Coherent Excitation of Phonon Polaritons in a Centrosymmetric Crystal

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We report the first coherent excitation of phonon polaritons in a centrosymmetric crystal. Energy dispersion and linewidth of the A_u upper-branch bulk polaritons in TiO_2 were determined by optical four-wave mixing.

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In recent years several four-wave-mixing (4WM) experiments have been performed to study polaritons in crystals with *non*centrosymmetric structure.[1] The excitation of polaritons in these crystals may involve contributions from the third-order susceptibility $\chi^{(3)}$ as well as contributions from two-stage processes associated to the second-order susceptibility $\chi^{(2)}$. The contribution from $\chi^{(2)}$ occurs in the following way: In the first stage, two incident lasers of frequencies ω_1 and ω_2 generate a polariton at frequency $\omega_p = \omega_1 - \omega_2$. In the second stage, the polariton couples with the laser beam at frequency ω_1 to generate a beam at $\omega_4 = 2\omega_1 - \omega_2$.[1,2]

These experiments cannot be performed in a material medium with inversion symmetry because $\chi^{(2)} = 0$ and the electric dipole selection rules do not allow the observation of resonant enhancement of $\chi^{(3)}$ due to polaritons. For this kind of material the studies of polaritons have been possible by use of techniques such as infrared absorption and hyper-Raman and neutron scattering, which present a poor spectral resolution.[3]

However, the observation of polaritons in centrosymmetric crystals by 4WM techniques should be possible if two of the four transitions involved in the process are of the electric dipole (ED) type and the others are of the magnetic dipole (MD) or the electric quadrupole (EQ) type. In both cases there are no parity selection rules preventing two-photon intermediate resonances between the opposite-parity states which correspond to polariton excitations. Then a two-stage nonlinear mixing would occur involving MD or EQ transitions. Of course, the effects resulting from MD or EQ resonances will be superimposed on the effects due to ED transitions which contribute to $\chi^{(3)}$. However, those effects can be minimized by choosing the laser frequencies such that ω_1, ω_2, and $\omega_1 \pm \omega_2$ are far from the resonances associated to $\chi^{(3)}$. On the other hand, the MD or EQ effects can be enhanced by the appropriate selection of the laser frequencies in order to be resonant with the MD or EQ transitions.

In this paper, we report an experiment which takes advantage of a strong electric quadrupolar nonlinear susceptibility in order to excite bulk polaritons in a centrosymmetric crystal.

Rutile (TiO_2) was the selected material because it has a high electric quadrupole susceptibility.[4] Furthermore, it is representative of a large number of compounds which have the same crystalline structure (D_{4h}^{14}) and show interesting electric and magnetic properties.[5]

The experimental arrangement used for the present work consisted of two homemade dye lasers pumped by the same frequency-doubled Nd-doped yttrium-aluminum-garnet laser. Both dye lasers were of the grazing-grating type[6] operating in the range of 5600–6200 Å with linewidths of ~ 0.2 cm^{-1}. The dye laser beams with 8-nsec duration time were overlapped temporally and spatially inside the sample with use of a 30-cm focal length lens and properly located mirrors. The 4WM output signal was sent through a 0.5-m double monochromator to a photomultiplier followed by a boxcar integrator and recorder. The laser beams propagated along the crystal c axis and the phase matching was achieved by adjustment of the crossing angle between the incident beams. The scanning of the dye lasers was controlled in order to maintain the 4WM signal frequency ω_4 constant while tuning $\omega_1 - \omega_2$. Phase matching was preserved by slightly rotating the sample around its a axis which is perpendicular to the incidence plane.

The signal intensity at frequency ω_4 as a function of $\omega_1 - \omega_2$ is shown in Fig. 1. The spectrum was obtained at room temperature with the laser fields $\mathbf{E}(\omega_1)$ and $\mathbf{E}(\omega_2)$ parallel to the crystallographic a direction. The angle between $\mathbf{k}_1$ and $\mathbf{k}_2$ corresponding to Fig. 1 was $\approx 1.5°$ outside of the sample. The electric field of the generated beam was found to be perpendicular to the incidence plane. Similar spectra could be obtained with good signal-to-noise ratio throughout the whole spectral range of interest [900 cm$^{-1} < \omega_1 - \omega_2 < 1500$ cm^{-1}].

For each given $\omega_p = \omega_1 - \omega_2$, we measured $I(\omega_4)$ as a function of $|\mathbf{k}_1 - \mathbf{k}_2|$ by varying the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$ in order to find the optimum phase matching. This procedure allows us to obtain the dispersion characteristics of the polaritons as a function of their wave vectors and the results are shown in Fig. 2(a).

The typical nonresonant background in these experiments has been found to be about 20% of the background produced in a coherent anti-Stokes Raman

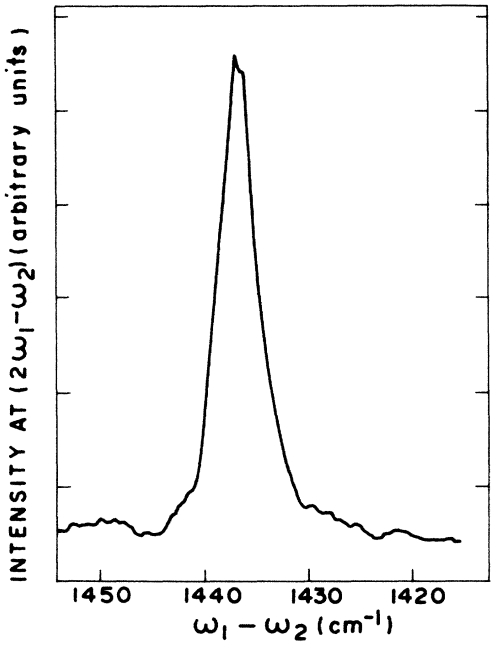

FIG. 1. Four-wave-mixing spectrum of TiO_2 at room temperature. The laser fields $\mathbf{E}(\omega_1)$, $\mathbf{E}(\omega_2)$, and $\mathbf{E}(\omega_4)$ are parallel and are incident on a crystal face perpendicular to the c axis.

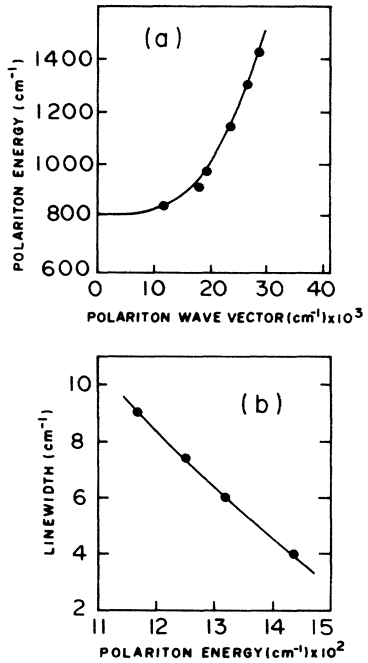

FIG. 2. (a) Dispersion relation for the A_u-phonon polariton in TiO_2. Points represent data obtained in the 4WM experiment. Solid line is a sketch of the dispersion relation starting at the A_u-(LO) phonon energy. (b) Observed linewidth of polaritons as a function of their energy. The solid line is a guide for the eyes.

scattering experiment with use of liquid benzene while the resonance enhancement is of the same order as that obtained on scanning through the 992-cm^{-1} mode of benzene.

We associate the observed resonances to the upper-branch A_u-phonon polaritons in TiO_2 because of their energy range. Accordingly, we obtain from Fig. 2(a) the energy $\omega(k \rightarrow 0) \cong 800$ cm^{-1} which is in reasonable agreement with the reported energy of the A_u(LO) infrared-active phonons.[7] Furthermore, the behavior of the resonance linewidth $\Gamma(\omega_p)$ agrees with the expected behavior for upper-branch polaritons. Namely, we observed a decrease of $\Gamma(\omega_p)$ for increasing values of ω_p as shown in Fig. 2(b).

The directions of the light beams and their polarizations impose the condition that the excited phonon polaritons must have wave vectors and polarizations perpendicular to the c axis. Thus, only the ordinary A_u-phonon polaritons are observed.

Notice that the energy of the ordinary polaritons differs from the reported energies of the extraordinary polaritons.[5a] This result is expected for any axial crystal.[3a]

In order to describe the nonlinear mixing occurring in this experiment, it is convenient to express the induced effective polarization per unit volume by[8]

$$\mathbf{P}_{\rm eff}^{\rm NL} = \mathbf{P}^{\rm NL} - (c/\omega_4)\mathbf{k}_4 \times \mathbf{M}^{\rm NL} - \tfrac{1}{6} i \mathbf{k}_4 \cdot \mathbf{Q}^{\rm NL}, \quad (1)$$

where $\mathbf{P}^{\rm NL}$, $\mathbf{M}^{\rm NL}$, and $\mathbf{Q}^{\rm NL}$ are the nonlinear dipole moment, the nonlinear magnetic moment, and the nonlinear quadrupole moment densities, respectively. $\mathbf{k}_4$ and ω_4 are the wave vector and frequency of the wave resulting from the interaction of two photons at ω_1 and one photon at ω_2.

For a centrosymmetric crystal, the effective polarization has contributions of the form

$$\mathbf{P}^{\rm NL} = \chi_a^{(2)} \vdots \mathbf{E}\nabla\mathbf{E} + \chi_b^{(2)} \vdots \mathbf{B}\mathbf{E} + \chi_c^{(3)} \vdots \mathbf{E}\mathbf{E}\mathbf{E}, \quad (2)$$

$$\mathbf{Q}^{\rm NL} = \eta_a^{(2)} \vdots \mathbf{E}\mathbf{E} + \eta_b^{(3)} \vdots \mathbf{E}\mathbf{E}\nabla\mathbf{E} + \eta_c^{(3)} \vdots \mathbf{B}\mathbf{E}\mathbf{E}, \quad (3)$$

$$\mathbf{M}^{\rm NL} = \xi_a^{(2)} \vdots \mathbf{E}\mathbf{E} + \xi_b^{(3)} \vdots \mathbf{E}\mathbf{E}\nabla\mathbf{E} + \xi_c^{(3)} \vdots \mathbf{B}\mathbf{E}\mathbf{E}, \quad (4)$$

where $\chi_\alpha^{(i)}$, $\eta_\alpha^{(i)}$, and $\xi_\alpha^{(i)}$ (with $i = 2, 3$; $\alpha = a,b,c$) represent the second- and third-order susceptibilities. $\mathbf{E}$ and $\mathbf{B}$ are the electric and the magnetic vectors of the incident lasers, respectively.

The various contributions to the induced polarization at the frequency $2\omega_1 - \omega_2$ can be folded into a single effective susceptibility, $\chi^{(3),\rm eff}$, so that

$$\mathbf{P}_{\rm eff}^{\rm NL} = \chi^{(3),\rm eff} \vdots \mathbf{E}(\omega_1)\mathbf{E}(\omega_1)\mathbf{E}(\omega_2)^*. \quad (5)$$

The light intensity at $2\omega_1 - \omega_2$ will be proportional to $|\chi^{(3),\rm eff}|^2$.

We do not expect an important resonant contribution for $|\chi^{(3),\rm eff}|^2$ originating from $\chi_c^{(3)}$ as is usual in 4WM experiments with centrosymmetric crystals.[3b] Although $\omega_1 + \omega_2$ is larger than the crystal band gap

(3.75 eV), a direct two-photon transition cannot explain the relatively narrow resonances observed. Furthermore, the fact that all Raman-active phonons have energies which are far from the $\omega_1-\omega_2$ values used in the experiment prevents a Raman-resonance enhancement of $\chi_c^{(3)}$. However, this susceptibility may give an important contribution to the nonresonant background.

For the geometrical configuration of electromagnetic fields used in the experiment, it is possible to deduce polarization selection rules introduced by each term of Eqs. (2)–(4). The calculation takes into account the symmetry properties of the nonlinear susceptibilities which are determined by the rutile crystalline structure. The nonnull contributions to $P_{\rm eff}^{\rm NL}(2\omega_1-\omega_2)$ will depend on the nonzero elements of χ, η, and ξ as well as on the directions and polarizations of the light beams. The results show that the resonance enhancement of the beam intensity at $\omega_4=2\omega_1-\omega_2$ originates from two-stage processes involving $\chi_a^{(2)}$ and or $\eta_a^{(2)}$ in a manner similar to the polariton excitation in Ref. 2 which involved the second-order electric dipolar susceptibility. This is in agreement with the observed enhancement of $|\chi^{(3),\rm eff}|^2$ which occurs when $\omega_1-\omega_2$ is scanned through the energy range expected for the A_u-phonon polaritons in TiO_2. Thus, we concluded that the resonant signal at ω_4 results from a quadrupole-assisted four-wave-mixing process. The occurrence of a two-step process involving one EQ and one ED transition in each step is essential in order to allow a two-photon resonant enhancement connecting the opposite-parity states associated to the phonon polaritons. Although electric quadrupole susceptibilities are usually expected to be small, the present results are not surprising because efficient second-harmonic generation in TiO_2 was reported a few years ago[4] and explained in terms of the high electric quadrupolar susceptibility of this crystal. It is important to notice that the second-harmonic generation efficiency in TiO_2 is about 3 orders of magnitude larger than in crystalline calcite.[4] Other reports of very large electric quadrupole effects have also appeared quite recently for centrosymmetric semiconductors.[9] Furthermore, in the present experiments the dye-laser frequencies are large enough to excite two-photon transitions through the crystal band gap which may contribute with a broad background and thus the nonlinear response may be even larger than in Ref. 4. For the conditions of the present experiment we estimate that on resonance, $\chi_{xxxx}^{(3),\rm eff}\approx 10^{-12}$ esu which has the same order of magnitude as in liquid benzene. Concerning the diagonal element of the effective susceptibility far from polariton resonances, an order-of-magnitude estimate gives the value $\sim 10^{-14}$ esu.

In conclusion, we emphasize that our experiments demonstrate a new type of spectroscopic application of four-wave-mixing processes. Polaritons in a centrosymmetric crystal could be studied by exploration of two-photon resonances between states of opposite parity. Further experiments are in progress to characterize better the microscopic origin of the bulk polaritons lifetime and to study infrared and silent phonons in TiO_2.

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