# Electron-Phonon Self-Energies in Many-Valley Semiconductors*

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The temperature dependence of band edges is discussed in many-valley semiconductors for intermediate and high temperatures. Electron-phonon self-energies are evaluated using a spherically, nonparabolic conduction band model. The intravalley and intervalley contributions to the electron-phonon scattering are shown to have the characteristics of Debye and Einstein functions, respectively. The results are shown to be in agreement with measurements of the temperature dependence of the indirect gap $\Gamma_{25'}-L_1$ in Ge.

It was noticed in the early days of semiconductor research that band gaps were temperature-dependent. A few measurements were made in the high-temperature limit where the change in the band gap $\Delta E_g$ is proportional to $T$, and Fan[1] presented a single spherical, parabolic band model which separated the effects of lattice expansion and electron-phonon scattering. Because our understanding of electron-phonon interactions and semiconductor band structures has been considerably refined, we have reopened the problem and found that temperature dependence can be used quantitatively as a tool for investigating the multiplicity of band edges.

We have evaluated the temperature dependence of the indirect gap $E_g=E(L_1)-E(\Gamma_{25'})$ in Ge, making appropriate approximations for the shape of the energy bands and the deformation potential matrix elements. These approximations will be discussed as they are introduced. It is the purpose of this investigation to illustrate how the electron-phonon self-energies can be evaluated in many-valley semiconductors and used to explain the observed temperature dependence of band edges. The presence of intervalley scattering is easily recognizable in our results, which suggests that accurate measurements of the temperature dependence of band edges can be used to investigate the band structure of semiconductors.

The temperature dependence of the indirect gap $E_g=E(L_1)-E(\Gamma_{25'})$ in Ge has been measured with a few tenths of a milli-electron volt accuracy.[2] This is shown semilogarithmically in Fig. 1. (Here the effect of thermal expansion has been removed by making use of the Grüneisen relation and experimental measurements of the specific heat,[3] the change in the energy gap with pressure,[4] and the Grüneisen constant.[5]) Note that below room temperature two activation energies are resolved of approximately 200° and 375°K. It is tempting to identify these with intervalley scattering caused by transverse acoustic ($TA$) and longitudinal acoustic ($LA$) phonons.

According to Fan, the electron-phonon self-energy term is given by

$$\Delta E_g=\sum_i \sum_q \frac{|M_{0q}{}^i|^2}{\epsilon_i(0)-\epsilon_i(q)\pm\hbar\omega_q}, \tag{1}$$

where $i$ denotes the band we are considering, $\epsilon_i(q)$ is the electron energy, and $M_{0q}{}^i$ is the deformation potential matrix element in scattering to a virtual state $q$ and the origin of coordinates $q=0$ which has been put at the band edge. For the excitation energies of interest ($\sim$1 eV) phonon energies $\hbar\omega_q$($\sim$0.1 eV) can be neglected in (1).

The matrix element $M_{0q}{}^i$ is given by[6]

$$M_{0q}{}^i=\mp\frac{1}{(MN)^{1/2}}\frac{2i}{3}qC_i\left(\frac{\hbar}{2\omega_q}\right)^{1/2}\begin{cases}(n_q)^{1/2}\\(n_q+1)^{1/2},\end{cases} \tag{2}$$

where $N$ is the total number of unit cells in the lattice,

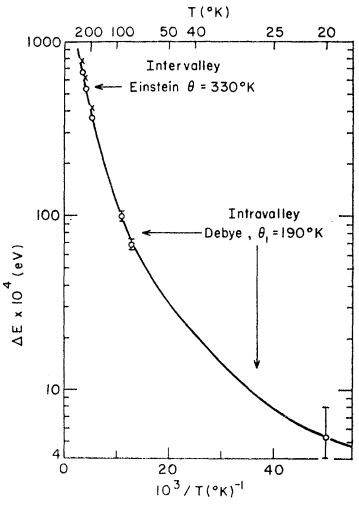


FIG. 1. Predicted and measured temperature change of the indirect gap $L_1-\Gamma_{25'}$ in Ge. The solid line is the theoretical fit taken from Eq. (5). The experimental points are taken from reference 2, the error bars being estimated from the difference in center of gravity of $TA$ phonon emission and absorption compared to $LA$ phonon emission and absorption. The ✕'s refer to the experimental values with thermal-expansion effects included. The parts of the curve dominated by intervalley and intravalley scattering are labeled explicitly.

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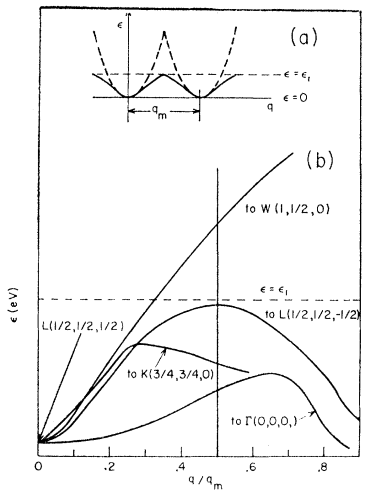


FIG. 2(a). $\epsilon(q)$ vs $q$ for spherically parabolic conduction bands and nonparabolic conduction bands. (b) Energy vs wave vector from the point $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ to other points in the Brillouin zone for Ge. Note the similarity of these curves, especially the one to $L$, to the nonparabolic band in Fig. 2(a).

$M$ is the mass of the ion, $n_q$ is the occupation number for the phonon $q$, and $C_i$ is an interaction parameter independent of $q$ and equal to $\frac{3}{2}$ of the corresponding deformation potential constant. The above expression for the matrix element $M_{0q}{}^i$ is an approximation based on the deformable ion model. With the interaction parameters taken to be independent of $q$, this approximation yields matrix elements with the same $q$ dependence as that obtained from the rigid ion model.

For the valence band edge a single-band model is adequate; for the conduction band edge one can include intervalley effects by dividing the Brillouin zone into eight similar zones [4 at $L=(1,1,1)$, 3 at $x=(1,0,0)$, and 1 at $\Gamma=(0,0,0)$]. The summation over $q$ in Eq. (1) is then written as a sum of integrals over each subzone separately. To obtain the temperature dependence of $L_1$ we include in the sum only the intravalley integral together with three intervalley integrals over the other $L$ subzones. Equation (1) then becomes

$$\Delta E_g(T)=-\frac{4\Omega\hbar}{9(2\pi)^3N}\left\{|C_v|^2\int d^3q\frac{n_q q^2}{\omega_q\epsilon_v(q)}+|C_c{}^{\text{intra}}|^2\int d^3q\frac{n_q q^2}{\omega_q\epsilon_c(q)}+3|C_c{}^{\text{inter}}|^2\int d^3q'\frac{n_{\mathbf{q}_m+\mathbf{q}'}(\mathbf{q}_m+\mathbf{q}')^2}{\omega_{\mathbf{q}_m+\mathbf{q}'}\epsilon_c(q')}\right\}, \quad (3)$$

where $v$ and $c$ refer to the valence and conduction bands, respectively, $\Omega$ is the volume of the unit cell, $\mathbf{q}_m$ is the phonon wave vector connecting the (1, 1, 1) valleys, and $\mathbf{q}'$ is the phonon wave vector measured from the minimum of the valley to which the electron has been scattered.

We restrict ourselves to the lowest conduction band and evaluate the integrals by assuming a sphericalized, nonparabolic conduction band dispersion relationship described by an energy-dependent effective mass similar to the one used for describing nonparabolic conduction bands[7] in InSb:

$$\epsilon(q)=\frac{\hbar^2q^2}{2m(\epsilon)},\quad \frac{1}{m(\epsilon)}=\frac{1}{m(0)}\left(1-\frac{\epsilon}{\epsilon_1}\right), \quad (4)$$

where $m(0)$ is the density of states effective mass at the $L_1$ band edge. A plot of $\epsilon(q)$ vs $q$ based on this model appears in Fig. 2(a) and a similar plot is made based on a parabolic band model for comparison. Our results are insensitive to the cutoff energy $\epsilon_1$; it was chosen to be 2 eV. This value is consistent with Fig. 2(b) which shows the variation of energy as a function of wave vector in Ge from the point $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ to (0,0,0), $(\frac{3}{4},\frac{3}{4},0)$, $(\frac{1}{2},\frac{1}{2},-\frac{1}{2})$, and $(1,\frac{1}{2},0)$ in the Brillouin zone.[8] We also see from Fig. 2(b) that the approximations involved in Eq. (4) are quite good. The dispersion relation gives a good description of the shape of the energy bands and the use of a spherical conduction band is a reasonable approximation to the actual energy band structure.

The intervalley terms can be evaluated by expanding the phonon energies about the (2,0,0) extrema. Retaining only the leading term in this expansion and using the Debye approximation, Eq. (3) becomes

$$\Delta E_g(T)=\frac{-4\Omega\hbar}{9(2\pi)^3N}\left[|C_v|^2\left(\frac{8\pi m_v}{\hbar^2u}I_1+\frac{4\pi}{u\epsilon_1}I_2\right)+|C_c{}^{\text{intra}}|^2\left(\frac{8\pi m_c}{\hbar^2u}I_1+\frac{4\pi}{u\epsilon_1}I_2\right)+3|C_c{}^{\text{inter}}|^2\left(\frac{19\pi m_c n_{q_m}}{3\hbar^2\omega_{q_m}}q_m{}^3+\frac{19\pi n_{q_m}}{60\epsilon_1\omega_{q_m}}q_m{}^5\right)\right], \quad (5)$$

where

$$I_1=\int_0^{q_m/2}n_q q\,dq,\quad I_2=\int_0^{q_m/2}n_q q^3dq,$$

$m_v$ and $m_c$ are the density-of-states effective masses at $\Gamma_{25'}$ and $L_1$, respectively, and $u$ is the velocity of sound. We find that the intravalley terms are given by functions similar to Debye functions with a cutoff $\theta_1$ equal to the average phonon energy of a given mode at the boundary of the subzone. The intervalley contribution has an Einstein character, being just proportional to $n_{q_m}=(e^{\theta/T}-1)^{-1}$.

Using the dispersion curves measured by neutron scattering,[9] we find that the (2,0,0) $TA$ and $LA$ phonon energies are 118° and 330°K, respectively. The $LA$ subzone Debye cutoff, $\theta_1$, for intravalley scattering is 190°K.

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$I_1$ and $I_2$ are evaluated numerically and a good fit to the experimental data (Fig. 1) can now be obtained by assuming that both intravalley and intervalley scattering are dominated by $LA$ phonons alone. (The conclusion that $TA$ phonons do not contribute appreciably to intervalley scattering is in good agreement with group theoretical considerations[10] which show that the $TA$ phonon is forbidden by time reversal.)

In the above we have assumed the $LA$ deformation potential constants $E_i(=\frac{2}{3}C_i)$ are $q$ independent; their values that are obtained by fitting to the experimental data are listed in Table I. We have assumed that the ratio

$$E_{\text{conduction}}^{\text{intravalley}}/E_{\text{valence}}^{\text{intravalley}}$$

is the same as that proposed by Philipp *et al.*[11]

The above values are in good qualitative agreement with valence gas free-electron deformation potentials ($\frac{2}{3}E_F\approx 10$ eV) and long wavelength deformation potentials near band edges.[11] Their exact magnitude depends somewhat on the approximations we have made in (5). By neglecting scattering from modes other than $LA$ we tend to overestimate average $LA$ deformation potentials.

We have also plotted[12] (Fig. 3) semilogarithmically $\Delta E_g(T)$ for the indirect gap $\Delta_5-\Gamma_{25'}$ in Si. Again two phonon activation energies are found, $\theta=575$°K and $\theta_1=275$°K. These values agree within experimental error with the longitudinal acoustic frequencies for (2,0,0) intervalley $LA$ scattering and subzone intravalley scattering as determined by neutron spectroscopy.[13] Intervalley scattering from the $\Delta_5$ edge (close to $X$) to the $L_1$ subzones would require (1,1,1) phonons which, in view of the isotropy of the $LA$ branch in Ge,[9] would also be expected to have energies close to 575°K.

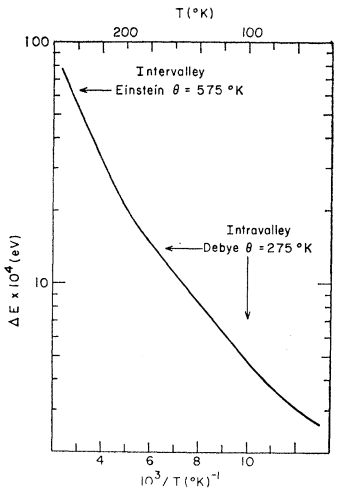


FIG. 3. Measured temperature change of the indirect gap, $\Delta_5-\Gamma_{25'}$, in Si.

It appears from our calculation for Ge that the temperature dependence of band edges can be made to yield valuable information concerning their location in the Brillouin zone. Our results are in good agreement with experiment and intervalley effects are quite evident. Extremely accurate (to 0.01 eV) measurements of temperature dependences might be helpful in identifying interband transitions[14] at higher energies as well.

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TABLE I. Averaged deformation potentials for scattering in each subzone and scattering between subzones.

| | Intravalley (eV) | Intervalley (eV) |
|---|---|---|
| Conduction band | 3.8 | 7.9 |
| Valence band | 6.7 | |

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