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Degenerate four-wave mixing in n-Ge due to intervalley redistribution of hot electrons

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Abstract. We have studied backward degenerate four-wave mixing at CO_2 laser wavelengths in n-type Ge. Phase conjugation due to redistribution of free electrons between equivalent valleys was observed. The effect is related to carrier heating by infrared radiation.

Keywords: degenerate four-wave mixing, phase conjugation, many-valley semiconductors, intervalley redistribution, carrier heating.

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1. Introduction

The degenerate four-wave mixing at CO_2 laser wavelengths has been observed in III-V compounds and $Hg_{1-x}Cd_xTe$, this being associated with free carrier optical nonlinearity [1-2]. This nonlinearity has a double origin, namely: the nonlinear dependence of carrier velocity on momentum, due to the nonparabolicity of the conduction band and the energy dependence of the scattering events.

In cubic many-valley semiconductors, a strong nonlinearity of the dielectric permittivity in the IR region is related to the redistribution of electrons between equivalent valleys [3–4]. There are two reasons for this redistribution. The first one is the energy displacement of valleys, which is caused by an oscillatory character of the carrier motion in the electric field **E** of the light wave. The energy of this motion is inverse to the effective mass of carriers in the direction of oscillation and therefore the energy displacement of the valley depends on the orientation of **E** relatively to axes of valleys. Another reason for redistribution is the consequence of the different carrier heating in various valleys by infrared radiation.

As a consequence of electron redistribution, the contribution of free carriers to the dielectric permittivity becomes anisotropic and dependent on the intensity of light, initiating the light-induced changes of the optical constants.

The existence of the optical nonlinearity caused by redistribution of electrons in n-Ge has been confirmed in our previous works [5–6] in which a self-induced birefringence of intensive IR CO_2 laser radiation was observed. The intervalley redistribution was shown to be related with the carrier heating and occurred only when the electric field **E** of the light wave is aligned nonsymmetrically relative to long axes of valleys in crystal. It was demonstrated that this mechanism of optical nonlinearity dominates over any other within the relatively narrow interval of free carrier concentrations $N_e \sim (3–5)\times10^{16}$ cm^{-3}. For more lightly doped samples the contribution of free carriers to the susceptibility of Ge is small. On the other hand, with carrier concentrations larger than 5×10^{16} cm^{-3}, the energy exchange between electrons from different valleys caused by electron-electron collisions becomes essential. This type of interaction decreases the difference between the electron temperatures in various valleys and tends to equalize the concentration of electrons in different valleys.

One important aspect of this optical nonlinearity is that it is large, with measured values of the third-order nonlinear susceptibilities $\chi^{(3)}$ as high as 2×10^{-9} esu at 300 K and 1×10^{-8} esu at 80 K [6]. Furthermore, the response time of hot electron-induced optical nonlinearity corresponds to the intervalley scattering time and is about 10^{-11}–10^{-12} s for Ge [7]. Hence it may be useful for self-interaction type of effects such as degenerate four-wave mixing and optical bistability.

In the present paper, we describe the observation and study of a phase conjugation of CO_2 laser IR radiation via degenerate four-wave mixing in n-Ge caused by hot electron-induced optical nonlinearity.

2. Experimental setup

The backward degenerate four-wave mixing (BDFWM) in n-Ge has been measured for IR light with wavelength $\lambda = 10.6\,\mu$m at 300 and 80 K. The samples were cut from Sb-doped Ge single crystals in the form of slabs with thickness $\ell = 0.32$ cm. Front and back surfaces were polished to optical quality and had no antireflection coatings. Carrier concentrations were measured by the Hall effect and were about 5×10^{16} cm^{-3} for both 300 K and 80 K.

The experimental arrangement is shown in Fig.1. The TEA-CO_2 laser was used as a light source. The laser produced a maximal peak power of about 2 MW in a 100 ns FWHM single pulse. The variation of the output peak power was about ±15% from one pulse to another, but no change of the pulse shape was observed. Therefore, in the experiment, measurements were performed with pulses of the same peak power within an accuracy of 3%. A set of calibrated CaF_2 attenuators allowed us to vary the intensity of the laser beam in the range of 5 MW/cm^2 to 40 MW/cm^2.

The laser beam was split by a beam splitter BS1 into two beams, one the pump beam with intensity I_1 and the probe beam with intensity I_3. The probe beam was about 10 times weaker than the pump beam. These beams were separately focused and impinged on the same spot on the sample with an angle of 3° between them. The mirrors M2, M3 equalized the optical path lengths of the pump and the probe beams within 1 cm. The counter-propagating pump beam with intensity I_2 was obtained by the Fresnel reflection of the first pump beam from the rear face of the sample. The phase conjugate beams (I_4) were observed on the same side of the sample as the first pump and probe beams by introducing a ZnSe beam splitter BS2 into the probe beam.

Pyroelectric detectors D1, D2 with a response time of about 3 ns were used to measure the peak power of the incident pump and probe beam pulses and their shape. The phase conjugate signals were measured by a HgCdTe detector D3 at 300 K.

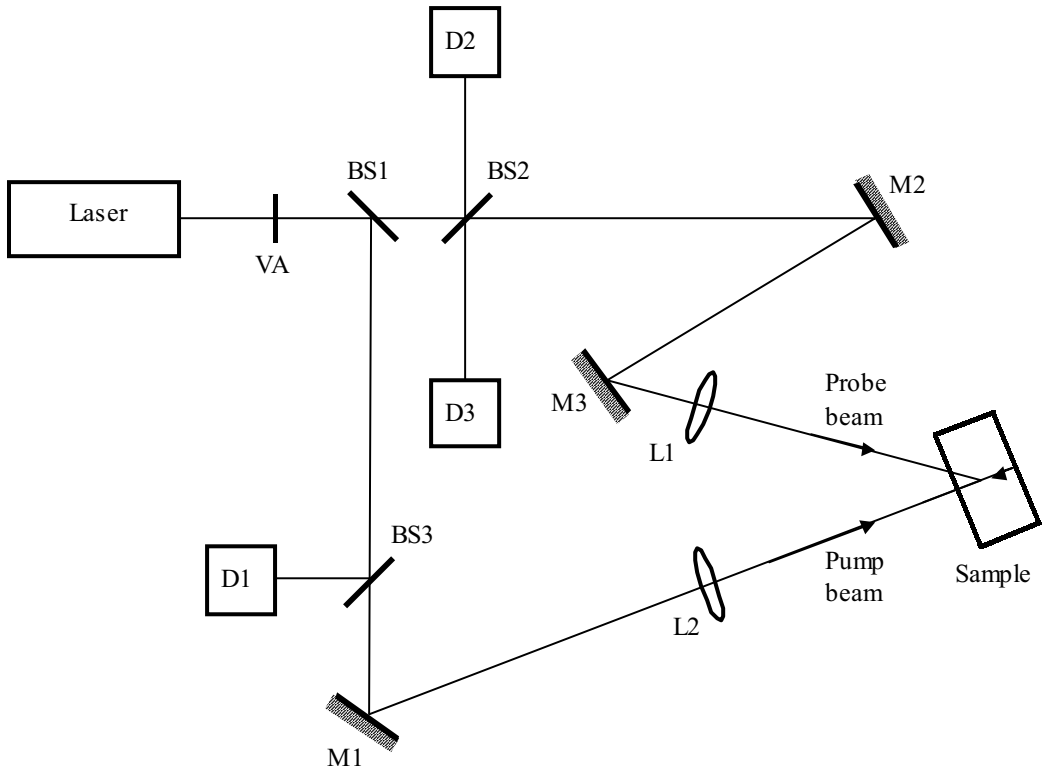

Fig. 1. Experimental setup for backward degenerate four-wave mixing in Ge crystal.

VA: variable attenuator; BS1, BS2, BS3: beam splitters; M1, M2, M3: mirrors; L1, L2: lens; D1, D2: pyroelectric detectors; D3: HgCdTe detector.

The propagation vectors of the pump and probe beams were orientated along the <110> axis of the crystal. The polarization of the beams was chosen parallel to <111> or <001> crystallographic axes. As well known for **E** || <111> orientation, the effective mass of the electrons along the **E** direction is higher in the valley located on <111> crystallographic axis than in other three valleys, and the carrier heating by the electric field of the light wave is smaller in it. Due to the different mean carrier energies in the valleys, the redistribution of the electrons between them takes place [8]. On the contrary, for the **E** ||<001> orientation, all valleys are settled down symmetrically to the field direction. The carrier heating is the same in them and therefore no redistribution of electrons between the valleys occurs.

It should be noted that the redistribution of hot electrons does not result in birefringence for orientation of **E** along the <111> axis in n-Ge [5]. Therefore, the polarization of the pump and probe beams remains unchanged with propagation.

3. Experimental results and discussion

Fig.2 represents the time traces of the pump wave I_1 and back reflected signal wave I_4 for the **E** along <111> crystallographic axis. As expected, the pulse duration of the back reflected signal wave I_4 is smaller than that of the pump wave I_1. At the same time, no delay is observed in the position of the signal pulse maximum as compared to the pump pulse maximum. A similar behaviour is observed also for the **E** along <001> crystallographic axis. Thus, the conclusion can be made that the response time of nonlinearity is at least much shorter than the pulse duration, i.e. the saturation of nonlinear response is reached during the pulse.

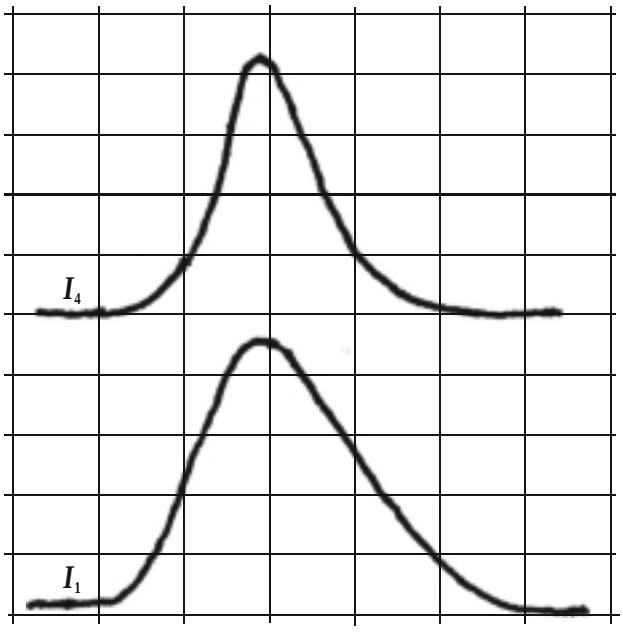

Fig.2. Time traces of the pump wave I_1 and phase conjugated wave I_4.

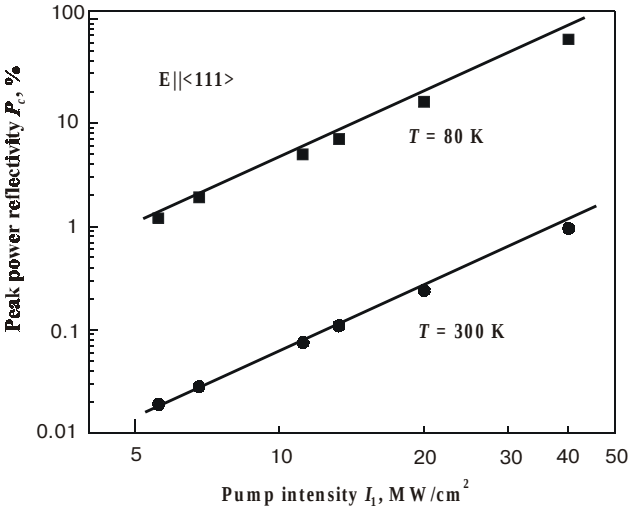

Fig.3. Dependence of BDFWM peak power reflectivity P_c on the pump wave intensity I_1.

Fig.3 shows a dependence of the normalized intensities I_4/I_1 of back reflected wave (BDFWM peak power reflectivity P_c) on the incident pump intensity I_1 for the **E** along <111> crystallographic axis. The reflectivity increases quadratically with the pump intensity I_1 (the slope of lines in a log-log plot equals of about two) thus indicating that only the third-order interaction contributes significantly to the BDFWM signals. For any given pumping intensity the reflectivity rises sharply as the sample temperature is decreased. By changing the temperature from 300 to 80 K, for example, the phase conjugated reflectivity can be increased from 1 % to 64 % at $I_1 = 40$ MW/cm^2.

It should be emphasised that for **E** || < 001> only a very weak phase conjugated signal has been detected at a maximum pump intensity used in the experiment. No dependence of the phase conjugated signal intensity on the sample temperature was observed. The estimated BDFWM reflectivity P_c is about 2×10^{-2} % at $I_1 = 40$ MW/cm^2 for both 300 K and 80 K.

As expected, the obtained value of the BDFWM reflectivity P_c and dependence of the P_c on the sample temperature differ substantially for various orientation of the electric field **E** of the light wave in crystal. This means that different optical nonlinearities lead to the generation of the phase-conjugated wave. Based on the fact that the BDFWM reflectivity increases sharply with decreasing sample temperature for the orientation of the electric field **E** along <111> crystallographic axis we conclude that the observed phase conjugated reflectivity is due to the redistribution of the hot electrons between equivalent valleys. The intervalley transition time in n-Ge is essentially smaller than the used laser pulse duration about 100 ns. Therefore, the optical nonlinearity connected with the redistribution of free electrons is sufficiently fast and can lead to the observed steady-state BDFWM.

For the orientation of the electric field **E** along <001> crystallographic axis, where the intervalley redistribution of the hot electrons does not occur, the observed phase

conjugated reflectivity can arise from the optical nonlinearity due to nonparabolicity of conduction band or that caused by bound electrons.

By using experimental values for BDFWM reflectivity P_c, we may evaluate the third-order nonlinear susceptibility $\chi^{(3)}$. Taking into account the Fresnel reflection R of incident and output waves from the crystal faces and the light absorption in the crystal the BDFWM reflectivity P_c may be written as [9]

$$P_c = \frac{1024\pi^4\omega^2\left|\chi^{(3)}\right|^2}{n^4c^4} I_1^2 \left(\frac{1-e^{-\alpha\ell}}{\alpha}\right)^2 e^{-2\alpha\ell} R(1-R)^4 \quad , \tag{1}$$

where ω is the optical frequency, α is the absorption coefficient and ℓ is the crystal thickness.

From (1) we obtain for the optical nonlinearity due to intervalley redistribution of the hot electrons $\chi^{(3)} = 1.9\times10^{-9}$ esu and $\chi^{(3)} = 9\times10^{-9}$ esu at 300 and 80 K, respectively, with the measured absorption coefficients $\alpha_{300k} = 2.15$ cm^{-1} and $\alpha_{80k} = 1$ cm^{-1}, while $R = 0.36$. These values for the third -order susceptibilities agree very well with that obtained by the self-induced birefringence experiments [5].

The BDFWM reflectivity measured for $\mathbf{E} \| <001>$ corresponds to the third-order nonlinear susceptibility $\chi^{(3)} = 2\times10^{-10}$ esu for both 300 K and 80 K that is close to the value of $\chi^{(3)}$ due to anharmonic motion of bound electrons in Ge [10].

4. Summary

We presented the first observation of the four-wave mixing in many-valley semiconductor *n*-Ge caused by hot electron-induced optical nonlinearity. High efficiency phase conjugation of the infrared CO_2-laser beams was demonstrated. The BDFWM reflectivities of about 65 % have been observed with pump intensity of about 40 MW/cm^2 at 80 K.

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