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# OPTICAL MIXING BY MOBILE CARRIERS IN InSb

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Optical frequency mixing of electromagnetic waves in InSb is investigated experimentally and analytically. Numerical results obtained from the general theory of nonlinear free carrier optical phenomena are compared with experimental results for the special case of mixing of two $CO_2$ laser beams in indium antimonide. The influence of nonparabolicity of the band and electron scattering processes on the measured nonlinear effect is considered. It is proved that nonlinearity associated with scattering of electrons by ionized impurities can in some cases be important in InSb.

## *1. Introduction*

The third-order nonlinear optical phenomena in semiconductors due to free electrons were for the first time detected by Patel et al. [1]. They observed the optical mixing (i.e. generation of radiation $2\omega_2-\omega_1$ and radiation $2\omega_1-\omega_2$) of two laser beams of frequencies $\omega_1$ and $\omega_2$ obtained from a $Q$-switched $CO_2$ laser in III—V semiconductors. In addition the sum frequency $3\omega_1$ was observed by them in InAs and GaAs. Generation of $2\omega_1-\omega_2$ radiation in GaAs with low electron concentrations was studied later by Wynne [2].

A large number of theoretical papers concerning nonlinear excitations of free carriers in semiconductors have been published [3–12]. Wolff and Pearson [3] have given a phenomenological theory of nonlinear optical effects due to the mobile carriers in semiconductors. They assumed that the only source of nonlinear properties of free electrons in semiconductors is due to the nonparabolicity of the energy band, so that the electron mass is energy-dependent. They started their calculations from the classical equation of motion. In such a treatment the distribution of electrons in the band as well as electron scattering processes have been neglected.

A more general and rigorous theory of nonlinear optical phenomena associated with free carriers in semiconductors has been proposed by one of us in a number of papers [4–8]. This theory is based on the solution of the nonlinear Boltzmann equation. It has been shown in papers [4–8] that there are two sources for nonlinear excitations of electrons

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in semiconductors. The first one is the energy dependence of the relaxation time and the second one is the above-mentioned nonparabolicity of the band. The treatment of nonlinear excitations of electrons from the point of view of the Boltzmann equation made it possible to find the third-order conductivity tensor which depends on both of the above-mentioned sources. The distribution of electrons in the band was taken into account.

The influence of the energy dependence of electron relaxation time on nonlinear phenomena was later considered by Kaw [9] and also by Krishnamurthy and Paranjape [10] who investigated the "heating" effect of a strong electric field of laser radiation on electrons. However Wang and Ressler [11] showed that the "heat-electron" approach to calculating the carrier-scattering contribution to nonlinear phenomena is inadequate, since it ignores changes described in terms of higher-order derivatives of the distribution function.

The results of experimental investigations of nonlinear optical phenomena in semiconductors presented in the literature [1, 2] are too scarce to be used for an experimental verification of the theories mentioned above. This was the main reason why we performed an experiment in which we measured the effect of optical frequency mixing due to the free electrons in indium antimonide. The frequencies $2\omega_2-\omega_1$, $2\omega_3-\omega_1$, $\omega_2+\omega_3-\omega_1$ of the radiation generated in the InSb samples result from the optical mixing of the laser beams of fundamental frequencies $\omega_1$, $\omega_2$, $\omega_3$, obtained from the $Q$-switched $CO_2$ high power laser. We measured the power of the generated $2\omega_2-\omega_1$ radiation as a function of temperature and electron concentration in InSb single crystals. From obtained experimental results it was possible to analyse the influence of a scattering processes and band nonparabolicity on the nonlinear excitation of electrons in indium antimonide. On the ground of a general theory of the nonlinear excitation of electrons in semiconductors [4–8] it was possible to derive the third-order conductivity tensor expressions for our experimental circumstances. Both the nonparabolicity of the band and the energy dependence of the electron relaxation time in InSb were taken into account.

The contribution to third-order conductivity tensor arising from the scattering of electrons by ionized impurities, optical and acoustic phonons was considered. Numerical calculations of the power of $2\omega_2-\omega_1$ radiation generated in InSb based on the theory presented in papers [4–8] were compared with the results of Wolff and Pearson's theory and with the experimental data obtained in this work.

## *2. Experiment*

The $CO_2$—$N_2$—He laser was operating in the $Q$-switched mode with the mirror rotating at 100 rps. The time of laser pulse was 1 μsec. The laser output consisted of several $P$ transitions of the $00^01-10^00$ band near 10.6 μ ($\omega_1$) as well as several $P$ and $R$ transitions of the $00^01-02^00$ band near 9.6 μ ($\omega_2$) and 9.3 μ ($\omega_3$). The laser radiation bands are shown in Fig. 1. It can be seen that each band is composed of a number of sharp lines. The frequency of each line corresponds to the particular rotational-vibrational transitions of $CO_2$ molecules. The power of the pulse was different for each band and equalled $P(\omega_1) = 1$ kW, $P(\omega_2) = 0.8$ kW, $P(\omega_3) = 0.7$ kW (that is the sum of powers in all lines

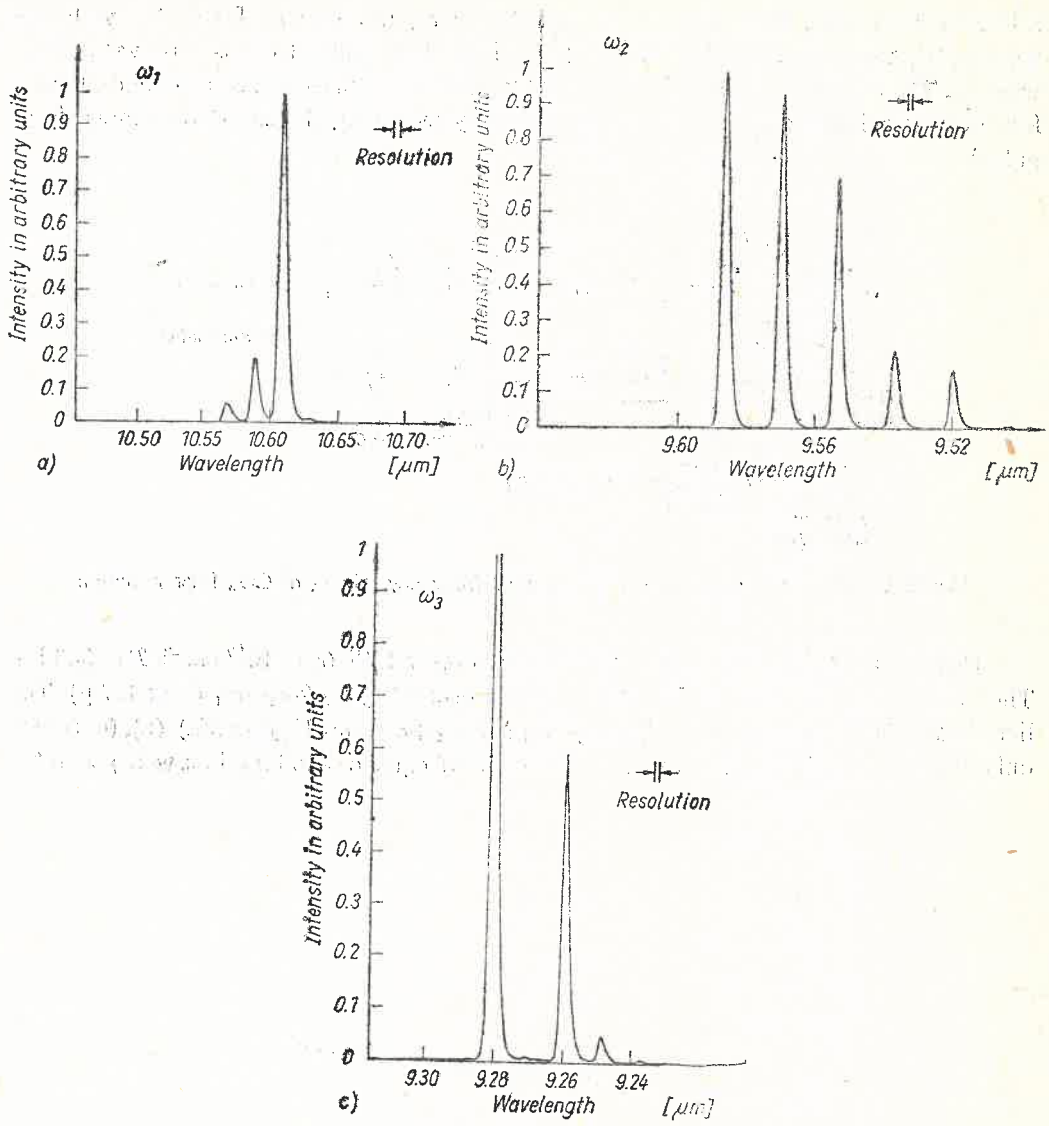



Fig. 1. Spectra of $Q$-switched $CO_2$ laser radiation: (a) 10.6 μ ($\omega_1$) transitions, (b) 9.6 μ ($\omega_3$) transitions, (c) 9.3 μ ($\omega_3$) transitions

of each band). The laser beam was focused by a NaCl lens on polished samples of InSb crystals (Fig. 2). The radiation generated in the sample by optical mixing of laser radiation was analysed by a grating monochromator of high resolution. An interference filter was employed which passed the radiation generated in the sample but retained the laser radiation. The analysed radiation was detected by a thin film of $Cd_xHg_{1-x}Te$ graded crystal acting as a photoresistor working at liquid nitrogen temperature. The detector pulses were passed through an amplifier of high sensitivity and observed on a CRT or summed by

a Boxcar Integrator. The trigger pulses synchronizing the Boxcar Integrator with the laser pulse, were obtained by reflecting the laser light pulse from the Brewster-angle window. The use of the Boxcar Integrator improved the signal-to-noise ratio and allowed for accurate relative measurements to be made by averaging the signal over many laser pulses.

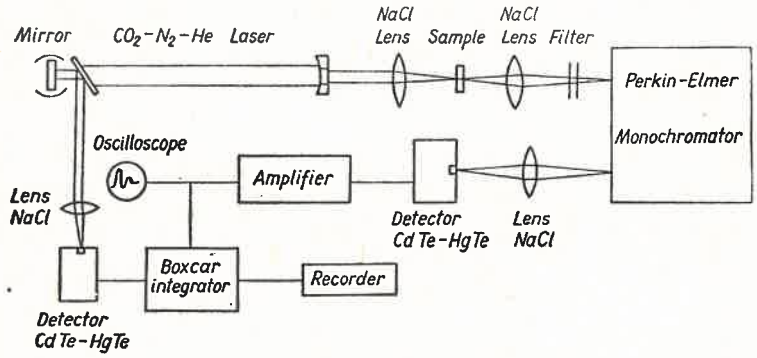
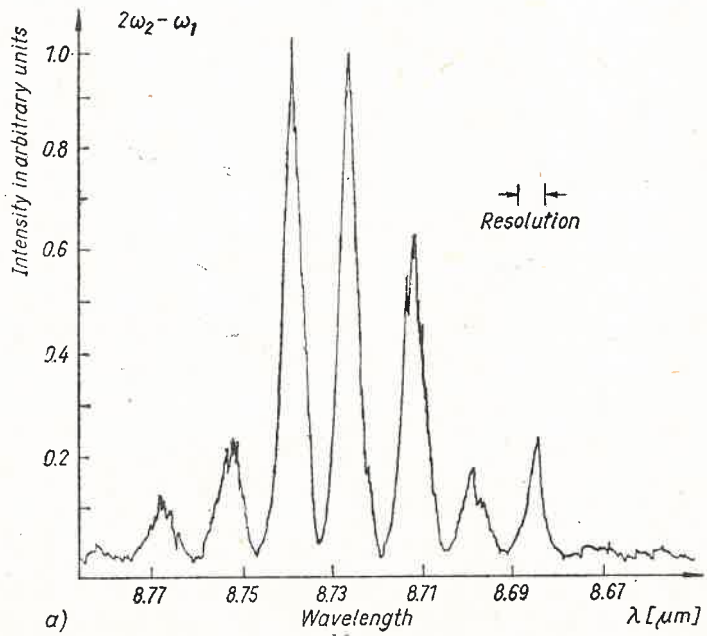



**Fig. 2. Experimental set-up for studying optical frequency mixing of $CO_2$ laser radiation**

Figures 3(a), (b) and (c) show mixed signals from $-n$ InSb ($n = 10^{17}$ cm$^{-3}$, $T = 300$ K). The positions of the lines in Fig. 3(a) are given occurately by $2\omega_2-\omega_1$ (near 8.7 μ). The lines in Fig. 3(b) and (c) are given by $2\omega_3-\omega_1$ and $\omega_2+\omega_3-\omega_1$ Figures 3(a), (b), (c) shown only three typical mixed bands, although all possible frequency combinations were generated



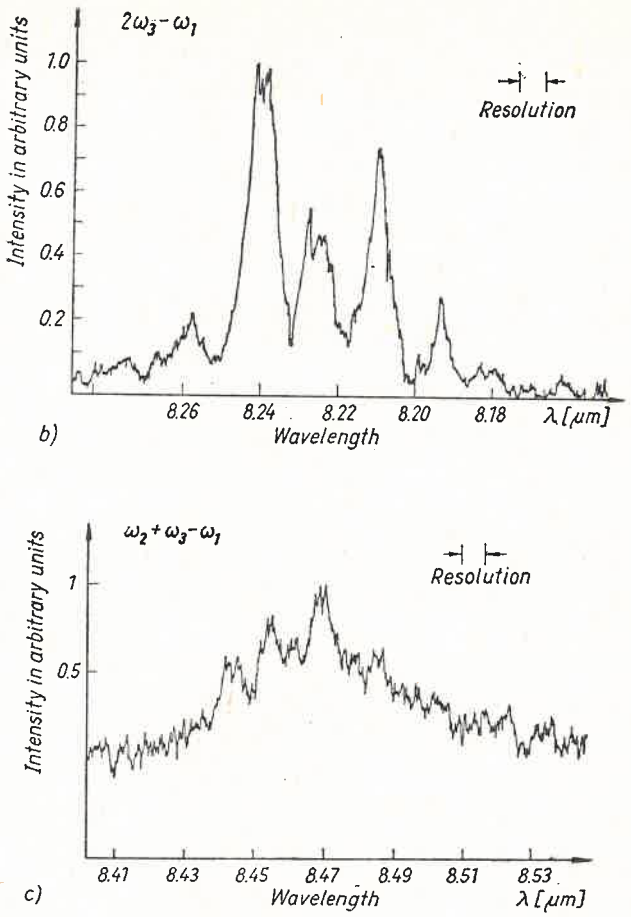



**Fig. 3. Output spectra from $n$–InSb: (a) mixed signal at 8.7 μ corresponding to $2\omega_2-\omega_1$, (b) mixed signal at 8.24 μ corresponding to $2\omega_3-\omega_1$, (c) mixed signal at 8.46 μ corresponding to $\omega_2+\omega_3-\omega_1$**

and could have been studied. The obtained frequencies of mixed lines correspond to ones expected from the frequencies of the laser radiation lines. The above experimental set-up was used for measurements of dependence of $2\omega_2-\omega_1$ radiation on temperature and electron concentration in InSb. The results are shown in Figs 5 and 6.

### *3. Interpretation*

The theory presented in papers [4–8] makes it possible to calculate the third-order conductivity tensor for semiconductors with nonparabolic energy band of ellipsoidal symmetry and for any mechanism of electrons scattering.

In the case of linear polarization in the same direction of $\omega_2$ and $\omega_1$ radiation, and assuming the presence of scalar momentum effective mass, the $2\omega_2-\omega_1$ conductivity can

be expressed in the form

$$\sigma_{np+sc}(2\omega_2-\omega_1) = \frac{q^4N}{9(2\omega_2-\omega_1)(-\omega_1)(\omega_2)^2\left\langle -\frac{df_0}{d\varepsilon}\right\rangle}\left\{\left\langle\frac{m^{*-1}}{\tau}\frac{d}{d\varepsilon}\left(\hat{F}\left\{\frac{df_0}{d\varepsilon}m^{*-1}\right\}\right)\right\rangle\right.$$

$$+\frac{(\omega_2-\omega_1)\omega_1^2+2\omega_2(\omega_1^2+\omega_2^2)}{(\omega_2-\omega_1)(-\omega_1)\omega_2}\left\langle m^{*-1}\frac{d}{d\varepsilon}\left(\hat{F}\left\{\frac{df_0}{d\varepsilon}\frac{m^{*-1}}{\tau}\right\}\right)\right\rangle$$

$$+i\left[\frac{(\omega_2-\omega_1)\omega_1^2+2\omega_2(\omega_1^2+\omega_2^2)}{(2\omega_2-\omega_1)(\omega_2-\omega_1)(-\omega_1)\omega_2}\left\langle\frac{m^{*-1}}{\tau}\frac{d}{d\varepsilon}\left(\hat{F}\left\{\frac{df_0}{d\varepsilon}\frac{m^{*-1}}{\tau}\right\}\right)\right\rangle\right.$$

$$\left.\left.-(2\omega_2-\omega_1)\left\langle m^{*-1}\frac{d}{d\varepsilon}\left(\hat{F}\left\{\frac{df_0}{d\varepsilon}m^{*-1}\right\}\right)\right\rangle\right]\right\}, \tag{1}$$

where the indices np and sc specify the contributions due to nonparabolicity and energy-dependent scattering, respectively. $\varepsilon$ — electron energy, $q$ — electronic charge, $N$ — electron concentration, $f_0$ — Fermi–Dirac distribution function, $m^*$ — effective electron mass, $\tau$ — relaxation time.
$\hat{F}$ is the operator

$$\hat{F}\{B\} = \gamma^{-\frac{1}{2}}\left(\frac{d\gamma}{d\varepsilon}\right)^{-1}\frac{d}{d\varepsilon}[\gamma^{\frac{1}{2}}B]. \tag{2}$$

The brackets $\langle\rangle$ in Eq. (1) are defined as follows:

$$\langle A\rangle = \int_0^\infty \gamma^{\frac{3}{2}}A(\varepsilon)d\varepsilon. \tag{3}$$

The function $\gamma(\varepsilon)$ in the above equations determines the nonparabolicity of the conduction band.

In the simplified version of Kane's band model (i.e. in which the energy of the spin-orbit interaction is assumed to be much larger than the energy gap $\varepsilon_g$) this function is given by the following relation:

$$\gamma(\varepsilon) = \varepsilon\left(1+\frac{\varepsilon}{\varepsilon_g}\right). \tag{4}$$

According to Ref. [13] the energy dependence of the effective electron mass is given by

$$m^{*-1} = m_0^{*-1}\left(\frac{d\gamma}{d\varepsilon}\right)^{-1}, \tag{5}$$

where $m_0^*$ is effective mass at the bottom of the conduction band. The energy-dependent relaxation time in Eq. (1) is different for each scattering mechanism.

According to paper [14], in the case of electron scattering by ionized impurities in InSb the relaxation time is given by

$$\tau = \tau_i \frac{1}{F} \gamma^{\frac{1}{2}} \left(\frac{d\gamma}{d\varepsilon}\right)^{-1}, \tag{6}$$

where

$$\tau_i = \frac{\kappa^2 (2m_0^*)^{\frac{1}{2}}}{\pi q^4 N}, \tag{7}$$

$\kappa$ is dielectric constant.

$$F_i = \left[1 + \frac{4\xi_1}{\xi_0}\left(1 - \frac{\xi_1}{8}\right)\right] \ln(\xi_0 + 1) - \frac{\xi_0}{\xi_0 + 1} - 2\xi_1\left(1 - \tfrac{5}{16}\xi_1\right), \tag{8}$$

with

$$\xi_0 = \frac{2\pi\kappa\hbar\gamma(\varepsilon)}{q^2(2m_0^* k_0 T)^{\frac{1}{2}}} \frac{1}{{}^0L_1^{\frac{1}{2}}(\eta, \beta)}, \tag{9}$$

and

$$\xi_1 = \frac{2\dfrac{\varepsilon}{\varepsilon_g}}{1 + \dfrac{2\varepsilon}{\varepsilon_g}}. \tag{10}$$

The generalized Fermi-Dirac integrals ${}^nL_k^m(\eta, \beta)$ are defined in [15] as follows:

$${}^nL_k^m(\eta, \beta) = \int_0^\infty \left(-\frac{df_0}{d\varepsilon}\right) x^n (x + \beta x^2)^m (1 + 2\beta x)^k dx, \tag{11}$$

with

$$x = \frac{\varepsilon}{k_0 T}; \quad \eta = \frac{\varepsilon_F}{k_0 T}; \quad \beta = \frac{k_0 T}{\varepsilon_g},$$

$\varepsilon_F$ is the Fermi level, $k_0$ — the Boltzmann constant, $T$ — temperature.

For electron scattering on acoustic phonons, the relaxation time is in the form [14]

$$\tau = \tau_{ac} \frac{1}{F_{ac}} \gamma^{-\frac{1}{2}} \left(\frac{d\gamma}{d\varepsilon}\right)^{-1}, \tag{12}$$

where

$$\tau_{ac} = \frac{\pi\hbar^2 v_L \varrho}{\sqrt{2}\, k_0 T E_d^2 (m_0^*)^{\frac{1}{2}}}, \tag{13}$$

$$F_{ac} = \left(1 - \frac{1.3\varepsilon}{\varepsilon_g + 2\varepsilon}\right)^2 + \left(\frac{v_L}{v_T}\right)^2 0.53 \tfrac{17}{72} \left(\frac{\varepsilon}{\varepsilon_g + 2\varepsilon}\right)^2. \tag{14}$$

$v_L$, $v_T$ is the longitudinal and transverse velocity of sound in crystals. $E_d$ — the deformation potential constant, $\varrho$ — the density of the crystal.

For electron scattering on optical phonons, the relaxation time is given by [14]

$$\tau = \tau_{op} \frac{1}{F_{op}} \gamma^{\frac{1}{2}} \left( \frac{d\gamma}{d\varepsilon} \right)^{-1}, \tag{15}$$

$$\tau_{op} = \frac{\sqrt{2}\Omega (k_0 \theta)^2}{8\pi (qq^*)^2 (m_0^*)^{\frac{1}{2}}}, \tag{16}$$

where $M$ is the reduced ionic mass, $\Omega$ — the volume of the elementary cell, $\theta$ — the Einstein temperature, $q^*$ — the effective ionic charge.
The function $F_{op}$ is given by [14]:

$$F_{op} = 1 - \frac{\frac{2\varepsilon}{\varepsilon_g}}{1 + \frac{2\varepsilon}{\varepsilon_g}} + \frac{3}{8} \left( \frac{\frac{2\varepsilon}{\varepsilon_g}}{1 + \frac{2\varepsilon}{\varepsilon_g}} \right)^2. \tag{17}$$

In analysing the pure effect associated with the nonparabolicity of the band, one has to neglect the energy-dependence of the relaxation time and assume $\tau = \text{const}$.
The result for $\sigma(2\omega_2 - \omega_1)$ is as follows:

$$\sigma_{np}(2\omega_2 - \omega_1) = \frac{5q^4 N}{9(2\omega_2 - \omega_1)(\omega_2)^2(-\omega_1)\varepsilon_g (m_0^*)^2 \tau}$$

$$\times \left\{ \frac{\omega_2^2(2\omega_2 - \omega_1) + \omega_1^2(4\omega_2 - \omega_1)}{(\omega_2 - \omega_1)(-\omega_1)\omega_2} + i \left[ \frac{(\omega_2 - \omega_1)\omega_1^2 + 2\omega_2(\omega_1^2 + \omega_2^2)}{(2\omega_2 - \omega_1)(\omega_2 - \omega_1)(-\omega_1)\omega_2 \tau} \right. \right.$$

$$\left. \left. - (2\omega_2 - \omega_1)\tau \right] \right\} \left\{ \frac{{}^0L_{-2}^{\frac{3}{2}} - \frac{12}{5} \beta^0 L_{-5}^{\frac{5}{2}}}{{}^0L_0^{\frac{3}{2}}} \right\}. \tag{18}$$

The pure effect associated with the energy dependence of the relaxation time can be calculated as follows

$$\sigma_{sc} = \sigma_{np+sc} - \sigma_{np}. \tag{19}$$

Note that the employed energy dependence of relaxation time takes into account not only the real energy band structure of the InSb crystal but also the mixing of valence $p$-like components into the total wave functions of the conduction electrons.

The effect of electron scattering by ionized impurities and optical phonons was considered by Rustagi [22] but the energy dependence of relaxation time used by him was incorrect because the electron wave functions concerned were not taken into account.

### 4. *Results and discussion*

Numerical calculations of the third-order conductivity tensor arising from: (a) nonparabolicity of the band, (b) scattering of electrons by ionized impurities, (c) scattering by acoustic phonons, (d) scattering by optical phonons were carried out in indium antimonide.

TABLE I

| | Symbol | Value | Reference |
|---|---|---|---|
| Band gap | $\varepsilon_g(0)$ | 0.23 eV | [16] |
| Effective mass | $m_0^*(0)$ | $0.0145\, m_0$ | [17] |
| Dielectric constant | $\varkappa$ | 17.5 | [18] |
| Reduced ionic mass | $M$ | $0.99 \times 10^{-22}$ g | [14] |
| Einstein temperature | $\theta$ | 238°K | [19] |
| Lattice constant | $a$ | $6.48 \times 10^{-8}$ cm | [14] |
| Callen's effective charge | $q^*$ | 0.13 q | [14] |
| Longitudinal sound velocity | $v_L$ | $3.4 \times 10^5 \frac{\text{cm}}{\text{sec}}$ | [20] |
| Transverse sound velocity | $v_T$ | $2.3 \times 10^5 \frac{\text{cm}}{\text{sec}}$ | [20] |
| Crystal density | $\varrho$ | 5.77 | [21] |
| Temperature-dependence of band gap | $\frac{\partial \varepsilon_g}{\partial T}$ | $9.6 \times 10^{-5} \frac{\text{eV}}{\text{K}}$ | [16] |

The values of parameters used in the calculations are given in Table I. After Ehrenreich [16] the dependence of effective mass on temperature in ISnb was assumed to be of the form

$$m_0^*(T) = \frac{m_0^*(0)\varepsilon_g(T)}{\varepsilon_g(0)}. \tag{20}$$

The obtained values of the third-order conductivity tensor as a function of electron concentration are given in Fig. 4. The biggest contribution to the conductivity tensor is due to the nonparabolicity of the band. The energy dependence of relaxation time gives a significant contributions — the biggest contribution arises from the scattering of electrons by ionized impurities.

The latter contribution increases strongly with increasing carrier concentration and becomes dominant for concentrations bigger than $10^{18}$ cm$^{-3}$. The energy-dependenc e o the relaxation time of electrons scattered by acoustic phonons decreases the effect of optica mixing.

Knowledge of the value of $2\omega_2 - \omega_1$ conductivity permits us to determine the density of radiation power generated in InSb. This power calculated from the theory presented in papers [4–8] were compared with the results of Wolff and Pearson's theory and with

power measured in this work, as is shown in Fig. 5. Curve *1* was calculated from the theory of Wolff and Pearson. Curves *2* and *3* show the results of calculations carried out in this work from the theory presented in papers [4–8]. The dependence shown by line *2* was obtained by assuming that the optical mixing effect is due only to the nonparabolicity

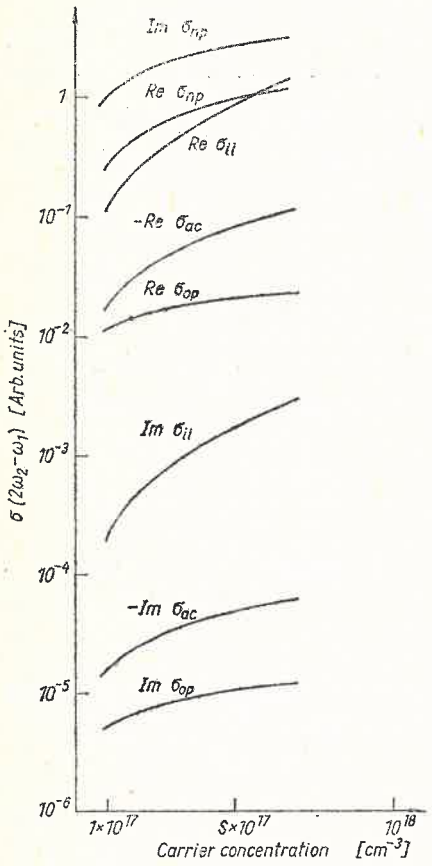



Fig. 4

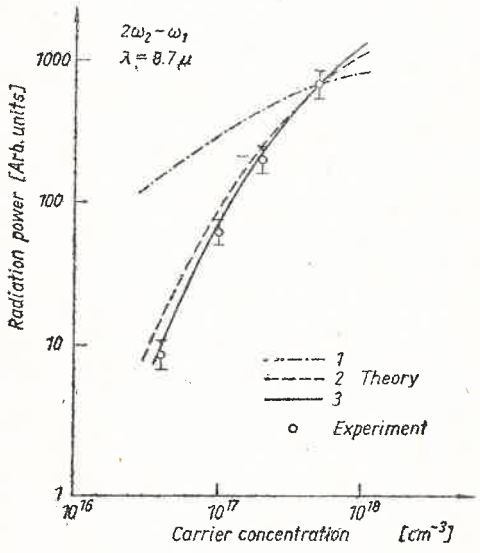



Fig. 5

Fig. 4. Real and imaginary parts of the third-order conductivity tensor $\sigma(2\omega_2-\omega_1)$ as a function of carrier concentration in $n$–InSb. $\sigma_{np}$ — conductivity due to band nonparabolicity, $\sigma_{ii}$, $\sigma_{ac}$, $\sigma_{op}$ — conductivity due to energy dependence of relaxation time of electron scattered by ionized impurities and acoustic and optical phonons

Fig. 5. Power of $2\omega_2-\omega_1$ radiation generated in $n$–InSb as a function of carrier concentration ($T = 300$ K). Theoretical results are normalized at the concentration $4.7\times10^{17}$ cm$^{-3}$. Theoretical curves are explained in the text

of the band. Taking into account the energy dependence of electron relaxation time leads to the function shown by line *3*, which is in full agreement with experimental results.

The dependence of the power of $2\omega_2-\omega_1$ radiation on temperature in InSb crystals was calculated and measured in this work for various electron concentrations (Fig. 6).

The dashed lines show the power of $2\omega_2-\omega_1$ radiation which was calculated on the assumption that the optical mixing effect is due only to the nonparabolicity of the conduction band. Considering simultaneously the energy dependence of relaxation time of electrons scattered by ionized impurities yields to the function shown by the solid curves. The contribution to optical mixing arising from the scattering by acoustic and optical phonons was negligible in comparison with the effect of scattering by ionized impurities.

It is concluded that the results of numerical calculations obtained from the theory presented in papers [4–8] show a much better agreement with the experimental values

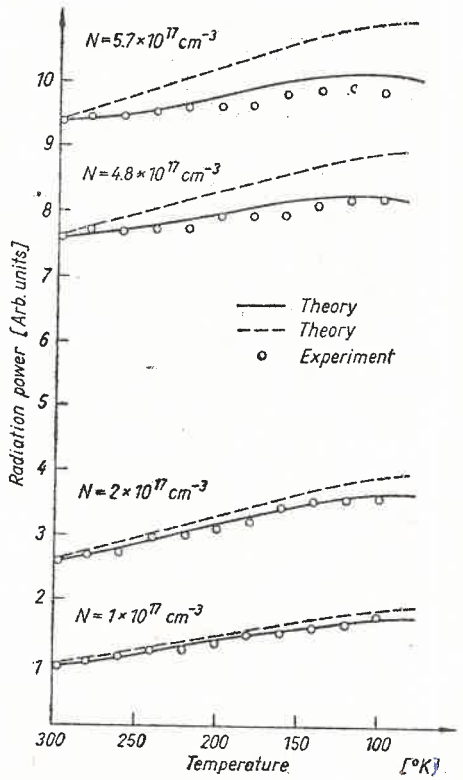



Fig. 6. Power of $2\omega_2-\omega_1$ radiation generated in $n$–InSb as a function of temperature for various carrier concentrations. Theoretical and experimental results are normalized at temperature $T = 300$ K. Dashed line was calculated assuming that the optical mixing effect is due only to band nonparabolicity. Solid line shows numerical results obtained in the case when the energy dependence of relaxation time of electrons scattered by charged centers is also included

of power of $2\omega_2-\omega_1$ radiation than the results obtained from Wolff and Pearson's theory. This is due to taking into account both, the statistical electron distribution in the band as well as the electron scattering processes. The investigations carried out in this work have proved that a particularly great contribution to the effect of optical mixing arises from scattering of electrons by ionized impurities.

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