Soft-mode spectroscopy in cubic BaTiO$_3$ by hyper-Raman scattering

H. Vogt and J. A. Sanjurjo*

*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80,
Federal Republic of Germany*

G. Rossbroich[†]

*II. Physikalisches Institut der Universität Köln, Zülpicher Strasse 77, 5000 Köln 41,
Federal Republic of Germany*

(Received 19 July 1982)

Hyper-Raman scattering from cubic BaTiO$_3$ is studied to clarify the controversies about the low-frequency dielectric response in this material. Applying the fluctuation-dissipation theorem, we obtain the imaginary part $\epsilon''(\Omega)$ of the dielectric function in the wave-number range from 3 to 150 cm^{-1}. $\epsilon''(\Omega)$ can be adequately described by a classical single-oscillator dispersion formula. In approaching the Curie temperature, we find a continuous decrease of the mode frequency Ω_0. The relative damping constant γ/Ω_0 exceeds 2, so that the mode may be referred to as intermediate between oscillator and relaxator. Because of the high damping $\epsilon''(\Omega)$ can be formally written as the sum of two overdamped oscillator contributions. This would lead to the concept of a soft-mode saturation and an extra dispersion mechanism as has been recently inferred from the far-infrared reflectivity spectrum. However, we do not find any evidence for this mode splitting and, so far, regard it as artificial.

I. INTRODUCTION

Although BaTiO$_3$ is a classical, most extensively studied ferroelectric, the soft-mode spectroscopy in this material has remained a challenging and still unsettled problem. The soft phonons at the center of the Brillouin zone are overdamped and moreover sandwiched between acoustic modes and an intense elastic peak. Hence their frequencies and damping constants are difficult to determine by neutron scattering.[1] On the other hand, the far-infrared reflectivity is very high and displays unusually broad bands, so that the Kramers-Kronig analysis yields mode parameters with a limited degree of precision.[2,3] Therefore, interest has been focused on the A_1 and E modes of the tetragonal phase, which, in contrast to the F_{1u} modes of the cubic phase, are also Raman active and hence can be studied rather accurately.[4-6]

Apart from the interpretation of two broad bands at 270 and 520 cm^{-1} in the A_1-mode spectra, general agreement has been achieved about the Raman data.[7] Nevertheless, a debate is still going on concerning the contribution of the optic phonons to the static dielectric constant $\epsilon(0)$. Many authors (see, for instance, Ref. 5 and other references therein) have found considerable discrepancies between the "clamped" version of $\epsilon(0)$ directly measured by

capacitance technique and the value $\epsilon^{LST}(0)$ calculated from the transverse- and longitudinal-optical-mode frequencies according to the Lyddane-Sachs-Teller (LST) relation. In order to explain these discrepancies an additional very-low-frequency pole in the dielectric function has been assumed resulting either from impurities[8] or an intrinsic disorder mechanism.[9]

In measuring the permittivity ϵ_c along the polar axis in the microwave region, Turik and Shevchenko[10] detected several relaxator-type contributions. Their results, however, are contradicted by those of Clemens et al.[11] who did not find any indication of the invoked extra dispersion mechanism in the frequency range up to 8 GHz. Recently, Tominaga et al.[12] measured the hypersonic dispersion in BaTiO$_3$ at room temperature and obtained the permittivity ϵ_a perpendicular to the polar axis in the 10-GHz region from the piezoelectric coupling between acoustic and optical phonons. Their values are still well above $\epsilon_a^{LST}(0)$, although an extra dispersion step between 10 GHz and the optical-phonon region seems rather unlikely. Thus the meaning of $\epsilon^{LST}(0)$ derived from the Raman data of the tetragonal phase has persisted as a somewhat open question.

A similar problem is encountered in the cubic phase above the Curie temperature T_C of about 403

K. In his interpretation of the far-infrared reflectivity spectrum Barker[13] concluded that the lowest-frequency F_{1u} mode shifts with temperature according to Cochran's theory of lattice instability and fully accounts for the Curie-Weiss law of $\epsilon(0)$. Luspin *et al.*,[14] however, observed a pronounced deviation from this behavior in a temperature interval of about 100° above T_C. From their improved reflectivity measurements these authors inferred that the frequency of the soft F_{1u} mode does not decrease continuously in approaching T_C, but stabilizes at about 60 cm^{-1} and merges into the frequency of the overdamped E mode of the tetragonal phase. In order to reconcile this result with the Curie-Weiss law of $\epsilon(0)$ the Ti ions have been assumed to fluctuate between the minima of a multiwell potential giving rise to an additional Debye-type contribution to the dielectric function.[15]

In this paper we utilize hyper-Raman (HR) scattering[16] as an independent experimental technique to help in clarifying the controversies about the cubic phase. The HR effect is a three-photon process by which two photons of the exciting light are simultaneously annihilated to give rise to one scattered photon. The parity selection rules are the same as those of one-photon infrared absorption and hence allow the observation of the Raman forbidden soft F_{1u} mode. The corresponding HR line appears in the spectral neighborhood of the second harmonic $2\omega_L$ of the incident laser radiation. As the cubic phase of BaTiO₃ is centrosymmetric, the elastic line at $2\omega_L$ is expected to be rather weak so that the mode softening can be studied down to very small HR shifts.

During the course of this work, Inoue and Asai[17] published HR spectra of cubic BaTiO₃ at three different temperatures. However, they did not study the frequency range below 10 cm^{-1} where the most important changes with temperature occur. Therefore, they have not been able to deduce the parameters of the soft mode and concluded that it might not exist.

The HR data presented here, cover the frequency and temperature range 3–150 cm^{-1} and 400–700 K, respectively. Applying the fluctuation-dissipation theorem we deduce the imaginary part $\epsilon''(\Omega)$ of the dielectric function from our HR spectra. Values of the mode frequency Ω_0 and the damping constant γ are obtained by fitting a classical single-oscillator dispersion formula to $\epsilon''(\Omega)$. Our results do not reveal a saturation of Ω_0, but show a continuous decrease when T_C is approached from above. The soft mode turns out to be always highly overdamped, so that, apart from its high-frequency tail, the dielectric function can be approximated by a Debye formula with $\tau = \gamma/\Omega_0^2$. We compare our results with the far-infrared reflectivity spectrum[13,14] and discuss the problem of the extra dispersion step. Particular attention is paid to ambiguities appearing in the description of the dielectric response by a classical dispersion formula with $\gamma/\Omega_0 > 2$.

In a forthcoming paper[18] our analysis will be complemented by a study of coherent second-harmonic generation (SHG) in cubic BaTiO₃. We shall show that this effect is compatible with inversion symmetry and does not arise from macroscopic remnants of the tetragonal phase. The responsible nonlinear source term in Maxwell's equations involves the spatial gradient of the electric field of the incident radiation, so that the observed SHG may be referred to as a spatial dispersion phenomenon. In discussing its microscopic origin we shall consider the influence of impurities as well as structural disorder.

II. EXPERIMENTAL DETAILS

The source of the exciting radiation was an acousto-optically Q-switched Nd-YAG laser ($\lambda_L = 1.06\ \mu$m) with a peak power of about 10 kW and a pulse repetition rate of 5 kHz. Details of our HR spectrometer have been described elsewhere.[19]

Measurements were performed on single crystals of BaTiO₃ received from two different sources.[20,21] They all were grown from the melt by a top-seeded solution method. After polishing, some of the samples were etched in hot phosphoric acid in order to remove preparation-induced surface layers[22] which could have given rise to spurious SHG and thus to an enhanced elastic peak at $2\omega_L$.

The sample temperature was kept constant within ±0.5 K. In order to estimate the influence of laser heating the sharp drop in SHG intensity at the phase transition was monitored for several laser powers differing by orders of magnitude. Within the uncertainty of T_C due to hysteresis effects we found this drop to occur at the same temperature. Thus significant changes of sample temperature by laser heating could be excluded.

HR scattering was observed in the backscattering configuration $X(YY)\bar{X}$, the directions X and Y approximately coinciding with cubic axes. In order to evaluate the instrumental background arising from the elastic peak at $2\omega_L$, we carefully measured the instrumental profile of the double monochromator as function of slit width. For this purpose we used the unbroadened second-harmonic light generated

in a LiIO₃ crystal under phase-matching conditions. In deducing the soft-mode parameters we discarded all data appreciably affected by the elastic peak. Our samples turned out to differ in the intensity at $2\omega_L$ and hence in the degree to which the low-frequency end of the HR spectrum was obscured. Only one sample (Sanders Association) permitted us to observe the inelastic HR scattering down to a wave-number shift of about 3 cm^{-1} at all temperatures.

The spectral slit width $\Delta\omega$ was 1.2 cm^{-1} in the region below 20 cm^{-1}. Too much time was consumed in taking the whole spectrum with this resolution. Therefore, we opened the spectrometer slits at higher wave numbers and properly adjusted the intensity scale. Even for $\Delta\omega = 7$ cm^{-1} the soft-mode HR signal dropped to 0.2 photon counts per second at 150 cm^{-1}.

III. RESULTS

Figure 1 presents the low-frequency HR spectrum of BaTiO₃ for various temperatures above T_C. The wave-number scale below 20 cm^{-1} has been expanded to show the significant changes with temperature which just occur in this region. All data refer to nearly the same laser power.

The fluctuation-dissipation theorem provides a relation between the spectral efficiency $S(\omega)$ for HR scattering at frequency $\omega = 2\omega_L - \Omega$ and the far-infrared dielectric function $\epsilon(\Omega)$.[23] We have
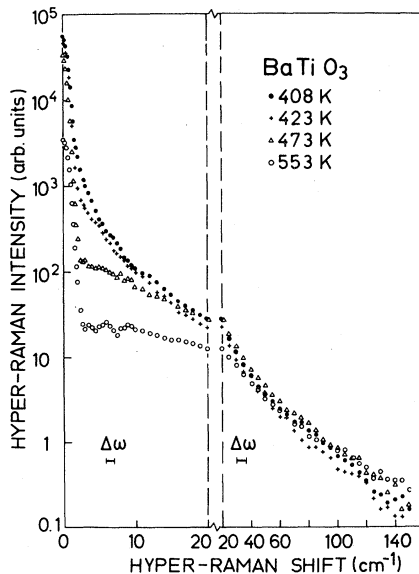

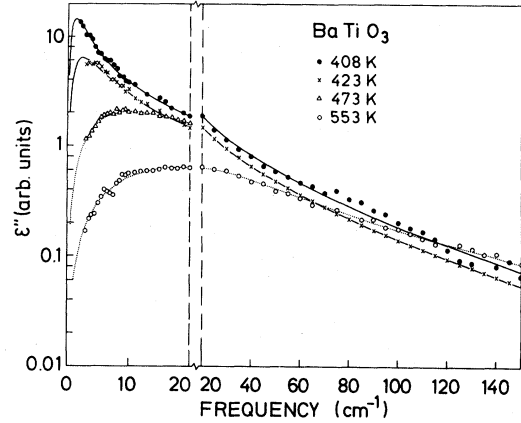FIG. 1. Hyper-Raman spectrum of cubic BaTiO₃ in the soft-mode region.

FIG. 2. Imaginary part of the dielectric function as deduced from the HR spectrum. The full and dotted curves present classical dispersion oscillator fits.

$$S(2\omega_L - \Omega) = A_{YY}[n(\Omega) + 1]\epsilon''(\Omega) , \qquad (1)$$

where $n(\Omega)$ is the Bose-Einstein population factor and $\epsilon''(\Omega)$ the imaginary part of $\epsilon(\Omega)$. A_{YY} contains the HR polarizability as well as the effective charge and is regarded as independent of Ω. In Fig. 2 we have plotted $\epsilon''(\Omega)$ as obtained by applying Eq. (1) to our HR data. At all temperatures $\epsilon''(\Omega)$ can be adequately described by a classical dispersion formula, i.e.,

$$\epsilon''(\Omega) = \frac{4\pi\rho\Omega_0^2\gamma\Omega}{(\Omega_0^2 - \Omega^2)^2 + \gamma^2\Omega^2} , \qquad (2)$$

where Ω_0, γ, and $4\pi\rho$ are the frequency, damping constant, and oscillator strength of the soft mode, respectively. We have fitted Eq. (2) to the experimental points by minimizing the mean square of the relative deviations. The fitting procedure converges unambiguously to a single set of the three parameters Ω_0, γ, and $4\pi A_{YY}\rho$, the situation being almost the same as in the case of the overdamped E mode in the tetragonal phase.[5,6] The quality of our fits is demonstrated by the full and dotted curves in Fig. 2. The values of Ω_0 and γ/Ω_0 obtained in this way are shown in Fig. 3 for 12 temperatures between T_C and 700 K. Our results are rather close to those of Barker[13] but differ considerably from the more recent ones of Luspin et al.[14] inasmuch as no saturation, but a continuous softening of Ω_0 is observed. The relative damping constant γ/Ω_0 always exceeds 2 and, owing to the decrease of Ω_0, becomes very high near T_C.

As shown in Fig. 4, $\epsilon''(\Omega)$ can be roughly approximated by a Debye formula with $\tau = \gamma/\Omega_0^2$, i.e.,
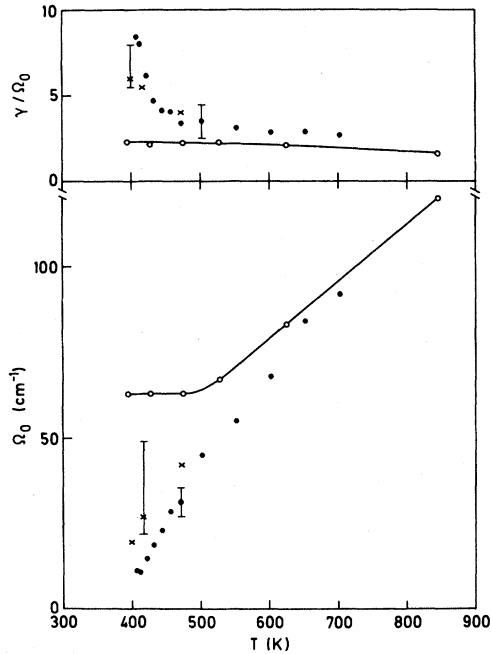
FIG. 3. Frequency and relative damping of the soft mode in BaTiO₃. Open circles: Ref. 14; crosses: Ref. 13; closed circles: this work.

FIG. 4. Comparison between an overdamped oscillator and a Debye relaxator description of the soft mode.

$$\epsilon''(\Omega) \simeq \frac{4\pi\rho\Omega_0^2\gamma\Omega}{\Omega_0^4 + \gamma^2\Omega^2} \ . \tag{3}$$

The relaxator model, however, fails in describing the high-frequency tail of $\epsilon''(\Omega)$, so that Ω_0 and γ have to be considered as independent fitting parameters. On the other hand, the combination γ/Ω_0^2 appears to be determined with a higher degree of accuracy than either γ or Ω_0.

IV. DISCUSSION

We shall focus our discussion on two problems: (a) the compatibility between our results and the far-infrared reflectivity and (b) the relation between the mode softening, as revealed by our measurements, and the Curie-Weiss law for $\epsilon(0)$.

In Fig. 5 we compare the shapes of $\epsilon''(\Omega)$ determined experimentally at 473 K as well as calculated from Eq. (2) for three sets of parameters Ω_0 and γ. The curves are normalized to reach the same maximum value. The mode parameters quoted by Luspin et al.[14] ($\Omega_0 = 63$ cm⁻¹, $\gamma = 138$ cm⁻¹) cannot be reconciled with our experimental data even if $\epsilon''(\Omega)$ is not calculated from Eq. (2), but from the factorized form of the dielectric function used by these authors. On the other hand, Barker's[13] parameters
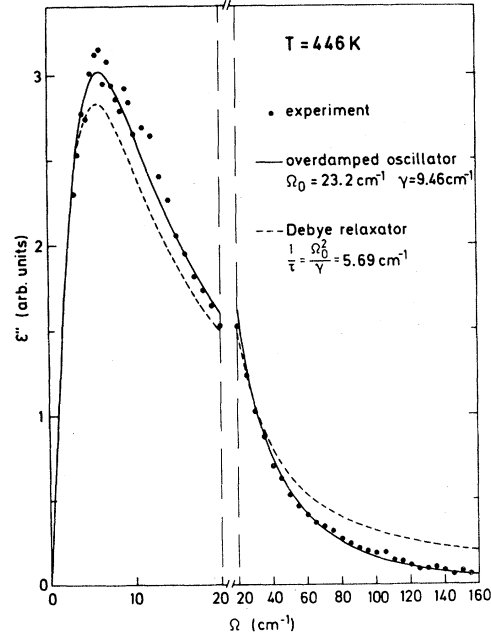
($\Omega_0 = 42$ cm⁻¹, $\gamma = 168$ cm⁻¹) are much more compatible with ours and lead to disagreement only on the high-frequency side. In addition, they give a rough idea of the accuracy by which Ω_0 and γ can be determined by our method. We estimate the errors in Ω_0 and γ to be $\pm15\%$ and $\pm30\%$, respectively.

Figure 5 also presents the far-infrared reflectivity spectrum $R(\Omega)$ at about 473 K for Ω below 150 cm⁻¹. The experimental data have been taken from Ref. 14 (closed circles) as well as Ref. 23 (open circles) on which Barker[13] has based his analysis. As $R(\Omega)$ is rather high and structureless, it is quite insensitive to Ω_0 and γ, certainly more than the HR line shape. We have calculated $R(\Omega)$ from a classical single-oscillator dispersion formula varying only $4\pi\rho$ and using the values of Ω_0 and γ obtained from the HR spectrum. Taking into account the contribution of the two other dispersion oscillators to $\epsilon(0)$, we have assumed $\epsilon(\infty) = 8$, where $\epsilon(\infty)$ indicates the level of the real part of $\epsilon(\Omega)$ on which the soft-mode dispersion is superimposed. For $\epsilon(0) = 1250$ we achieve reasonable agreement with the experimental data. Direct capacitance measurements of $\epsilon(0)$, however, yield values around 1900 (Refs. 24 and 25), which should give rise to an increased reflectivity $R(\Omega)$ as shown by the full curve. At this point we have to consider surface effects lowering $R(\Omega)$. Moreover, we must stress
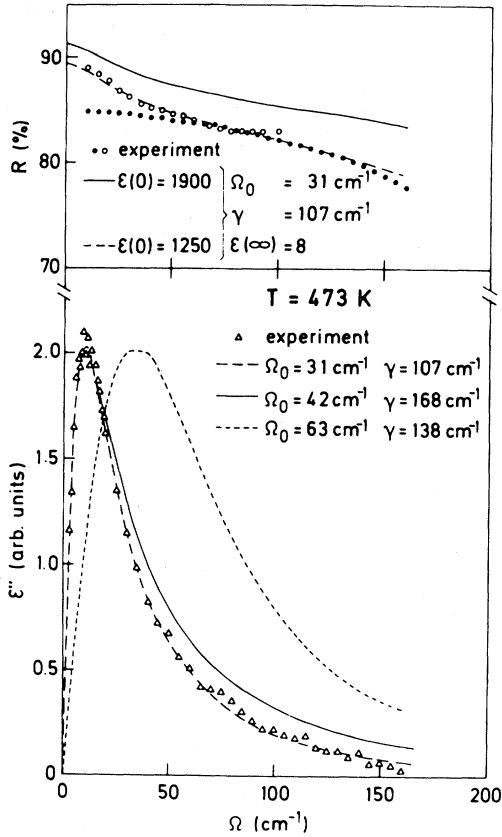
FIG. 5. Lower half: The imaginary part of the dielectric function as measured experimentally and as calculated for three sets of parameters Ω_0 and γ; short dashes: Ref. 14; solid line: Ref. 13; long dashes and triangles: this work. Upper half: The far-infrared reflectivity in the soft-mode region. Closed circles: Ref. 14; empty circles: Ref. 23. The two curves present $R(\Omega)$ as calculated from a classical dispersion formula with the parameters indicated in the figure.

that the infrared studies have been performed on flux-grown crystals with $T_C \simeq 395$ K, whereas our HR data and the cited capacitance measurements refer to melt-grown samples with $T_C \simeq 403$ K. In view of such a large difference in T_C, the discrepancy in $\epsilon(0)$ is to be expected and can by no means be interpreted as evidence of an extra dispersion mechanism below the spectral region under study. We should note that higher values of T_C and $\epsilon(0)$ indicate smaller impurity concentrations, so that our samples may be considered as purer than the flux-grown ones.

In Fig. 6 we have plotted the square of the mode frequency (closed circles) as a function of temperature. In order to have a definite measure of accuracy we have repeated our fitting procedure keeping
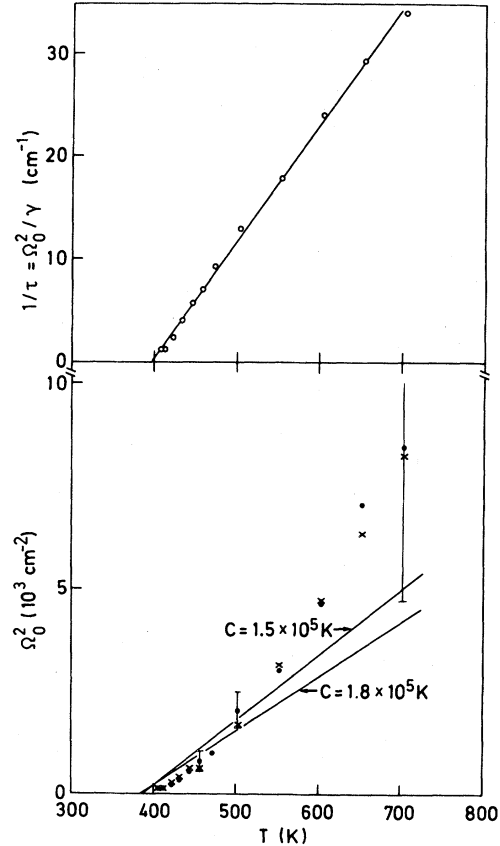

FIG. 6. Mode softening or critical slowing down in BaTiO$_3$. See text for explanation.

Ω_0 fixed and optimizing only $4\pi A_{YY}\rho$ and γ. The error bars indicate the frequency interval in which the mean-square deviation varies by a factor of 2. The temperature dependence of Ω_0^2 can also be obtained from $4\pi A_{YY}\rho$, i.e., the total HR intensity. We have

$$4\pi A_{YY}\rho(T) \sim \Omega_0^{-2}(T) \qquad (4)$$

if the HR polarizability is independent of temperature and all scattering conditions remain constant. The crosses in Fig. 6 represent $\Omega_0^2(T)$ as follows from Eq. (4). The factor of proportionality has been calibrated by use of $\Omega_0 = 31$ cm^{-1} at 473 K.

Combining the Curie-Weiss law of $\epsilon(0)$ and the generalized LST relation,[13-15] we expect a linear increase of Ω_0^2 with temperature. This is shown by the two straight lines referring to the Curie constants C quoted in the literature for melt-grown crystals.[24,25] All the TO- and LO-mode frequencies involved have been determined by HR scattering. There seems to be a systematic deviation from the expected linear behavior of Ω_0^2. However, it is difficult to decide whether it results from experimental

errors in Ω_0^2 or indicates an inadequacy of the LST relation written in its usual form.[26,27]

As mentioned before, the relaxation time $\tau = \gamma/\Omega_0^2$ is obtained with a higher degree of precision than either of the parameters Ω_0 or γ. Therefore, we have also plotted $1/\tau$ as a function of temperature in Fig. 6. Undoubtedly, there is a mode softening or critical slowing down with a characteristic one-mode frequency continuously decreasing from the infrared to the millimeter wave region. As our values of Ω_0 explain the correct order of magnitude of $\epsilon(0)$, it is quite probable that the soft mode, as revealed by our measurements, fully accounts for the Curie-Weiss law of $\epsilon(0)$ and does not need to be complemented by an extra pole in $\epsilon(\Omega)$. Of course, this conclusion should be confirmed by accurate dielectric measurements up to 3 cm^{-1} (90 GHz).

Our one-mode description seems to contradict the two-mode model used in Refs. 14 and 15. Nevertheless, we should admit that, due to the high damping, $\epsilon(\Omega)$ can be formally written as a sum of two overdamped oscillator contributions. Hence the assumption of two different dispersion mechanisms can be reconciled with our experimental results although it introduces a complication that has to be justified by substantial physical arguments. In order to clarify this point, let us consider some elementary transformations of formula (2).

Because of $\gamma > 2\Omega_0$ the poles of $\epsilon(\Omega)$ become purely imaginary and $\epsilon(\Omega)$ can be written as a difference of two Debye relaxator terms. We obtain

$$\epsilon''(\Omega) = \frac{4\pi\rho\Omega_0^2\gamma\Omega}{\Omega_+^2 - \Omega_-^2}\left[\frac{1}{\Omega^2 + \Omega_-^2} - \frac{1}{\Omega^2 + \Omega_+^2}\right],$$

(5)

with

$$\Omega_\pm^2 = \frac{1}{2}[\gamma^2 - 2\Omega_0^2 \pm \gamma(\gamma^2 - 4\Omega_0^2)^{1/2}] > 0. \quad (6)$$

Introducing a characteristic frequency Ω_m intermediate between Ω_- and Ω_+ ($\Omega_- \leq \Omega_m \leq \Omega_+$), we may recast $\epsilon(\Omega)$ into the sum of two overdamped oscillator contributions, i.e.,

$$\epsilon''(\Omega) = \frac{4\pi\rho\Omega_0^2\gamma\Omega}{\Omega_+^2 - \Omega_-^2}\left[\frac{1}{\Omega^2 + \Omega_-^2} - \frac{1}{\Omega^2 + \Omega_m^2}\right.$$

$$\left. + \frac{1}{\Omega^2 + \Omega_m^2} - \frac{1}{\Omega^2 + \Omega_+^2}\right]$$

$$= \sum_{\mu=1}^{2}\frac{4\pi\rho_\mu\Omega_\mu^2\gamma_\mu\Omega}{(\Omega_\mu^2 - \Omega^2)^2 + \gamma_\mu^2\Omega^2}. \quad (7)$$

The parameters of the first mode are given by

$$\Omega_1 = (\Omega_m\Omega_-)^{1/2}, \quad \gamma_1 = \Omega_- + \Omega_m,$$

and (8)

$$\rho_1 = \frac{1 - \Omega_-/\Omega_m}{1 - \Omega_-/\Omega_+}\rho,$$

while the parameters of the second mode follow from these equations when Ω_- and Ω_+ are interchanged.

The artificial parameter Ω_m provides the possibility to assume any value of Ω_2 between $(\Omega_-\Omega_+)^{1/2} = \Omega_0$ and Ω_+, and to adjust Ω_1 correspondingly. For instance, we may identify Ω_2 with the saturating mode frequency reported by Luspin et al.[14] Then Ω_1 increases from 7.5 cm^{-1} at 408 K up to 43 cm^{-1} at 703 K, whereas in the same temperature interval the relative oscillator strength $\rho_1/(\rho_1 + \rho_2)$ drops from 0.98 to 0.1. A mode with such parameters is difficult to detect by infrared spectroscopy. Therefore, the inability to cover the spectral region below 10 cm^{-1} may be the reason why the authors of Ref. 14 have only found an Ω_2 component and have failed to observe the whole soft mode, i.e., the sum of the Ω_1 and Ω_2 contributions.

Dielectric data alone do not substantiate the mode splitting as they can be described by a phenomenological single-mode model and do not indicate two distinct dispersion mechanisms. It has been argued that the F_{1u} mode saturates because it has to continuously merge into the corresponding E mode of the tetragonal phase.[14,15] Although this hypothesis is rather suggestive, we should point out that the phase transition is of first order, so that a jump in frequency is expected for both components (A_1 and E) into which the soft F_{1u} mode is divided at T_C. In the case of the E component the extremely high damping may partly obscure this discontinuity. In addition, we should not overinterpret the physical meaning of Ω_0 or (Ω_1, Ω_2). So far, these frequencies have only been used as phenomenological fitting parameters. Microscopic models are required to understand the origin of the high damping and its influence on the mode softening.

ACKNOWLEDGMENTS

*On leave from Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas, 13100-Campinas, S.P. Brasil.

†Present address: Max-Planck-Institut für Strahlenchemie, 4300 Mülheim a.d. Ruhr, Federal Republic of Germany.

[1]J. Harada, J. D. Axe, and G. Shirane, Phys. Rev. B <u>4</u>, 155 (1971).

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

[3]J. M. Ballantyne, Phys. Rev. <u>136</u>, A429 (1964).

[4]M. DiDomenico, S. H. Wemple, S. P. S. Porto, and R. P. Baumann, Phys. Rev. <u>174</u>, 522 (1968).

[5]A. Scalabrin, A. S. Chaves, D. S. Shim, and S. P. Porto, Phys. Status Solidi B <u>79</u>, 731 (1977).

[6]G. Burns and F. H. Dacol, Phys. Rev. B <u>18</u>, 5750 (1978).

[7]J. A. Sanjurjo, R. S. Katiyar, and S. P. Porto, Phys. Rev. B <u>22</u>, 2396 (1980).

[8]G. Burns, Phys. Lett. <u>43A</u>, 271 (1972).

[9]C. A. S. Lima, A. Scalabrin, L. C. M. Miranda, H. Vargas, and S. P. S. Porto, Phys. Status Solidi B <u>86</u>, 373 (1978).

[10]A. V. Turik and N. B. Shevchenko, Fiz. Tverd. Tela (Leningrad) <u>19</u>, 2807 (1977) [Sov. Phys.—Solid State <u>19</u>, 1644 (1977)].

[11]R. Clemens, G. Luther, and H. E. Müser, Phys. Status Solidi A <u>64</u>, 637 (1981).

[12]Y. Tominaga, M. Udagawa, S. Ushioda, T. Nakamura, and H. Urabe, Phys. Rev. B <u>23</u>, 1664 (1981).

[13]A. S. Barker, Jr., Phys. Rev. <u>145</u>, 391 (1966).

[14]Y. Luspin, J. L. Servoin, and F. Gervais, J. Phys. C <u>13</u>, 3761 (1980).

[15]J. L. Servoin, Y. Luspin, and F. Gervais, Ferroelectrics <u>37</u>, 523 (1981).

[16]R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Lett. <u>14</u>, 681 (1965); H. Vogt, in *Light Scattering in Solids II*, Vol. 50 of *Topics in Applied Physics,* edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1982), p. 207.

[17]K. Inoue and N. Asai, J. Phys. (Paris) Colloq. <u>42</u>, C6-430 (1981).

[18]H. Vogt and G. Rossbroich (unpublished).

[19]H. Vogt and G. Neumann, Phys. Status Solidi B <u>92</u>, 57 (1979).

[20]Sanders Association Inc., Nashua, New Hampshire.

[21]J. Albers, Sonderforschungsbereich 130, Ferroelektrika, Universität Saarbrücken, Federal Republic of Germany.

[22]H. E. Müser, W. Kuhn, and J. Albers, Phys. Status Solidi A <u>49</u>, 51 (1978).

[23]H. Vogt and G. Rossbroich, Phys. Rev. B <u>24</u>, 3086 (1981).

[24]C. J. Johnson, Appl. Phys. Lett. <u>7</u>, 221 (1965).

[25]I. Camlibel, M. DiDomenico, Jr., and S. H. Wemple, J. Phys. Chem. Solids <u>31</u>, 1417 (1969).

[26]A. S. Barker, Jr. and J. J. Hopfield, Phys. Rev. <u>135</u>, A1732 (1964).

[27]J. Petersson, Phys. Status Solidi B <u>53</u>, K79 (1972).