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Phase-transition analysis through soft-phonon–polariton behavior in the temporal domain: A_1-symmetry investigation of the $PbTiO_3$ perovskite

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We have studied the A_1-symmetry lowest-frequency phonon behavior of $PbTiO_3$ near the tetragonal-to-cubic phase transition, by a temporal-domain experiment. Study of the soft-phonon–polariton dispersion as a function of wave-vector value, at different temperatures up to T_c at 493 °C, allowed us to deduce its contribution to the static dielectric constant. Good agreement with measured values of the dielectric constant, which is associated with the nonappearance of a relaxational mode in the temporal response, clearly demonstrate the displacive origin of the transition.

I. INTRODUCTION

Development of intense subpicosecond-pulse technology has led to an increase in the number of studies using time-resolved nonlinear-spectroscopy. The work we describe here uses the two complementary characteristic features of ultrashort pulses, inasmuch as they allow a direct excitation and a temporal-evolution study of low-frequency phonon modes and relaxation motions in a crystal.

The three-pulse technique used permits, as previously demonstrated,[1] a complete description of the phonon-polariton regime. The advantage of an easy measurement of this wave-vector-dependent dispersion lies in the subsequent access to the relevant contribution of a given oscillatory mode to the dielectric constant. As a consequence, such a measurement, as a function of temperature, can lead to a two-parameter study of a phase transition. Soft-phonon–polariton behavior and its dielectric-constant contribution with direct measurements of the static dielectric constant allow us to consider the two potentially different characters associated with a phase transition, namely whether the transition is of order-disorder or displacive origin.

We present in this paper an investigation on lead titanate $PbTiO_3$. This crystal is known as a text-book example[2] of a displacive-character phase transition, from tetragonal to cubic symmetry. Nevertheless, recent Raman experiments[3] stressed discrepancies with dielectric-constant measurements and the authors concluded that this transition exhibits a mixed character. The problem of the description of the phase transition of perovskites is in fact troublesome as can be seen from recent quasicontradictory publications concerning $KNbO_3$ in the spectral domain.[4,5] An attempt to reconcile these conclusions has been made using a temporal-domain analysis.[6]

The first part of this paper will be devoted to symmetry considerations and associated selection rules, and to the general features of the signal discussed in the light of other experimental arrangements and results, which lead also to oscillatory excitations. Section III will be devoted to the description of the polariton regime. This behavior will be exploited as a way to determine the dielectric constant. Evolution of the phonon-polariton frequency up to the phase-transition temperature will be described in Sec. IV for different wave-vector values. The soft-mode behavior and the deduced dielectric-constant evolution is compared to clamped values and we are lead to the character of the symmetric part of this transition.

II. EXPERIMENTAL SETUP AND GENERAL FEATURES OF THE SIGNAL

We recall as a preliminary point the essential characteristics of the experimental setup. Femtosecond pulses (<100 fs) with a central wavelength of 620 nm from a colliding-pulse mode-locked dye laser and amplified at 20-Hz repetition rate are divided into three parts. Two of them form the pump-pulse excitation pair. A typical energy of 1 μJ per pulse is used for the experiment. The angle between the beams, tuned around 1°, defines the grating spacing and the phonon-polariton wave-vector value. The third part of the laser beam is focused in an ethylene glycol jet to produce a spectral continuum of light from which a central wavelength at 650 nm is selected by an interference filter. This probe beam goes through a variable delay line and is focused onto the crystal by the same lens as the pump-pair beam. The diffraction efficiency as a function of temporal delay is detected by a photodiode.

The point which is of primary concern is related to the physical mechanisms involved in a coherent excitation by two ultrashort pulses. Typical temporally resolved signals are depicted in Fig. 1. Apart from the electronic polarizability change, third order in the electric-field strength, which appears as an instantaneous process, the diffracted signal is composed of several features which depend on the pump-pulse energy and polarization configurations of pump and probe pulses.

There exists a long-lived process which dominates the response at positive time delays, when the pump-pulse polarizations are linear and parallel to each other. Its efficiency as a function of pump fluence, measured at a time delay of ~ 3 ps, where the oscillatory part of the signal becomes small, presents a fourth-power dependence;[7] this behavior is consistent with a two-photon absorption

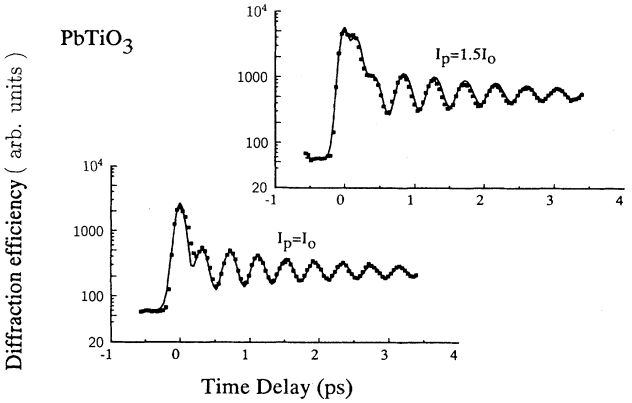

FIG. 1. Evolution of the temporal response, in a configuration where all the beams are polarized along y (or x axis), for two different values of pump fluence. The discrete points are experimental data and the continuous line is the theoretical fit.

(TPA) process, a fact which we have demonstrated previously.[8] In fact, modulation of the fluence in the sample, through the interference effect between the two pump pulses, leads to a modulation in the population of the free carriers created by TPA. We emphasize that this grating, in which complicated decay depends on diffusion and recombination processes, exists only, of course, for parallel polarizations of the pump pair. As the general characteristics of the signal are drastically independent on this TPA process, the overall study described here will be limited to this pump-pair polarization configuration.

The third general feature corresponds to the existence of several oscillatory parts. The one which is close to zero delay is highly damped and leads to a broadening of the electronic response; the other superimposed on the long-lived process, is characterized by a damping rate of several ps. The higher the energy density impinging the sample, the more the contribution near zero delay contributes. The fitting of results concerning various geometrical and polarization configurations leads us to conclude that we are dealing with the same frequency and the same phase. More insight into the processes involved will be the subject of a different publication; nevertheless, a qualitative explanation may be given now. At early times, the dielectric constant is directly modulated through the vibrational motion of the atoms; the damping rate is quite high, in agreement with the large spectral width of the phonon Raman mode. This temporal feature is comparable to results obtained by Dougherty, Wiederrecht, and Nelson on $KNbO_3$.[6] Moreover, the TO-phonon–polariton driven by the pump pair is associated with an induced field $E_{\rm pol}$, which is directed along z; this modulated field will give rise to a modulation of the refractive index through the electro-optic effect. The symmetry-allowed coefficients r_{33} and r_{13} lead, therefore, to a signal, after a rise time of ~ 100 fs, for y- and z-polarized probe pulses. This mechanism has been previously put forward for the description of polariton generation and propagation in $LiNbO_3$ (Ref. 9) and of coherent phonon oscillations in GaAs.[10] The main advantage of the special driving of phonon-polariton through electro-optic effect stands in a better accuracy in the knowledge of the vibrational frequency. The last fact which is of importance for this study is to recognize that we are dealing with only one vibrational motion, in phase with the pump-pair pulses. We are therefore located in the electronic ground state, in contrast to other studies where an electronic-induced displacement is observed.[11]

III. PHONON-POLARITON BEHAVIOR AND DIELECTRIC-CONSTANT DETERMINATION

The excitation process using two spectral broadband pulses can be described in the same manner as previously stated[12,13] for two monochromatic exciting beams $E_1(\omega_1)$ and $E_2(\omega_2)$ if one assumes that $E_{p1}\leftrightarrow E_1(\omega+\delta\omega)$ and $E_{p2}\leftrightarrow E_2(\omega-\delta\omega)$ with $2\delta\omega=\Omega$, the frequency of the driven phonon polariton. The scattering process may also be considered in the same way. Consequently, the phonon-polariton wave vector of frequency Ω will satisfy the relation

$$K^2(\Omega)=K^2(\omega_{p1})+K^2(\omega_{p2})-2K(\omega_{p1})K(\omega_{p2})\cos\phi\ , \quad (1)$$

where ϕ is the angle inside the crystal between the two pump pulses. This general formulation takes into account the wavelength and anisotropy dispersions of the refractive index. It has been applied using parameters obtained on $PbTiO_3$.[14]

In this series of experiments, the mean propagation direction of the beams being directed in a plane perpendicular to the c axis (z direction) of the tetragonal crystal (C^1_{4v}), the phonon-polariton wave vector is also perpendicular to the c axis and there is no anisotropy dispersion. The induced dipole moment is directed along z; so we are in the presence of pure A_1(TO) modes. As the spectral width of the pulses allows the excitation of modes lower than $\sim 200\ \text{cm}^{-1}$, the only driven mode is the lowest one, with Raman wave number $\omega_{\rm TO}$ and located at 147 cm^{-1}.[15] We are in the middle of the wave-vector dispersive region, in contrast to the experiments of Dougherty, Wiederrecht, and Nelson[6] and Planken[9] which are performed respectively in the phononlike region (for $KNbO_3$) and photonlike region (for $LiNbO_3$). The dielectric strengths of the two other allowed A_1(TO) modes is ten times smaller,[2] and we expect that the lowest mode will correctly describe the phonon part of the dielectric constant parallel to the c axis. Fitting the experimental points to a simple model, with an undamped single oscillator, of the form

$$\varepsilon_{\parallel}(\Omega)=c^2\frac{K^2}{\Omega^2}=\varepsilon_{\parallel\infty}+[\varepsilon_{\parallel}(0)-\varepsilon_{\parallel\infty}]\frac{\omega_{\rm TO}^2}{\omega_{\rm TO}^2-\Omega^2}\ , \quad (2)$$

where $\varepsilon_{\parallel}(0)$ and $\varepsilon_{\parallel\infty}$ are the static and optical dielectric constants, lead to a value of $\varepsilon_{\parallel}(0)$ consistent with the results directly measured at 1 KHz and 1 MHz.[3] Thus we are confident in the fact that this mode dominates the dielectric behavior along the ferroelectric c axis and that no additional excitation takes place in the dielectric response between the frequency of the dielectric data and the phonon-polariton resonances.

IV. TEMPERATURE BEHAVIOR OF THE PHONON-POLARITON MODE

Ferroelectric $PbTiO_3$ has tetragonal symmetry below the phase-transition temperature T_c, located at 495 °C. Above T_c, the crystal becomes paraelectric and its structure is cubic. For the study of the temperature-dependent phonon-polariton frequency, the crystal is placed in an electrically heated furnace, in which temperature is measured close to the crystal by a thermocouple. The poor stability in the value of the furnace temperature did not allow us to approach the transition temperature closer than several degrees.

In Fig. 2, the diffracted signal as a function of delay is displayed for three different temperatures. One can see that the value of the phonon-polariton frequency decreased dramatically for higher temperatures and tends toward a finite nonzero value; we have also verified that oscillations do not persist above T_c. This behavior is characteristic of a first-order phase transition. Figure 3 shows the evolution of the phonon-polariton frequency as a function of temperature for several of the wave vectors probed. For each K value, the temperature dependence can be fitted to an adequate power law. Since theory suggests $\Omega(A_1(\mathrm{TO})) \propto P_s$, the spontaneous polarization, we have fitted the temperature dependence of the measured phonon-polariton data to the P_s dependence, as did Burns and Scott.[2] Devonshire theory can be used to determine the P_u and Ω_u, polarization and frequency values respectively, at the superheating temperature T_u:

$$P_s = P_u \left\{ 1 + \left[\frac{3}{4} \frac{T_u - T}{T_c - T_0} \right]^{1/2} \right\}^{1/2} , \tag{3a}$$

$$\Omega = \Omega_u + C(T_u - T)^{\gamma} , \tag{3b}$$

$$C = \frac{1}{4}\sqrt{3} \frac{\Omega_u}{(T_c - T_0)^{1/2}} . \tag{3c}$$

The curves in Fig. 3 correspond to a fit of Eq. (3b). Successive values obtained for ω_u and γ at increasing K values are 21.5, 28.5, 30.5 cm^{-1} and 0.59, 0.56, 0.57. The wave number values Ω_u at different K can be compared to previously published values obtained from Raman experiments, and are 50 cm^{-1} (Ref. 3) and 65.8 cm^{-1}.[2] Although this power law adequately fits our results, we will not discuss the validity of the model or the physical meaning of γ parameters.

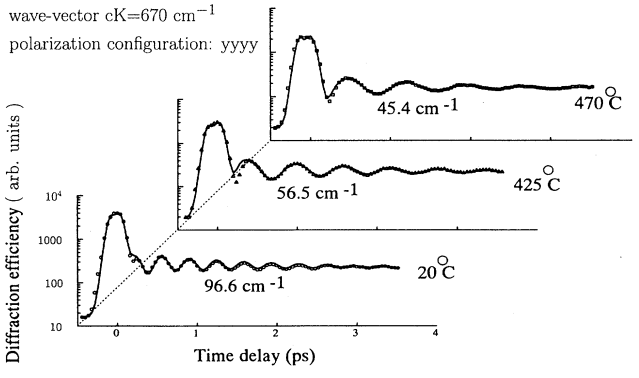

FIG. 2. Evolution of the temporal response for three different temperatures. The wave numbers correspond to fitted phonon-polariton frequencies. Experimental data are plotted as discrete points and theoretical results are plotted as continuous lines.

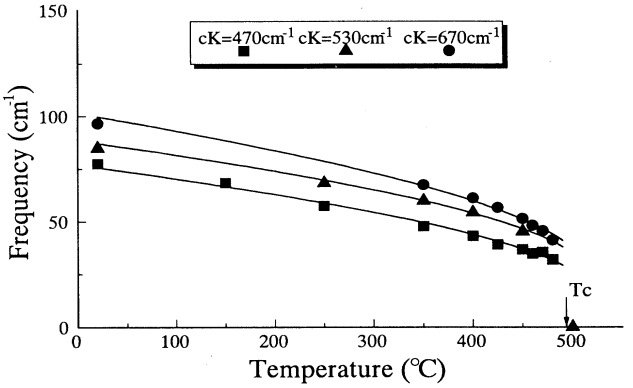

FIG. 3. Evolution of phonon-polariton frequency as a function of temperature, at different wave-vector values. The lines correspond to a fit to Eq. 3(b).

Study of Fig. 2 reveals no evidence of the contribution from a relaxational mode to the phase transition for this symmetry. Nevertheless, its detection in the actual measurement is questionable, and depends on the possible temporal and weight characteristics of this contribution with respect to the long-lived process, which persists at all temperatures studied. To confirm this point, we have deduced, for each temperature, an estimate of the static dielectric constant from a fit of Eq. (2), by using ω_{TO} and $\varepsilon_{\parallel\infty}$ values given in the literature;[3,16] several of the fits are reproduced in Fig. 4. We find that by comparing (Fig. 5) our values to measurements of the clamped dielectric constant,[3] good agreement is obtained and leads us to believe that the lowest-frequency phonon-polariton mode contribution to $\varepsilon_{\parallel}(0)$ prevails over all other processes over the whole temperature range probed; in fact, the

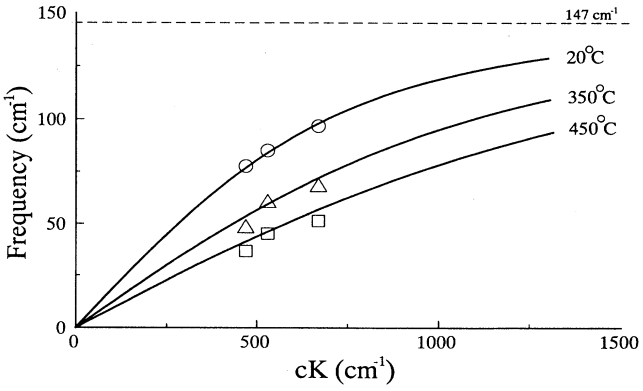

FIG. 4. Evolution of phonon-polariton frequency as a function of wave-vector values, at different temperatures. The lines correspond to a fit to Eq. (2).

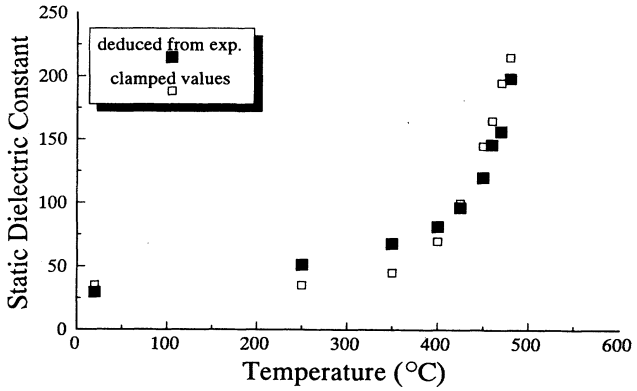

FIG. 5. Evolution of the static dielectric constant as a function of temperature. Full squares correspond to values deduced from phonon-polariton dispersion curves; empty squares correspond to direct measurements of the dielectric constant.

havior of the temporal response can be accounted for without any contribution from a relaxational mode.

V. CONCLUSION

We have shown that phonon-polariton behavior can be used as a sensitive tool for the measurement of the changes that take place in a crystal when a phase transition is approached. In the case of $PbTiO_3$, accurate measurement of the phonon-polariton frequency as a function of K leads to an estimate of the photon-polariton contribution to the static dielectric constant. Knowledge of this dual characterization allowed us to verify that the phase transition is of first order and to conclude with a high degree of confidence that it is of displacive origin. This is in contrast with $KNbO_3$ perovskite for which temporal results obtained by Dougherty, Wiederrecht, and Nelson[6] showed a relaxational contribution in the A_1 symmetry part of the phase transition.

Enhancement of the phonon-polariton part to the overall signal is the result of a contribution from an electro-optic effect and from free carriers promoted by a two-photon absorption process. The polarization configuration necessary to drive nonsymmetric modes will cancel the excitation of these processes. It will be studied in a separate publication.

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[1]J. Etchepare, G. Grillon, A. Antonetti, J. C. Loulergue, M. D. Fontana, and G. E. Kugel, Phys. Rev. B **41**, 12 362 (1990).

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

[3]M. D. Fontana, H. Idrissi, and K. Wojcik, Europhys. Lett. **11**, 419 (1990); M. D. Fontana, H. Idrissi, G. E. Kugel, and K. Wojcik, J. Phys. Condens. Matter **3**, 8695 (1991).

[4]J. P. Sokoloff, L. L. Chase, and D. Rytz, Phys. Rev. B **38**, 597 (1988); **40**, 788 (1989).

[5]M. D. Fontana, A. Ridah, G. E. Kugel, and C. Carabatos, J. Phys. C **21**, 5853 (1988); Phys. Rev. B **40**, 786 (1989).

[6]T. P. Dougherty, G. P. Wiederrecht, and K. A. Nelson, Ferroelectrics **120**, 79 (1991); G. P. Wiederrecht, T. P. Dougherty, and K. A. Nelson, *Ultrafast Phenomena VIII*, edited by J. L. Martin, A. Migus, G. A. Mouron, and A. H. Zewail, Springer Series on Chemical Physics, Vol. 55 (Springer, Berlin-Heidelberg, 1993).

[7]J. Etchepare, G. Grillon, A. Antonetti, J. C. Loulergue, M. D. Fontana, and G. H. Kugel, Ann. Phys. (Paris) **16**, 111 (1991).

[8]J. C. Loulergue and J. Etchepare, Ferroelectrics **125**, 501 (1992).

[9]P. C. M. Planken, L. D. Noordam, J. T. M. Kennis, and A. Lagendijk, Phys. Rev. B **45**, 7106 (1992); P. C. M. Planken, thesis, University of Amsterdam (1991).

[10]G. C. Cho, W. Kütt, and H. Kurz, Phys. Rev. Lett. **65**, 764 (1990); W. Kütt, T. Pfeifer, T. Dekorsy, and H. Kurtz, in *Ultrafast Phenomena VIII* (Ref. 6).

[11]H. J. Zeiger, J. Vidal, T. K. Cheng, E. P. Ippen, G. Dresselhaus, and M. S. Dresslhaus, Phys. Rev. B **45**, 768 (1992).

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

[13]J. J. Wynne, R. Dorsinville, and R. R. Alfano, Phys. Rev. B **40**, 1885 (1989).

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

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

[16]W. Kleeman, F. J. Schäfer, and D. Rytz, Phys. Rev. B **34**, 7873 (1986).