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Third-order nonlinear susceptibilities and polariton modes in $PbTiO_3$ obtained by temporal measurements

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Temporal measurements of the third-order susceptibility were performed in $PbTiO_3$ with use of a forward nondegenerate four-wave-mixing technique. We resolved, on a femtosecond time scale, the transient behavior of the lowest A_1 polariton mode and measured its dispersion versus the magnitude of the wave vector. The deduced value of the dielectric constant $\epsilon_{\parallel}(0)$ is in good agreement with previous estimations.

I. INTRODUCTION

Lattice-dynamics behavior of oxydic perovskites has been the subject of considerable attention over the last two decades, particularly in regard to their structural phase transition. Their knowledge is a key point for a full comprehension of a number of nonlinear properties of these materials, including large electro-optical effects, high second-harmonic generation efficiency, and important third-order nonlinearities.

Nonlinear spectroscopy techniques have been extensively used to elucidate problems related to lattice dynamics. Apart from the directivity of the signal and its enhancement due to resonance effects, a main advantage of a nonlinear optical method, with respect to conventional Raman experiments, concerns its ability to give access to any definite value of the excited phonon wave vector by choosing the appropriate geometrical arrangement for the incoming actinic beams, a point of prime importance especially when studying polar modes of crystals. Among four-wave-mixing processes available, coherent antistokes Raman spectroscopy has been chosen by Coffinet and De Martini[1] and Wynne[2] to study polariton dispersion curves in, respectively, GaP and $LiNbO_3$, whereas Delfyett, Dorsinville, and Alfano[3] used a Raman-induced phase conjugation spectroscopy (RIPS) technique to perform spectral and temporal measurements of the third-order nonlinear susceptibility of $LiNbO_3$.

Very recently, the development of femtosecond optical lasers[4] has made possible the coherent driving of Raman-active optical vibrations by impulsive stimulated excitation.[5] This approach has been exploited by Cheung and Auston[6] for a coherent impulse excitation and detection of phonon polaritons by the electro-optic effect in $LiTaO_3$. We present here a nondegenerate four-wave-mixing technique which enables us to drive the low-frequency polar model of $PbTiO_3$ directly, to resolve, on a femtosecond time scale, the transient behavior of polaritons, and to measure their dispersion as a function of the wave-vector value.

II. THEORETICAL BACKGROUND

The optical nonlinear technique we decided to implement uses two different frequencies, ω_p and ω_t, issued from a femtosecond pulse laser system.[7] The relevant combination of the three incoming fields to the nonlinear process, $E_t E_p E_p^*$, corresponds to the excitation of $X(-\omega_t;\omega_t,\omega_p,-\omega_p)$, a third-order susceptibility tensor. Our specific experimental arrangement (Fig. 1) possesses a forward-folded boxcar geometry, where the two pump pulses at angular frequency ω_p generate the nonlinear phenomena, and the probe pulse, at angular frequency ω_t, is temporarily delayed to study with a subpicosecond resolution, the transient nonlinear processes involved. Working at Bragg-angle incidence for the probe pulse direction allows fulfillment of phase-matching conditions. For the specific application we are concerned with, the ω_t value is unimportant as its only role consists of probing the nonlinearity excited by the lone ω_p pump pulses.

As stated here before, the spectral width associated with 50-fs pulses enables direct resonant excitation of low-frequency lattice modes included in the spectral range lower than $\simeq 250\ cm^{-1}$. Since the temporal width of the pulses is much shorter than the characteristic lifetime of

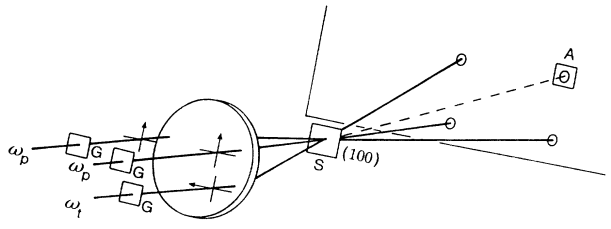

FIG. 1. Experimental scheme: pulses at frequency ω_p create a transient perturbation in the crystal S, which is probed by pulses at frequency ω_t; the signal is collected through the analyzer A, whereas polarization of the incoming pulses are defined by Glan polarizers.

the phonons, the measured nuclear response function of the material will appear as a combination of damped sinusoidal functions, each being written in the form

$$Y_\sigma(t) = B_\sigma \sin(\Omega_\sigma t + \Psi_\sigma)\exp(-\gamma_\sigma t), \quad (1)$$

where B_σ is proportional to the Raman efficiency, Ω_σ stands for the angular frequency of the Raman mode σ, and ψ_σ and γ_σ stand for its relative phase and damping constant, respectively. Other third-order phenomena, with different temporal characteristics, may be generated during the nonlinear interaction: among them, electronic third-order polarizability will give rise to an instantaneous response, with regard to the pulse temporal widths, and will be described by a δ function; resonant or nonresonant processes may also be present and the temporal behavior of each of them will be described by an exponential function with a characteristic relaxation time τ_n. The total nonlinear transient response, taking account of all processes considered here before will be written as[8]

$$S(t) = \left[A\delta(t) + \sum_\sigma B_\sigma \sin(\Omega_0 t + \Psi_\sigma)\exp(-\gamma_\sigma t) + \sum_n C_n \exp\left(-\frac{t}{\tau_n}\right)\right]^2, \quad (2)$$

where pump and probe pulses are approximated by Dirac functions. In the actual calculations, we performed first a convolution product of the response functions with the pump-pulse temporal shape—described by a sech^2 function—and second a convolution with the probe pulse.

The crystal under study in this Rapid Communication is the ferroelectric phase of $PbTiO_3$ perovskite, which is the stable isomorph at room temperature. Our choice of lead titanate relies on the existence of underdamped well-defined Raman bands in the low-frequency region.[9,10] Among these modes, several are soft in character, i.e., their frequency moves as one approaches the transition temperature to the paraelectric (cubic) phase, a phenomenon which can be potentially studied by the present technique. In fact, $PbTiO_3$ appeared for a long time to be a "textbook example" of a displacive phase transition, a statement which has to be made with care in view of very recent Raman works.[11]

Ferroelectric $PbTiO_3$ has a tetragonal (C_{4v}^1) space symmetry and selection rules associated with $X_{ijkl}^{(3)R}$ tensor elements can be used, as in spontaneous Raman spectroscopy, to discriminate among modes belonging to different symmetries. We recall the relation between $X_{ijkl}^{(3)R}$ elements and the polarizability derivative elements associated with a normal mode Q,[12]

$$X_{ijkl}^{(3)R}(-\omega_t;\omega_t,\omega_p,-\omega_p) \propto \frac{\partial a_{ij}}{\partial Q}\frac{\partial a_{kl}}{\partial Q}, \quad (3)$$

where $\partial a_{ij}/\partial Q$ represents the ij element of the polarizability associated with the normal mode Q. Among 21 nonzero elements allowed by symmetry, 11 are independent; their number is further reduced, due to symmetry properties inherent to the A_1 and E Raman-active modes. We expect three independent elements associated with each A_1 mode Ω, and two other ones for each E mode Ω' (Table I). A_1 and E modes being simultaneously ir active, we are concerned with polar modes, which can therefore experience a splitting into LO and TO components; TO components may furthermore interact with the transient induced dipoles and experience a dispersive behavior, the polariton regime, in the low value range of the wave vector $\mathbf{K}$. It is thus necessary to relate a phonon wave vector to each actual excitation geometry. If we assume that ω_{p1} refers to the central frequency of the pump pulse and ω_{p2} to $\omega_{p1}+\Omega$, the phonon wave vector of frequency Ω will satisfy the relation

$$K^2(\Omega) = K^2(\omega_{p1}) + K^2(\omega_{p2}) - 2K(\omega_{p1})K(\omega_{p2})\cos(\phi), \quad (4)$$

where φ is the angle value inside the crystal between the two pump pulses. The moduli of the $\mathbf{K}(\omega_{p1})$ and $\mathbf{K}(\omega_{p2})$ wave vectors in the crystal were calculated, making use of refractive index values $n_0(\omega)$ and $n_e(\omega)$ deduced from a dispersion equation of the refractive indices parametrized by Singh, Remeika, and Potopowicz.[13] Using a typical value of $\varphi = 1°$ inside the crystal, a central frequency $\omega_{p1} = 620$ nm and $\Omega = 100\ \mathrm{cm}^{-1}$ leads for $\mathbf{K}(\Omega)$ a value of $8.1\times10^2\ \mathrm{cm}^{-1}$: Such a magnitude is by far smaller than what can be reached by conventional right-angle Raman scattering or phase conjugate four-wave mixing ($-10^4\ \mathrm{cm}^{-1}$) and turns out to lie within the dispersive region of polaritons.

III. EXPERIMENTAL RESULTS

We present results obtained on a single crystal of $PbTiO_3$,[14] approximately $0.7\times5\times5$ mm[13] in size. In order to generate pure A_1 symmetry phonons, the exciting geometry $x-\Delta y(zz)x+\Delta y$ (Ref. 15) was used for the pump beams; so the polariton was propagating in the pseudo [010] direction and polarized along the [001] direction. Thus the phonons are all extraordinary and geometrical dispersion is not anticipated.[16] The experiments were performed using a 50-fs temporal pulse width, emitting at a central frequency of 620 nm at a 10-Hz repetition rate; their energy density reached roughly 1 $\mathrm{GW/cm}^2$. The probe pulse, at 650 nm and with much lower energy, was obtained by interaction in a 1-mm jet of ethylene glycol; its linear polarization was at 90° from the direction of polarization of the pump pulses. The

TABLE I. Form of the nonlinear coefficients and related properties in a crystal of symmetry C_{4v}^1.

Symmetry of the mode	$X_{ijkl}^{(3)R}$ element	$\frac{\partial a_{ij}}{\partial Q}\frac{\partial a_{kl}}{\partial Q}$
$A_1(z)$	$X_{xxxx} = X_{xxyy}$	aa
$A_1(z)$	X_{zzzz}	bb
$A_1(z)$	$X_{yyzz} = X_{xxzz}$	ab
$E(x)$	$X_{zxzx} = X_{zxxz}$	cc
$E(y)$	$X_{yzyz} = X_{yzzy}$	dd
	$X_{xyxy} = X_{xyyx}$	0

diffracted signal polarization was analyzed through an analyzer directed along the y axis, the relevant nonlinear susceptibility elements generated correspond to $X^{(3)}_{yyzz}$.

In Fig. 2, the diffraction efficiency is plotted versus the temporal delay between pump and probe pulses. It is typical of the behavior of $PbTiO_3$ nonlinear response and corresponds to results obtained with a angle $\varphi = 0.88°$ inside the sample. Apart from an instantaneous response, which corresponds to the third-order electronic nonlinearity of the material, the signal reveals an interference between an $A_1(TO)$ oscillatory mode and a low-relaxation component. This one, which shows a steep intensity dependence on exciting laser intensity, seems consecutive to a two-photon absorption process and may then correspond to a relaxation from this population grating.[17,18] In this work the primary concern is with the characterization of the oscillatory mode, which frequency and damping are measured with a high accuracy. As a result of the interaction with the long-lived process, we can see from Eq. (2) that first, the signal is linearly proportional to the oscillatory contribution and, second, we measure directly the frequency value Ω, and not 2Ω.

Figure 3 displays the evolution of the polariton frequency as a function of $\mathbf{K}(\Omega)$ vector values, which variations were obtained from geometrical modification of the φ value. We note that the dispersion character is similar to that encountered for underdamped polaritons and that the polariton frequency tends toward zero value with $\mathbf{K}$. So we have fitted the experimental points to an undamped single-oscillator model of the form

$$\epsilon_{\parallel}(\Omega) = \frac{c^2K^2}{\Omega^2} = \epsilon_{\parallel\infty} + [\epsilon_{\parallel}(0) - \epsilon_{\parallel\infty}]\frac{\omega_{TO}^2}{\omega_{TO}^2 - \Omega^2}, \qquad (5)$$

where $\epsilon_{\parallel}(0)$ and $\epsilon_{\parallel\infty}$ are the static and optical dielectric constants. Using[10] $\epsilon_{\parallel\infty} = 7.211$ and $\omega_{TO} = 147\ cm^{-1}$, the fitting of the polariton dispersion curve leads to a value $\epsilon_{\parallel}(0) = 27 \pm 3$, consistent with that deduced from the generalized Lyddane-Sachs-Teller relation.[10] We actually verified that in the low-frequency regime, $\epsilon_{\parallel}(0)$ can be accurately estimated from a fitting of the experimental values to a single oscillator model, the contribution coming from the two other $A_1(TO)$ modes, located at 359 and 559 cm^{-1}, being negligible.

It is noticeable that this value is very close to the clamped dielectric data, which proves that, at room temperature, no other excitation contributes to the dielectric constant in the low-frequency range.

IV. CONCLUSION

We have shown that nonliner interaction, using femtosecond pulses in a forward four-wave-mixing arrangement, allows an easy description of polariton behavior. The polarization combination described in this work gives direct access to the lowest $A_1(TO)$ pure phonon frequency variation of a $PbTiO_3$ single crystal as a function of wave-vector value. From a fit to a single-harmonic-oscillator model, an accurate value of $\epsilon_{\parallel}(0)$ can be deduced in good agreement with previously measured values.

Complementary work is in progress, using various polarization arrangements, at a temperature in the vicinity of the transition to the cubic phase. This would demonstrate the existence of a central peak in $PbTiO_3$, as it has been recently proposed; indeed, a measure in the temporal domain can be a more suitable technique to extract information in the near-zero frequency range and may therefore give better access to the reality of the displacive character of the phase transition.

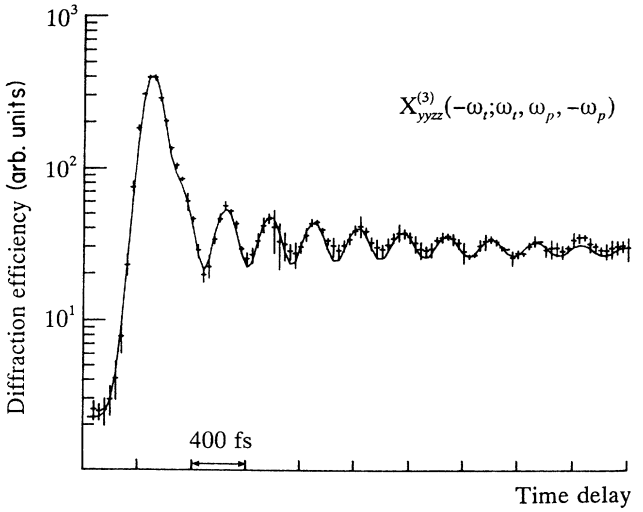

FIG. 2. Efficiency of the four-wave mixing process, in logarithmic scale, as a function of the time delay; the wave vector $\mathbf{K}$ is in the x-y plane, polarization of the pump along z axis of the crystal, probe and signal polarization along y; the theoretical fit has been obtained using Eq. (2).

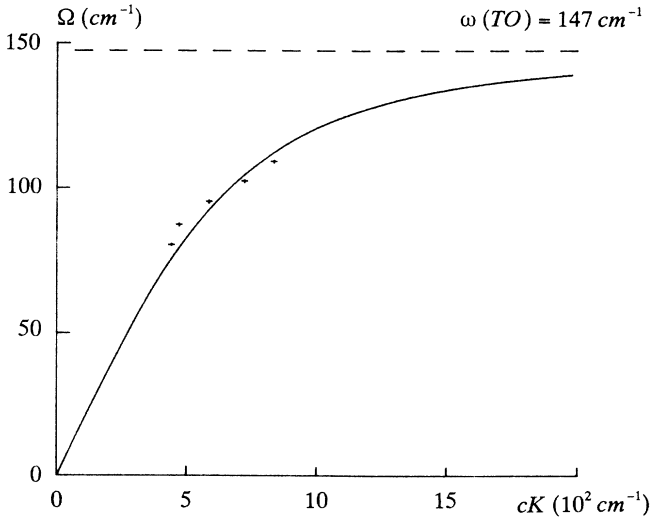

FIG. 3. Dispersion of the mode frequency Ω vs wave vector cK value, for the $A_1(TO)$ polariton; the crosses represent the experimental data taken with different angles φ between the pump beams; the solid curve gives the theoretical fit of the dielectric function using Eq. (5) for $\epsilon_{\parallel}(0) = 27$.

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[1]J. P. Coffinet and F. De Martini, Phys. Rev. Lett. **22**, 60 (1969).

[2]J. J. Wynne, Phys. Rev. Lett. **29**, 650 (1972).

[3]P. J. Delfyett, R. Dorsinville, and R. R. Alfano, Phys. Rev. B **40**, 1885 (1989).

[4]L. Fork, B. I. Greene, and C. V. Shank, Appl. Phys. Lett. **38**, 671 (1981).

[5]Y. Yan and K. A. Nelson, J. Chem. Phys. **87**, 6240 (1987).

[6]K. P. Cheung and D. H. Auston, Phys. Rev. Lett. **55**, 2152 (1985).

[7]A. Migus, A. Antonetti, J. Etchepare, D. Hulin, and A. Orszag, J. Opt. Soc. Am. B **2**, 584 (1985).

[8]J. Etchepare, G. Grillon, and J. Arabat, Appl. Phys. B **49**, 425 (1989).

[9]G. Burns and B. A. Scott, Phys. Rev. B **7**, 3088 (1973).

[10]R. A. Frey and E. Silberman, Helv. Phys. Acta **49**, 1 (1976).

[11]M. D. Fontana, H. Idrissi, and K. Wojcik, Europhys. Lett. **11**, 419 (1990).

[12]S. A. Akhmanov and N. I. Koroteev, Usp. Fiz. Nauk **23**, 405 (1977) [Sov. Phys. Usp. **20**, 899 (1977)].

[13]S. Singh, J. P. Remeika, and J. R. Potopowicz, Appl. Phys. Lett. **20**, 135 (1972).

[14]Crystal supplied by K. Wojcik, Institute of Physics, 40007 Katowice, Poland.

[15]S. P. S. Porto, J. A. Giormaine, and T. C. Damen, Phys. Rev. **147**, 608 (1966).

[16]R. Calus, L. Merten, and J. Brandmuller, *Light Scattering by Phonon-Polaritons* (Springer-Verlag, Berlin, 1975).

[17]L. R. Williams, E. B. Gamble, Jr., K. A. Nelson, S. De Silvestri, A. M. Weinger, and E. P. Ippen, Chem. Phys. Lett. **139**, 244 (1987).

[18]F. W. Deeg and M. D. Fayer, J. Chem. Phys. **91**, 2269 (1989).