducible representations of the $m3m$ (O_h) point

group. The T_{2u} is silent (not Raman or infrared active) and even in the ferroelectric phase seems very unimportant (very small oscillator strength), so it will not be mentioned again even when the tetragonal phase is discussed. The $3T_{1u}$ modes are all infrared but not Raman active. The lowest frequency, transverse branch, of these modes is called the soft mode. In the ferroelectric tetragonal phase below T_c each of these T_{1u} modes splits into modes that transform as the A_1+E irreducible representation of the $4mm$ (C_{4v}) point group. Thus, in the tetragonal phase there are $3A_1+3E$ modes and each of these are Raman as well as infrared active. Due to the long-range electrostatic forces, each of these modes splits into a transverse- and longitudinal-optical (TO and LO) mode. Then, depending on the direction of propagation of the mode, the direction of the very-small-k value with respect to its polarization (mechanical separation of charge), one can measure A_1(TO), A_1(LO), E(TO), or E(LO) modes. The A_1 modes are associated with the clamped dielectric constant along the ferroelectric c axis, ϵ_c, while the E modes are associated with ϵ_a, the clamped dielectric constant perpendicular to the c axis.

III. PREVIOUS WORK

The experimental results on $BaTiO_3$ seem to have followed a rather tortuous path. Since in this paper we present some results for the temperature dependence of the lowest TO modes in the tetragonal phase we mention some of the previous experimental results.

The early experimental infrared[10-12] work reported results on the high-temperature phase and the E modes below T_c. All the results showed that the lowest E(TO) and T_{1u}(TO) modes were overdamped and accounted for a very large ϵ_a (via the Lyddane-Sach-Teller relationship[1-8]). The A_1 modes were not measured. The mode assignments in the early[13,14] Raman work were in agreement except for the lowest E(TO) mode. For this mode they did not agree with each other or with the infrared measurements.[10-12] However, later Raman work[15] showed an overdamped E(TO) in agreement with the infrared measurements. A still later Raman paper[16] gave the other E modes in agreement with the work in Refs. 13 and 14 but A_1 modes in disagreement with the work in these references. A comparison could not be made with infrared results because such measurements on the A_1 modes had not been made. Pinczuk *et al.*[17] have cleared up the A_1 mode problem by using polariton techniques at room temperature. Their results are in good agreement with the earlier work.[13,14] The A_1 results in $BaTiO_3$ were also checked by using the powder Raman technique and by looking at the system[18] $Pb_{1-x}Ba_xTiO_3$ for $0 \leq x \leq 1$. These results[18] agree nicely with the polariton results of Pinczuk *et al.*[17]

From neutron diffraction[19,20] one finds that for certain directions of k and certain polarizations the modes are well defined except at $k \approx 0$, while for other directions and polarizations the modes are very low in energy and highly damped throughout the Brillouin zone. Thus, the lowest transverse-optical branch is very anisotropic and highly damped.

Somewhat surprising results were found when the temperature dependence of the A_1 modes were measured in the tetragonal phase.[21] First, throughout the entire tetragonal phase, most of the contribution to ϵ_c comes not from the lowest A_1 mode but from the next-highest A_1 mode. Second, the value of ϵ_c determined from the modes is considerably lower than the clamped value measured by capacitance techniques.[22] Further, the ratio of the ϵ_c values determined by these two methods, which is 2.4 at room temperature, increases to 5.0 at 100 °C where the capacitance measurements were terminated. So this disagreement has a large temperature dependence.

IV. RESULTS-E(TO) MODE

Figure 1 shows the experimental results for the lowest overdamped E(TO) in $BaTiO_3$ at two temperatures. This mode is quite strong and our results are in agreement with the several results reported much earlier by infrared[10-12] and Raman techniques.[15,16,23] The sample was obtained from Sanders Corp. and has a $T_c = 135$ °C, but as pre-

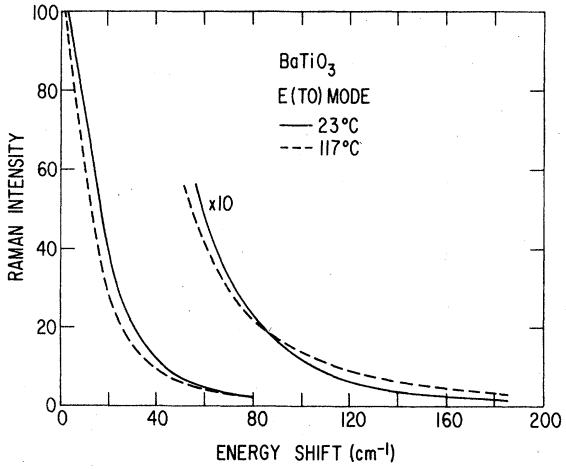

FIG. 1. Experimental Raman results for the lowest E(TO) mode in $BaTiO_3$ at two temperatures. The results are normalized to 100 at 2 cm^{-1}.

viously noted,[18] the same results are obtained from "butterfly" crystals except that for these $T_c = 120$ °C. Note that in Fig. 1, when the data is normalized to 100 at 2 cm^{-1}, the higher-temperature results are narrower for $\omega < 80$ cm^{-1} but extend out further at larger ω. From this observation one immediately knows that at higher temperatures the ratio of the damping to harmonic frequency will increase.

To fit the data the rather standard approach of a damped harmonic oscillator was used. With the use of a velocity-dependent damped harmonic oscillator the Raman-Stokes response I is simply[16]

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = E\,, \tag{1a}$$

$$I = A(1+n)(\omega\gamma)\omega_0^2/[(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2]\,, \tag{1b}$$

where ω_0 is the undamped harmonic frequency, γ is the damping constant, A is a frequency-independent constant, n is the Bose-Einstein factor $(e^{\hbar\omega/kT} - 1)^{-1}$, and the other symbols have their usual meaning.

The experimental data were fit using a least-squares criterion and Eq. (1b) to obtain ω_0 and γ at each temperature. The results are shown in Fig. 2 (where $\frac{1}{3}\gamma$ is plotted so that it can be conveniently shown on the same scale as ω_0). The fits to the experimental data are so good that, on the scale shown in Fig. 1, no difference between experiment and the fit would be seen. There is really no room for a frequency-dependent γ,[24] as has been pointed out previously.[25]

The results shown in Fig. 2 are unexpected, first because ω_0 increases right up to T_c while one expects it to decrease, and second because γ increases rather rapidly. The latter has also been observed[26] in $PbTiO_3$. In fitting overdamped modes considerable care should be used because such modes are rather easy to fit with many different functional forms.[27] All we can say is that the form in Eq. (1) is the usual one used in this field and we claim no deeper justification. However, one can check the importance of various experimental backgrounds that might be expected to cause ω_0 and γ to vary.

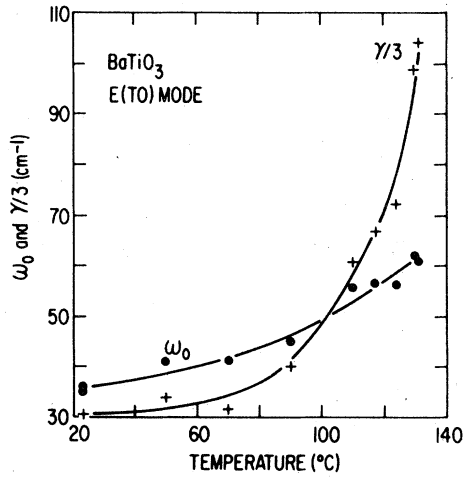

FIG. 2. Temperature dependence of ω_0 and γ obtained by fitting the experimental data. γ has been divided by 3 so that only one scale need be used.

TABLE I. Results obtained by fitting the room-temperature experimental data with various corrections.

Data and correction	ω_0 (cm^{-1})	γ (cm^{-1})
(a) Data	35.39	94.24
(b) Data +0.5	38.44	109.12
(c) Data +1.0	44.74	137.76
(d) Data +1.5	58.17	234.07
(e) Data +2.0	87.92	513.39
(f) Data $-(1-\frac{1}{20}\omega)$	35.48	94.30
(g) Data $-(5-\frac{5}{20}\omega)$	35.83	94.25
(h) Data $+(\frac{1}{200}\omega)$	35.39	94.24

Table I is a compilation of various additions or subtractions to the data that one might expect. However, before we discuss these results we should point out that changing the least squares to a least fourth power or several other criteria made very little difference on ω_0 and γ. Similar conclusions were reached if less of the experimental data was used. For example, using 78 data points to $\omega = 392$ cm^{-1} or 31 data points to 57 cm^{-1} caused changes in ω_0 of only 0.3% and in γ of only 1%. We finally used the data to 200 cm^{-1} which contained 58 data points and is normalized to 100 at 2 cm^{-1}. The results in Table I are all for 23 °C but similar results were found at the other temperatures. (a) The "raw" data were used. In (b)–(e) 0.5–2.0 is added to each data point. These additions are what would result if the base line were actually lower than we think it is. As can be seen the effects can be quite large for a 2% addition. However, we think that a 2% addition is well outside our understanding of the experimental data. (f) and (g) represent much more likely corrections that would be due to a background of elastic laser scattering. In (g) the correction is 4.5% at $\omega = 2$ cm^{-1}, going to zero at $\omega = 20$ cm^{-1}. We think that this is larger than we should substract and yet, as can be seen in Table I, the changes in ω_0 and γ are quite small. This is a very encouraging result. (h) is an attempt to model the overall spectrometer response, since the throughput decreases at longer wavelength. Again we are encouraged by the result.

In summary, a correction for elastic laser

scattering and overall spectrometer response affect ω_0 and γ only by small amounts. The results in Fig. 2 are from just the raw data without any corrections. We can not claim any high accuracy for these results. All we can say is that from right-angle Raman scattering one obtains data as shown in Fig. 1, and least-squares fits to such data, with no other conditions placed on the results, will give values of ω_0 and γ shown in Fig. 2.

V. RESULTS-A_1(TO)

We have already reported, in a brief but fairly complete paper,[21] the temperature dependence of the A_1 modes to T_c. Here we would like to emphasize these same results and show by means of Fig. 3 what could not be shown in that brief paper.[21]

The lowest A_1(TO) mode at room temperature occurs at about[17] 170 cm^{-1} and is very weak in right-angle Raman measurements. However, it gets considerably stronger in forward scattering measurements.[17] The next two higher A_1 modes occur at about 270 and 520 cm^{-1} right on top of other broad lines. However, in forward scattering these A_1(TO) modes can be moved to lower energy leaving these broad lines behind. The top spectrum of Fig. 3 shows this polariton result at near forward scattering and Ref. 21 or 17 can be consulted for details. The arrows point to the $3A_1$(TO) modes. As can be seen the lowest mode now has considerable intensity and the next two modes are moved away from the broad background lines. By varying θ, it is rather easy to see that, indeed, there are $3A_1$(TO) modes as well as two broad background modes. At T_c these $3A_1$(TO) modes *abruptly disappear and the two broad background features remain* as shown in the bottom of Fig. 3. There has been considerable discussion about these broad features[28,29] and we can add nothing new here.

We would like to discuss related work on the A_1 phonons in $BaTiO_3$. Chaves *et al.*[30] and Scalabrin *et al.*[31] have measured the A_1(TO) modes in $BaTiO_3$ by right-angle scattering and fit their data using, in addition to the frequencies and damping constants of the modes, coupling coefficients between the modes. Their calculations, using real coupling coefficients as opposed to imaginary coupling terms, which they conclude are much smaller,[30] yield frequencies of the modes which are not at all close to peaks in the Raman spactra. This result, which seems rather unphysical to us, occurs because of the very large mode-mode coupling coefficients. However, we believe a very serious experimental problem, not properly taken into account by these authors,[30,31] is that, by using only right-angle scattering geometry the broad modes, that remain above T_c, as well as the $3A_1$(TO) are being measured together. One really should use polariton techniques to separate these features.

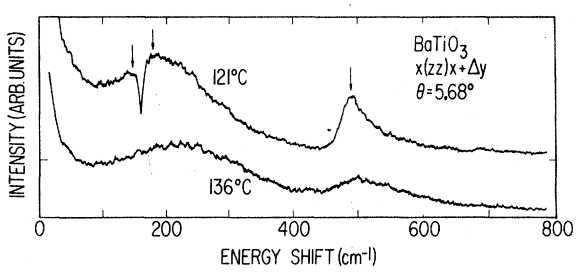

FIG. 3. Experimental near forward scattering in $BaTiO_3$ above and below T_c. The top figure shows the A_1(TO) modes while only the broad features are observed above T_c as can be seen in the bottom figure.

Thus, in summary, we emphasize that the $3A_1$ modes obey the appropriate selection rules and that there are other broadbands that can be seen both below and above T_c. The E modes also abruptly disappear at T_c. Thus, the appropriate selection rules are, indeed, obeyed in $BaTiO_3$. These broad features appear only for[18] $x = 0.9$ and $x = 1.0$ in the $Pb_{1-x}Ba_xTiO_3$ system, and thus seem to be only related to $BaTiO_3$.

VI. DISCUSSION

The object of this paper is to give the results for ω_0 and γ as a function of temperature for the lowest overdamped E(TO) in the tetragonal phase of $BaTiO_3$. These results, obtained by fitting the right-angle Raman spectra, are shown in Fig. 2. ω_0 increases right up to T_c which is surprising in terms of the soft-mode theory. Further, γ increases sharply as T_c is approached. However, it is troublesome, at least to the authors, to draw strong conclusions from rather small changes in a line shape. After all, to a first approximation the E_1(TO) modes appear to have about the same shape at all temperatures (Fig. 1). On the other hand, we certainly can emphasize that the 12 zone-center optical modes (A_1 and E) in the tetragonal phase, disappear abruptly at T_c in accordance with the selection rules and are not observed in the cubic phase. (However, other wide lines persist into the cubic phase.)

We can compare our results with several others that have been published. DiDomenico *et al.*[16] have measured this E_1(TO) mode at 10, 30, and 60 °C. They find that the intensity of the entire feature decreases very rapidly with temperature, a result in sharp disagreement with our results. We find very little decrease with temperature.[18]

Their three values of ω_0 increase faster with temperature (50 cm^{-1} at 60 °C) than those shown in Fig. 2. Their γ increases faster (140 cm^{-1} at 60 °C). The reasons for these differences are not known.

Lazay and Fleury[23] give values of ω_0 and γ for this E(TO) mode to 117 °C. However, their values of ω_0 are taken to agree (via the Lyddane-Sachs-Teller relation) with the value of the damped dielectric constant along the a axis (ϵ_a) measured by Wemple *et al.*[22] Thus, their values should not be compared with those shown in Fig. 2. However, their highest value of ω_0 (= 45 cm^{-1} at 117 °C) is somewhat smaller than that shown in Fig. 2 which is really another way of saying that the values of ω_0 shown in Fig. 2 give values of ϵ_a, somewhat smaller than those of Wemple *et al.*[22] The more interesting point is that experimental values of ϵ_a,[22] at least to 126 °C, decrease as T_c is approached from below and show no sign of increasing. Unfortunately results between 126 °C and T_c are not determined.[22] However, we should note that these results for ϵ_a,[22] are in complete agreement with those of Fig. 2 where we find that ω_0 *increases* right up to T_c, which, via the Lyddane-Sachs-Teller relation, means that ϵ_a will *decrease* right up to T_c. This, however, is not what conventional wisdom would say.

Lastly, the results in Fig. 2 can be compared with much more sophisticated measurements of ω_0 and γ. These are the measurements of Nakamura and colaborators[32,33] and Heiman and Ushioda[34] who use polariton techniques (forward Raman scattering) to reduce the effective linewidth of the overdamped E(TO) mode. Using this technique one may obtain experimental curves that do not fall monotonically as ω is increased (from the laser line), as in Fig. 1, but that show a peak at a small value of ω.[32,33] Background effects, such as those discussed with reference to Table I, play no important role in fitting lines with a peak for $\omega > 0$. Thus, ω_0 and γ determined from these types of polariton experiments[32,33] should be more certain than values determined from overdamped modes measured by right-angle Raman scattering. Unfortunately the peak from this mode occurs at very low values of ω (below 10 cm^{-1}) which makes observations difficult. Nevertheless, Tominaga and Nakamura[33] report values of ϵ_a, ω_0, and γ from 6 to 40 °C. ϵ_a is separately determined in this experiment and is needed to deconvolute the experimental line shape so that ω_0 and γ may be determined. Their results[32] for ω_0 to 40 °C increase faster (ω_0 = 43 cm^{-1} at 40 °C) than those shown in Fig. 2. Their values of γ are larger than those shown in Fig. 2 (γ = 126 cm^{-1} at 40 °C) but increase with temperatures at about the same rate. Since the experimental approach is so different from that reported here it is difficult to guess why these small differences occur. It certainly would be nice if these polariton techniques could be extended to T_c.

As can be seen, all of the experimental results show that both ω_0 and γ increase as the temperature increases from room temperature. However, we find that this increase continues up to T_c.

VII. CONCLUSIONS

We can only conclude from the results shown in Fig. 2 that the harmonic frequency of the "soft" E(TO) in $BaTiO_3$ in the tetragonal phase *increases* right up to T_c. This implies that ϵ_a *decreases* right up to T_c, which agrees with other capacitance measurements[22] to $T = T_c - 9$ °C. We also know that at room temperature[17] it is not the lowest A_1(TO) mode that has the largest dielectric strength but rather the next-higher A_1(TO) mode and that this situation persists right up to T_c.[21] Also, there is a large discrepancy between ϵ_c obtained from the A_1 modes and ϵ_c measured by capacitance techniques.[21,35] Further we know from the $Pb_{1-x}Ba_xTiO_3$ system[18] this E(TO) mode is overdamped only for $x = 0.9$ to 1 which is the same region where the broadbands appear that occur below[28,29] and above T_c. Thus, $BaTiO_3$ indeed behaves rather strangely, at least in the tetragonal phase. On the other hand the A_1 and E modes do obey the proper selection rules and disappear abruptly above T_c, and reappear as the temperature is lowered below T_c.

VIII. SUPPLEMENTARY COMMENT

Recently a paper by Scalabrin *et al.*[36] came to our attention. In this paper the lowest E(TO) mode was measured to 121 °C using the same approach as in this paper. Their results, for ω_0 and γ, look quite similar to our results to 121 °C although their ω_0 does not rise quite as steeply between 100 and 121 °C as the solid line shown here in Fig. 2. However, our data above 121 °C indicates that both ω_0 and γ continue to increase to T_c. Nevertheless, the agreement to 121 °C is encouraging.

It is also interesting to note that Scalabrin *et al.*[36] apparently find no decrease in intensity of this E(TO) mode as the temperature is increased in agreement with what we find and contrary to an early publication.[16]

Also in this paper[36] the temperature dependence of the A_1(TO) modes are shown but these results appear to be the same as those reported earlier[31] and we have already commented on these results

in Sec. V. Scalabrin *et al.*[36] also note the large difference between the measured clamped dielectric constant along the c axis and what is calculated from the modes. We have previously reported and commented on this effect.[21,35,37]

We would also like to comment on another recent paper by Scalabrin *et al.*,[38] where an anomalous temperature dependence of the linewidth of the A_1(TO) 270-cm^{-1} mode is reported. As discussed in Sec. V, we believe there is a serious experimental problem when right-angle scattering geometry is used. What is being measured are two lines and polariton techniques should be used to separate these two modes.

[1]F. Jona and G. Shirane, *Ferroelectric Crystals* (MacMillan, New York, 1962).

[2]E. Fattuzzo and W. J. Merz, *Ferroelectricity* (Wiley, New York, 1967).

[3]W. Kaenzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 4, pp. 1–197.

[4]R. A. Cowley, Philos, Mag. 11, 673 (1965).

[5]See, *Structural Phase Transitions and Soft Modes*, edited by E. J. Samuelson, E. Anderson, and J. Feder (Universitetsforlaget, Oslo, 1971).

[6]R. Blinc, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).

[7]G. Shrane, Rev. Mod. Phys. 46, 437 (1974).

[8]W. Cochran, Phys. Rev. Lett. 3, 412 (1959); Adv. Phys. 9, 387 (1960); 10, 401 (1961).

[9]P. C. Kwok and P. B. Miller, Phys. Rev. 151, 387 (1966); P. B. Miller and P. C. Kwok, Solid State Commun. 5, 57 (1967); W. Cochran and A. Zia, Phys. Status Solidi 25, 273 (1968).

[10]W. G. Spitzer, R. C Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. 126, 1710 (1962).

[11]T. M. Ballantyne, Phys. Rev. 136, A429 (1964).

[12]A. S. Barker, Jr., Phys. Rev. 145, 931 (1966).

[13]J. L. Parsons and L. Rimai, Solid State Commun. 5, 423 (1967); L. Rimai, J. L. Parsons, J. T. Hickmott, and T. Nakamura, Phys. Rev. 168, 623 (1968).

[14]A. Pinczuk, W. T. Taylor, E. Burstein, and I. Lefkowitz, Solid State Commun. 5, 429 (1967).

[15]M. DiDomenico, Jr., S. P. S. Porto, and S. H. Wemple, Phys. Rev. Lett. 19, 855 (1967).

[16]M. Di Domenico, Jr., S. H. Wemple, S. P. S. Porto, and R. P. Bauman, Phys. Rev. 174, 522 (1968).

[17]A. Pinczuk, E. Burstein, and S. Ushioda, Solid State Commun. 1, 139 (1969).

[18]G. Burns and B. A. Scott, Solid State Commun. 9, 813 (1971); G. Burns, Phys. Rev. B 10, 1951 (1974).

[19]G. Shirane, J. D. Axe, and J. Harada, Phys. Rev. B 2, 3651 (1970).

[20]J. Harada, J. D. Axe, and G. Shirane, Phys. Rev. B 4, 155 (1971).

[21]G. Burns, Phys. Lett. A 43, 271 (1973); G. Burns and B. A. Scott, Solid State Commun. 13, 417 (1973).

[22]S. H. Wemple, M. DiDomenico, Jr., and I. Camlible, J. Phys. Chem. Solids 29, 1797 (1968); I. Camlible, M. DiDomenico, and S. H. Wemple, J. Phys. Chem. Solids 31, 1417 (1970).

[23]P. A. Fleury and P. D. Lazay, Phys. Rev. Lett. 26, 1331 (1971); P. D. Lazay and P. A. Fleury, in *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971), p. 406.

[24]D. Heiman, S. Ushioda, and J. P. Remeika, Phys. Rev. Lett. 34, 886 (1975).

[25]G. Burns, Phys. Rev. Lett. 37, 229 (1976).

[26]G. Burns and B. A. Scott, Phys. Rev. B 7, 3088 (1973); G. Burns and B. A. Scott, Phys. Rev. Lett. 25, 162 (1970).

[27]B. D. Silverman, Phys. Rev. B 9, 203 (1974).

[28]M. P. Fontana and M. Lambert, Solid State Commun. 10, 1 (1972); A. M. Quittet and M. Lambert, *ibid.* 12, 1053 (1973).

[29]G. A. Barbosa, A. Chaves, and S. P. S. Porto, Solid State Commun. 11, 1053 (1972).

[30]A. Chaves, R. S. Katiyar, and S. P. S. Porto, Phys. Rev. B 10, 3552 (1974).

[31]A. Scalabrin, S. P. S. Porto, and A. S. Chavas, in *Light Scattering in Solids*, edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), p. 861.

[32]L. Loughman, L. W. Davis, and T. Nakamura, Phys. Rev. B 6, 3322 (1972).

[33]Y. Tominaga and T. Nakamura, J. Phys. Soc. Jpn. 39, 746 (1975).

[34]D. Heiman and S. Ushioda, Phys. Rev. B 9, 2122 (1974).

[35]G. Burns and E. Burstein, Ferroelectrics 7, 297 (1974).

[36]A. Scalabrin, A. S. Chaves, D. S. Shim, and S. P. S. Porto, Phys. Status Solidi B 79, 731 (1977).

[37]G. Burns, Phys. Rev. B 13, 215 (1976).

[38]A. Scalabrin, S. P. S. Porto, H. Vargas, C. A. S. Lima, and L. C. M. Miranda, Solid State Commun. 24, 291 (1977).