Theoretical and experimental study of Raman scattering and infrared reflectivity in indium phosphide

B. H. Bairamov, I. P. Ipatova, V. A. Milorava, and V. V. Toporov
A. F. Ioffe Physico-Technical Institute, Academy of Sciences of the USSR, 194021 Leningrad, USSR

K. Naukkarinen
Electron Physics Laboratory, Helsinki University of Technology, 02150 Espoo, Finland

T. Tuomi
Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

G. Irmer and J. Monecke
Sektion Physik der Bergakademie Freiberg, 9200 Freiberg, German Democratic Republic
(Received 9 September 1987; revised manuscript received 18 May 1988)

Room-temperature Raman and infrared-reflectivity measurements are performed on semi-insulating InP doped with Fe and on n-type InP doped with Sn and S in the concentration range from 6.8×10^{17} to 1×10^{19} cm^{-3}. In the Raman spectra low(ω_-)- and high(ω_+)-frequency coupled plasmon–LO (Γ)-phonon modes are observed. The ω_--mode linewidth shows a definite concentration dependence with the lines narrowing as the concentration is increased. A broad minimum due to the coupled plasmon-phonon modes of the infrared-reflectivity spectrum shifts towards high photon energies with increasing carrier concentration. The spectra are calculated by using the same semiclassical model of permittivity as in the interpretation of the Raman spectra. From the best fit to the experiment, energy values and damping constants of the ω_- and ω_+ modes are obtained. The carrier concentrations also determined from the infrared spectra with the aid of the model are in good agreement with those obtained from the Raman spectra.

INTRODUCTION

In polar semiconductors, when the frequency of free-electron plasma excitations—plasmons—is close to the frequency of the longitudinal-optical phonons, the two excitations interact via their macroscopic electric fields. Usually frequencies of coupled plasmon–LO(Γ)-phonon modes $\omega_\pm$ are determined assuming that no damping occurs. Recently, for correct interpretation of the Raman scattering data in the frequency region of the upper coupled plasmon–LO(Γ)-phonon mode in the n-type GaP lattice damping was also taken into account.[1]

In this paper we use the same approach as in the case of GaP for the analysis of our experimental data on Raman scattering in InP crystals. We also compare these data with those obtained by infrared-reflectivity measurements made on the same samples as used in the Raman study.

THEORY OF RAMAN SCATTERING BY COUPLED PLASMON-PHONON MODES INCLUDING PHONON AND ELECTRON DAMPING

The efficiency of Raman scattering by coupled longitudinal-plasmon–$LO(\Gamma)$-phonon modes is given by[2]

$$I\sim\frac{n_2}{n_1}\omega_2^4\left[\frac{\partial\alpha}{\partial E^L}\right]^2(n_1+1)A\,\mathrm{Im}\left[-\frac{1}{\epsilon}\right]. \qquad (1)$$

Including phonon damping the function A in Eq. (1) can be given by[1]

$$A=1+2C\omega_T^2\frac{\omega_p^2\Gamma(\omega_T^2-\omega^2)-\omega^2\gamma(\omega^2+\Gamma^2)}{\omega_p^2\Gamma[(\omega_T^2-\omega^2)^2+\omega^2\gamma^2]+\omega^2\gamma(\omega_L^2-\omega_L^2)(\omega^2+\Gamma^2)}+C^2\frac{\omega_T^4}{\omega_L^2-\omega_T^2}\frac{\omega_p^2[\Gamma(\omega_L^2-\omega_T^2)+\gamma(\omega_p^2-2\omega^2)]+\omega^2\gamma(\omega^2+\Gamma^2)}{\omega_p^2\Gamma[(\omega_T^2-\omega^2)^2+\omega^2\gamma^2]+\omega^2\gamma(\omega_L^2-\omega_T^2)(\omega^2+\Gamma^2)}, \qquad (2)$$

in which C is a dimensionless constant called the Faust-Henry coefficient. $\omega=\omega_1-\omega_2$ is the Raman frequency, ω_1 and ω_2 are the incident and scattered photon frequencies, respectively, n_1 and n_2 are the refractive indices of the crystal at ω_1 and ω_2, and ω_L and ω_T are the frequencies of the LO(Γ) and TO(Γ) phonons.

The permittivity in the long-wavelength limit in the presence of free carriers can be given as the sum of lattice

 ©1988 The American Physical Society

and plasma contributions

$$\epsilon(\omega)=\epsilon_\infty\left[1+\frac{\omega_L^2-\omega_T^2}{\omega_T^2-\omega^2-i\omega\gamma}-\frac{\omega_p^2}{\omega(\omega+i\Gamma)}\right], \quad (3)$$

where

$$\omega_p=\left[\frac{ne^2}{m^*\epsilon_\infty\epsilon_0}\right]^{1/2} \quad (4)$$

is the plasma frequency, γ the phonon damping constant and Γ the plasmon damping constant, n and m^* the concentration and the effective mass of the free carriers, respectively, and ϵ_∞ is the optical relative permittivity.

For the calculation of the coefficient A the Faust-Henry coefficient is needed. A theoretical value of $C=-0.14$ is given in Ref. 3 for InP. We calculated the influence of C on the frequency and linewidths of the coupled modes in the range of C from 0 to -5. It was found that the values of ω_+ and Γ_+ are not much affected. Recently the Faust-Henry coefficient of undoped InP at 1.06 μm has been determined from Raman scattering measurements.[4] We used this value, $C=-0.53$, which is different from those obtained in previous measurements.[5,6]

In the calculation of the coefficient A we used the values $\omega_T=303.7$ cm^{-1} and $\omega_L=344.5$ cm^{-1}, $\gamma=1.2$ cm^{-1}, which were measured in semi-insulating InP. Usually the frequencies of the coupled plasmon-LO(Γ)-phonon modes are deduced in the limit of zero damping as the roots of the equation $\epsilon(\omega)=0$ and are given by the equation

$$\omega_\pm^2=\tfrac{1}{2}\{\omega_L^2+\omega_p^2\pm[(\omega_L^2+\omega_p^2)^2-4\omega_p^2\omega_T^2]^{1/2}\}, \quad (5)$$

which may not be valid at high damping values.

THEORY OF INFRARED REFLECTIVITY

At normal incidence of light the reflectivity R is given by

$$R=\left|\frac{\sqrt{\epsilon(\omega)}-1}{\sqrt{\epsilon(\omega)}+1}\right|^2, \quad (6)$$

where $\epsilon(\omega)$ is given by Eq. (3).

Parameters in this semiclassical model are the phonon frequencies ω_T and ω_L, the plasma frequency ω_p given by Eq. (4), and the damping constants γ and Γ. The frequencies of the coupled phonon modes ω_- and ω_+ are defined by Eq. (5).

In another model by Kukharskii[7]

$$\epsilon(\omega)=\epsilon_\infty\frac{(\omega^2+i\Gamma_-\omega-\omega_-^2)(\omega^2+i\Gamma_+\omega-\omega_+^2)}{\omega(\omega+i\Gamma)(\omega^2+i\gamma\omega-\omega_T^2)}. \quad (7)$$

In this model two additional parameters are the damping constants Γ_- and Γ_+ of the coupled plasmon-phonon modes.

The coupled and single oscillator modes are related to each other through the equation

$$\omega_-\omega_+=\omega_p\omega_T. \quad (8)$$

Both models were used for the fitting of the experimental data to theory. As a result of the fitting procedure the frequencies and the damping constants are obtained.

The carrier concentration is calculated according to Eq. (4) from the values of ω_p. Because InP has a nonparabolic conduction band, the effective mass m^* in Eq. (4) depends on the carrier concentration. This dependence obtained by the $\mathbf{k}\cdot\mathbf{p}$ theory[8,9] is

$$\frac{1}{m^*}=\frac{1}{m_0^*}-\frac{\phi}{E_g}, \quad (9)$$

where $m_0^*=0.08m_e$, $E_g=1.35$ eV, and $\phi=0.4078(3\pi^2n)^{2/3}h^2$.

RESULTS AND DISCUSSION

The Raman spectra measured in the frequency range up to 550 cm^{-1} are shown in Fig. 1. For all spectra a high-resolution scan near the interesting features was also recorded. The spectrum of the undoped semi-insulating InP (the lowest curve in Fig. 1) consists of two narrow lines of the LO(Γ) and TO(Γ) phonons having a linewidth of 1.2 and 0.8 cm^{-1} and a frequency of 344.5 and 303.7 cm^{-1}, respectively. These values of the phonon frequencies are in good agreement with previous measurements.[6–8]

Figure 1 also shows the spectrum for sample 1 with

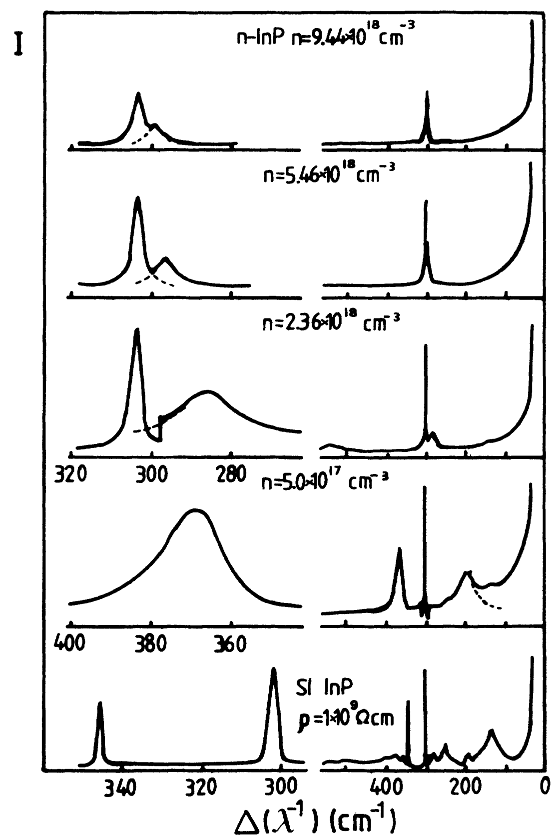

FIG. 1. Raman spectra of n-type InP samples "semi-insulating," 1, 2, 3, and 5 in this order from bottom to top. On the left a high-resolution scan of a part of the spectrum is shown. The spectral resolution is 1.6 cm^{-1}. $T=295$ K.

TABLE I. Frequencies and linewidths (in units of cm^{-1}) of low- and high-frequency plasmon–LO(Γ)-phonon modes ω_-,Γ_- and ω_+,Γ_+, respectively, for doped n-type InP obtained from Raman scattering and infrared-reflectivity data, and calculated values of electron concentrations n (in cm^{-3}).

	Raman scattering					Infrared reflectivity				
Sample	ω_-	Γ_-	ω_+	Γ_+	n	ω_-	Γ_-	ω_+	Γ_+	n
1	200	50	369	17	5.0×10^{17} [a]	192		368		4.9×10^{17}
2	286	14	539	45	2.4×10^{18} [a]	284		538		2.3×10^{18}
3	296	6.4			5.5×10^{18} [b]					
4						298	11	858	80	7.1×10^{18}
5	299	5			9.4×10^{18} [b]	300	10	901	85	8.8×10^{18}

[a]Data calculated from the measured values of ω_+ and Γ_+.
[b]Data calculated from the measured values of ω_- and Γ_-.

$n=5.0\times10^{17}$ cm^{-3}. There is a line corresponding to the TO(Γ) phonon. In addition this spectrum shows new peaks at 200 and at 369.2 cm^{-1} corresponding to ω_- and ω_+, respectively. The asymmetric shoulder on the low-frequency side of the ω_- mode is due to the contribution from the Raman scattering by free electrons centered at the zero-frequency shift.

It is clearly seen that the frequencies of the ω_+ and ω_- mode increase with increasing concentration of free carriers. The intensity of the ω_+ mode is small or negligible in comparison with that of the ω_- mode. In the spectrum of sample 5 with $n=9.44\times10^{18}$ cm^{-3} shown in the top of Fig. 1 we observe the largest value of the ω_- mode which is equal to 299 cm^{-1} and the smallest value of $\Gamma_-=5$ cm^{-1}.

The measured values of frequencies and linewidths of the plasmon–LO(Γ)-phonon lines and the calculated free-carrier concentrations for samples 1–5 are shown in Table I. All of the observed features as well as concentration dependence of the intensities of the ω_- and ω_+ modes are in good agreement with the predictions of Eq. (2).

Figure 2 shows the measured and calculated (solid lines) infrared-reflectivity spectra of the same samples 1, 2, and 5 as in Fig. 1 and that of an additional sample 4. The carrier concentrations given in the figure are those calculated from Eq. (3). The plasma resonance minimum

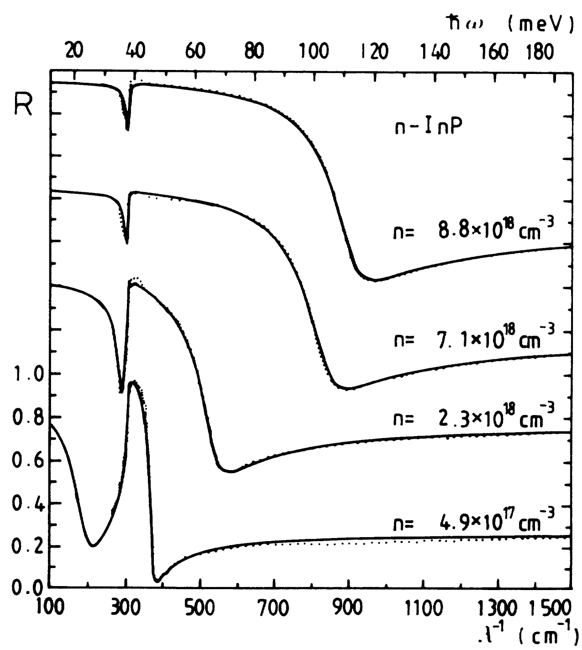

FIG. 2. Infrared-reflectivity spectra of the n-type InP samples 1, 2, 4, and 5 in this order from bottom to top. The carrier concentrations shown are the calculated ones. The minimum at about 300 cm^{-1} is due to the transverse-optical (TO) phonon. The position of the second minimum, called the plasma minimum, depends on the electron concentration. $T=300$ K.

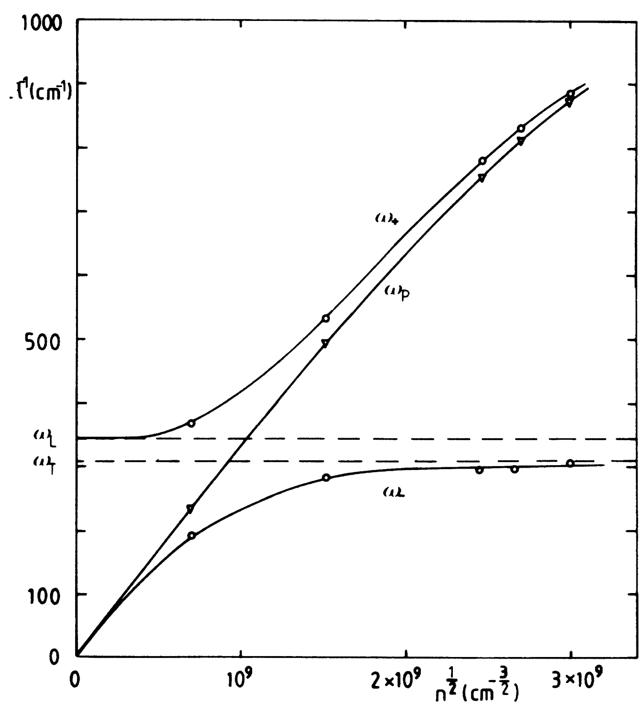

FIG. 3. The frequencies of the coupled plasmon-phonon modes ω_- and ω_+ and the plasma frequency ω_p as a function of the square root of the electron concentration $n^{1/2}$ (solid curves). The frequencies of the longitudinal- (ω_L) and transverse- (ω_T) optical phonons are marked with dashed lines.

is very close to the TO-phonon line in the spectrum of the relatively lightly doped sample 1.

When the carrier concentration is larger, $n = 2.3 \times 10^{18}$–8.8×10^{18} cm^{-3} (samples 2–5), the plasma minimum is shifted towards higher photon energies as seen from Fig. 2.

It turned out that all infrared spectra were adequately well explained by the semiclassical model. However, the damping constants Γ_- and Γ_+ of the coupled modes are not included in this model. The other model by Kukharskii, from which the damping constants can be obtained, could be successfully applied only to the spectra of the heavily doped samples 4 and 5. Table I shows the results of the calculations.

A comparison between the results obtained from the inelastic light scattering and the infrared-reflectivity measurements is presented in Table I. The values of carrier concentrations are well in agreement with each other (within less than 10%).

The frequencies of the coupled phonon modes ω_- and ω_+ obtained by the fitting procedure from the infrared spectra agree well with those measured directly by Raman scattering. It is noticed that ω_+ modes are not observed in the Raman spectra of the heavily doped samples, whose electron concentration is larger than 5×10^{18} cm^{-3}. On the other hand, in this carrier concentration range the values of ω_+ (as well as ω_-) can be calculated from the infrared-reflectivity spectra (samples 4 and 5). In the heavily doped samples ω_+ is close to ω_p and ω_- approached ω_T. This is seen from Fig. 3, in which the frequencies of ω_-, ω_+, and ω_p are plotted as a function of the square root of the carrier concentration (solid curves). The dashed lines represent the constant values of ω_T and ω_L. If the effective mass were independent of carrier concentration, the ω_+ curve would asymptotically approach at large values of n the straight line given by Eq. (4). Because of the concentration dependence of m^* this is not the case as seen from Fig. 3, where the ω_+ curve is bowed slightly towards the similar ω_p curve.

It is possible to estimate the mobility of the electrons from the half-widths of the LO-phonon–plasmon modes. The results were presented in Ref. 10.

[1] G. Irmer, V. V. Toporov, B. H. Bairamov, and J. Monecke, Phys. Status Solidi B **119**, 595 (1983).

[2] M. V. Klein, in *Light Scattering in Solids,* Vol. 8 of *Topics in Applied Physics,* edited by M. Cardona (Springer, Berlin, 1975).

[3] M. Cardona, in *Light Scattering in Solids III: Recent Results,* Vol. 51 of *Topics in Applied Physics,* edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1982).

[4] N. Suzuki and K. Tada, Jpn. J. Appl. Phys. **23**, 291 (1984).

[5] A. Mooradian and G. B. Wright, Solid State Commun. **4**, 431 (1966).

[6] M. Selders, F. Yi Chen, and R. K. Chang, Solid State Commun. **12**, 1057 (1973).

[7] A. A. Kukharskii, Fiz. Tverd. Tela (Leningrad) **14**, 1744 (1972) [Sov. Phys.—Solid State **14**, 1501 (1972)].

[8] E. O. Kane, J. Phys. Chem. Solids **1**, 24 (1957).

[9] A. Raymond, J. L. Robert, and B. Pistoulet, in *Proceedings of the Sixth International Symposium on Gallium Arsenide and Related Compounds, Edinburgh Conference, 1976,* edited by C. Hilsum (Institute of Physics Conference, Bristol, 1977) Ser. No. 33a, p. 105.

[10] B. H. Bairamov, I. P. Ipatova, V. V. Toporov, G. Irmer, J. Monecke, J. Jahne, K. Naukkarinen, and T. Tuomi, in *18th International Conference on the Physics of Semiconductors,* edited by O. Engström (World Scientific, Sinagpore, 1987), Vol. 2, p. 1701.