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Band-Gap–Resonant Nonlinear Refraction in III-V Semiconductors

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We present experimental measurements of the resonance of the large intensity dependence of refractive index in InSb near the band-gap energy at 77 K and derive a semiempirical theory for this effect which fits the measurements well, both in absolute magnitude and wavelength dependence, using only measurable parameters. The size of the effect in other nondegenerate direct–band-gap III-V compound semiconductors and at other temperatures is predicted.

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Direct–narrow-gap semiconductors present unique situations which give large optical saturation effects in solids at low powers, particularly in the region near the band-gap energy where the effective optical matrix element for direct transitions is large and the density-of-states changes rapidly whence such saturation leads both to nonlinear absorption and to a strong intensity dependence of refractive index. We have observed this nonlinear refraction at 77 K in the semiconductor InSb obtaining $dn/dI \equiv n_2$ as high as 1 cm^2/kW [equivalent to an effective degenerate $\chi^{(3)}(\omega;\omega, -\omega,\omega)$ of ~ 1.0 esu]. This effect has already proved to be the important mechanism in the observation of optical bistability,[1,2] optical transistor action,[2,3] and degenerate four-wave mixing[4] thus demonstrating nonlinear optical devices operating at milliwatt powers.

In this paper, we present the first measurements of the resonance of nonlinear refraction (n_2) in the semiconductor InSb near its optical band gap at 77 K under which conditions nondegenerate (Boltzmann) statistics prevail. A semiempirical model is derived which uses only measurable parameters and predicts the size and sign of nonlinear refraction due to saturation and the frequency dependence of its resonance for nondegenerate direct–band-gap III-V compound semiconductors in general when excitonic effects are negligible; this is compared with the experimental results.

Existing models which have been proposed for band-gap–resonant nonlinear refraction have either adopted a full-density-matrix approach[5,6] leading to adjustable parameters (e.g., T_2) which are difficult to explain and measure, or have been restricted to low temperatures (dynamic Burstein-Moss shift)[5,7]; in no case has it been possible to explain the detailed resonance of n_2. The present theory is one extreme limit of the density-matrix approach, with intraband relaxation being sufficiently strong to thermalize the carrier distribution in times much less than the recombination time. For these thermal distributions, the simple Kramers-Krönig relations, not generally valid for nonlinear optical processes,[8] are again applicable because the quantum-mechanical phases of the carriers have been randomized by the thermalizing collisions. The theory rests on the following mechanism:

(i) A fraction of optical absorption in the semiconductor at the photon energy of interest (which may be below the band gap) results in the creation of free electrons and holes in the semicon-

ductor bands.

(ii) The electrons and holes thus created relax rapidly to thermal distributions, which then decay with a single interband recombination time τ_R.

(iii) The thermal populations of the band states partially block (i.e., saturate) the absorption which would otherwise exist in the spectral region above the band-gap energy; this alteration of the absorption spectrum in turn affects the refractive index seen by the incident photons (which may be below the band-gap energy) through the Kramers-Krönig relations. Thus the incident field alters its own refractive index.

For the present comparison, we make two further simplifications: *Every* absorbed photon creates a free electron and hole (in the region below the band gap this may be accomplished by, for example, a phonon-assisted transition,[9] although the precise mechanism for absorption near the gap is not understood); the Fermi-Dirac distributions are approximated by Boltzmann distributions (this is valid for the carrier densities used in the experiments and will normally be the case in relatively pure III-V compound semiconductors at 77 K or above).

Pumping the semiconductor with incident radiation of photon energy $\hbar\omega$ and intensity I leads to generated populations of electrons and holes,

$$\Delta N = \alpha(\hbar\omega) I\tau/\hbar\omega, \tag{1}$$

in the steady state where $\alpha(\hbar\omega)$ is the absorption coefficient at photon energy $\hbar\omega$. We may write the direct interband absorption coefficient for III-V compound semiconductors (neglecting excitonic interaction) for photon energies $\hbar\omega'$, above the band-gap energy, in the parabolic-band approximation as[10]

$$\alpha_d(\hbar\omega') = \frac{(8\sqrt{2})m^{1/2}e^2}{3\hbar^2 c}\left(\frac{\mu}{m}\right)^{3/2}\frac{1}{n_0}\frac{mP^2}{\hbar^2}\frac{(\hbar\omega'-E_G)^{1/2}}{\hbar\omega'}\,[1-f_e(E_c)-f_h(E_v)], \tag{2}$$

where μ is the reduced effective mass, $\mu = m_c m_v/(m_c+m_v)$ (m_c and m_v are the conduction- and valence-band effective masses, respectively) and P is the momentum matrix element

$$P = -(i\hbar/m)\langle S|p_z|Z\rangle$$

defined by Kane.[11] We consider only the absorption between the heavy hole and conduction bands and neglect the much weaker light-hole–band contribution. The absorption is weighted according to the occupation probabilities $f_e(E_c)$ and $f_h(E_v)$ of electrons and holes in the conduction and valence bands, respectively, at the energies appropriate for the direct transition at photon energy $\hbar\omega'$,

$$E_c = \frac{m_v}{m_c+m_v}(\hbar\omega'-E_G);\quad E_v = \frac{m_c}{m_c+m_v}(\hbar\omega'-E_G).$$

Using the Boltzmann approximation and the usual parabolic density of states, we may write the changes Δf_e and Δf_h in f_e and f_h in the presence of the radiation field explicitly as

$$\Delta f_e(E_c) = 4\pi^{3/2}\left(\frac{\hbar^2}{2m_c}\right)^{3/2}\frac{\Delta N}{(kT)^{3/2}}e^{-E_c/kT};$$
$$\Delta f_h(E_v) = 4\pi^{3/2}\left(\frac{\hbar^2}{2m_v}\right)^{3/2}\frac{\Delta N}{(kT)^{3/2}}e^{-E_v/kT}. \tag{3}$$

Because the effective mass of holes is always $\gtrsim 10$ times larger than that of electrons in direct-band-gap III-V compound semiconductors, we may neglect Δf_h in comparison to Δf_e for all the energy range of interest, and the change in the absorption coefficient at energy $\hbar\omega'$ is

$$\Delta\alpha_d(\hbar\omega') \simeq -\frac{16\pi^{3/2}}{3}\frac{e^2\hbar}{m_c}\left(\frac{\mu}{m_c}\right)^{3/2}\frac{mP^2}{\hbar^2}\frac{1}{n_0}\frac{\Delta N}{(kT)^{3/2}}\frac{(\hbar\omega'-E_G)^{1/2}}{\hbar\omega'}\exp\left[\frac{-\mu(\hbar\omega'-E_G)}{m_c kT}\right]. \tag{4}$$

From the Kramers-Krönig relations[12] we may write the change in refractive index at photon energy $\hbar\omega$ as

$$\Delta n(\hbar\omega) = \frac{\hbar c}{\pi}\int_0^\infty \frac{\Delta\alpha_d(\hbar\omega')}{(\hbar\omega')^2-(\hbar\omega)^2}\,d(\hbar\omega'). \tag{5}$$

Hence, using (1), (4), and (5) we may write n_2 ($\equiv \Delta n/I$ in this approximation) as

$$n_2 \simeq \frac{-8\sqrt{\pi}}{3}\frac{e^2\hbar^2}{m}\frac{\mu}{m_c}\frac{mP^2}{\hbar^2}\frac{1}{n_0}\frac{1}{kT}\frac{\alpha(\hbar\omega)\tau_R}{(\hbar\omega)^3}J\left(\frac{\mu(\hbar\omega-E_G)}{m_c kT}\right), \tag{6}$$

where

$$J(a)=\int_0^\infty \frac{x^{1/2}e^{-x}}{x-a}\,dx$$

and we have made the restrictions $|\hbar\omega - E_G| \ll E_G$ and $kT \ll E_G$ to simplify the integral so that it can be expressed as a function of only one parameter. The function J is calculated numerically and is plotted in Fig. 1. Note that n_2 is negative; i.e., this is a self-*de*focusing nonlinearity.

In the present Boltzmann (i.e., nondegenerate) approximation, the change in refractive index is proportional to intensity: At high intensities where the carrier density exceeds the limits of the Boltzmann approximation the nonlinearity will itself saturate and can only be described with use of the full Fermi-Dirac statistics (which must also be used if the initial carrier concentration is large); this presents no difficulties in principle.

The experimental measurements were performed with an Edinburgh Instruments model-PL3 CO laser together with a continuously variable attenuator which preserves the Gaussian beam form.[13] Several samples of InSb were used, all from the same crystal (n type, $\sim 4\times 10^{14}$ cm^{-3} net carrier concentration) with thicknesses between 50 μm and 1 cm. They were all anti-reflection coated on both faces and mounted with indium solder to copper tails in a conventional reservoir cryostat filled with liquid nitrogen. The samples could be rotated out of the beam to facilitate absolute absorption measurements. The linear absorption was measured by using a Laser Precision cw power meter with laser powers of a few milliwatts. The sample lengths were chosen to provide a good overlap of measurements between samples and the results were corrected for residual surface losses in absorption experiments by normalizing each sample's results to those of the next longest sample, and, for the longest sample, by using the average surface loss of the thinner samples. The absorption results are shown in Fig. 2. The nonlinear refraction was measured with use of the method of beam profile distortion[14] due to self-defocusing, in which the intensity profile of the transmitted laser beam is observed in the diffraction far field and the shape of this profile is compared with calculated curves. From this comparison, the nonlinear phase lead in the center of the beam at the exit face of the crystal is deduced and the intensity dependence of the refractive index is then simply calculated from a knowledge of the incident beam power and Gaussian spot size with due allowance for linear absorption[14]; this analysis assumes $n=n_0+n_2I$, and detailed investigations at 1822 cm^{-1} in the near field confirmed *self-defocusing*. Because of the self-defocusing the beam in the far field becomes larger with increasing power and the intensity in the far field beam center actually decreases: The simplest point of comparison is when this central intensity passes

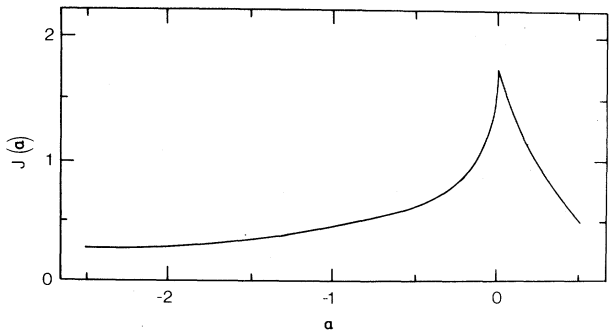

FIG. 1. The dimensionless resonance function $J(a)$ plotted against dimensionless energy parameter $a = \mu(\hbar\omega - E_G)/m_c kT$.

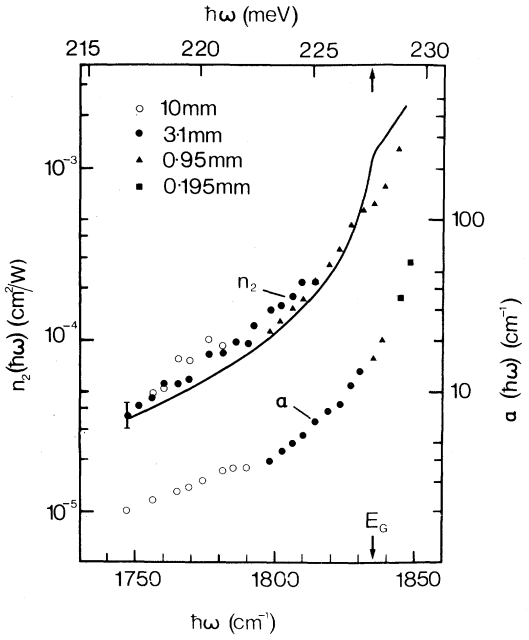

FIG. 2. Measured n_2 and absorption coefficient α as a function of photon energy $\hbar\omega$ compared with theory for n_2. The error in α measurements is of the order of the point size. The solid line is calculated with use of the measured α (smoothed for clarity) from Eq. (6). All the parameters in this theoretical curve are based on measured values.

through its (first) maximum which occurs for ~2.2 rad central phase lead at the crystal exit face (i.e., slightly more than $\lambda/2$ lead); if I_i is the incident intensity in the beam center at this point, the deduced nonlinear refraction n_2 is therefore $n_2 = 2.2\lambda\alpha/[2\pi I_i(1-e^{-\alpha l})]$, where l is the crystal length. This degree of phase lead is readily achieved with tens of milliwatts for the spot sizes ($1/e^2$ diameter of ~300–400 μm) used in these experiments, although for photon energies significantly above the band-gap energy, such a phase lead cannot be achieved without carrier densities which exceed the limits for the Boltzmann approximation ($\lesssim 10^{15}$ cm^{-3} in InSb at 77 K) and the method can no longer be used. The results for n_2 are shown in Fig. 2. These also were taken with use of several different sample thicknesses, and were corrected for surface losses. On the thinner samples, a 1:30 mark space ratio chopper was used to prevent sample heating. The beam profiles were observed with use of a scanning mirror arrangement with a PbSnTe detector.

In Fig. 2 the experimental n_2 are compared with the theory [Eq. (6)] by using the measured α with the following values of the relevant parameters: $\mu/m_c \sim 0.97$ ($m_c \simeq 0.014m$; $m_v \simeq 0.4m$); $mP^2/\hbar^2 \simeq 11$ eV; $n_0 \simeq 4$; $E_G \simeq 1835$ cm^{-1} (Ref. 15); $\tau_R \sim 400$ ns; τ_R is the least accurately known of all the parameters but the value used here for comparison with theory lies between two published values for conditions similar to those used in this experiment, namely 800 (Ref. 16) and 200 ns (Ref. 17). Except within the uncertainty of τ_R, there are no adjustable parameters in this comparison.

As can be seen from Fig. 2, the agreement between theory and experiment for n_2 is good in overall magnitude (and sign). The resonance form fit is not perfect, but there is a significant steady rise in the experimental n_2/α ratio (~2 between 1750 and 1830 cm^{-1}) confirming some resonance rather than direct proportionality between n_2 and α. This can be used to predict such band-gap resonant nonlinear refraction in other III-V compound semiconductors. The n_2 however depends on the particular $\alpha(\hbar\omega)$; a more useful comparative figure is the change in refractive index for one excited electron-hole pair in unit volume, $\sigma \equiv n_2\hbar\omega/\alpha(\hbar\omega)\tau$. Since P^2 and n_0 are substantially constant and $\mu/m_c \sim 1$ for all III-V compound semiconductors, we can predict

$$\sigma \sim 1.7\times 10^{-17}\,\frac{1}{T}\,\frac{1}{(\hbar\omega)^2}\,J\left(\frac{\hbar\omega - E_G}{kT}\right)\ \text{cm}^3$$

near the direct bandgap in nondegenerate III-V compound semiconductors (here the temperature is given in degrees kelvin and $\hbar\omega$ in electron volts). To observe this effect in other materials would require (i) photon energy between $\frac{1}{2}kT$ above and a few kT below the band-gap energy so that J is large, and (ii) an absorption mechanism efficient in creating free carriers (particularly for photon energies below the band gap). A full consideration of residual Coulomb electron-hole correlation effects, more important for wider-band-gap materials even in the absence of actual excitonic resonances, is beyond the scope of this paper, but as these enhance the absorption they may also further enhance the nonlinear refraction.

In conclusion, we have presented a theory, using only measurable parameters, for the large band-gap–resonant nonlinear refraction seen in InSb, which agrees well with new detailed experimental results both in magnitude and resonance form, and predicts the existence of this effect for other semiconductors.

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