PHYSICAL REVIEW B VOLUME 17, NUMBER 8 15 APRIL 1978

Experimental observation of the upper polariton branch in isotropic crystals

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(Received 11 October 1977)

The dispersion of phonon polaritons on the upper branch of a crystal of cubic GaP has been measured for the first time by the method of attenuated total reflection. The results allow accurate evaluation of the high-frequency dielectric constant. Two-particle states make no contribution to the polariton dispersion in GaP in the frequency region explored.

I. INTRODUCTION

It is well known that in a polar diatomic crystal the transverse-optical (TO) phonon couples to transverse-electromagnetic waves and the resulting polariton dispersion curves form two branches with very different dispersion behavior as a function of the wave vector k.[1] We need only to mention that the upper polariton branch (UPB), with which we are going to deal, approaches asymptotically the uncoupled electromagnetic wave $\omega = ck/\epsilon_\infty^{1/2}$ as $k \to \infty$ and its frequency approaches that of the longitudinal-optical (LO) phonon as $k \to 0$.

Since the first experimental observation of the Raman scattering by polaritons[2] in GaP, the dispersion of phonon polaritons has been measured in a large number of substances, from simple diatomic cubic to very complex uniaxial and biaxial crystals.[3] The experimental work has been so far concerned mainly with the Raman scattering by polaritons and the measurement of the dispersion of the lower branches. As pointed out by Mills and Burstein,[1] in isotropic crystals the UPB cannot be observed by inelastic (Raman) scattering of light. Nonlinear interaction processes, such as two-photon absorption, frequency mixing, etc., should allow the excitation of polaritons on the upper branch of cubic as well as anisotropic media.[1] Exciton UPB dispersion has been measured by two-photon absorption in CuCl.[4] As far as we know the only experiment concerned with the phonon UPB in a cubic crystal is that by Faust and Henry[5] on GaP, a frequency-mixing experiment in which the polaritons are excited by an external source. In uniaxial crystals the UPB can in principle be observed by Raman scattering as the index of refraction for ordinary and extraordinary waves can be considerably different.[6] By means of a photographic detection method, Raman scattering and associated parametric luminescence have been observed in the UPB of several uniaxial crystals,[3,7] but with the usual Raman technique it turned out to be experimentally very difficult and only recently has successful observation of the UPB in ZnO been reported.[8]

In the present paper we show that the attenuated-total-reflection (ATR) method can be advantageously used for observing this polariton branch and report the first detailed measurement of the dispersion of the phonon UPB in a cubic crystal, GaP.

II. THEORY

The ATR method[9] was suggested in 1968 by Otto[10] as a means of coupling radiation to surface excitations. Since then, it has been widely used to study all kinds of surface polariton modes (plasmon, phonon, exciton, etc.).[11] Only recently[12] it was recognized that with a slight modification, i.e., direct contact between total reflection prism and sample, this technique[13] [transverse-magnetic (TM) reflection] could be used to measure the dispersion of bulk phonon polaritons. Most of the work done before now has been concerned with a thorough study of the bulk polaritons in α-quartz, including directional dispersion of polar phonons, spatial damping, and polariton dispersion inside reststrahlen bands.[11,14,15]

The principle of the TM reflection experiment[12] is shown in Fig. 1(a). The sample with dielectric constant $\epsilon(\omega)$ is in close contact with the prism (in our case hemicylinder), an isotropic transparent medium with index of refraction n. A TM-polarized[16] radiation $\vec{E}_i$ is incident at the angle ϑ upon the prism-sample plane interface. It has a wave-vector component parallel to the surface.

$$k_x = (\omega/c) n \sin\vartheta . \tag{1}$$

From boundary conditions it follows that this radiation couples only to excitations in the sample having an equal wave-vector component in the x direction.

For a diatomic cubic crystal like GaP the dispersion relation of phonon polaritons is given by

$$\epsilon(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(\omega_{to}^2 - \omega^2 - i\omega\gamma) = c^2k^2/\omega^2 \tag{2}$$

and the TM reflectivity at an angle of incidence ϑ

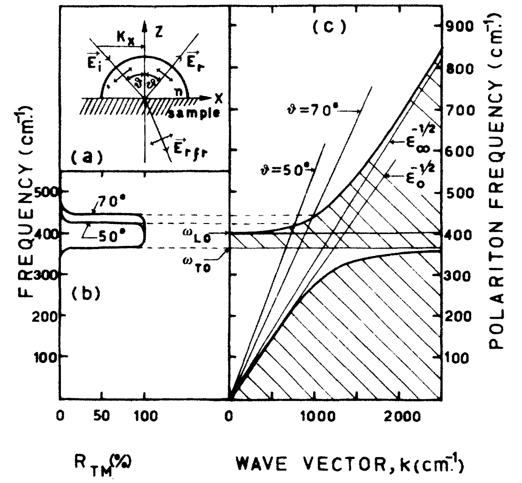

FIG. 1. (a) Schematic diagram of the TM reflection experiment. $\vec{E}_i$, $\vec{E}_r$, and $\vec{E}_{rfr}$ refer to the incident, reflected, and refracted EM waves, respectively. (b) Calculated TM reflectivity with $n = 2.37$ (KRS 5) at $\vartheta = 50°$ and $\vartheta = 70°$. (c) Calculated polariton dispersion curves of GaP. ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constant, respectively. $\omega_{TO} = 366$ cm^{-1} and $\omega_{LO} = 403$ cm^{-1}. The regions of high reflectivity are shown as hatched areas.

is given by

$$R_{TM}(\omega, k) = \left| \frac{\epsilon^{1/2} k \cos\vartheta - n(k^2 - k_x^2)^{1/2}}{\epsilon^{1/2} k \cos\vartheta + n(k^2 - k_x^2)^{1/2}} \right|^2 . \qquad (3)$$

When a refracted ray $\vec{E}_{rfr}$ is present, it has a real wave-vector component in the z direction

$$k_z = (k^2 - k_x^2)^{1/2} \qquad (4)$$

which couples to excitations in the sample propagating in the z direction.

From Eq. (3) we see that total reflection ($R_{TM} = 1$) occurs when $k^2 - k_x^2 \leq 0$ and that the lines separating areas of total and reduced reflectivity are the dispersion curves of the bulk phonon polaritons, as shown in Fig. 1(c). On these lines the z components become zero and the measured wave vectors, Eq. (1), are equal to those of the bulk phonon polaritons propagating parallel to the surface. Provided a suitable material (i.e., a suitable refractive index n) for the prism is available, a large range of k space in the first Brillouin zone can be explored by varying the angle of incidence ϑ.

With the damping parameter γ included in the dielectric function (2), Eq. (3) gives smoothed reflection curves, as shown for two values of ϑ in Fig. 1(b). The inflection points in these curves give the intercepts of the light lines with the dispersion curves.

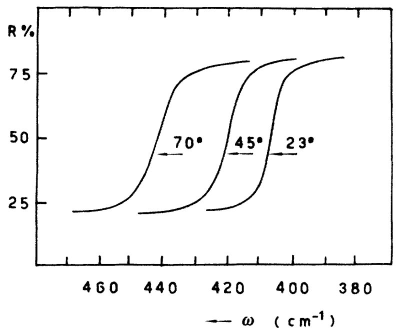

FIG. 2. Experimental TM reflection curves of GaP obtained at the indicated angles of incidence with KRS5 hemicylinder. Only the relevant frequency range is shown.

III. EXPERIMENT

The TM reflection curves were measured using a Perkin Elmer Model 180 ir spectrophotometer and a RIIC TR-5 Micro ATR unit. As total reflection prism a KRS5 hemicylinder was used. The sample was a GaP single crystal of 2 × 4 × 7 mm with polished surfaces. One point was obtained by a reflectivity measurement in air at large (70°) angle of incidence. The inflection points could be determined rather precisely in the experimental curves, the accuracy being better than ±2 cm^{-1} for all the measurements made. Three experimental curves are shown in Fig. 2. Our data, shown in Fig. 3 together with the calcu-

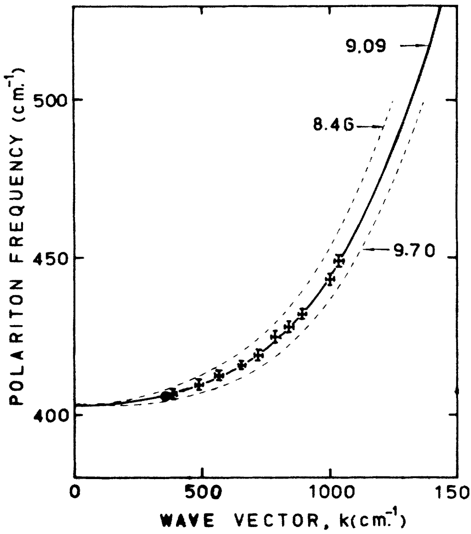

FIG. 3. Calculated and measured upper branch polariton dispersion in GaP. The dashed and solid lines are calculated with the indicated values of ϵ_∞. The accuracy of the experimental points is represented by the error bars. The solid circle refers to a reflectivity measurement in air at $\vartheta = 70°$.

lated UPB, are quite accurate since we can set the angle of incidence ϑ with a comparable degree of accuracy. The spread in the angle of incident radiation, due to the beam divergence in the infrared spectrometer, does not affect the position of the inflection points.

IV. DISCUSSION

The dielectric parameters used in the calculation of the dispersion curve were those obtained by Barker[17] with his multiple-oscillator model for the lattice in GaP. Two additional curves have been added in Fig. 3 with slightly different values of the high-frequency dielectric constant ϵ_∞, one of which ($\epsilon_\infty = 8.46$) was that used for GaP before Barker's work. There is a very good agreement between our results and the curve calculated with the value $\epsilon_\infty = 9.09$ taken from Ref. 17.

The UPB is much more sensitive to the value of ϵ_∞ than the lower polariton branch, as can be seen also in Fig. 3 where, if drawn in the figure, the corresponding three lower branches would have been hardly distinguishable from one another. Our measurement of the UPB thus represents a further check of Barker's value for ϵ_∞ in GaP (see also, e.g., Marschall and Fischer[18] and Valdez and Ushioda[19]).

We wish to point out that the great sensitivity of the UPB to the value of ϵ_∞ can give rise to some difficulty when comparing the results obtained by Raman scattering with the calculated curves (see Ref. 8) since one has to take into account the variations of the index of refraction of the samples, at the laser frequency used, in the measured range of the polariton frequency.

Gallium phosphide is known to have several two-phonon bands[20] in the frequency range 400–500 cm^{-1}. The fact that our results fit quite closely the calculated UPB seems to indicate that in this frequency region two-particle states do not contribute to the polarition dispersion. This is in agreement with the previous works by Barker,[17] Ushioda and McMullen,[21] and a more recent one by Mavrin and Sterin.[22] In Ref. 22 a negligible contribution was explicitly assumed from this region to the weighted density function of two-particle states taken into account in the polariton dispersion relation.

V. CONCLUSION

We have reported the first measurement of the phonon UPB in a cubic crystal, GaP, and shown that the method employed (ATR or TM reflection) is a simple, accurate, and straightforward technique for the observation of this branch of the polariton dispersion, the only limitations being connected with the choice of a suitable material for the prism. It turns out to be particularly useful for isotropic materials whose UPB cannot be observed by Raman scattering, but is likewise applicable to uniaxial and biaxial crystals in which it allows the measurement of both the ordinary and the extraordinary UPB. An accurate evaluation of the high-frequency dielectric constant is possible through this method. In the case of low-refractive-index crystals, an appreciable portion of the UPB can be very conveniently measured by TM reflection in air,[23] i.e., with $n = 1$ in Eqs. (1) and (3).

ACKNOWLEDGMENT

We would like to thank J. B. Valdez, G. Mattei, M. J. Delaney, and S. Ushioda for helpful comments.

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