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Quasimodes and a central peak in $BaTiO_3$

M D Fontana†, K Laabidi† and B Jannot‡

† Laboratoire Matériaux Optiques à Propriétés Spécifiques, CLOES, Université de Metz et Supelec, F-57078 Metz Cédex 3, France

‡ Laboratoire de Physique, Université de Bourgogne, BP 138, F-21004 Dijon Cédex, France

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Abstract. The $z(yz)y$ Raman spectrum of a single-domain $BaTiO_3$ crystal in the tetragonal phase (z is the ferroelectric axis) is carefully measured and analysed to determine the quasimodes. In this scattering geometry, the phonon wave vector q is at 45° to the ferroelectric axis, and only mixed modes of $A_1 + E$ character are observed. We show that a modification of the Merten equation is necessary to take account of the large damping of the lowest $E(TO_1)$ soft mode. We describe an attractive application of these calculations to the accurate frequency determination of the heavily damped soft mode from knowledge of the well defined frequency of the other modes. This careful analysis lets us make unambiguous the presence of a central component in the Raman spectrum of $BaTiO_3$.

1. Introduction

Phonons that cannot be described by one of the irreducible representations of the point groups are called quasimodes or mixed-symmetry phonons [1, 2]. This situation occurs when the polarization direction of the phonon does not coincide with one of the crystallographic axes.

Although Raman spectroscopy constitutes an extensively used technique which provides essential information about lattice dynamics in various compounds easily and nearly directly, the scattering geometries leading to quasimode observation are generally avoided.

In uniaxial crystals and with right-angle scattering geometry, pure transverse and longitudinal phonons with a well defined symmetry character may be detected by Raman scattering when they propagate along the x, y or the optic z axis. For the C_{4v} group, phonons polarized along the z axis correspond to the totally symmetric irreducible representation A_1 whereas phonons polarized in the (x, y) plane, normal to z, have an E symmetry character. In the opposite case when it is propagating between the z and $x(y)$ axes, the phonon can have a mixed A_1–E symmetry character, as clearly established by Loudon [1] and Arguello *et al* [2] . The frequency of such a phonon is intermediate between those of the pure corresponding A_1 and E phonons. Inversely, frequencies of the quasiphonons can be used to find those of the pure phonons. This is particularly useful when a phonon line is not observable owing to its intensity being too weak. This application of the quasimodes was demonstrated by Burns and Scott in $PbTiO_3$ [3].

$BaTiO_3$ is a prototype ferroelectric material and its cubic–tetragonal phase transition was considered for a long time as a good example of a displacive phase transition driven by the softening of the lowest-frequency phonon. Despite extensive investigations, this soft mode response remains an unsolved problem due to large contradictions concerning the determination of its frequency and damping [4–6].

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In this study, we utilize the quasimode scattering measurements in tetragonal $BaTiO_3$ (C_{4v} group) to clarify the controversies about the characteristics of the lowest-frequency phonon of E-symmetry which cannot be easily determined in a pure phonon symmetry configuration.

The resolution of the E(TO$_1$) spectrum is of great importance since its interpretation is generally related to the mechanism of the phase transitions in $BaTiO_3$. The E(TO) spectrum exhibits at low frequency an intense and broad profile apparently centred around 0 cm^{-1}. It is usually fitted to a damped harmonic oscillator corresponding to the E(TO) phonon expected at low frequency. Several series of parameters, that is, phonon frequency and damping, have been found by various authors to provide a satisfactory adjustment of the experimental Raman spectrum [4–6]. A large damping constant was needed in each investigation. Thus the damping-to-frequency ratio can reach a value of 2.8 [5]. This renders the accurate determination of the phonon frequency which seems to decrease as the temperature is lowered in the tetragonal phase, difficult. In addition, the broad profile impedes the possible detection of a relaxational 'central peak', if any. This question is of increasing interest in the light of the dispersion step recently detected by dielectric measurements [7]. To date the possibility of detecting a quasi-elastic scattering was not considered. The paper is devoted to the measurement of the quasimode spectrum in $BaTiO_3$, which is shown to be able to discriminate between the relaxational central peak and the soft phonon peak and to solve the ambiguity about the value of the soft E(TO) frequency.

2. Quasimode scattering

2.1. Experimental results

A single crystal of $BaTiO_3$ grown by the Czochralsky method was excited by an He–Ne laser line and Raman spectra were recorded in a right-angle geometry with a double Spex monochromator. According to group theory (C_{4v} point group), four optical modes of E symmetry, one of B_1 symmetry and three of A_1 symmetry are expected. Raman measurements are performed on various scattering geometries like in previous investigations [4, 5]. The values of the frequency and linewidth for each phonon are obtained by the fit with the standard damped harmonic oscillator. They are compiled in table 1 and labelled according to [8]. Our results are shown to be in good agreement with those derived from previous Raman [4–6] and infrared [10] investigations, if we dismiss the lowest E(TO$_1$)phonon, which needs a special treatment as will be shown below. The characteristics of this phonon will be determined below from a method that differs from the usual fit of the Raman lineshape, but is based on the dispersion of the quasimode.

Therefore, we focus our attention on the determination of the quasimodes visible in the $z(yz)y$ configuration. This spectrum, which is reported in figure 1, strongly differs from the E(TO) spectrum recorded in the $z(xz)y$ configuration. In the E spectrum, the low-frequency scattering intensity is so large that it renders difficult the clear observation of the second, weak peak around 190 cm^{-1}, which is more resolved in another configuration [9].

The $z(yz)y$ Raman spectrum shown in figure 1 corresponds to the observation of quasimodes since the propagating direction is at an angle $\theta = 45°$ to the optical c axis. Three main peaks are detected around 150, 215 and 306 cm^{-1} and four lines with a smaller intensity are located around 182, 470, 495 and 715 cm^{-1}. The lines at 182 and 715 cm^{-1} are enlarged in the inset of figure 1 to be more visible. Frequency and damping are determined for each quasimode and are reported in table 2. Quasimodes occur in polar phonons for which the polarization is neither parallel nor normal to the propagation direction. Two situations can

Table 1. The frequencies of the optical modes of $BaTiO_3$ in the Brillouin zone centre of the tetragonal phase. The notation is frequency (damping) in cm^{-1}.

Modes	IR results [9]	Raman data [5]	Our Raman results
$E(TO_1)$	35(95)	38	
$A_1(TO_2)$	180(4)	178	176(25)
$E(TO_2)$	182(1.8)	180	178(9)
$E(LO_2)$	180(9)	180	178(9)
$A_1(LO_2)$	187(9)	189	
$A_1(TO_1)$	280(120)	276	274(56)
B_1		304	303(4)
$E(TO_4)$	306(9)	308	306(7)
$E(LO_4)$	305.6(9)	308	307(6)
$E(LO_1)$	465(12)	466	466(5)
$A_1(LO_1)$	469(12)	471	471(11)
$E(TO_3)$	482(21)	498	488(21)
$A_1(TO_3)$	507(45)	515	518(48)
$E(LO_3)$	706(22)	722	708
$A_1(LO_3)$	729(34)	725	720(39)

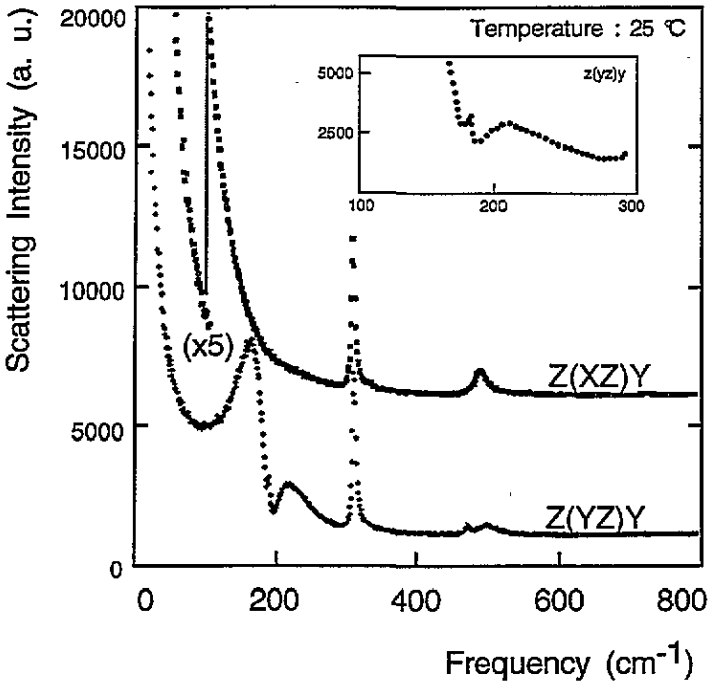

Figure 1. Raman spectra of single-domain $BaTiO_3$ crystal recorded at room temperature for two scattering geometries. The inset shows with a different scale weak peaks around 182 and 715 cm^{-1} detected in the $z(yz)y$ configuration.

be encountered according to the respective magnitudes of the electrostatic and short-range forces in the crystal [1]. In the C_{4v} group these forces are respectively evaluated from the LO–TO frequency splitting for each mode symmetry and from the separation between A_1 and E components of the same phonon. With regard to the data reported in table 1, the long-

range forces appear to be dominant in $BaTiO_3$ and the $z(yz)y$ spectrum can be attributed to transverse or longitudinal phonons of mixed symmetry. This hypothesis can be checked in tables 1 and 2 since each quasimode frequency is indeed found to be intermediate between the frequency of one of the bare E(TO or LO) phonons and that of a bare A_1 phonon.

Table 2. Characteristics of the quasimodes measured in the $z(yz)y$ scattering geometry: (a) frequency and damping obtained by fitting the experimental spectra; (b) frequency deduced from (1) with $\theta = 45°$; (c) frequency deduced from (4) with $\theta = 45°$ when introducing the soft phonon damping.

Quasimode	Combination of modes	(a) Experimental frequency (cm^{-1})	(b) Calculated frequency (cm^{-1})	(c) Calculated frequency (cm^{-1})
QM1	$E(TO_1)$–$A_1(TO_2)$	154(61)	168	154
QM2	$A_1(LO_2)$–$E(LO_2)$	182(5)	180	182
QM3	$E(TO_2)$–$A_1(TO_1)$	217(54)	213	216.7
QM4	$E(TO_4)$–$E(LO_4)$	306(7)	307	306
QM5	$A_1(LO_1)$–$E(LO_1)$	469(18)	468	468
QM6	$E(TO_3)$–$A_1(TO_3)$	495(6)	502	498
QM7	$A_1(LO_3)$–$E(LO_3)$	716(4)	714	715

The relation of the spatial dispersion for the quasimodes was clearly established by Merten [11]. We interpret our quasimode data in this framework and we attempt to deduce the $E(TO_1)$ phonon characteristics.

2.2. *Analysis of the quasimodes*

The quasimode frequency ω_θ for an angle θ is determined as

$$\varepsilon_c(\infty)\cos^2\theta\prod_j[\omega^2_{A_1}(LO_j)-\omega^2_\theta]\prod_j[\omega^2_E(TO_j)-\omega^2_\theta]+\varepsilon_a(\infty)\sin^2\theta\prod_j[\omega^2_E(LO_j)-\omega^2_\theta]$$
$$\times\prod_j[\omega^2_{A_1}(TO_j)-\omega^2_\theta]=0 \qquad (1)$$

where $\varepsilon_a(\infty)$ and $\varepsilon_c(\infty)$ are the high-frequency dielectric permittivities along the a and c axes, taken as the squares of the refractive indices. This equation was established by Merten [11] from the Kurosawa form of the dielectric function as

$$\varepsilon(\omega)=\varepsilon(\infty)\prod_j[\omega^2(LO_j)-\omega^2]\Big/\prod_j[\omega^2(TO_j)-\omega^2]. \qquad (2)$$

In a first stage, using (1), we derive, from the frequencies of the bare phonons given in table 1, the quasimode dispersion, that is the values ω_θ, which are compared with experimental data for $\theta = 45°$. The calculated value is found to be very close to the experimental quasimode frequency for each of the seven phonons except for the lowest mode, for which a significant difference is observed (see table 2). The value of 168 cm^{-1} for the lowest quasimode is found irrespective of the value of the $E(TO_1)$ phonon.

This shows that the values of the soft phonon frequency that were previously reported [4, 5, 6, 9] are not consistent with our quasimode data. Two origins of this discrepancy can be invoked: either the description of the quasimode by equation (1) is inadequate in

$BaTiO_3$, or the $E(TO_1)$ frequency is erroneous. A third possibility is that the discrepancy could originate from both these reasons simultaneously. We assume that the difficulty arises from the large damping of the lowest $E(TO_1)$ phonon. Therefore we modify the Merten equation by introducing a damping constant parameter γ_E for the $E(TO_1)$ phonon. Equation (2) becomes then

$$\varepsilon_a(\omega) = \varepsilon_a(\infty)\left(\prod_j[\omega_E^2(LO_j) - \omega^2] \Big/ \prod_{j\neq 1}[\omega_E^2(TO_j) - \omega^2]\right) \Big/ \omega_E^2(TO_1) - \omega^2 + i\omega\gamma_E(TO_1). \tag{3}$$

Now, $\omega_E(TO_1)$ and $\gamma_E(TO_1)$ denote the real frequency and the damping factor of the complex frequency corresponding to the $E(TO_1)$ phonon. The quasimode dispersion (1) is thus rewritten as

$$\varepsilon_c(\infty)\cos^2\theta[[\omega_E^2(TO_1) - \omega_\theta^2]^2 + \omega_\theta^2\gamma_E^2(TO_1)]\prod_j[\omega_{A_1}^2(LO_j) - \omega_\theta^2]\prod_{j\neq 1}[\omega_E^2(TO_j) - \omega_\theta^2]$$
$$+ \varepsilon_a(\infty)\sin^2\theta[\omega_E^2(TO_1) - \omega_\theta^2]\left(\prod_j[\omega_E^2(LO_j) - \omega_\theta^2]\prod_j[\omega_{A_1}^2(TO_j) - \omega_\theta^2]\right) = 0. \tag{4}$$

Equation (4) is used to deduce the characteristics of the $E(TO_1)$ phonon, i.e. the parameters $\omega_E(TO_1)$ and $\gamma_E(TO_1)$ from the experimental values of the quasimode frequencies (for $\theta = 45°$), and those of the A_1 and other E phonons. We find $\omega_E(TO_1) = 48\ cm^{-1}$ and $\gamma_E(TO_1) = 120\ cm^{-1}$ with a good accuracy. The values given in the literature [5, 6] are thus incompatible with the quasimode experimental frequencies. The parameters $\omega_E(TO_1)$ and $\gamma_E(TO_1)$ deduced from equation (4) are also able to fit the broad Raman profile.

We repeat the calculation of the quasimode dispersion curves as a function of the angle θ, but with equation (4) instead of equation (1). Now, we use $\omega_E(TO_1) = 48\ cm^{-1}$ and $\gamma_E(TO_1) = 120\ cm^{-1}$ in addition to the frequencies of the other phonons with pure symmetry. Results exhibited in figure 2 show that in this case a good agreement is achieved between the calculated and the experimental quasimode frequencies. It is thus clearly demonstrated that the seven peaks displayed in the $z(yz)y$ spectrum are caused by the scattering of quasimodes. We can remark that the branches no 2, 4, 5 and 7 are non-dispersive. The lowest branch no 1 exhibits a very large dispersion and therefore needs the use of equation (4) where the damping $\gamma_E(TO_1)$ is introduced. Figure 3 illustrates the large dependence of the dispersion in the lowest curve on the damping of the $E(TO_1)$ phonon. The measurement of the lowest quasimode therefore constitutes an excellent way to determine the characteristics of a highly damped bare phonon.

3. Quasi-elastic scattering

Since the lowest peak lies at relatively high frequency around 154 cm^{-1} at room temperature, the $z(yz)y$ spectrum can be used to detect a quasi-elastic scattering, which should correspond to a relaxation process. Raman scattering measurements have been consequently performed in the tetragonal phase as a function of temperature. The transitions to the orthorhombic and the cubic phases are expected to occur around 7 and 136 °C respectively. Figure 4 shows the quasimode spectrum at 25 and 120 °C. The temperature dependence of the quasimodes

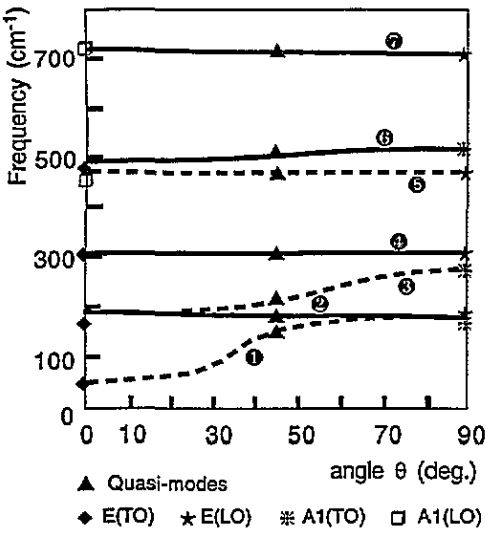

Figure 2. Quasimode dispersion curves calculated with equation (4), including damping.

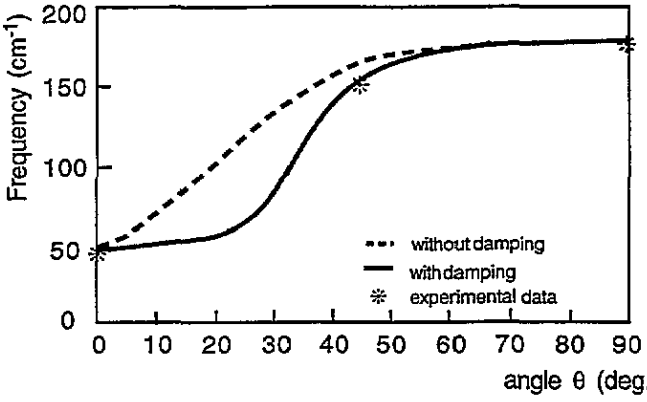

Figure 3. The lowest branch of figure 2, as calculated from two versions of the quasimode dispersion equation, one including the soft phonon damping (4), the other without (1).

that can be thus derived is shown [9] to be consistent with that of the bare phonons only if the modified form of equation (1) is used. This reinforces the model used above.

A remarkable change is observed in the spectrum below 100 cm^{-1}, in both the scattering intensity and the lineshape profile. A large quasi-elastic scattering is detected, and the lowest quasimode peak becomes a shoulder of this broad signal when the temperature increases.

This low-frequency spectrum is carefully measured with better resolution conditions. Results are reported in figure 5 as a function of temperature. First, the scattered intensity between 3 and 15 cm^{-1} weakly decreases as the temperature increases up to 70 °C. Then the intensity strongly rises on heating, particularly in the close vicinity of the tetragonal–cubic phase transition.

According to the selection rules prediction, the spectrum $z(yx)y$ does not exhibit any Raman line. Only the intense Rayleigh peak is observed in this configuration. Consequently the spectrum $z(yx)y$ is used as the reference spectrum for the purely elastic scattering of $BaTiO_3$. Therefore this scattering, which is remarkably temperature independent between 25 and 135 °C, is reported in figure 5 for comparison with the low-frequency $z(yz)y$ spectrum. This comparison clearly emphasizes that the spectrum displays, in addition to the Rayleigh line, a temperature-dependent and intense quasi-elastic scattering.

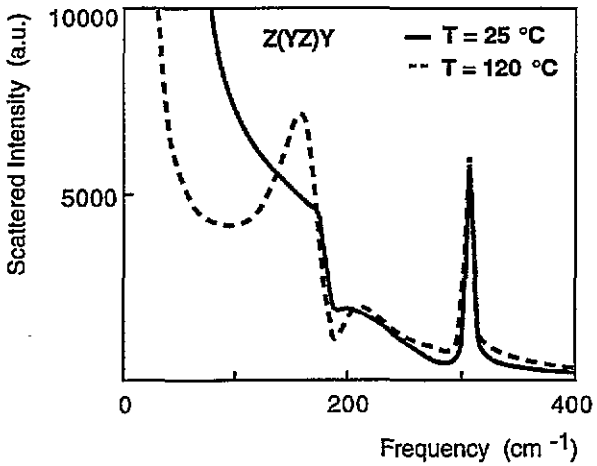

Figure 4. The lowest-frequency quasimode spectrum in $BaTiO_3$ at two temperatures of the tetragonal phase.

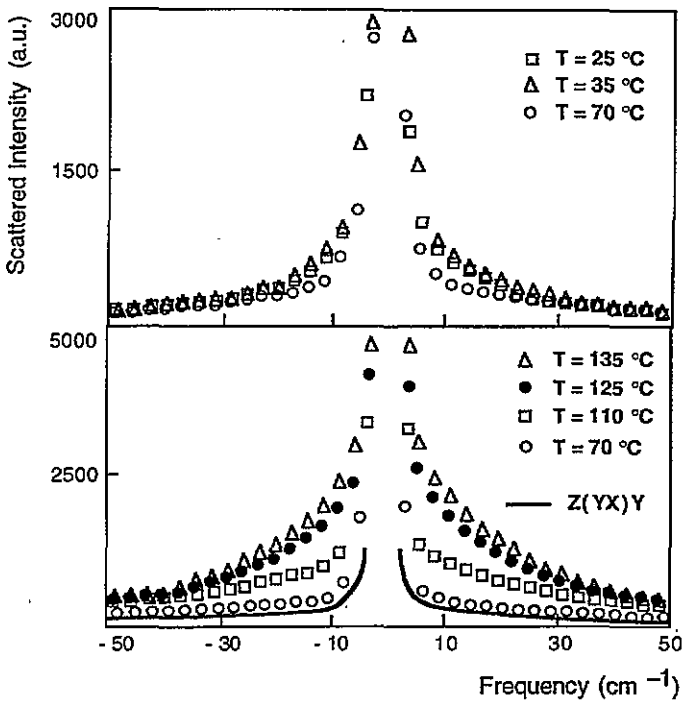

Figure 5. The evolution with temperature of the central-peak component in the $z(yz)y$ spectrum in the tetragonal phase. The spectrum recorded in the extinction geometry $z(yx)y$ is also given as a 'zero-level' reference for the pure elastic scattering. It is temperature independent over the whole range 25 °C–135 °C.

This proves that the quasi-elastic scattering detected in the $z(yz)y$ configuration is intrinsic and cannot be attributed to leakage from other mode symmetries. Absent in the

$z(yx)y$ configuration, the quasi-elastic scattering occurs as well in the $z(xz)y$ geometry (*E-symmetry modes*) [12] but its observation is more difficult owing to the presence of the intense and broad soft phonon peak (see figure 1). Our study shows that the central peak in $BaTiO_3$ can be unambiguously detected in the quasimode configuration and that it is extremely anisotropic.

The central peak appears to be related to the tetragonal–orthorhombic and tetragonal–cubic phase transitions since its intensity increases on approaching these transitions.

It is shown and reported elsewhere [13] that the central peak is due to a relaxation process in the 100 GHz range, which is able to interpret the large dispersion of the dielectric permittivity ε_a along the tetragonal a axis, and thus to explain the large discrepancy in ε_a between the low-frequency capacitance value and the high-frequency Lyddane–Sachs–Teller value. Consistently with earlier x-ray [14] and EPR [15] studies, this central peak is attributed to the relaxational motion of the off-centre Ti ion [13] in the plane perpendicular to the z axis.

Our results therefore differ considerably from those reported by Sokoloff *et al* [16]. These authors have detected a central peak in the A_1 symmetry attributed to a dynamic disorder of Ti ions along the polar c axis and thus related to the dielectric permittivity ε_c. In fact anomalies in the tetragonal $BaTiO_3$ connected to the phase transitions are expected to concern principally the motion along the a axis and the very large permittivity ϵ_a. Therefore the results obtained by Sokoloff *et al* are not consistent with the results derived from other techniques.

4. Conclusion

In contrast to the previous measurements, our Raman investigation of the quasimode spectrum allows us to determine the frequency and damping of the overdamped soft E(TO) phonon in the tetragonal phase. The angular dependence of each quasimode frequency shows that the agreement between experimental and calculated values is achieved only if the damping of the lowest-frequency mode is taken into account in Merten's equation. The quasimode configuration gives also the first clear evidence of a central peak in $BaTiO_3$: its intensity increases when both the orthorhombic and the cubic phases are approached. These observations are consistent with earlier x-ray [14] and EPR [15] studies, which indicated the order–disorder mechanism of these two phase transitions in $BaTiO_3$.

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