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Resonant Raman scattering from polaritons in ZnSe †

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Raman scattering from polaritons was studied near resonance in ZnSe. Detailed dispersion curves were determined experimentally for different incident frequencies and compared with theoretical results. Measurements of linewidth and relative scattered intensities were also performed. The observed polariton dispersion curves showed a deviation from theory near the same frequencies for which line broadening occurred, indicating the necessity of including relaxation effects depending on polariton frequency. Structure in the polariton intensity as a function of frequency, not observed before, may also be related to damping.

I. INTRODUCTION

Since the first observations of Raman scattering by phonon polaritons in GaP, reported by Henry and Hopfield,[1] and in ZnO, reported by Porto, Tell, and Damen,[2] several materials were investigated and showed equivalent results.[3] However, in spite of the enormous activity in resonant Raman scattering[3] the only report on resonant Raman scattering from polaritons is a brief report related to ZnSe dating from 1969.[4] This deficiency is possibly due to certain difficulties in combining the special features of near-forward scattering geometry with the unavoidable increased absorption of near-resonant incident and scattered radiations. The main difficulties in recording polariton spectra with sufficiently small acceptance angles and slits, together with convenient laser frequency rejection, are nevertheless somewhat compensated by the enhanced cross sections characteristic of near-resonance scattering.

Our results were precise enough to allow for a detailed comparison with the classical dispersion theory of Born and Huang[5] and for a qualitative verification of certain deviations suggested by quantum-theoretical predictions.[6] Our results implemented those of Ref. 4, the only existing report on resonance effects on Raman scattering by polaritons, in several aspects: (a) by reducing the acceptance angle and slits width the real linewidth was measured; (b) by using four different incident frequencies instead of two; (c) by taking a significantly larger number of data points increasing also the range of observation angle; (d) by significantly increasing the precision in relative intensities of scattered radiation.

II. EXPERIMENTAL METHOD

In order to consistently measure the scattering cross sections at different observation angles we had to avoid the current technique of using concentric rings determining the acceptance angle, because of obvious disadvantages. Instead, we used a rotatory table built from a Karl Lambrecht precision rotator to which three corner reflectors were adapted. The well-collimated laser beam is made colinear with the rotator axis as shown in Fig. 1. The laser beam reaches the crystal after three reflections on the three-corner reflector. The active volume is determined by the intersection between the laser beam inside the crystal, with the monochromator acceptance angle limited by an iris diaphragm placed between the crystal and the monochromator. The acceptance angle outside the crystal was smaller than 15′ and the rotator plate allowed for a precision of 20″ in the crystal position. The zero angle was determined by use of the polariton shift in both directions of rotation.

Photon counting was used together with a multichannel analyzer. A double 1-m monochromator with stepping motor, together with an S-5 photomultiplier, were used in a conventional Raman-scattering arrangement. Signal integration times of up to 60 sec were used.

In order to reduce back reflection, which normally hampers measurements of polariton spectra because of the strong TO scattered radiation at $2K_i$ and polariton-scattered radiation at ill-defined angles due to multireflection, we have immersed the sample in α-bromonapthalene, a high-refractive-index liquid.

Figure 2 gives an example of spectra with and

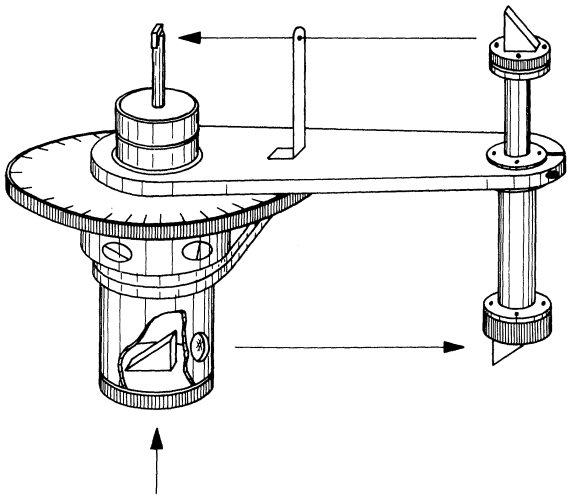

FIG. 1. Rotating table for near-forward scattering.

without the index-matching liquid. Note two important features: (i) the TO-phonon back-reflected radiation (180°) at 206 cm^{-1} is significantly reduced and (ii) the polariton line shows a measurable reduction in linewidth with the index-matching liquid.

III. EXPERIMENTAL RESULTS

Figure 3 shows the experimental dispersion curves as taken with an argon-ion laser operating at wavelengths of 4765, 4880, 4965, and 5145 Å. In order to better realize the variation of the dispersion curves with excitation frequency, we have included these curves in one single figure together

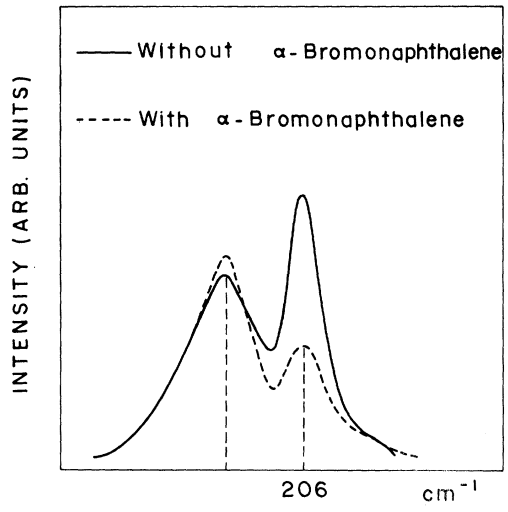

FIG. 2. Raman spectra of polariton and spurious backward TO phonon (206 cm^{-1}) with and without the index-matching liquid.

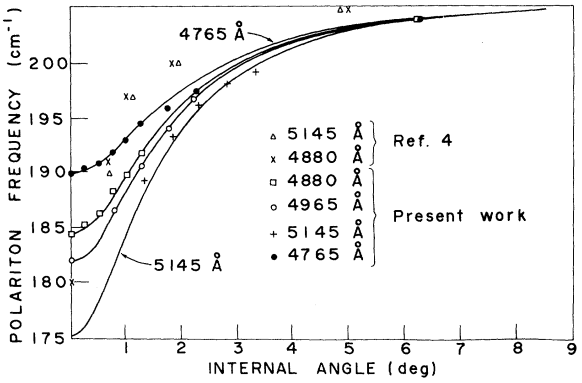

FIG. 3. Polariton dispersion curves for different incident wavelengths. Data from Ref. 4 included for comparison.

with the classical dispersion curves as calculated from Huang's approach.[5] Thus, the following relation was used:

$$\left[\left(\frac{\partial K}{\partial \omega}\right)_{\omega=\omega_L}\right]^2 + \left(\frac{\omega_L}{\omega}\right)^2 \delta^2 = \frac{\epsilon_0 \omega_0^2 - \epsilon_\infty}{\omega_0^2 - \omega^2}, \quad (1)$$

where ω_L is the laser frequency, ϵ_0 and ϵ_∞ are the dc and high-frequency dielectric constants of the crystal, and ω and K are the polariton frequency and wave vector, respectively. Note from Eq. (1) that the polariton frequency explicitly depends upon $\partial\omega/\partial K$ at ω_L, even at forward scattering. This allows for an experimental determination of $(\partial\omega/\partial K)_{\omega_L}$ at all laser frequencies with good precision and subsequent calculation of the dispersion curves, a procedure certainly more precise than the interpolations used in Ref. 4. The values of $\partial\omega/\partial K$ calculated from Eq. (1) and forward results are included in Table I. $\partial\omega/\partial K$ at 5145 Å is an extrapolation because the forward intensity at this wavelength is vanishingly small.

Note from Fig. 4 that there is a small deviation from the classical theory without damping for polariton frequencies around 200 cm^{-1}. Though small, this deviation is well established and consistently observed for all incident frequencies.

TABLE I. Values of $(\partial\omega/\partial K)_{\omega_L}$ calculated from Eq. (1) and forward results.

ω_L (cm^{-1})	$\left(\frac{\partial\omega}{\partial K}\right)_{\omega_L}$
20 984	0.217
20 491	0.239
20 140	0.247
19 434	0.265

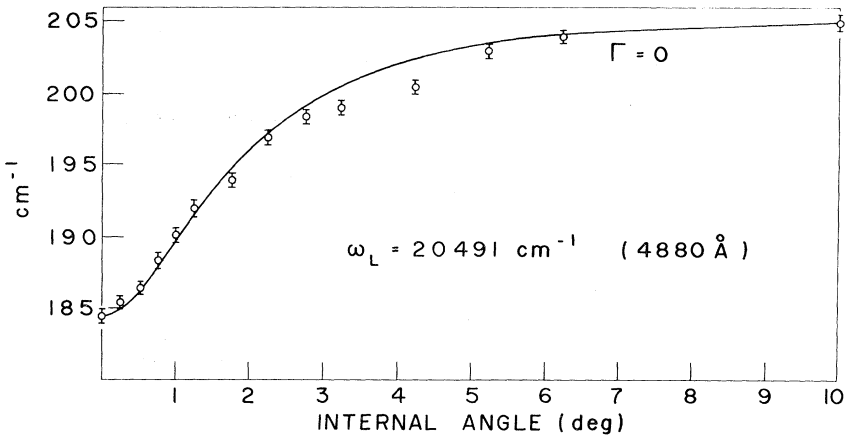

FIG. 4. Polariton dispersion curve for an incident wavelength of 4880 Å.

Figure 5 gives the polariton bandwidth as a function of the polariton frequency for all incident laser frequencies. The dispersion-determined linewidth is at all frequencies at least four times smaller than the observed linewidth. Note that for all excitation frequencies the linewidth starts to increase with reduction of polariton frequency around 200 cm^{-1}, and reduces again below 190 cm^{-1}.

Figure 6 gives the polariton integrated intensity as a function of the polariton frequency for all incident frequencies used in our experiments. The polariton intensity is proportional to the ratio of the electro-optic coefficient to the mechanical susceptibility coefficient characterizing the response to ionic displacements in a deformation potential.[7] In contrast to the conclusions in Ref. 4, based on rather inadequate number of data points, a single value of the above-mentioned ratio is not capable of accounting for our results.

If we combine the results of Figs. 5 and 6 we see that the peak intensity of the polariton Raman line suffers a reduction from expected values at frequencies between 195 and 200 cm^{-1}.

The deviations from classical theory described here are predicted by theories that include damping.[6] However, the results in Fig. 5 indicate that damping must be dependent upon the polariton frequency, what makes a direct comparison with such theories of questionable value. The observed broadening at 195 cm^{-1} may be related to a coincidence with a high two-phonon density of states that increases the damping coefficient.

IV. CONCLUSIONS

Polariton dispersion curves taken with sufficient precision showed predicted dependence on incident frequency near resonance. Small but measurable deviations from classical theory indicated the ne-

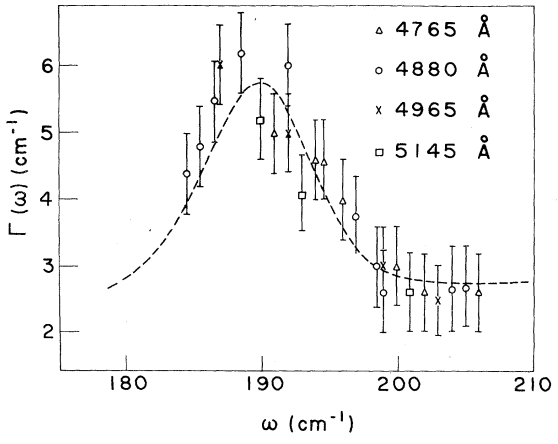

FIG. 5. Linewidth dependence on polariton frequency for different incident wavelengths.

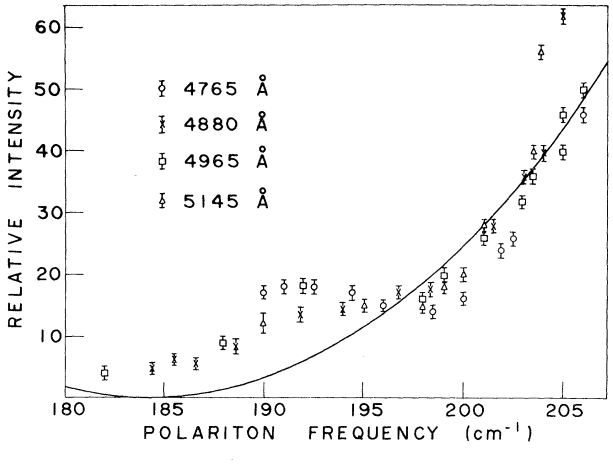

FIG. 6. Raman intensities as a function of polariton frequency. Intensities for different incident wavelengths are normalized at 195 cm^{-1}. The solid line is a better fit curve for $C = 2.6$ (C from Ref. 4).

cessity of including damping. Linewidth strong dependence on polariton frequency was observed to be the same for all incident frequencies. It was suggested that damping, to be introduced in future, more advanced theoretical approaches, must be frequency dependent. The significant variation of scattered intensity, as a function of polariton frequency observed for all incident frequencies, is not accounted for by present theories and though the observed function may be related to the frequency dependent damping we were unable to relate these effects in a consistent model.

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