Observation of THz Phonon-Polariton Beats in $LiTaO_3$

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We report on the impulsive excitation and phase-sensitive detection of terahertz phonon polaritons in the ferroelectric $LiTaO_3$ using femtosecond pulses. The coherent propagation of the polaritons and their dephasing is investigated in detail. Polaritons with frequencies below 1.5 THz clearly show that there is a resonance at 0.95 THz that has not been found in previous Raman and IR reflectivity studies. This resonance allows the coherent excitation of two polaritons of different frequencies. This leads to the first observation of phonon-polariton beats.

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Recent developments in laser technology have led to the generation of light pulses that are much shorter than the oscillation period of many lattice vibrations (phonons). Therefore these pulses can be used for the impulsive excitation and phase-sensitive detection of phonons [1]. In addition, due to their large bandwidth, short pulses allow the simultaneous excitation of several stationary states of different energy, thereby opening the way to the observation of quantum and polarization beats. Recently, these beats have been observed for extended states like excitons [2–5] and exciton polaritons [6].

Polaritons are a very general type of excitation. Whenever light propagates through a medium with resonances, the coupling between light and polarization leads to mixed light-polarization states, called polaritons. Near a resonance the coupling leads to an avoided crossing in the dispersion of the polariton. As a result two polariton dispersion branches appear.

The ratio between polarization and electric field of the polariton is described by the dielectric constant. Far away from resonance the dielectric constant is real and shows a weak dependence on frequency so that the polaritons can be described well with a refractive index. Close to resonance, however, the polaritons become strongly dispersive which leads to spreading and damping of the polaritons.

A previous cw Raman study on phonon polaritons in $LiTaO_3$ revealed an anomaly in the dispersion for low frequencies [7]. It was suggested that bulk polaritons with frequencies below 1.4 THz cannot exist due to crystal domain variations. In a previous time-resolved study, ultrashort polaritons were excited in $LiTaO_3$ via the optical Čerenkov effect, but no anomaly was found for frequencies below 1.4 THz [8]. These ultrashort polaritons are generated in a divergent cone and have no well-defined wavevectors and frequencies. Polaritons can also be generated and studied with alternative nonlinear optical techniques like impulsive stimulated Raman scattering [9, 10] and difference-frequency mixing [11].

In this Letter we report on the impulsive excitation and phase-sensitive detection of phonon polaritons in $LiTaO_3$ with well-defined wavevector, frequency, and direction of propagation. The polaritons are excited via difference-frequency mixing of two ultrashort pulses. Excitation via stimulated Raman scattering will be of minor importance since the $\chi^{(2)}$ of $LiTaO_3$ is very large. The pulses are generated by a colliding-pulse-mode-locked laser and amplified in a six-pass dye amplifier that is pumped with a copper-vapor laser. The pulses have a pulse duration of 60 fs, a central wavelength of 625 nm, a bandwidth of 8 THz, and an energy of 5 μJ. The repetition rate of the system is 6.8 kHz. The pulses are split into three. All three parts are focused into the crystal with a 40 cm lens to a focus of 200 μm. Two of the three pulses serve as excitation pulses and are polarized along the optical axis in order to attain the highest efficiency for the mixing process. The angle between these two excitation beams defines the wavevector of the nonlinear polarization and thereby the wavevector of the polariton for which the mixing process is phase matched. An angle of 0.57° is required to generate a wavevector of 1000 cm^{-1} . The polariton frequencies that correspond to this wavevector are generated with the highest efficiency out of the frequency spectrum of the excitation pulses. Because the two excitation pulses have equal central frequency and bandwidth, two counter-propagating polaritons of equal frequency and equal absolute wavevector are generated. The polaritons are probed with the third pulse (probe) via the electro-optic effect. This beam makes an angle of 2° with the excitation beams. The electric field associated with the polariton strongly modulates the refractive index of the probe that is polarized along the optical axis. The resulting index grating diffracts the probe. In our experiment we measure the first-order diffracted light intensity as a function of the time delay between the two excitation pulses and the probe.

The signal in the diffracted direction is influenced by two interference effects. The first effect is the interference of the two counter-propagating polaritons with each other. This leads to a standing wave which implies that the index grating goes on and off with the double polariton frequency. This effect will only be observed when the probe is focused at about the same spot the two pumps

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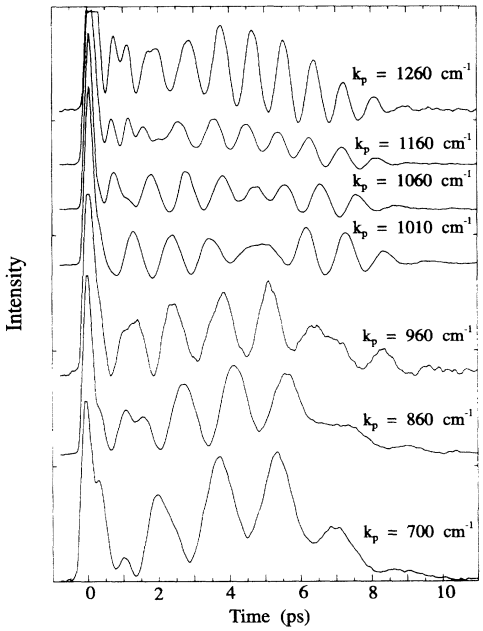

FIG. 1. Time-resolved measurement of phonon polaritons with seven different wavevectors. Between 800 and 1200 cm^{-1} the signal transients become irregular due to the interference of polaritons of different frequency.

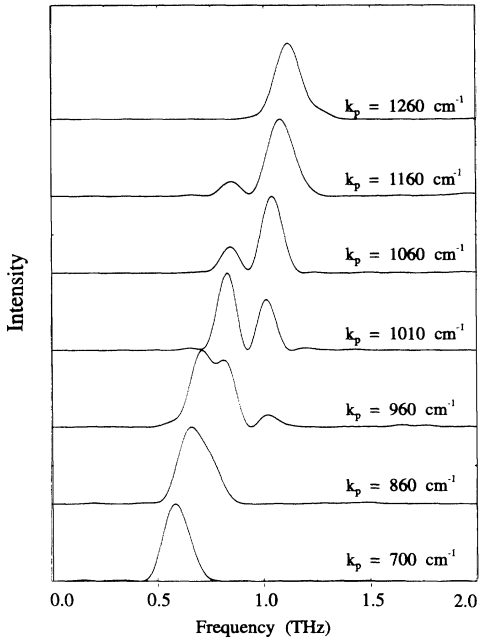

FIG. 2. Fourier transforms of the signal transients of Fig. 1.

are focused at. If the probe is focused next to this spot only one of the two polaritons will propagate into the focus of the probe after some time and will diffract the probe. In this case just the envelope function of the polariton would be observed if there was no interference with background scattered light. However, there is always some background scattered light from zero-order diffraction of the focused probe and scattering from inhomogeneities at the surface of the crystal. The interference of this light with the light diffracted by the polariton leads to a signal oscillating with the polariton frequency.

In Fig. 1 a set of measurements is presented where the probe is focused 260 μm next to the common focus of the two exciting pulses in the plane that is spanned by the two excitation beams. In these measurements the central value of the polariton wavevector k_p is varied around 1000 cm^{-1}. Time delay zero can be recognized from the signal that arises from a strong electronic $\chi^{(3)}$ effect that is only present when the probe has time overlap with the two excitation pulses. For small time delays the double frequency is observed due to interference of the two counter-propagating polaritons. The signal is large and regular for k_p >1200 cm^{-1} and for k_p <800 cm^{-1}. However, for values of k_p between 800 and 1200 cm^{-1}, the signal appears to become weaker and irregular. For k_p = 1010 cm^{-1} a jump in phase is observed. In Fig. 2 the corresponding Fourier transforms of the signal transients of Fig. 1 are presented. The traces between 800 and 1200 cm^{-1} show two clearly resolved frequencies. We also note that there is no value for k_p at which a polariton with a frequency of 0.95 THz can be excited.

In Fig. 3 the polariton frequency is shown as a function of k_p. In this figure also other measurements have been included. The dispersion of the polaritons is strongly influenced by the TO-phonon resonance at 6 THz. In addition we note that there is an avoided crossing in the dispersion curve around 1 THz which indicates a second resonance. Because of this resonance at 0.95 THz we can excite coherently at one particular value of k_p two polaritons with different frequency. This explains the observation of beats in Fig. 1. The solid curves in Fig. 3 are fits using the definition of Barker and Loudon for the dispersion of polaritons [12]. In this fit the two resonances are described as damped harmonic oscillators. We derive from the fit that the resonance at 0.95 THz is 60 times weaker than the resonance at 6 THz.

We compare the time-resolved measurements of the polaritons around 1 THz with numerical solutions of the coupled equations that describe the interaction between light and matter. These equations are the Maxwell wave equation containing the nonlinear source term by which the polaritons are excited and the Bloch equation for the polarization of a two-level system,

$$\left(\frac{\partial}{\partial z}+\frac{1}{v_g}\frac{\partial}{\partial t}\right)E=-\frac{i}{2\epsilon_0 cn\omega_3}\frac{\partial^2}{\partial t^2}Pe^{-i\omega_3 t}-e^{-i\omega_3 t}\frac{i\chi^{(2)}}{2\epsilon_0 cn\omega_3}\frac{\partial^2}{\partial t^2}E_1E_2^*,\quad \frac{\partial}{\partial t}P=\frac{iN\mu^2}{2\hbar}E+i(\omega_3-\omega_0)P-\frac{P}{T_2},\qquad(1)$$

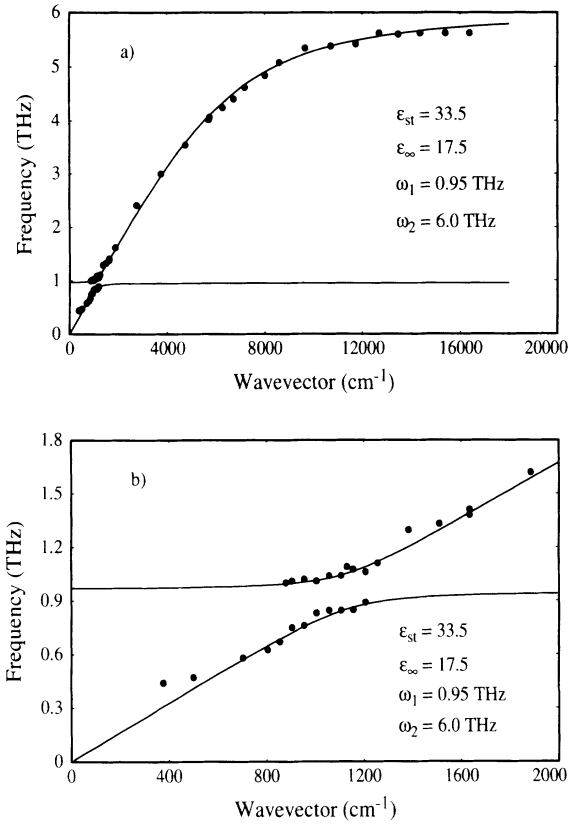

FIG. 3. Dispersion curve of $LiTaO_3$ in the frequency interval between 0 and 6 THz (200 cm^{-1}). The solid curves are the result of a fit in which the resonances are described as damped harmonic oscillators.

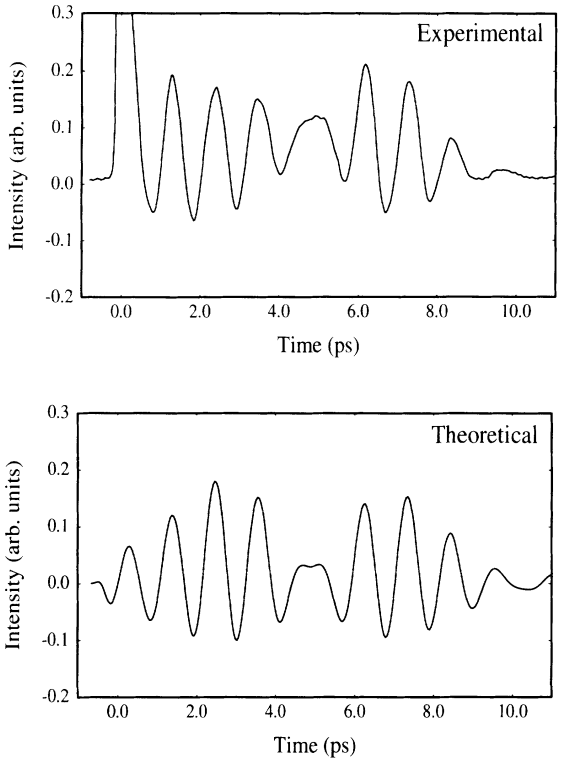

FIG. 4. Experimental and numerically calculated time-resolved signal transient that arises from the coherent excitation of two polaritons of the lower and the upper branch of the dispersion curve at k_p = 1010 cm^{-1}.

with the electric field of the polariton defined by $Ee^{i(k_p z-\omega_3 t)}$, the polarization of the polariton defined by $Pe^{i(k_p z-\omega_3 t)}$, E_1 and E_2 the envelope functions of the two excitation fields, v_g the group velocity, ϵ_0 the vacuum permittivity, c the velocity of light in vacuum, n the refractive index, ω_3 the angular frequency of the light in case there would be no interaction ($\omega_3 = k_p c/n$), $\chi^{(2)}$ the second-order susceptibility, N the density of excited oscillators, μ the transition dipole matrix element, ω_0 the resonance frequency, and T_2 the dephasing time.

In the Maxwell equation the slowly varying amplitude approximation is used and it is assumed that all other resonances are so far away in frequency that their effect on the dielectric response can be well described with the refractive index n and the group velocity v_g. Therefore the polarization P in these equations is only the polarization associated with the resonance at 0.95 THz. It is also assumed that this polarization is not affected by population changes.

These equations are numerically solved using a modified Runge-Kutta method by which a fourth-order accuracy in both time and space is achieved [13]. The equations are integrated in time. At each time point the spatial profiles of electric field and polarization in the crystal are calculated. Far away from resonance the polaritons, which form the eigenstates of the coupled system, have different frequencies, group velocities, and electric-field amplitudes so that little interference will be observed. Near resonance however, the two polaritons have about equal group velocities, equal electric-field strengths, but still different frequencies so that beats are observed. We also derive from these solutions and from the experimental results that around resonance the polaritons become very dispersive. In Fig. 4 the experimental signal transient for k_p=1010 cm^{-1} is compared with the calculated result at the same wavevector. The only parameters that enter the calculation are the strength of the coupling $N\mu^2$ between the light and the resonance, the frequency of the resonance ω_0, and the dephasing time T_2. From the comparison between calculated and experimental results we derive a value for T_2 of 4 ps at room temperature.

The resonance at 0.95 THz has not been found in previous Raman [14] or IR reflectivity [15] studies. This may be due to the fact that the resonance is rather weak and in a frequency regime where these techniques are not very sensitive. In contrast, our experiment demonstrates

clearly the avoided crossing in the polariton dispersion. Therefore the measurement of this dispersion appears to be a very sensitive probe for resonances. In a previous cw Raman study on polaritons in $LiTaO_3$ [7], it was observed that for decreasing k the dispersion flattens out, which agrees very well with our observation for the upper branch of the dispersion in Fig. 3.

We suggest the following explanation for the resonance at 0.95 THz. It has been found that the effects of the 6 THz phonon on the dielectric parameters of $LiTaO_3$ can be described very well with a potential that is extremely anharmonic with three minima in one unit cell [16]. This agrees with the observation that above T_c the Li ion is found not only at the centrosymmetrical position but also at positions ± 0.037 nm displaced along the optical axis [17]. In the ferroelectric phase the minima of this potential have different energies due to the electric field every unit cell experiences due to the spontaneous polarization. We used this potential for a quantum-mechanical calculation of the vibrational levels and found that the vibrational ground state is localized in the well with the lowest minimum. The first excited state is 6 THz above the ground state and is close in energy to the ground state of the middle well. As a result both states get delocalized and have an energy splitting of 1 THz. Because the two states have a small difference in thermal population, the 0.95 THz resonance can be assigned to this tunneling resonance between the two wells. This explanation agrees with the fact that such a low-frequency resonance is not observed in $LiNbO_3$ [11], because the potential in this crystal has only one minimum. The explanation is also supported by our observation that the strength and frequency of the resonance are temperature dependent because such a tunneling resonance will be influenced by changes in the vibrational state populations and the spontaneous polarization.

In conclusion, we report on the impulsive excitation of THz phonon polaritons with femtosecond pulses in $LiTaO_3$. We observe phonon-polariton beats due to the coherent excitation of polaritons of the lower and the upper branch of the dispersion that is associated with a newly discovered resonance at 0.95 THz.

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