Mechanism for the Photoreflectance Effect

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Recently a new differential reflectance technique has been reported in which the band-edge reflectance of a semiconducting crystal is modulated by irradiation of the surface with an intense ultraviolet light beam. It is proposed that the reflectance changes are caused in part by the blocking of interband transitions which occurs when electrons are pumped from the valence to the conduction band. A calculation shows the reflectance change to consist of a sharp oscillation at the band edge. The magnitude of the oscillation is in reasonable agreement with experiments on cadmium sulfide.

$\mathbf{R}$ECENTLY, Wang *et al.*[1] have reported a new differential reflectance technique in which the band-edge reflectance of a semiconducting crystal is modulated by an intense ultraviolet light beam. In this *photoreflectance* effect, the modulating beam pumps electrons from filled to unfilled bands. This pumping can alter the reflectance of the crystal by two mechanisms. By producing additional free carriers, the pumping can shorten the Debye length near the crystal surface. This can change the surface electric fields and lead to Franz-Keldysh reflection effects.[2,3] Alternatively, the pumping can alter the reflectance simply by changing the effective densities of states for interband transitions. In crystals with carrier concentrations of 10^{16} per cm^3 or higher the Debye length is of the order of 100 Å or less, while typical absorption lengths above the band edge are of the order of 1000 Å. Thus, in these crystals the major part of the pumping and of the interaction of the reflected beam take place in field-free regions of the crystal. Consequently, it appears likely that in these crystals the second mechanism may play a significant role in the photoreflectance effect. The magnitude of the change in reflectance to be expected from this mechanism is estimated in the calculation described below.

For normal incidence, the reflectivity R of a crystal is given in terms of its dielectric constant n and extinction coefficient κ by

$$R = \frac{n^2 + n^2\kappa^2 + 1 - 2n}{n^2 + n^2\kappa^2 + 1 + 2n}. \quad (1)$$

The optical constants are in turn related to ϵ_1 and ϵ_2, the real and imaginary parts of the dielectric constant, by

$$n^2(1-\kappa^2) = \epsilon_1,$$
$$n^2\kappa = \tfrac{1}{2}\epsilon_2. \quad (2)$$

Since we are concerned with an effect which is limited to a very small frequency range near a band edge, we will assume that the material constants are independent of frequency and obtain from (1) and (2) an expression for the relative reflectivity change $\Delta R/R$ due to changes $\Delta\epsilon_1$ and $\Delta\epsilon_2$ which are caused by pumping, namely,

$$\frac{\Delta R}{R} = \frac{1}{n(1+\kappa^2)}\left[\frac{n(1-\kappa^2)-1}{n^2(1+\kappa^2)+1-2n} - \frac{n(1-\kappa^2)+1}{n^2(1+\kappa^2)+1+2n}\right]\Delta\epsilon_1$$
$$+ \frac{1}{n(1+\kappa^2)}\left[\frac{(2n-1)\kappa}{n^2(1+\kappa^2)+1-2n}\right.$$
$$\left. - \frac{(2n+1)\kappa}{n^2(1+\kappa^2)+1+2n}\right]\Delta\epsilon_2. \quad (3)$$

To simplify the calculation of $\Delta\epsilon_1$ and $\Delta\epsilon_2$, we ignore exciton effects and assume uniform pumping throughout the crystal. We work with the expression[4]

$$\epsilon_{cv}{}^j(E) = 1 - \frac{\hbar^2 e^2}{\pi^2 m}$$
$$\times \int d^3k \frac{f_{cv}{}^j(f_v - f_c)}{(E - E_{cv} + i\hbar/\tau)(E + E_{cv} + i\hbar/\tau)}, \quad (4)$$

which gives the contribution of transitions between the valence and conduction bands to the jj element of the dielectric constant. The integral is over the Brillouin zone, $E_{cv} = E_{cv}(\mathbf{k})$ is the band gap at $\mathbf{k}$, $f_{cv}{}^j$ is the oscillator strength assumed independent of $\mathbf{k}$, f_v and f_c are the Fermi factors for the valence and conduction bands, and τ is a relaxation time. Equation (4) contains a factor of 2 to account for the assumed spin degeneracy of both bands.

Pumping influences $\epsilon_{cv}{}^j$ by changing f_v and f_c. We assume that electrons pumped out of the valence band are immediately replenished by electrons from hole traps above the valence band edge. Then the change in $\epsilon_{cv}{}^j$ due to pumping is

$$\Delta\epsilon_{cv}{}^j(E) = \frac{\hbar^2 e^2}{\pi^2 m}$$
$$\times \int d^3k \frac{f_{cv}{}^j \Delta f_c}{(E - E_{cv} + i\hbar/\tau)(E + E_{cv} + i\hbar/\tau)}. \quad (5)$$

[1] E. Y. Wang, W. A. Albers, Jr., and C. E. Bleil, in *II-VI Semiconducting Compounds, 1967 International Conference*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 136.

[2] B. O. Seraphin and N. Bottka, Phys. Rev. **139**, A560 (1965).

[3] B. O. Seraphin and N. Bottka, Phys. Rev. **145**, 628 (1966).

[4] H. R. Phillip and H. Ehrenreich, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1967), Vol. 3, Chap. 4.

In the approximation $\tau \rightarrow \infty$, the real part of (5) is

$$\Delta\epsilon_1(E) = \frac{\hbar^2 e^2}{\pi^2 m} f_{cv}{}^j \mathcal{P} \int d^3k \frac{\Delta f_c}{(E-E_{cv})(E+E_{cv})}, \quad (6)$$

and the imaginary part is

$$\Delta\epsilon_2(E) = -\frac{\hbar^2 e^2}{2\pi m E} f_{cv}{}^j \int_{E_{cv}=E} dS \frac{\Delta f_c}{|\nabla_k E_{cv}|}. \quad (7)$$

For small changes, Δf_c is related to $\Delta\rho$, the excess carrier concentration created by pumping, through the relation

$$\Delta f_c = \frac{\partial f_c}{\partial E_f} \frac{\partial E_f}{\partial \rho} \Delta\rho,$$

where E_f is the effective Fermi level for the conduction band. The derivative $\partial E_f/\partial\rho$ can be determined from the expression for the equilibrium carrier concentration. For an isotropic conduction band with effective mass $m_c{}^*$, the expression is

$$\rho = \sqrt{2} \frac{(m_c{}^* kT)^{3/2}}{\pi^2 \hbar^3} F_{1/2}(E_f/kT),$$

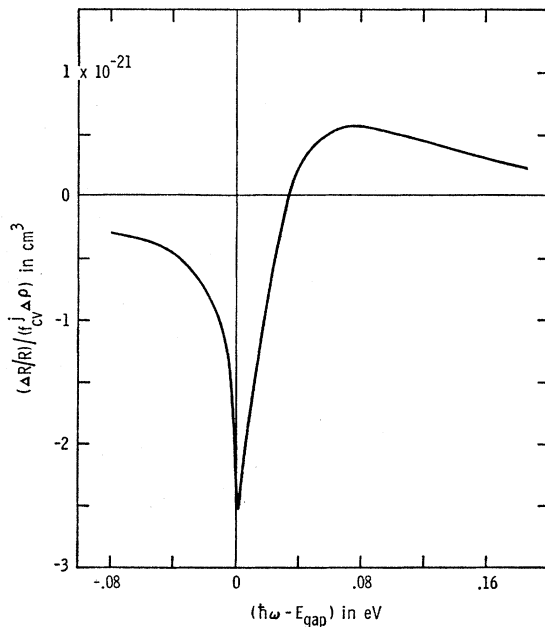where $F_{1/2}$ is a Fermi integral[5] and E_f is measured from

Fig. 1. Differential reflectance at a band edge of CdS per unit oscillator strength per unit change in electron density as a function of photon energy.

[5] A. C. Beer, M. N. Chase, and P. F. Choquard, Helv. Phys. Acta **28**, 529 (1955).

the bottom of the conduction band. The result is

$$\Delta f_c = \frac{\sqrt{2}\pi^2 \hbar^3}{(m_c kT)^{3/2} F_{-1/2}(E_f/kT)}$$

$$\times \frac{\exp[(E-E_f)/kT]}{\{\exp[(E-E_f)/kT]+1\}^2} \Delta\rho. \quad (8)$$

When (8) is inserted in (6) and (7), and these in turn are inserted in (3), an expression is obtained for $\Delta R/R$ which depends linearly on $\Delta\rho$. We have evaluated this final expression numerically in the approximation of parabolic energy bands with extrema at $\mathbf{k}=0$. The parameters used were $m_c{}^* = 0.2$ electron masses, $m_v{}^* = \infty$, $E_{gap} = 2.5$ eV, $\rho = 3\times10^{17}$ electrons/cm^3, $T = 300°$K, $n = 2.6$, and $\kappa = 0.10$. These were chosen to fit CdS, for which experimental photoreflectance data are available,[1] but are sufficiently representative that our calculated $\Delta R/R$ should be typical of behavior at M_0 edges in a number of semiconductors.

Our result is given in Fig. 1, where $(\Delta R/R)/(f_{cv}{}^j\Delta\rho)$ is plotted as a function of photon energy. This curve results from transitions between a single valence and conduction band, both twofold, i.e., spin-degenerate. The curve amounts to an oscillation near the band-gap energy consisting of a sharp dip at the band gap followed by a broad peak above the gap. In these features it resembles theoretical Franz-Keldysh curves calculated for an M_0 edge.[2,3] Carrier lifetime effects have been shown to significantly broaden and diminish sharp structure in the Franz-Keldysh curves.[3] Therefore, we expect that with lifetime effects included, our curve would show an oscillation consisting of a dip and peak of roughly the same magnitude and breadth. Such behavior is consistent with the experimental $\Delta R/R$ curves.[1]

To get an idea of the magnitude of the oscillation we must estimate the product $f_{cv}{}^j\Delta\rho$. From pseudopotential wave-function matrix elements for CdS,[6] we calculate the oscillator strength to be about 4. In the photoreflectance experiments[1] the modulating ultraviolet flux was estimated to be about 10^{17} photons/cm^2 sec.[7] Then, assuming that the electrons are created in a sheath of thickness 10^{-5} cm and have a lifetime between 10^{-4} and 10^{-6} seconds, we infer for $\Delta\rho$ a value between 10^{16} and 10^{18} electrons/cm^3. These factors imply an oscillation in $\Delta R/R$ between 10^{-4} and 10^{-2}, which is compatible with the observed oscillation in CdS of about 3×10^{-4}.[1]

We conclude on the basis of the above that this mechanism, namely, change in effective density of states, makes a significant and perhaps dominant contribution to the observed photoreflectance effect.

[6] T. K. Bergstresser and M. L. Cohen, Phys. Rev. **164**, 1069 (1967).

[7] W. A. Albers (private communication).