Theory of Nonlinear Infrared Absorption in p-Type Germanium

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We present a theory of the saturation of inter–valence-band absorption in p-type Ge by high-intensity light with a wavelength near 10 μm. The absorption coefficient decreases with intensity in a manner closely approximated by an inhomogeneously broadened two-level model. The saturation intensity is calculated as a function of excitation wavelength and temperature and found to be in good agreement with measured values.

Free-hole transitions between the heavy- and light-hole bands in p-type Ge are primarily responsible for the absorption of light with wavelengths in the 11- to 9-μm range. Absorption due to this process has been found to saturate at high light intensities.[1-4] Thus p-type Ge can be used as a saturable absorber to passively mode lock CO_2 lasers. In this Letter, we present a theory of the saturation of heavy-hole band to light-hole band transitions in p-type Ge at high light intensities.

Previously saturable absorption in p-type Ge has been analyzed by modeling the Ge valence bands as an ensemble of two-level systems whose level populations approach one another at high light intensities.[2-5] This model predicts that the dependence of the absorption coefficient as a function of intensity is given by

$$\alpha(I,\omega)=\alpha_0(\omega)[1+I/I_s(\omega)]^{-1/2}, \quad (1)$$

where $\alpha_0(\omega)$ is the absorption coefficient at low intensity, and $I_s(\omega)$ is the saturation intensity. This behavior was found to be reasonably well satisfied experimentally.[2-4] However, attempts to calculate $I_s(\omega)$ as a function of photon energy using the two-level model and a multistep cascade relaxation produced results that were in qualitative disagreement with experiment.[2,5] There has also been a theoretical discussion of the saturation based on a spherical, parabolic band model,[6] but this study produced a result for the absorption coefficient which was quite different from that of Eq. (1) and which is in qualitative disagreement with experimental results. Here we describe the Ge valence bands using degenerate $\vec{k}\cdot\vec{p}$ perturbation theory. This is the first time the saturable absorption has been discussed in a model which realistically accounts for the anisotropic and nonparabolic Ge valence bands. Our calculated results are in close numerical agreement with Eq. (1) and for the first time give results for $I_s(\omega)$ as a function of photon energy which are in good agreement with the experimental values. There are no adjustable parameters in the theory.

Both energy and wave vector are conserved in the inter–valence-band optical transition. Thus only holes in a narrow region of the heavy-hole band can directly participate in the absorption. As the light intensity becomes large, the population of these states in the heavy-hole band is decreased and the absorption coefficient is reduced. The absorption coefficient is given by

$$\alpha(I,\omega)=\frac{4\pi^2}{\epsilon^{1/2}m^2\omega c}\frac{Ne^2}{3}\sum_{\vec{k}}[f_h(\vec{k})-f_l(\vec{k})] \times|\vec{P}_{hl}(\vec{k})|^2\frac{1/\hbar\pi T_2(\vec{k})}{[\Omega(\vec{k})-\omega]^2+[1/T_2(\vec{k})]^2}, \quad (2)$$

where the subscripts h (l) designate the heavy- (light-) hole band, N is the density of holes, ϵ is the dielectric constant, m is the free-electron mass, $\hbar\omega$ is the photon energy, $f_i(\vec{k})$ is the probability that a hole state with wave vector $\vec{k}$ is occupied in band i, $|\vec{P}_{hl}(\vec{k})|^2$ is the squared momentum matrix element between the Bloch states in the heavy- and light-hole bands (summed over the two degenerate states in each band), and $\Omega(\vec{k})$ is the angular frequency associated with the energy difference $[\epsilon_h(\vec{k})-\epsilon_l(\vec{k})]$ where $\epsilon_i(\vec{k})$ is the energy of the hole with wave vector $\vec{k}$ in band i. The phase relaxation time $T_2(\vec{k})$ is given by

$$\frac{2}{T_2(\vec{k})}=\sum_{c\vec{k}'}[R_{h\vec{k}\to c\vec{k}'}+R_{l\vec{k}\to c\vec{k}'}], \quad (3)$$

where $R_{a\vec{k}\to b\vec{k}'}$ is the rate at which a hole in band a with wavevector $\vec{k}$ is scattered into a state in band b with wave vector $\vec{k}'$.

In p-type Ge the scattering rate of holes occurs on a subpicosecond time scale. Since the experimental studies use lasers with nanosecond pulse durations, transient effects are damped out. Hence, we calculate the steady-state distribution functions which are determined by the following

equations:

$$\beta(\vec{k}, I)[f_h(\vec{k}) - f_l(\vec{k})] = -\sum_{c\vec{k}'}[R_{h\vec{k}\to c\vec{k}'} f_h(\vec{k}) - R_{c\vec{k}'\to h\vec{k}} f_c(\vec{k})], \quad (4a)$$

$$\beta(\vec{k}, I)[f_h(\vec{k}) - f_l(\vec{k})] = \sum_{c\vec{k}'}[R_{l\vec{k}\to c\vec{k}'} f_l(\vec{k}) - R_{c\vec{k}'\to l\vec{k}} f_c(\vec{k}')], \quad (4b)$$

where

$$\beta(\vec{k}, I) = \frac{2\pi^2}{\epsilon^{1/2} m^2 \omega c} \frac{e^2 I}{3\hbar\omega} |\vec{P}_{hl}(\vec{k})|^2 \times \frac{1/\hbar\pi T_2(\vec{k})}{[\Omega(\vec{k}) - \omega]^2 + [1/T_2(\vec{k})]^2}. \quad (4c)$$

These equations state that the rate of optical excitation out of (into) a state is equal to the net rate of scattering into (out of) the state. The left-hand sides of Eqs. (4a) and (4b) give the net rate of optical excitation out of a state with wave vector $\vec{k}$ in the heavy-hole band into a state with wave vector $\vec{k}$ in the light-hole band. Here $\beta(\vec{k}, I)$ describes the strength of the optical interaction.

Using Eqs. (4), we obtain an expression for the steady-state difference in occupation probabilities,

$$f_h(\vec{k}) - f_l(k) = \frac{f_h^e(\vec{k}) - f_l^e(\vec{k})}{1 + \beta(\vec{k}, I)[T_h(\vec{k}) + T_l(\vec{k})]} + \frac{T_h(\vec{k})F(\vec{k}, I) - T_l(\vec{k})G(\vec{k}, I)}{1 + \beta(\vec{k}, I)[T_h(\vec{k}) + T_l(\vec{k})]}, \quad (5)$$

where $f_i^e(\vec{k})$ is the equilibrium value for the distribution function,

$$\frac{1}{T_h(\vec{k})} = \sum_{c\vec{k}'} R_{h\vec{k}\to c\vec{k}'}, \quad (6a)$$

$$F(\vec{k}), I) = \sum_{c\vec{k}'} R_{c\vec{k}'\to h\vec{k}}[f_c(\vec{k}') - f_c^e(\vec{k}')], \quad (6b)$$

and $T_l(\vec{k})$ and $G(\vec{k}, I)$ are defined for the light-hole band analogous to Eqs. (6a) and (6b), respectively. The function $F(\vec{k}, I)$ is the difference in the feeding rate of free holes from the equilibrium feeding rate for the state with wave vector $\vec{k}$ in the heavy-hole band. The first term in Eq. (5) gives the population difference that would occur for the states at $\vec{k}$ if the populations of the states that feed those at $\vec{k}$ were given by their equilibrium values. The second term in Eq. (5) accounts for the change in the populations of the states that feed those at $\vec{k}$. For those values of $\vec{k}$ which are important in the integral in Eq. (2), the first term in Eq. (5) is found to be significantly greater than the second.

For the hole concentrations and temperatures at which most saturable absorption measurements have been performed (room temperature, $N \lesssim 10^{16}$ cm^{-3}), phonon scattering is the dominant scattering mechanism. Phonon scattering was calculated on the basis of the deformable potential model, where the deformation parameters were taken from the mobility fits of Brown and Bray.[7] Following Ref. 7 we neglect angular dependence in the phonon scattering matrix elements and take the scattering rates to be the same function of energy for the heavy- and light-hole bands. Energy relaxation of the excited holes is determined by optical-phonon scattering. The optical-phonon spectrum is relatively flat for small k with an average energy of about 0.037 eV. We neglect the energy of the acoustic phonons; this is a reasonable approximation for the region of interest (small k). Acoustic-phonon scattering mixes states with approximately the same energy but different values of $\vec{k}$. The effect of acoustic-phonon scattering is not negligible because of the anisotropy of the valence bands.

If there is no angular dependence in the phonon scattering matrix elements, the functions $F(\vec{k})$ and $G(\vec{k})$ depend only on $\epsilon_h(\vec{k})$ and $\epsilon_l(\vec{k})$, respectively. We use Eq. (4) to write one-dimensional integral equations for these functions. If we take the optical-phonon energy as discrete and neglect the acoustic-phonon energy, these integral equations can be reduced to a set of algebraic equations which we solve numerically. Once these functions are determined, the absorption coefficient is calculated by numerically integrating Eq. (2). The one-hole energies and the momentum matrix elements are found from degenerate $\vec{k}\cdot\vec{p}$ perturbation theory.[8] The cyclotron-resonance parameters of Hensel and Suzuki[9] were used.

The calculated values of $\alpha(I, \omega)$ were compared with the expression in Eq. (1). The numerical results could be fitted by this expression to an accuracy of about 5% for intensities less than $25I_s$. (This is the range of intensities which has been explored experimentally.) If only the first term in Eq. (5) is retained, the calculated $\alpha(I, \omega)$ has precisely the form of Eq. (1). The second term in Eq. (1) is smaller than the first; it leads to the small deviations of the calculated $\alpha(I, \omega)$ from the expression in Eq. (1).

For those temperatures and hole densities for which hole-impurity and hole-hole scattering is small compared to phonon scattering, the calculated I_s is independent of hole concentration. At room temperature, I_s has been found experimen-

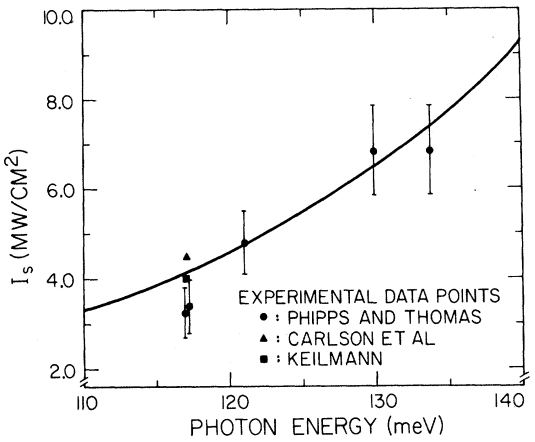

FIG. 1. Saturation intensity vs photon energy for p-type Ge at 295°K. The experimental data are from Refs. 2, 3, and 4. Error bars are given only in Ref. 2.

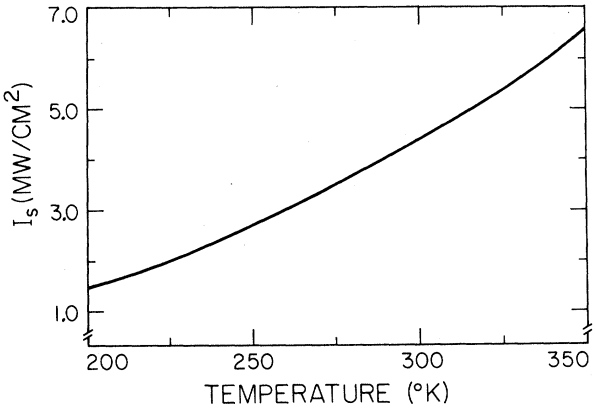

FIG. 2. Calculated saturation intensity vs temperature for p-type Ge and light with a wavelength of 10.6 μm.

tally to be independent of hole concentration for concentrations less than about 4×10^{15} cm^{-3}.[1]

Measurements of saturable absorption in p-type Ge have been interpreted in terms of the inhomogeneously broadened two-level model which produces Eq. (1), and values of $I_s(\omega)$ are reported.[2-4] In Fig. 1, we compare measured values of $I_s(\omega)$ at room temperature as a function of photon energy with the calculated values. In the range of photon energies considered, $I_s(\omega)$ was found to increase monotonically with photon energy. The increase in $I_s(\omega)$ with increasing ω is primarily a result of the larger density of states in the heavy-hole band for the higher-energy holes involved in the optical transition. There is good agreement between theory and experiment. There are no adjustable parameters in the theory.

In Fig. 2, we present the results of a calculation of the temperature dependence of $I_s(\omega)$ for light with a wavelength of 10.6 μm. I_s increases monotonically with temperature. This increase in I_s with temperature is due to the increased rate of phonon scattering at higher temperature. Because of the rather strong dependence of I_s on temperature, it should be possible to tune the saturation behavior of p-type Ge with temperature.

Many semiconductors have a valence-band structure which is similar to that of Ge, and saturation of inter-valence-band absorption should be observable in these materials. In addition to Ge, the effect has also been observed in p-GaAs.[1] The theory presented here should apply for these materials as well as for Ge.

Using this theory, we can determine the hole distribution as a function of laser intensity and frequency. Knowledge of the hole distribution function allows an interpretation of "pump-probe" experiments. In these experiments the absorption of a low-intensity light beam (probe) is measured as a function of frequency in the presence of a high-intensity laser (pump) of fixed frequency.[4,10-12]

In conclusion, we have presented a theory of the saturation of inter-valence-band absorption in p-type Ge. We have found that the saturation is closely approximated by an inhomogeneously broadened two-level model. We have calculated the saturation intensity as a function of photon energy and found good agreement with experimental values. We have predicted the dependence of the saturation intensity on temperature.

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Theory of Non-Ohmic Conduction from Charge-Density Waves in $NbSe_3$

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A theory of non-Ohmic conduction from depinning of charge-density waves by an electric field is presented. It is based on Zener-type tunneling of the charge-density waves across a gap at the Fermi surface that is determined by the pinning frequency. The theory applies to relatively pure specimens for which the pinning is due to approach to commensurability or cooperative action of impurities.

The remarkable transport properties of the quasi one-dimensional conductor $NbSe_3$ have attracted a great deal of interest. In the complex unit cell there are three chains of Nb atoms. Transport,[12] and x-ray[3] studies indicate two Peierls transitions to charge-density-wave states, one at $T_P = T_1 = 142$ K and one at $T_2 = 58$ K. Below the two transitions there are resistivity peaks from gaps opening up at the Fermi surface (FS). Hall data are consistent with a loss of 20% of the FS at T_1 and 60% of the remaining at T_2. The resistivity peaks are strongly frequency and field dependent. At microwave frequencies (9.6×10^9 Hz), the anomaly below T_2 is completely wiped out and that below T_1 nearly so. The non-Ohmic conductivity can be expressed in the form

$$\sigma = \sigma_a + \sigma_b \exp(-E_0/E), \quad (1)$$

where σ_a is the low-field conductivity and $\sigma_a + \sigma_b$ approximately that expected if the charge-density waves (CDW's) were not present.

The field E_0 is temperature dependent with a minimum of about 1.5 V/cm below T_1 and 0.1 V/cm below T_2. X-ray studies show that the CDW's are present with undiminished magnitudes in fields large enough to wipe out at least half of the resistivity anomalies.[3] The evidence is that the CDW's are weakly pinned and can be released to move freely by application of small electric fields. When moving, they transport carriers by the mechanism proposed by Fröhlich[4] and do not add to the resistivity. There is no evidence that they add to the conductivity which would be present in the absence of CDW's, although scattering by the $2k_F$ phonons which correspond to the state of macroscopic occupation in the CDW should be eliminated.

I propose here a simple theory based on Zener-type tunneling which relates the field E_0 with the frequency of the oscillations of the CDW about pinning positions, ω_P. Although based on a model of commensurability pinning, the theory could also apply to impurity pinning. The wavelength of an incommensurate CDW can always be expressed approximately as the ratio of two integers such that $N_W \lambda_W \simeq N_L a$, where N_W refers to the number of wavelengths, λ_W, of the CDW and N_L to the number of lattice periods, a, required to bring then into approximate coincidence. The pinning period is then $b = N_L a$, where a is the lattice period. It is presumed that the pinning sites are fixed relative to the crystal lattice. Although I discuss a one-dimensional model, it is presumed that there is a substantial coherence distance perpendicular to the chain direction.

A quite different theory for the field-dependent conductivity based on impurity pinning has been given by Lee and Rice.[5] Their prediction that E_0 should be proportional to the square of the impurity concentration, c_i, is in approximate agreement with data of Ong *et al.*[6] on the resistivity anomaly below T_2. The data show that E_0 approaches a limiting value as $c_i \to 0$, but this limit could be determined by impurities responsible for the residual resistivity. Impurity pinning will be discussed briefly later in this note.