TEMPERATURE DEPENDENCE OF THE ENERGY GAP IN SEMICONDUCTORS

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Synopsis

A relation for the variation of the energy gap (E_g) with temperature (T) in semi-conductors is proposed:
$$E_g = E_0 - \alpha T^2/(T + \beta)$$
where α and β are constants. The equation satisfactorily represents the experimental data for diamond, Si, Ge, 6H–SiC, GaAs, InP and InAs.

In the present note we wish to suggest the following relation for the temperature dependence of the energy gap in semiconductors:

$$E_g = E_0 - \alpha T^2/(T + \beta) \tag{1}$$

where E_g is the energy gap which may be direct (E_{gd}) or indirect (E_{gi}), E_0 is its value at $0°K$, and α and β are constants.

Most of the variation in the energy gap with temperature is believed to arise from the following two mechanisms:

(1) A shift in the relative position of the conduction and valence bands due to the temperature-dependent dilatation of the lattice[1][2]). Theoretical calculations[2]) show that the effect is linear with temperature at high temperatures. In that region this effect accounts for only a fraction (about 0.25) of the total variation of the energy gap with temperature. At low temperatures the thermal expansion coefficient is nonlinear with T; indeed for a number of diamond structure solids it even becomes negative[3]) over a certain temperature interval. Correspondingly the dilatation effect on the energy gap is also nonlinear.

(2) The major contribution comes from a shift in the relative position of the conduction and valence bands due to a temperature-dependent electron lattice interaction. Theoretical treatments[4-9]) show that this leads to a temperature dependence of the following form:

$$T \ll \theta$$
$$\Delta E_g \propto T^2$$
$$T \gg \theta$$
$$\Delta E_g \propto T$$
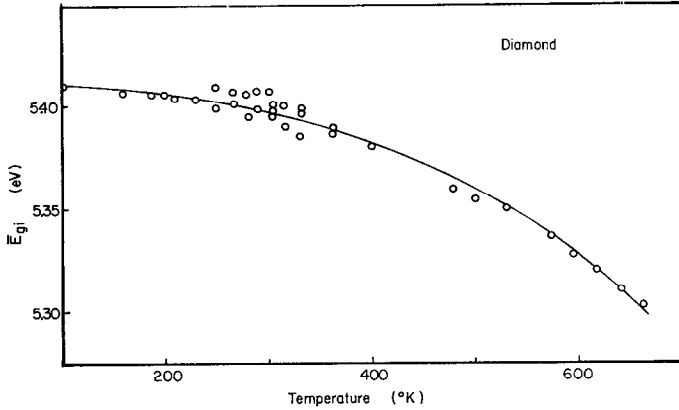
where θ is the Debye temperature.

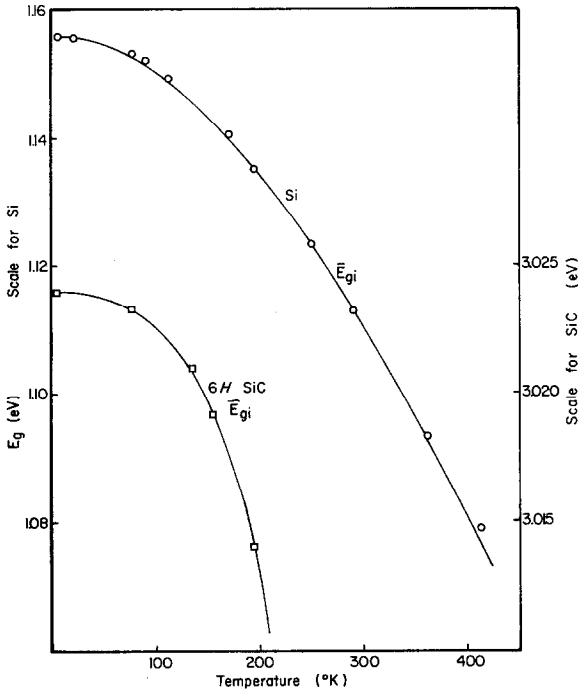Fig. 1. Variation of the energy gap with temperature for diamond. The curve represents equation (1).

Fig. 2. Silicon and 6H SiC.

Eq. (1) is consistent with the theoretical results if we assume that $\beta \sim \theta$. The constants in eq. (1) were evaluated from the experimental data for a member of semiconductors and are recorded in table I. In some cases the available data are for the difference between the energy gap and the binding energy of the exciton (E_x). This is indicated by a bar above E; thus
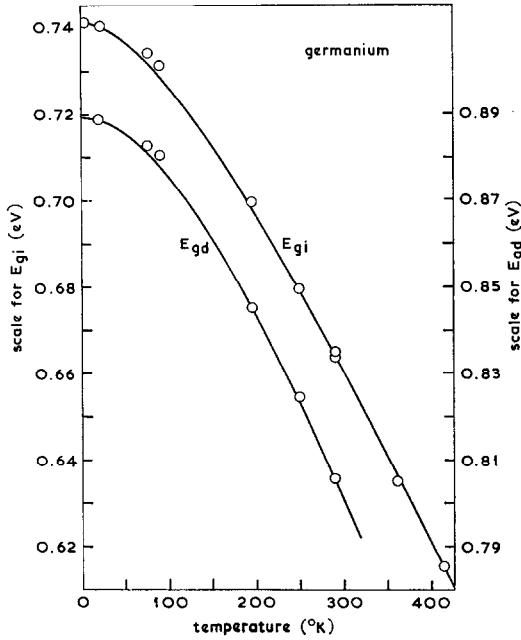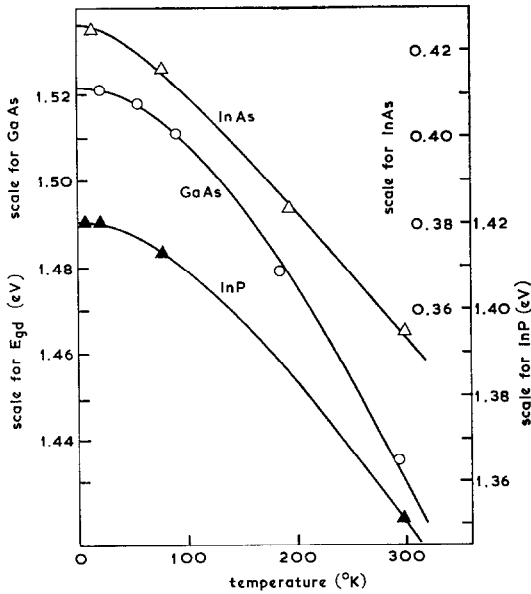
Fig. 3. Germanium, indirect and direct gaps.

Fig. 4. GaAs, InP and InAs.

$\bar{E}_{gi} = E_{gi} - E_x$. The exciton binding energy is usually quite small and to a first degree of approximation its temperature dependence may be neglected.

In figs. 1 to 4 the curves obtained from eq. (1) are compared with the experimental points. In most cases the agreement between the two is seen to be satisfactory, the deviation $\{E_g(\text{calc.}) - E_g (\text{obs.})\}$ is of the same order as the uncertainties in the experimental points. For the 77°K and 90°K points for $Ge(E_{gd})$ and $Ge(E_{gi})$ the deviation of the curve from the ex-

TABLE I

Substance	Type of gap	E_0 (eV)	α ($\times 10^{-4}$)	β	Source of E_g data	Debye θ (°K)
		Values of the parameters in equation (1)				
Diamond	$\bar{E}_{gi}$	5.4125	−1.979	−1437	ref. 10	2220 [16]
Si	$\bar{E}_{gi}$	1.1557	7.021	1108	ref. 11	645 [17]
Ge	E_{gi}	0.7412	4.561	210	ref. 11	374 [17]
Ge	E_{gd}	0.8893	6.842	398	ref. 11	
6H SiC	$\bar{E}_{gi}$	3.024	−0.3055	−311	ref. 12	~1150 [a]
GaAs	E_{gd}	1.5216	8.871	572	ref. 13	344 [b]
InP	E_{gd}	1.4206	4.906	327	ref. 14	301 [c]
InAs	E_{gd}	0.426	3.158	93	ref. 15	248 [b]

[a]) estimated from $h\nu_0/k$, where ν_0 is the infrared resonance frequency taken from ref. 18.
[b]) calculated from elastic constants.
[c]) calculated from estimated values of elastic constants.

perimental points is greater than the experimental uncertainty. The errors in these cases are about 0.002 eV. However, when we compare β with the Debye temperature, we are somewhat disappointed. For Si, Ge, GaAs, InP and InAs, β correlates with θ within a factor of roughly 2.5. But for diamond and SiC, β turns out to be negative. The cause of this anomaly is discussed below.

As a matter of fact if E_g is plotted versus $T^2/(T + \theta)$ (see fig. 5) the relationship is linear above $T \sim \theta/10$; at low temperatures ($< \theta/10$) the linear relations appear to give values which are a little too high. The exact limit upto which linearity extends is not easy to locate in fig. 5 because of too few points in the low temperature region.

When the measurements of the energy gap are made at high temperatures ($T \sim \theta$), it has been customary to obtain the energy gap at 0°K by a linear extrapolation of the E_g, T plot. Results obtained above show that a much better estimate of $E_g(0°K)$ can be obtained by plotting E_g versus $T^2/(T + \theta)$. We may illustrate it with the case of the indirect energy gap for germanium. The experimental value at 0°K is 0.7412 eV. If we consider only those experimental points which are at $T > 195°K$, an E_g, T plot would give $E_g(0°K) \approx 0.78$ eV, while an E_g, $T^2/(T + \theta)$ plot give $E_g(0°K) = 0.74$ eV.

Fig. 6 shows E_g versus $T^2/(T + \theta)$ for diamond and SiC. For diamond, for $T > \theta/8$, a linear relationship appears to be reasonable. In the case of
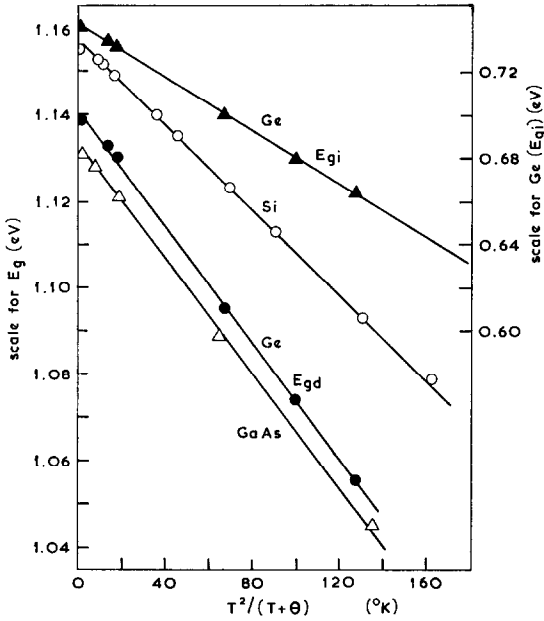
Fig. 5. E_g versus $T^2/(T + \theta)$. To accomodate on the same graph, the points for Ge(E_{gd}) have been increased by 0.25 eV and those for GaAs decreased by 0.39 eV.
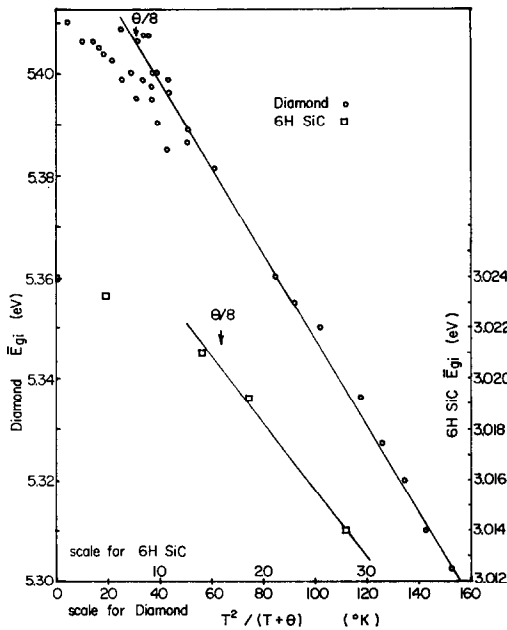

Fig. 6. E_g versus $T^2/(T + \theta)$ for diamond and 6H SiC.

SiC only two points are available for $T > \theta/8$ and any conclusion is somewhat arbitrary. Nevertheless, the trend of the points does seem to indicate that the curve is flattening off to a linear type of relation. In obtaining the constants, listed in table I, for these two substances we have forced the curve to pass through the low temperature points and in so doing β has turned out to be negative. This also indicates that the constants for these two substances as given in table I may not be satisfactory for distant extrapolation.

We may add that with $\beta = \theta$ it is still possible to achieve agreement over the whole temperature range by introducing one more constant. For diamond such an equation is

$$\bar{E}_{gi} = 5.4461 - \frac{(7.917 \times 10^{-4}\, T^2 + 55.4)}{T + 2220.}$$

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