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COHERENT EXCITATION OF POLARITONS IN GALLIUM PHOSPHIDE*

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The coherent excitation of polaritons has been achieved in the III-V semiconductor GaP for the first time by a nonlinear, optical parametric process. We are able to describe the polariton dispersion curve in the ω-k space and to measure the absorption coefficient of the crystal near the Reststrahl band. The results are discussed on the basis of recent theories on the polariton disperson and damping in GaP.

A high-intensity, coherent polariton field has been excited in the polar III-V semiconductor gallium phosphide by mixing two coherent optical waves whose wavelengths lie in the transmission gap of the crystal. This method for the creation in a medium of coherent, Raman-active optical phonons or other elementary excitation is sometimes called "coherent excitation[1]."

Four pairs of interacting frequencies have been chosen in order to excite resonantly the polarization field near the lattice resonance (Reststrahl) at 366 cm^{-1} covering, in the lower branch of the optical dispersion curve, a range of infrared wavelengths in which the excitation exhibits a mixed (electromagnetic and phonon) character.[2,3] In our experiment (Fig. 1) two Raman cavities pumped by a Q-switched ruby laser were used to generate two (Stokes) beams of coherent light at different frequencies (ω_1 and ω_2). The two beams were focused by a common high-quality achromatic lens (20-cm $f/1$) in the crystal where the polariton field at frequency $\omega_q = \omega_1 - \omega_2$ is generated. Small diaphragms were used in front of the lens in order to reduce the convergence of the beams reaching the crystal to about 5×10^{-3}. The angle θ made by the two beams $\vec{k}_1$ and $\vec{k}_2$ in

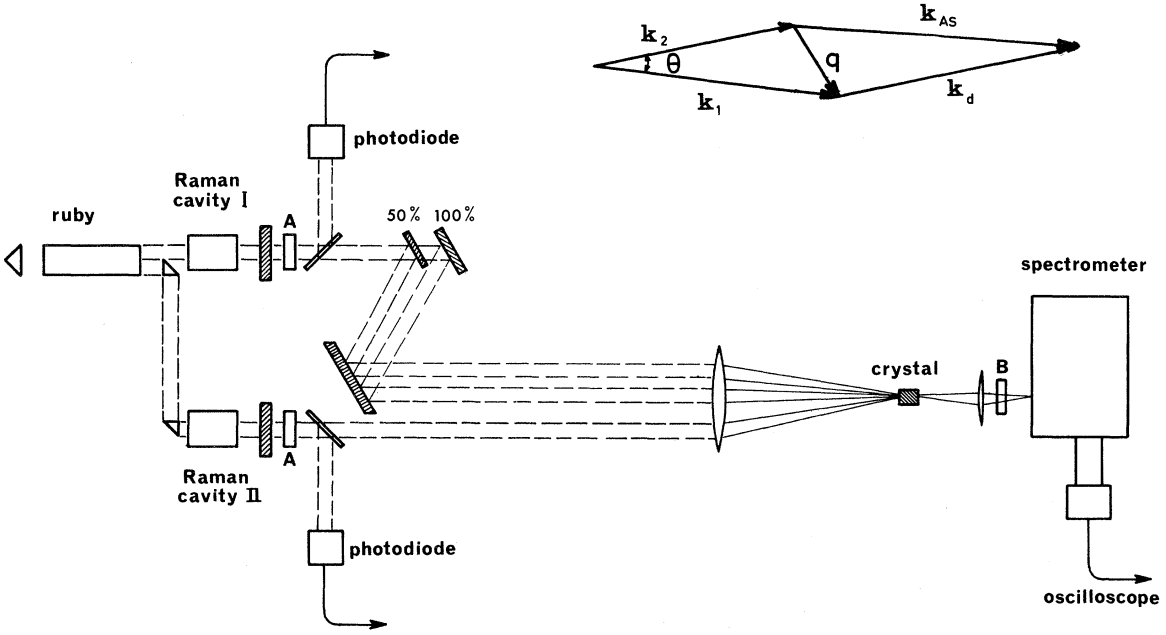

FIG. 1. Schematic diagram of the experimental apparatus.

the crystal was set to a previously calculated value in order to secure the phase matching of the polariton generation process.[4] Small variations of θ were made possible in our experiment in a simple and reproducible way in order to sweep over the polariton resonance in the k-vector space for each set of exciting frequencies. Valuable physical information about the dynamics of the polariton field in GaP was thus obtained and it will be discussed later in the paper. The excitation of the coherent polariton field was probed by a third beam $\vec{k}_d$ of frequency ω_d, that was focused by the common lens in the focal region of the $\vec{k}_1$ and the $\vec{k}_2$ beams. The scattered beam $\vec{k}_{as}$ at frequency $\omega_a = \omega_d + \omega_q$ (or $\omega_a = \omega_d - \omega_q$)[5] was analyzed by a double-stage Jarrell-Ash Model No. 82-410 spectrometer and detected by a 56CVP photomultiplier. For simplicity the $\vec{k}_d$ beam was supplied by one of the two Raman oscillators. The direction of $\vec{k}_d$ was calculated in order to match the momentum-conservation requirement for the polariton scattering process $\vec{k}_{as} = \vec{k}_d \pm \vec{q}'$. (We call $\vec{q} = \vec{q}' + i\vec{q}''$ the propagation vector of the polariton at frequency ω_q.) The direction of $\vec{k}_d$ could be easily changed to adjust the phase matching during the experiment. A large-aperture lens collected the $\vec{k}_{as}$ beam focusing it on the slit of the spectrometer. The filters A and B were used to block out the 6943-Å radiation coming from the laser. The GaP crystal was 6 mm long and had its (311) direction parallel to the lens axis. More details about the experimental setup will be given in a forthcoming paper. The intensities of the three interacting beams k_1, k_2, k_d were about 500 kW with a pulse width of 20 nsec. In these conditions the crystal did not suffer damage on the surface. Working at a difference frequency of 354 cm^{-1} (when the polariton is very phononlike), at perfect phase matching the energy of the scattered beam was 10^{-6}-10^{-7} times the exciting beam intensity, a result which is in order-of-magnitude agreement with the anti-Stokes generation in usual stimulated-Raman-scattering experiments.[6] According to the theory, the intensity of the k_{as} beam was found to be proportional to the product of the intensities of the interacting beams, $I_1 I_2 I_d$. The materials used as Raman generators were some highly Raman-active liquids. We list them together with the difference frequencies ω_q: nitrobenzene-benzene (354 cm^{-1}), nitrobenzene-toluene (340 cm^{-1}), nitrobenzene-fluorobenzene (335 cm^{-1}), deuterated benzene–carbon disulfide (289 cm^{-1}). Before reporting the results of our measurements made in GaP using the method describing above, we give a simplified theory of the nonlinear process we are dealing with.

We assume that the two exciting beams $E_1 = \mathcal{E}_1 \times \exp(-i\vec{k}_1 \cdot \vec{r})$, $E_2 = \mathcal{E}_2 \exp(-i\vec{k}_2 \cdot \vec{r})$ are not depleted along the interaction path. With this simplifying hypothesis the growth of the polariton field (E_q, Q) is described by the following set of equations[7]:

$$\left[\nabla^2 + \frac{\omega_q^2 \epsilon_\infty}{c^2}\right] E_q = -\frac{\omega_q^2}{c^2}\frac{\omega_0^2 \mu}{e}(\epsilon_0 - \epsilon_\infty) Q - \frac{4\pi\omega_q^2}{c^2} P^{\mathrm{NL}}(\omega_q),$$

$$\mu D_q Q = e E_q + F^{\mathrm{NL}}(\omega_q), \tag{1}$$

$D_q = \omega_0^2 - \omega_q^2 - i\omega_q\Gamma$; μ is the reduced mass, and e the electric charge associated with the TO lattice mode at frequency ω_0. Q is the lattice displacement within the primitive cell and E_q is its associated electric field. $P^{\mathrm{NL}}(\omega_q)$ and $F^{\mathrm{NL}}(\omega_q)$ are, respectively, the nonlinear polarization at frequency ω_q and the nonlinear force. The nonlinear interaction of the electromagnetic and phonon fields can be described in terms of a phenomenological energy density function[6,8] U^{NL} that for the overall process may be written in the form

$$U^{\mathrm{NL}} = -[d_E(E_1 E_2 {}^*E_q{}^* + E_d E_{as}{}^* E_q{}^*) + N d_Q(E_1 E_2 {}^* Q^* + E_d E_{as}{}^* Q^*)]. \tag{2}$$

N is the number of primitive cells per cm^3 and the quantities d_E and d_Q are the nonlinear coupling coefficients for the interactions. They can be taken to be real and constant over the entire range of infrared frequencies covered by our experiment.[9] The nonlinear polarization and force are given by

$$P^{\mathrm{NL}}(\omega_q) = -\partial U^{\mathrm{NL}}/\partial E_q{}^*,$$

$$F^{\mathrm{NL}}(\omega_q) = -\partial U^{\mathrm{NL}}/\partial Q^*.$$

Solving the set (1) and taking $E_q = 0$ at the boundary $r = 0$, we obtain the equation of evolution of the polariton field in the following form:

$$E_q = \frac{\beta \mathcal{E}_1 \mathcal{E}_2{}^*}{|2\vec{q}'|\{|\Delta\vec{q}'| - \gamma + i|\vec{q}''|\}} \exp(-i\vec{q}' \cdot \vec{r}) \times \{\exp(i\Delta\vec{q}' \cdot \vec{r}) - \exp(-\vec{q}'' \cdot \vec{r})\}, \tag{3}$$

where

$$\beta = -\frac{4\pi\omega_q^2}{c^2}\left(d_E + \frac{(\epsilon_0-\epsilon_\infty)\omega_0^2 d_Q N}{4\pi e D_q}\right),$$

$$\gamma = \frac{|\vec{q}''|^2}{|2\vec{q}'|}, \quad \Delta\vec{q}' = (\vec{k}_1-\vec{k}_2)-\vec{q}'.$$

Equation (3) shows that, for $\Delta\vec{q}'=0$, the polariton field grows from zero to a maximum value $\beta\mathcal{E}_1\mathcal{E}_2^*/|2\vec{q}'|\{-\gamma+i|\vec{q}''|\}$ in a path about equal to the inverse absorption coefficient $\alpha^{-1}=1/|2\vec{q}''|$. For $|\vec{r}|>\alpha^{-1}$, E_q keeps constant all along the interaction path. A more precise analysis[10] that takes into account the growth of the Stokes field together with that of the idler E_q shows that the expression (3) is indeed appropriate to describe the polariton growth if the absorption coefficient α is larger than the "gain" of the Raman (or parametric) process. This is always satisfied in our case. This result is most important in our experiment for the following reasons: (a) The measurement of the physical quantities under investigation (e.g., the infrared absorption coefficient α of the crystal or the nonlinear coupling coefficients near the lattice resonance) is not affected by surface effects because, in the less favorable experimental condition, E_q is zero at the surface and small in the absorption layer. The quantities measured in our experiment always correspond to the behavior of the bulk of the crystal regardless of the large absorption of the Reststrahl band. This consideration demonstrates the interest of the present method against the reflection methods of the linear and nonlinear optical spectroscopy of solids[9,11] in proximity of a lattice resonance. (b) The absence of an exponential gain of the polariton field rules out in the analysis of the k-space resonance curves any spurious effect due to the interaction.

The polariton scattering process may be considered in a way similar to the polariton generation process. We still assume that the diffusing field $E_d = \mathcal{E}_d \exp(-i\vec{k}_d\cdot\vec{r})$ is not depleted along the interaction path and the Maxwell equation for the E_{as} field is found to be, to a good approximation,

$$\left[\nabla^2 + \frac{\omega_a^2}{c^2}\epsilon_a\right]E_{as} = -\frac{4\pi\omega_a^2}{c^2}\left(d_E + Nd_Q\frac{e}{\mu D_q^*}\right)E_d E_q^*. \tag{4}$$

We can solve this equation by assuming, for simplicity's sake and without loss of general validity of the results, that the fields E_q, E_d, E_{as} have a common direction of propagation in the phase-matched condition. With this hypothesis the solution of (4) leads to a simple expression for the anti-Stokes intensity:

$$I_{as} \simeq |R|^2(\sin\tfrac{1}{2}|\Delta\vec{k}_a|\,l/\tfrac{1}{2}|\Delta\vec{k}_a|\,l)^2 l^2 \tag{5}$$

(l = interaction path) apart from small terms proportional to $l\alpha^{-1}$ and α^{-2}. In the above expression $\Delta\vec{k}_a$ is the phase mismatch of the optical beams k_1, k_2, k_d, k_{as} corresponding to the polariton phase mismatch $\Delta\vec{q}'$. The value of the function depending on $\Delta\vec{k}_a$ in the expression of I_{as}, for all the experimental conditions we consider in the paper, is always near unity. The function $|R|^2$ in (5) gives the dependence of I_{as} on the nonlinear coefficients and on the phase mismatch $\Delta\vec{q}'$:

$$|R|^2 = \frac{16(\pi\omega_a\omega_q)^4 I_d I_1 I_2}{c^8|\vec{k}_{as}|^2|\vec{q}'|^2(|\Delta\vec{q}'|^2+|q''|^2)}\left|\left(d_E + Nd_Q\frac{(\epsilon_0-\epsilon_\infty)\omega_0^2}{4\pi e D^*}\right)\left(d_E + Nd_Q\frac{e}{\mu D^*}\right)\right|^2 \tag{6}$$

(for $|\vec{q}'|\gg|\vec{q}''|$). For $\vec{q}''$ independent of $\vec{q}'$, $|R|^2$ is a Lorentzian function of $|\Delta\vec{q}'|$ and both the determination of the position of its maximum in q' space and the analysis of its width can give useful information on some physical quantities of the crystal. In our experiment for each frequency of the excited polariton field we produced small variations $|\Delta\vec{q}'|$ around a preset, approximate value of $|\vec{q}'|$ by varying the angle θ in order to sweep over the polariton resonance (Ref. 4). By looking, for each polariton frequency, at the curve of the anti-Stokes intensity determined experimentally as a function of $|\Delta\vec{q}'|$ we were able to determine the true value of $\vec{q}'$ and the absorption coefficient of the crystal $\alpha = |2\vec{q}''|$. This last quantity is equal to the full width of the Lorentzian function $I_{as}(\Delta q')$. Furthermore, the

values of the maxima of the $I_{as}(\Delta q')$ curves corresponding to different polariton frequencies allowed us to study the dispersion of the nonlinear optical polarizability in the range of frequency we investigated.[9] We shall report about these last quantities in a forthcoming paper. The perturbation on the value of the interaction path l introduced by the very small variation of θ produced in order to describe the resonant curves at various frequencies has been found to be negligible even with the largest absorptions we measured.

In Fig. 2 we report the dispersion curve of the polariton near the Reststrahl band. The curve *a* has been drawn on the basis of the infrared data given by Kleinman and Spitzer[11] by assuming a constant damping of the lattice TO vibration. Curve *b* has been drawn by Barker[12] as a result of his recent theory that accounts for a more complex damping process involving a frequency-dependent damping constant Γ in the expression for the far-infrared dielectric constant of GaP. Physically, that corresponds to including explicitly in the damping the effect of some particular combination (two-phonon) bands of the spectrum. Our experimental points lie very close to the curve *a* in substantial agreement with earlier Raman data of Henry and Hopfield.[13]

Figure 3 reports the results of our measurement of ihe infrared absorption coefficient $\alpha = |2\vec{q}''|$. Curve *a* corresponds to the frequency-independent damping theory (Kleinman and Spitzer[11]) and *b* is again calculated on the basis of the Barker's multiple-oscillator damping theory.[12]

As is shown by our experimental results in Figs. 2 and 3 the simple model of a single oscillator with constant damping, of Kleinman and Spitzer,[11] looks very satisfactory for GaP. However, the resonance curve $I_{as}(\Delta q')$ corresponding to a polariton frequency of 354 cm^{-1} shows a substantial asymmetric broadening in the lower part of its quasi-Lorentzian profile toward increasing $|\vec{q}'|$. This behavior is somewhat reminiscent of an analogous asymmetric broadening in the frequency domain and toward the lower frequency of the 90° spontaneous Raman line from the TO mode of GaP at 366 cm^{-1}.[12] This effect has been attributed[12] to a selective damping process involving the two-phonon band TA(*X*) + LA(*X*) peaked

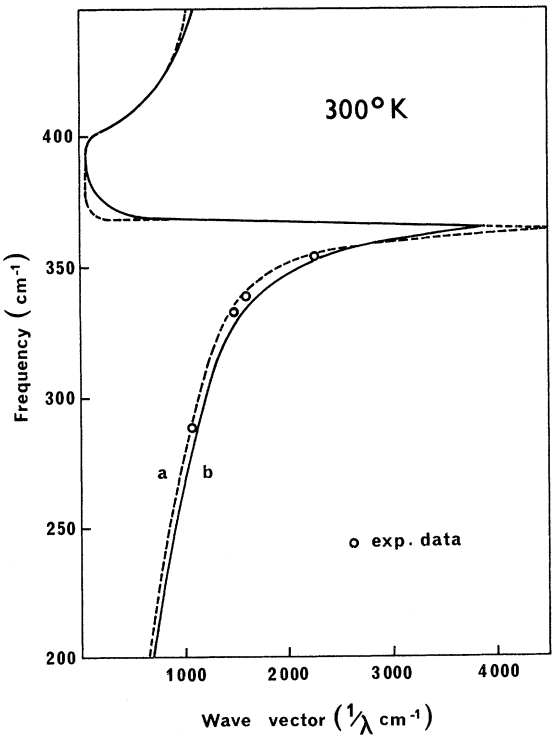

FIG. 2. Dispersion curve of the LO phonons and polaritons in GaP. Curve *a* has been drawn on the basis of the infrared data of Kleinman and Spitzer (Ref. 11). Curve *b* has been drawn on the basis of the multiple-oscillator theory for the lattice resonance [A. S. Barker, Phys. Rev. 118, 118 (1960)].

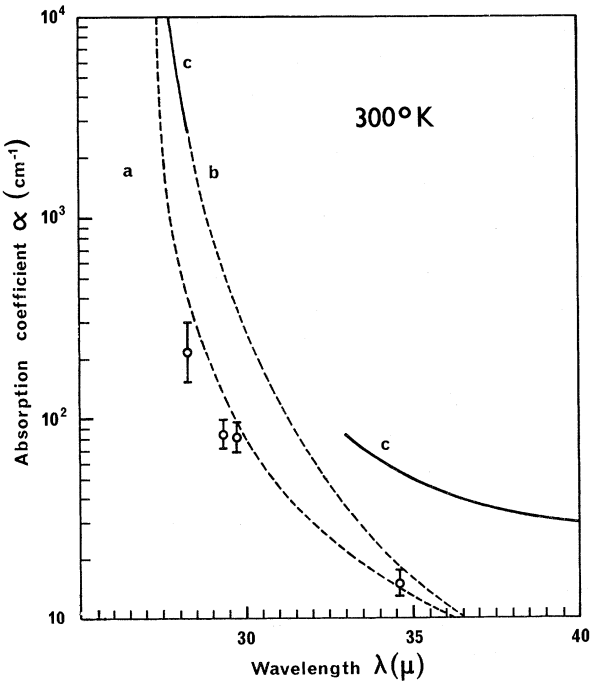

FIG. 3. Absorption coefficient of GaP versus wavelength. Curves *a* and *b* correspond to curves *a* and *b* of Fig. 2. Curve *c* shows the results of a previous experimental investigation on the absorption coefficient of GaP using conventional methods (A. S. Barker, Ref. 12). Curve *c* is reported without structure. Our experimental points lie near the curve *a*.

at a frequency of 357 cm^{-1}. Some interesting considerations may be made by comparing in Fig. 3 the values of α obtained in our experiment with the experimental curve c obtained by Barker.[12] The branch of curve[14] c for $\lambda \geq 32\ \mu$ has been obtained by usual transmission and reflection methods.[11] The branch of curve c nearest the TO resonance has been obtained by Kramers-Kronig analysis of reflectivity measurements. (In the range of wavelengths 28-32 μ both methods have been found by Barker[12] to give results insufficiently precise.) As an explanation of the very large discrepancy between our results (which are essentially free from surface effects) and the classical reflectivity data, we may suggest the existence of a very large anharmonicity of the crystal near the surface with a large effect of damping by two-phonon energy transfer.

An alternative method to our anti-Stokes technique of detecting the generation of the polariton field should be the detection of the associated far-infrared radiation outside the crystal.[1,7,10,15] Although this effect could be of some interest in itself, it will not lead to more physical information on the polariton dynamics than has been given by our present method.[16] An experiment attempting to detect outside the crystal the coherent far-infrared radiation arising from polaritons in GaP is in progress in our laboratory. We present in this Letter what we believe to be the first experimental application of a new kind of spectroscopy in solid-state physics: a spectroscopy in the momentum space. We believe that this kind of spectroscopy should be of valuable interest for the study of elementary excitations that exhibit a large group velocity.

We wish to thank Professor J. Ducuing and Professor N. Bloembergen for stimulating discussions. One of us (F.D.M.) is indebted to Professor C. H. Townes for early discussions on the problem of infrared generation from optical phonons. Thanks are due to Mr. J. Ehrhart for calculations concerning the method of "coherent excitation" and to Dr. H. Rodot of Laboratoire Associé au Centre National de la Recherche Scientifique, Bellevue, for the growth of large single crystals of gallium phosphide.

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[14]The branch of curve c for $\lambda \geq 32\ \mu$ has been drawn in Fig. 3 by omitting the structure arising from combination bands and local modes. For the exact spectrum, see Ref. 12.

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[16]The anti-Stokes process we are dealing with may be viewed as a combination of two separated processes taking place in the same crystal: the polariton field generation and the polariton field detection. As far as detection is concerned, the process of mixing in a piezoelectric crystal an infrafred field E_q and an optical probe field E_d, giving rise to an optical field E_{as}, has been proposed as a possible general technique for far-infrared detection (C. H. Henry, private communication). On this process is based a method for the study of the dispersion of the nonlinear optical polarizability in noncentrosymmetric crystals (Ref. 9).