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Polaron Effects on the Optical Properties of Semiconductors*

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The optical-absorption coefficient of a polar semiconductor is calculated for light energies comparable to the width of the gap in an effort to determine some effects of the electron-phonon interaction. The self-energy given by the one-quantum cutoff approximation is used. The result is a shifting down of the absorption edge and some weak structure at an energy of one phonon above the edge.

I. INTRODUCTION

The polaron has been a popular model on which to develop many-body techniques. As a result, several approximations exist. Our object is to use the polaron self-energy from one of them to see if polaron effects can have a significant effect on a measurable quantity, namely, the optical-absorption spectrum near the absorption edge.

We use a result discussed by Whitfield and Puff[1] and by Velický.[2] It is the self-energy calculated in the one-quantum cutoff approximation, i.e., the electron is dressed by no more than one phonon at a time. It is

$$\Sigma(\vec{P}, \omega, l) = \frac{ie^2\omega_0 m_l}{2\hbar^2\bar{\epsilon}p} \times \ln\left| \frac{[(2m_l/\hbar^2)(\hbar\omega \mp \hbar\omega_0 - \Delta\delta_{l,c} + \mu)]^{1/2} - p}{[(2m_l/\hbar^2)(\hbar\omega \mp \hbar\omega_0 - \Delta\delta_{l,c} + \mu)]^{1/2} + p} \right| , \quad (1)$$

where l is a band index; we consider two bands, conduction and valence ($l = c, v$). ω_0 is the frequency of the longitudinal optical mode, m_l is the effective mass in band l, $\bar{\epsilon} = \epsilon_\infty\epsilon_0/\epsilon_\infty - \epsilon_0$, where ϵ_∞, ϵ_0 are the high-frequency and static dielectric constants, δ is a Kronecker δ, Δ is the band gap, and μ is the chemical potential. The upper sign is for $l = c$, the lower sign for $l = v$ and $p = |\vec{P}|$.

Implicit in this expression is the assumption that the bands are isotropic and parabolic with direct minimum gap at $k = 0$. We further assume that $m_v < 0$ and $-m_v > m_c$.

The real part of Σ gives the shift in the quasiparticle energy with respect to the noninteracting energy; the imaginary part gives the inverse lifetime. The Σ we are using is entirely real (stable polaron) if $\hbar\omega < \hbar\omega_0 + \Delta - \mu$ for $l = c$, and $\hbar\omega > -\hbar\omega_0 - \mu$ for $l = v$, and

$$\Sigma \sim -\frac{m_l}{p}\tan^{-1}\left(\frac{p}{[(-2m_l/\hbar^2)(\hbar\omega \mp \hbar\omega_0 - \Delta\delta_{l,c} + \mu)]^{1/2}}\right) .$$

Consequently, there is an energy shift into the gap for both bands of polaron states, and we can expect a lowering of the absorption edge.

When $\hbar\omega > \hbar\omega_0 + \Delta - \mu$ for $l = c$, and $\hbar\omega < -\hbar\omega_0 - \mu$ for $l = v$, Σ is entirely imaginary, which means that the polaron can decay into an electron and a phonon (since the electron is dressed by only one phonon). Thus, in this approximation, the polaron is unstable if it has an energy greater by one phonon than the energy of the electron spectrum edge–not the polaron spectrum edge.

II. FORMULA FOR OPTICAL ABSORPTION

We use an expression due to Bonch-Bruevich[3,4]:

$$\alpha(\omega) = [2e^2 |V(k)|^2 / c\epsilon^{1/2}\pi m^2\omega] \int d^3k\, dE \times \{\mathrm{Im}G_r(\vec{k}, v, E - \hbar\omega)\mathrm{Im}G_r(\vec{k}, c, E) \times [n_F(E - \hbar\omega) - n_F(E)]\}, \quad (2)$$

where G_r is the retarded Green's function

$$G_r = \begin{cases} G\ , & E > \mu \\ G^*, & E < \mu \end{cases} ,$$

$V(k)$ is the interband-momentum matrix element, which we have assumed varies slowly with k so that it can be taken out of the integrand, n_F is the Fermi function, and we replace the above difference of Fermi functions by 1 since we are working at $T = 0$.

This formula is an approximation to the Kubo formula for conductivity. To reach the above form from the Kubo formula, one factors the two-particle Green's function contained in the latter into a product of one-particle Green's functions. This procedure is justified when the energy gap Δ is much greater than a phonon energy $\hbar\omega_0$ by the "asymptotic theorem."[3,4]

When we recall that $\mathrm{Im}G_r$ is the quasiparticle density of states, Eq. (2) is seen to have the same form as the golden-rule expression for α. However, we have the density of states of noninteracting polarons, not electrons.

From (1) we get the Green's function using Dyson's equation

$$G=(G_0^{-1}-\Sigma)^{-1},$$

$$G_0=\hbar\left[\hbar\omega-\frac{\hbar^2k^2}{2m_l}-\Delta\delta_{l,c}+\mu+i\xi\,\mathrm{sign}\left(\frac{\hbar^2k^2}{2m_l}+\Delta\delta_{l,c}-\mu\right)\right]^{-1}$$

G_0 is the free Green's function, where $\xi\to 0$.

The integrations are done in the Appendix; the result is for $\hbar\omega<\Delta+\hbar\omega_0$:

$$\alpha(\omega)=\frac{4\pi^3e^2|V|^2}{c\epsilon^{1/2}m^2\omega}(-x^2)\left\{\frac{-\hbar^2x}{\bar{m}}+2\frac{g_v^2\hbar}{x^2}\sin^{-1}\left[x\Big/\left(-2\frac{m_v}{\hbar}\omega_0\right)^{1/2}\right]-2\frac{g_c^2\hbar}{x^2}\times\sin^{-1}\left[x\Big/\left(2\frac{m_c}{\hbar}\omega_0\right)^{1/2}\right]-2\frac{g_v^2\hbar}{x}\left(-2\frac{m_v\omega_0}{\hbar}-x^2\right)^{-1/2}+2\frac{g_c^2\hbar}{x}\times\left(2\frac{m_c\omega_0}{\hbar}-x^2\right)^{-1/2}\right\}^{-1}, \quad (3)$$

where x is the solution of

$$\frac{-\hbar^2x^2}{2\bar{m}}+\hbar\omega-\Delta-2\frac{g_v^2\hbar}{x}\sin^{-1}\left[x\Big/\left(-2\frac{m_v\omega_0}{\hbar}\right)^{1/2}\right]+2\frac{g_c^2\hbar}{x}\sin^{-1}\left[x\Big/\left(2\frac{m_c\omega_0}{\hbar}\right)^{1/2}\right]=0,$$

with

$$g_l^2=e^2\omega_0m_l/2\hbar^2\bar{\epsilon},\quad \bar{m}=m_cm_v/m_v-m_c.$$

As $x\to 0$, we find

$$\hbar\omega=\Delta-\frac{2g_c^2\hbar}{(2m_c\omega_0/\hbar)^{1/2}}+2\frac{g_v^2\hbar}{(-2m_v\omega_0/\hbar)^{1/2}},$$

which is the polaron absorption edge.

In this neighborhood

$$x=\left[\frac{2\bar{m}}{\hbar^2}\left(\hbar\omega-\Delta-\frac{2g_v^2\hbar}{(-2m_v\omega_0/\hbar)^{1/2}}+\frac{2g_c^2\hbar}{(2m_c\omega_0/\hbar)^{1/2}}\right)\right]^{1/2},$$

$$\alpha\sim(\bar{m}/\hbar^2)x.$$

For $\hbar\omega\lesssim\Delta+\hbar\omega_0$,

$$x=[(2\bar{m}/\hbar)(\hbar\omega-\Delta)]^{1/2},\quad \alpha\sim(\bar{m}/\hbar^2)x.$$

Thus, the polaron effects do not change the shape of the absorption edge, but shift its position down. For example, for PbS the shift is of the order of 2.6×10^{-3} eV.

For $\Delta+(m_c/\bar{m})\hbar\omega_0>\hbar\omega>\Delta+\hbar\omega_0$, α equals (3) plus these terms:

$$\frac{8\pi^3e^2v^2\bar{m}}{\hbar^2c\epsilon^{1/2}m^2\omega}\frac{(\hbar\omega-\Delta-\hbar\omega_0)}{\omega_0(\hbar\omega-\Delta)^{1/2}}\left[-g_v^2\left(\Delta-\hbar\omega-\frac{m_v}{\bar{m}}\hbar\omega_0\right)^{-1/2}+g_c^2\left(\Delta-\hbar\omega+\frac{m_c}{\bar{m}}\hbar\omega_0\right)^{-1/2}\right]. \quad (4)$$

At $\hbar\omega=\Delta+1.5\hbar\omega_0$, this added structure amounts to about 0.2% of the total absorption and is negative for PbS.

Since the first effect does not change the qualitative shape of the absorption and since the second effect is so small, it is understandable why polaron effects are not reported in standard absorption experiments, but only in more sensitive experiments such as the magnetoabsorption experiment of Johnson and Larsen.[5]

APPENDIX: INTEGRATION OF (2)

In polar coordinates (2) is

$$\alpha(\omega)=\frac{8\pi e^2|V|^2}{c\epsilon^{1/2}m^2\omega}\int dk\,dE\,k^2\,\mathrm{Im}\left[\left(E-\hbar\omega-\frac{\hbar^2k^2}{2m_v}+\mu-i\xi+i\frac{g_v^2\hbar}{k}\ln\left|\frac{[(2m_v/\hbar^2)(E-\hbar\omega+\hbar\omega_0+\mu)]^{1/2}+k}{[(2m_v/\hbar^2)(E-\hbar\omega+\hbar\omega_0+\mu)]^{1/2}-k}\right|\right)^{-1}\right]$$
$$\times\mathrm{Im}\left[\left(E-\frac{\hbar^2k^2}{2m_c}-\Delta+\mu+i\xi+i\frac{g_c^2\hbar}{k}\ln\left|\frac{[(2m_c/\hbar^2)(E-\hbar\omega_0-\Delta+\mu)]^{1/2}+k}{[(2m_c/\hbar^2)(E-\hbar\omega_0-\Delta+\mu)]^{1/2}-k}\right|\right)^{-1}\right]$$

In the range of E there are values for which the ln factors in the first and second components of the integrand are real, so those components become δ functions:

$$\alpha(\omega) \sim -\pi \int_0^{\hbar\omega-\hbar\omega_0-\mu} dk\, dE\, k^2\, \mathrm{Im}\Bigg[\Bigg(E - \hbar\omega - \frac{\hbar^2k^2}{2m_v} + \mu - i\frac{g_v^2\hbar}{k}$$

$$\times \ln\left|\frac{[(2m_v/\hbar^2)(E-\hbar\omega+\hbar\omega_0)]^{1/2}+k}{[(2m_v/\hbar^2)(E-\hbar\omega+\hbar\omega_0)]^{1/2}-k}\right|\Bigg)^{-1}\Bigg]\delta\Bigg[E - \frac{\hbar^2k^2}{2m_c} - \Delta + \mu + \frac{2g_c^2\hbar}{k}$$

$$\times \tan^{-1}\left(\frac{k}{[(-2m_v/\hbar^2)(E-\hbar\omega+\hbar\omega_0+\mu)]^{1/2}}\right)\Bigg]$$

$$-\pi^2\int_{\hbar\omega-\hbar\omega_0-\mu}^{\Delta+\hbar\omega_0-\mu} dk\, dE\, k^2\delta\left[E-\hbar\omega-\frac{\hbar^2k^2}{2m_v}+\mu+\frac{2g_v^2\hbar}{k}\tan^{-1}\left(\frac{k}{[(-2m_v/\hbar^2)(E-\hbar\omega+\hbar\omega_0)]^{1/2}}\right)\right]$$

$$\times\delta\left[E-\frac{\hbar^2k^2}{2m_c}-\Delta+\mu+2\frac{g_c^2\hbar}{k}\tan^{-1}\left(\frac{k}{[(2m_c/\hbar^2)(\hbar\omega_0+\Delta-E-\mu)^{1/2}]}\right)\right]$$

$$+\pi\int_{\Delta+\hbar\omega_0-\mu}^{\infty} dk\, dE\, k^2\delta\left[E-\hbar\omega-\frac{\hbar^2k^2}{2m_v}+\mu+2\frac{g_v^2\hbar}{k}\tan^{-1}\left(\frac{k}{[(-2m_v/\hbar^2)(E-\hbar\omega+\hbar\omega_0+\mu)]^{1/2}}\right)\right]$$

$$\times\mathrm{Im}\left[\left(E-\frac{\hbar^2k^2}{2m_c}-\Delta+\mu+i\frac{g_c^2\hbar}{k}\ln\left|\frac{[(2m_c/\hbar^2)(E-\hbar\omega_0-\Delta+\mu)]^{1/2}+k}{[(2m_c/\hbar^2)(E-\hbar\omega_0-\Delta+\mu)]^{1/2}-k}\right|\right)^{-1}\right]$$

The first integral is zero unless

$$\hbar\omega-\hbar\omega_0>\Delta+\frac{\hbar^2k^2}{2m_c}-\frac{g_c^2\hbar}{k}\tan^{-1}\left(\frac{k}{[(-2m_c/\hbar^2)(E-\hbar\omega_0-\Delta+\mu)]^{1/2}}\right)$$

The second integral is zero unless

$$\Delta+\hbar\omega_0>\hbar\omega+\frac{\hbar^2k^2}{2m_v}-2\frac{g_v^2\hbar}{k}\tan^{-1}\left(\frac{k}{[(2m_v/\hbar^2)(-E+\hbar\omega-\hbar\omega_0-\mu)]^{1/2}}\right)>\hbar\omega-\hbar\omega_0\,,$$

$$\Delta+\hbar\omega_0>\frac{\hbar^2k^2}{2m_c}+\Delta-2\frac{g_c^2\hbar}{k}\tan^{-1}\left(\frac{k}{[(2m_c/\hbar^2)(\Delta+\hbar\omega_0-E-\mu)]^{1/2}}\right)>\hbar\omega-\hbar\omega_0\,.$$

The third integral is zero unless

$$\infty>\hbar\omega+\frac{\hbar^2k^2}{2m_v}-2\frac{g_v^2\hbar}{k}\tan^{-1}\left(\frac{k}{[(-2m_v/\hbar^2)(\hbar\omega-E-\hbar\omega_0-\mu)]^{1/2}}\right)>\Delta+\hbar\omega_0\,.$$

These restrictions determine the limits of the k integration. For simplicity we neglect the $\tan^{-1}$ factors in these inequalities. Since these factors are slowly varying with k and are multiplied by the coupling constant, neglecting them causes a very small error in the determination of the k limits. In addition, the E in the $\tan^{-1}$ terms in the δ-function arguments is replaced by the value of E at which the rest of the argument goes to zero. This is the first step in a self-consistent procedure for finding the zeros of the arguments. Then we have

$$\alpha(\omega)\sim\pi\int_0^{[(2m_c/\hbar^2)(\hbar\omega-\hbar\omega_0-\Delta)]^{1/2}} dk\, k^2\,\mathrm{Im}\Bigg[\frac{\hbar^2k^2}{2\bar{m}}+\Delta-\hbar\omega+i\frac{g_v^2\hbar}{k}$$

$$\times\ln\left|\frac{[(2m_v/\hbar^2)(\hbar^2k^2/2m_c+\Delta+\hbar\omega_0-\hbar\omega)]^{1/2}+k}{[(2m_v/\hbar^2)(\hbar^2k^2/2m_c+\Delta+\hbar\omega_0-\hbar\omega)]^{1/2}-k}\right|-2\frac{g_c^2\hbar}{k}$$

$$\times\tan^{-1}\left(\frac{k}{[(-2m_c/\hbar^2)(\hbar^2k^2/2m_c-\hbar\omega_0)]^{1/2}}\right)\Bigg]^{-1}$$

$$+\pi^2\int_0^{(2m_c\omega_0/\hbar)^{1/2}} dk\,k^2\delta\left[\hbar\omega+\frac{\hbar^2k^2}{2m_v}\right.$$

$$-\frac{\hbar^2k^2}{2m_c}-\Delta-2\frac{g_v^2\hbar}{k}\tan^{-1}\left(\frac{k}{[(-2m_v/\hbar^2)(\hbar^2k^2/2m_v+\hbar\omega_0)]^{1/2}}\right)+2\frac{g_c^2\hbar}{k}$$

$$\left.\times\tan^{-1}\left(\frac{k}{[(-2m_c/\hbar^2)(\hbar^2k^2/2m_c-\hbar\omega_0)]^{1/2}}\right)\right]+\pi\int_0^{[(2m_v/\hbar^2)(\Delta+\hbar\omega_0-\hbar\omega)]^{1/2}} dk\,k^2\,\mathrm{Im}\left[\hbar\omega+\frac{\hbar^2k^2}{2\bar{m}}-\Delta+i\frac{g_c^2\hbar}{k}\right.$$

$$\left.\times\ln\left|\frac{[(2m_c/\hbar^2)(\hbar\omega+\hbar^2k^2/2m_v-\hbar\omega_0-\Delta)]^{1/2}+k}{[(2m_c/\hbar^2)(\hbar\omega+\hbar^2k^2/2m_v-\hbar\omega_0-\Delta)]^{1/2}-k}\right|-2\frac{g_v^2\hbar}{k}\tan^{-1}\left(\frac{k}{[(-2m_v/\hbar^2)(\hbar^2k^2/2m_v+\hbar\omega_0)]^{1/2}}\right)\right]^{-1}.$$

The first and third integrals are zero unless $\hbar\omega>\hbar\omega_0+\Delta$, as their upper limits indicate.

To do the second integral we use

$$\delta(f(x))=\left(\frac{df}{dx}\right)_{x_0}^{-1}\delta(x-x_0)\ ,$$

where x_0 is the zero of $f(x)$. To find x_0 we neglect the $\tan^{-1}$ terms as we did when finding the k limits of integration. The result is Eq. (3).

To do the first and third integral we approximate

$$\frac{(ig^2\hbar/k)\ln|\ \ |}{[\hbar\omega-\hbar^2k^2/2\bar{m}-\Delta-(2g^2\hbar/k)\tan^{-1}(\ \ )]^2+[(g^2\hbar/k)\ln|\ \ |]^2}$$

by

$$\frac{(ig^2\hbar/k)\ln|\ \ |}{(\hbar\omega-\hbar^2k^2/2\bar{m}-\Delta)^2}\ ,$$

which, considering the smallness of the $\tan^{-1}$ and ln terms, is good except where $\hbar\omega-\hbar^2k^2/2\bar{m}-\Delta=0$. But this point is outside the range of integration for $\hbar\omega<\Delta+(m_c/\bar{m})\hbar\omega_0$. The integral can now be done exactly; the result is Eq. (4).

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