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RESONANCE RAMAN SCATTERING AT THE INDIRECT GAP OF GALLIUM PHOSPHIDE

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We have measured the resonance enhancement of the LO and TO phonon Raman scattering cross-sections near the indirect gap of GaP at 300K and 77K. The result shows fine structures in the enhancement factor as a function of the incident laser energy. These structures were found to correspond to electronic transitions from the Γ-point to the X-point assisted by TA, LA and TO phonons at the X-point.

The resonant Raman scattering effect has been observed in many semiconductors for incident laser energies near the direct gap [1], but there has been no study of resonance enhancement of first-order Raman cross-sections near an indirect gap. (Enhancement of second-order Raman cross-sections at indirect gaps have been observed [2].) In this paper we report on the resonance Raman scattering in GaP near the indirect gap (~ 2.3eV) at the X-point. The electronic transitions at the indirect gap were studied in detail by Dean and Thomas [3] and more recently by several groups [4]. The basic features observed in these absorption measurements are several stepped increases in the absorption constant with increasing photon energy. Each step corresponds to the formation of indirect excitons assisted by either emission or absorption of different X-point phonons. Recent work using wavelength-modulated absorption measurements [4] reveals three prominent peaks (corresponding to steps in the ordinary absorption measurements) which are ascribed to indirect exciton formation assisted by TA, LA and TO phonon emission at the X-point.

The usual expression for the Raman scattering cross-section is derived by third order perturbation theory and contains two matrix elements of the electron-radiation interaction (H_{ER}) and one electron-phonon interaction (H_{EL}) matrix element [5]. In order to consider the resonance enhancement at an indirect gap, one must modify this theory by adding an interaction Hamiltonian between electrons and X-point phonons (H^{X}_{EL}), and consider fifth order processes involving H^{X}_{EL} twice. No microscopic theory of this kind has yet been reported; hence, no concrete theoretical expression exists with which to compare present experimental results. However, on simple physical grounds, one can anticipate the results to some extent. Since absorption signifies strong coupling between the incident radiation and the electronic system of the crystal, we may expect some structures in the Raman enhancement factor corresponding to the structures found in the absorption constant near the indirect gap. Because of the involvement of the X-point phonons in the transition process, the absorption constant is a sensitive function of the crystal temperature. Thus, we should expect an analogous dependence of the Raman enhancement factor on temperature. These are the considerations that motivated the present experiment.

The sample was a single crystal of intrinsic GaP with the dimensions of approximately 2mm x 2mm x Ø.Ø5mm. The large face was the (111) plane of the crystal. This thin sample was glued to an X-cut quartz plate at the edges. The incident laser beam was directed normal to the surface of the sample through the quartz plate, and the scattered light emerging at about 1.8^{o} from the forward direction was collected and analyzed. This sample configuration and scattering geometry was chosen in order to correct the Raman cross-section for the effect of absorption of the incident and scattered light in GaP. In the wavelength range of interest, quartz is completely transparent and the Raman cross-section of the phonon peaks in quartz shows no enhancement. Thus, we used the 465 cm^{-1} line of quartz phonon as the comparison standard. We measured the ratios of the LO and TO phonon scattering intensities of GaP to that of the 465 cm^{-1} line of quartz as a function of the incident laser energy. Since the scattered light emerging from quartz gets attenuated by the GaP sample on the way to the spectrometer, the ratios I(TO)/I(Qtz) and I(LO)/I(Qtz) are automatically corrected for absorption in GaP.

The exciting light was produced by a dye laser pumped by an argon ion laser, and the incident laser power level ranged between 1Ø mW and 1ØØ mW. The incident light was linearly polarized and the polarization of the scattering light was not analyzed. the spectra were recorded digitally, and the peak height ratios of the LO and TO phonon lines with respect to the 465 cm^{-1} line of quartz were plotted against the incident laser energy as illustrated in Fig. (1) for 77k. Figure (2) shows several sample spectra at 77k from which the data in Fig. (1) were obtained.

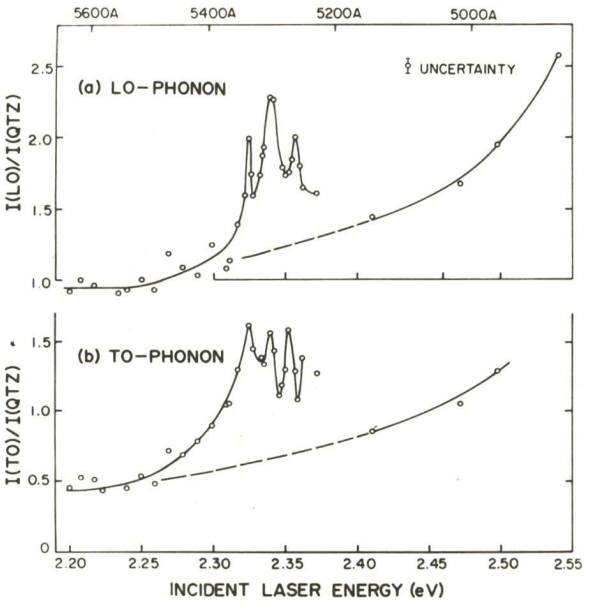

Figure 1 LO and TO phonon resonance enhancement factors vs. incident laser energy at 77K

In Fig. (2) the two peaks at 367 cm^{-1} and 4Ø3 cm^{-1} are the TO and LO phonon peaks of GaP, respectively, and the quartz phonon peak used for intensity calibration appears at 465 cm^{-1}. The structure seen below the TO phonon peak is due to bulk polaritons. In Fig. (1) we see that the Raman cross-section for both LO and TO phonons increase gradually as the incident laser energy approaches the indirect gap at ~2.3 eV. Both the LO and TO phonon cross-sections show three peaks in the enhancement factor. The energies at which these peaks occur at 77K are listed in Table 1 along with the energies of the absorption steps measured at 77K for the present sample. We note that the enhancement factors, I(LO)/I(Qtz) and I(TO)/I(Qtz), for the indirect gap is very small (~ 2) even at these peaks compared with the enhancement factors of

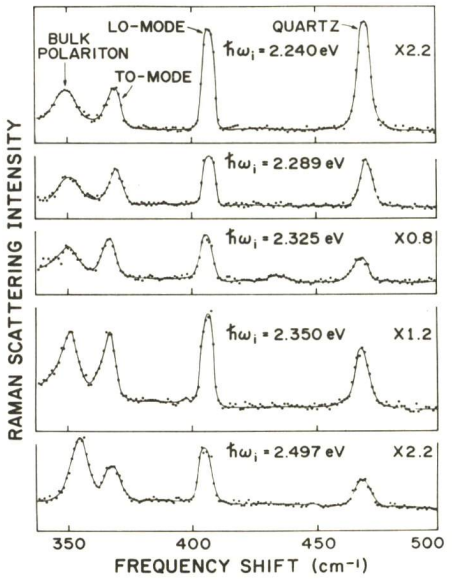

Figure 2 Sample spectra at 77K for different incident laser energies

observed in Fig. (1) were absent.

10^2 - 10^3 observed at the direct gap [6]. By making comparisons with the assignments given by Dean and Thomas [3] and by more recent wavelength modulated absorption measurements [4], we could assign the three peaks in the enhancement factor to specific X-point phonon assisted electronic transition processes as indicated in Table 1. The gradual rise in the enhancement factor toward the higher energies beyond the indirect gap region is due to the direct gap at ~ 2.8 eV. The data at room temperature (not shown here) show vaguely defined structures in the enhancement factor near and below the indirect gap energy, but the clear structures

Table 1

Assignment	Peak Position I(TO)/I(Qtz)	Peak Position I(LO)/I(Qtz)	Absorption Steps (eV)
$E_g(X)$	--	--	2.314
TA_E	2.323	2.325	2.325
LA_E	2.339	2.340	2.335
TO_E	2.353	2.356	2.351

The most interesting results of the present experiment can be summarized as follows: 1) the enhancement of the Raman cross-section at the indirect gap for one phonon scattering actually occurs, although the enhancement factor (~ 2) is very small compared with the 10^2 - 10^3 increase at the direct gap observed for most crystals; 2) the enhancement factor is strongly temperature dependent as expected; and 3) at 77K fine structures in the enhancement factor due to different X-point phonon assisted processes are observed.

An earlier work [7] reported that no enhancement was observed at the indirect gap of GaP. This work was done before dye lasers became available and the data points were too far apart in the region of the indirect gap; in addition the enhancement factor observed here is too small to be noticed by the earlier measurement. As we suggested earlier, the resonance enhancement at an indirect gap involves fifth order perturbation term rather than the usual third order term at a direct gap; thus, it is understandable that the enhancement factor measured here is down by

a factor of $10^2 - 10^3$.

We believe this is the first time that fine structures in the Raman enhancement factor of the type shown in Fig. (1) were measured. The appearance of the three well defined peaks in the resonance factors suggests that the intermediate electronic states responsible for the resonance are discrete indirect exciton levels. Table 1 shows that the resonances occur when the incident photon energy coincides with the steps in the absorption constant. This means that the resonance takes place with the incident photon and not with the scattered photon. It is interesting to note the similarity between the energy dependence of the Raman enhancement factor and the first derivative of the absorption constant obtained by the wavelength modulation method [4]. In both cases three peaks corresponding to the formation of indirect excitons assisted by TA, LA and TO phonon emission are observed. Under certain resonance conditions one expects the resonance factor to vary as $|\partial\chi/\partial\omega|^2$ where χ is the electronic susceptibility of the sample at the incident laser frequency [1]. Since the wavelength modulated absorption experiment measures basically the same quantity, the above noted similarity is not surprising. More detailed analysis of the data will be reported in a later publication.

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