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Temperature dependence of semiconductor band gaps

K. P. O'Donnell and X. Chen

University of Strathclyde, Glasgow, G4 0NG Scotland, United Kingdom

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The application of a simple three-parameter fit to the temperature dependence of semiconductor band gaps is justified on both practical and theoretical grounds. In all trials the fit is numerically better than that obtained using the widely quoted Varshni equation. The formula is shown to be compatible with reasonable assumptions about the influence of phonons on the band-gap energy. Approximate analytical expressions are derived for the entropy and enthalpy of formation of electron-hole pairs in semiconductors.

In this letter we advocate the use of a new three-parameter fit to the temperature dependence of semiconductor band gaps. This fitting improves upon the semi-empirical Varshni equation¹ both numerically, since it gives better fits to the data, and theoretically, since the parameters of the fit may be related to an intrinsic interaction of semiconductors, namely the electron-phonon coupling. Similar expressions to ours have appeared in the literature^{2,3} but the practical and theoretical justification of this kind of data fit have not previously been worked out in detail. We emphasize that our approach is empirical: we aim simply to describe the data as well as possible with the minimum number of free parameters.

The Varshni relation for the temperature dependence of semiconductor band gaps is

$$E_g(T) = E_0 - \alpha T^2 / (T + \beta), \quad (1)$$

where α and β are fitting parameters characteristic of a given material.¹ The theoretical basis of this much-used relation^{4,5} is unfortunately rather weak, since β , which is supposed to be related to the Debye temperature, may in certain important cases be negative.¹ Moreover, at low temperature, Eq. (1) predicts a quadratic temperature dependence, whereas experiment finds (an approximate) temperature independence at very low temperatures. This point was noted by Manoogian and Leclerc² who devised the equation

$$E_g = E_D^0 (1 + AT^x) + B \left[\theta_1 \coth \left(\frac{\theta_1}{2T} \right) + \theta_2 \coth \left(\frac{\theta_2}{2T} \right) \right]. \quad (2)$$

The first term on the right is included to describe the effect of lattice expansion on the band gap, by means of the parameters A and x . The coth terms represent contributions from electron-phonon coupling, with acoustic (θ_1) and optical (θ_2) terms being averaged separately. $\theta = \hbar v/k$ is the mode energy expressed as a temperature. With six parameters to fit, the procedure is somewhat tricky, but fits^{5,6} to experimental data on the group-IV semiconductors seem to yield reasonable values of θ_1 and θ_2 . In addition the lattice contribution was found to vary as $T^{0.7}$ for all three semiconductors C, Si, and Ge. A simplified form of Eq. (2), which sets $x = 2/3$ and considers only one average phonon energy is used by Donofrio *et al.*⁷

Viña *et al.*³ fit data on the critical-point energies of germanium to the Varshni relation (their Table I), but point out that they can also fit these data to an expression

$$E = a - b \left(1 + \frac{2}{e^{\theta/T} - 1} \right), \quad (3)$$

which represents a decrease in the energy thresholds "proportional to Bose-Einstein statistical factors for phonon emission plus absorption." The term within the brackets in Eq. (3) readily reduces to $\coth(\theta/2T)$ so that Eq. (3) can be written in a form

$$E = a - b \coth(\theta/2T), \quad (3a)$$

which is comparable with Eq. (2).

Recently, Collins *et al.*⁸ have used an empirical fit with a distribution of phonon energies. They write

$$E_g(T) = E' + \int d\omega f(\omega) [n(\omega, T) + \frac{1}{2}] - a(c_{11} + 2c_{12})\Delta V(T)/3V_0. \quad (4)$$

The last term on the right accounts for lattice expansion. The phonon term is numerically integrated using the approximation $f(\omega) = c\omega g(\omega)$ where $g(\omega)$ is the empirical density of phonon states and $n(\omega, T)$ is the Bose-Einstein occupation number. This approach owes a great deal to theoretical work by Allen and co-workers.^{9,10} A good fit to experiment is obtained at the expense of a high computing overhead in the work of Collins *et al.*⁸ Rather poor fits are obtained using the full theoretical treatments.

In this letter we advocate the equation

$$E_g(T) = E_g(0) - S \langle \hbar\omega \rangle [\coth(\langle \hbar\omega \rangle / 2kT) - 1] \quad (5)$$

as a direct replacement of the Varshni equation. $E_g(0)$ is the band gap at zero temperature, S is a dimensionless coupling constant, and $\langle \hbar\omega \rangle$ is an average phonon energy. We adopt this notation from the vibronic model of Huang and Rhys.¹¹ Data taken from the literature¹²⁻¹⁴ concerning GaAs, GaP, Si, and diamond are to be fitted. Following the methods of Thurmond¹⁵ we use Eq. (5) to derive expressions for the thermodynamic functions: the Gibbs energy, enthalpy, and entropy of formation of electron-hole pairs in a semiconductor. Finally we justify, without proof, the applicability of the new equation on the basis of simple thermodynamics.

Data for GaAs, GaP, Si, and C were obtained from the literature. Table I shows the best fit values of the param-

TABLE I. Fit parameters for temperature dependence of semiconductor band gaps.

	Temp. range (K)	$E_g(0)$ (eV)	S	$\langle\hbar\omega\rangle$ meV	Ref.
Si	0-300	1.170	1.49	25.5	13.
GaAs	10-1000	1.521	3.00	26.7	12
GaP	10-1300	2.338	3.35	43.6	12
C	100-700	5.450	2.31	94.0	14

ters $E_g(0)$, S , and $\langle\hbar\omega\rangle$ in each case. The excellent fits obtained are shown in Fig. 1. In each case, they are statistically better than Varshni fits to the same data. The silicon data show some anomalies which will be described in detail elsewhere.

At high temperatures, $kT \gg \langle\hbar\omega\rangle$ and

$$E_g(T) \rightarrow E_g(0) - 2SkT. \quad (6)$$

The slope of the E_g vs T curves approach the limiting value

$$\left(\frac{dE_g}{dT} \right)_{\max} = -2Sk. \quad (7)$$

It appears from Table I that the limiting values for silicon and diamond are somewhat smaller than for the other semiconductors. However, the range of applicability of a data fit never exceeds the range of the measurements. A wider range on the Si data is obviously desirable, while the diamond data is also seen to have a restricted range if the large value of the mean phonon energy is taken into account.

The entropy and enthalpy of formation of electron-hole pairs may be obtained from Eq. (5) following the method of Thurmond who identifies $E_g = \Delta E_{cv}$ as the Standard Gibbs energy.¹⁵ Thus,

$$\begin{aligned} \Delta S_{cv}(T) &= -\frac{d}{dT} \Delta E_{cv}(T) \\ &= \frac{S\langle\hbar\omega\rangle^2}{2k} \left(\frac{\text{csch}(\langle\hbar\omega\rangle/2kT)}{T} \right)^2 \end{aligned} \quad (8)$$

is the entropy of formation of electron-hole pairs and the enthalpy, $\Delta H_{cv} = \Delta E_{cv} + T\Delta S_{cv}$, can be evaluated using Eqs. (5) and (8). At high temperature, Eq. (8) becomes

$$\Delta S_{cv}(T) \rightarrow -2Sk. \quad (9)$$

The temperature dependence of the entropy for formation of electron-hole pairs in silicon is plotted by way of example in Fig. 2 using parameters from Table I. This plot differs appreciably from previous estimates¹⁶ which used a polynomial fit to the data of Bludau *et al.*¹³ Extrapolation is always a dangerous procedure but we may be fairly confident that the entropy of formation for e - h pairs in silicon saturates near room temperature with a value close to $3k$.

Finally, we offer a brief justification from thermodynamics of the form of Eq. (5). It has been known for a very long time that temperature-dependent electron-phonon interactions effectively determine semiconductor band

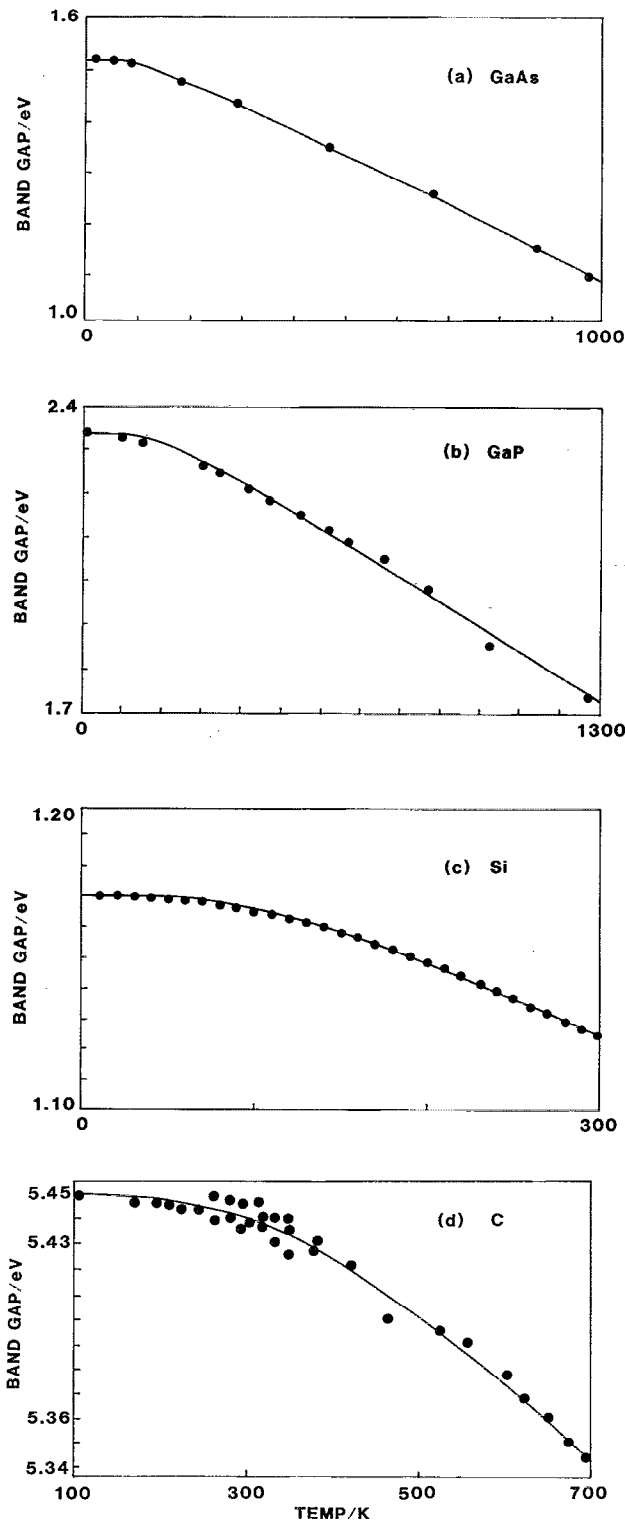


FIG. 1. Energy band gaps as a function of temperature of (a) gallium arsenide, (b) gallium phosphide, (c) silicon, and (d) diamond.

gaps.¹⁷ The reasoning is as follows. The band gap reflects the bond energy. An increase in temperature changes the chemical bonding as electrons are promoted from valence band to conduction band. In the intrinsic temperature range, direct effects due to thermal band-to-band excitations are negligible. The lattice phonons on the other hand have relatively small energies and are excited in large num-

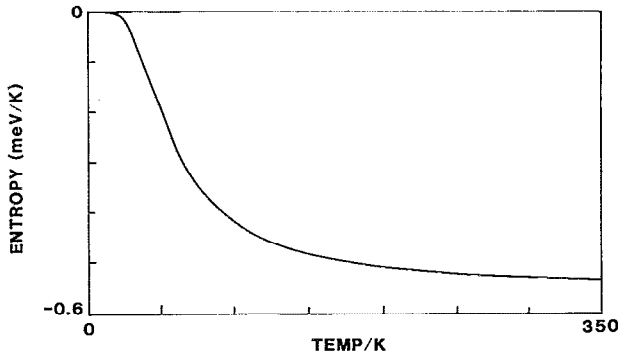


FIG. 2. Entropy of formation of electron-hole pairs in silicon, calculated using Eq. (8).

bers at moderate temperatures. They influence the bonding through various orders of electron-phonon interaction.^{9,10} Since any such effect depends on phonon numbers, the dependence on temperature should take the form $(\Delta E_g)_{\text{phonons}} \sim n(\omega, T) \sim \coth(\hbar\omega/2kT)$. We now show that the dependence of band gap on lattice expansion takes nearly the same analytic form. The (static) lattice contribution to the temperature dependence

$$(\Delta E_g)_{\text{lattice}} = - \left[\frac{\partial E_g}{\partial p} \right]_v \cdot B \frac{\Delta V(T)}{V_0}, \quad (10)$$

where $[\partial E_g / \partial p]_v$ is the pressure dependence, B is the bulk modulus equal to $1/3 (c_{11} + 2c_{12})$ and $V_0, \Delta V(T)$ are the lattice volume and its change with temperature, respectively. Using a standard thermodynamic result of Gruneisen¹⁸

$$\frac{B \Delta V}{V_0} = \gamma \frac{\bar{E}}{V} \quad (11)$$

we find

$$(\Delta E_g)_{\text{lattice}} = - \left[\frac{\partial E_g}{\partial p} \right]_v \cdot \gamma \frac{\bar{E}}{V}, \quad (12)$$

where γ is the Gruneisen parameter and \bar{E} is the mean thermal energy of the sample given by

$$\bar{E} = \hbar \int \omega g(\omega) [n(\omega, T) + \frac{1}{2}] d\omega \quad (13)$$

which for a single effective mode $g(\omega) = \delta(\omega - \omega_0)$ is simply

$$\bar{E} = \hbar \omega_0 [n(\omega_0, T) + \frac{1}{2}]. \quad (14)$$

Hence $(\Delta E_g)_{\text{lattice}}$ depends on \bar{E} , which is seen to depend on the phonon occupation number, and on V , which varies only weakly with temperature. The simple theory therefore predicts that the lattice contribution to $\Delta E_g(T)$ should vary in a similar way to the whole shift. This is in fact found to be the case in practice, in contradiction of the power law of the fitting Eq. (2) proposed by Manoogian and Leclerc.⁵ Since lattice and phonon contributions to the band-gap shift have very similar (averaged) temperature dependences, the use of a simple fitting equation is justified.

In summary, we have shown that a reasonable three-parameter thermodynamic function may be used with good effect to fit the temperature dependences of the fundamental band gaps for technologically important semiconductors with room-temperature gaps in the range from 1.0 to 5.5 eV.

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