Temperature dependence of the energy gap in semiconductors

A. MANOOGIAN AND J. C. WOOLLEY
Department of Physics, University of Ottawa, Ottawa, Ont., Canada K1N 9B4

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It is shown that the equation $\Delta E = \alpha T^2/(T + \beta)$, which is commonly used to describe the temperature variation of energy gaps in semiconductors, is a second order approximation of the electron–phonon interaction term in the recently proposed equation $\Delta E = UT^s + V\theta[\coth(\theta/2T) - 1]$. The calculation shows that the parameters α and β of the approximate equation can describe the characteristics of semiconductors only if the relation $\theta/T \ll 1$ holds, with the validity limited by the magnitude of the existing dilation effect. In this case it is found that $\beta = \theta/2$ where θ is the effective Einstein vibrational frequency, in temperature units, of the phonon spectrum in the material. A comparison of the two equations when fitted to experimental data is presented and discussed.

On montre que l'équation $\Delta E = \alpha T^2/(T + \beta)$, qu'on utilise communément pour décrire la variation en fonction de la température des bandes interdites dans les semiconducteurs, est une approximation du second ordre du terme d'interaction électron–phonon dans l'équation proposée récemment $\Delta E = UT^s + V\theta[\coth(\theta/2T) - 1]$. Le calcul montre que les paramètres α et β de l'équation approximative ne peuvent décrire les caractéristiques des semiconducteurs que sous la condition $\theta/T \ll 1$, la validité étant limitée par la grandeur de l'effet de dilatation existant. Dans ce cas on trouve que $\beta = \theta/2$, où θ est la fréquence de vibration Einstein effective, en unités de température, du spectre de phonons dans la substance. Une comparaison des deux équations, ajustées aux données expérimentales, est présentée et discutée.

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1. Introduction

The variation of the energy gap E_g of a semiconductor with temperature is of interest from both academic and technological viewpoints, and much work has been carried out to determine the experimental variations of E_g with temperature. When such values have been determined, they are usually fitted to some convenient equation, such as those discussed below, for one of two reasons. (a) It may be required to find a mathematical form to represent the experimental data so that interpolation or some other computation can be carried out. In this case the physical significance of the parameters is of no interest and one merely requires the best and simplest fit to the experimental data. (b) In a more fundamental investigation, the aim may be to obtain an understanding of the relevant theory or properties of the material concerned. In this case the form of the equation and the significance of the parameter values are the important factors.

It may be argued in case (b) that fitting to semi-empirical equations is of limited use when more detailed theories are available. However, even in recent work, e.g., the theoretical analysis by Allen and Cardona (1) of the temperature variation of the energy gap of germanium, the agreement between the calculated band gap change ΔE_g and the experimental value is no better than $\pm 25\%$. While this is very good as a test of the theoretical analysis, it is not satisfactory for the applications indicated in case (a) above. Moreover, analysis of this type has so far been limited to such well understood materials as germanium whereas experimental workers may need to deal with energy gap values of new ternary and quaternary compounds. Thus there is still need for semi-empirical equations, not only to give good fits to the experimental data for use in computations etc. but also for analysis of the results on new, more complex, materials where the fitted parameters provide at present the only guide to the behaviour of these compounds and alloys.

The temperature variation of the energy gap in semiconductors is known to be due to the sum of the effects of lattice dilation and electron–phonon interaction. The effect of lattice dilation contributes an amount in the order 2 to 20% to the temperature shift, depending on the semiconductor. Some years ago Varshni (2) suggested the equation

$$[1] \quad \Delta E = \alpha T^2/(T + \beta)$$

to describe the temperature variation of the energy gap and this equation is commonly used to analyze such data. The constant β was interpreted as being related to the Debye temperature θ_D, with $\beta \sim \theta_D$.

Recently, Manoogian and Leclerc (3) suggested an empirical equation to describe the energy gap temperature variation which included terms for the effects of both lattice dilation and electron–phonon interaction. The single frequency form of this equation, written so as to give $\Delta E = 0$ at $T = 0$ K, is

$$[2] \quad \Delta E = UT^s + V\theta[\coth(\theta/2T) - 1]$$

where U, s, V, and θ are constants independent of temperature. The first term represents the effect of lattice dilation and the second term the electron–phonon interaction. The second term is proportional to the average energy of a system of noninteracting harmonic oscillators with constant θ, where $\theta = h\nu/k$ and ν is the frequency of excitation. This term is obtained from the Einstein approximation for lattice vibrations as follows:

$$\begin{aligned}\langle E\rangle &= h\nu\{1/2 + (e^{h\nu/kT} - 1)^{-1}\}\\ &= (h\nu/2)\coth(h\nu/2kT)\\ &= (k\theta/2)\coth(\theta/2T)\end{aligned}$$

The dynamic part of the energy gap shift in semiconductors is taken to be proportional to this energy and is written as $V\theta\coth(\theta/2T)$, where V is a parameter to be determined. Whenever the Einstein model is used to fit any set of data, the procedure is to find the θ which produces the best fit. When [2], with two θ's, was applied to data of the group IV-A semiconductors (3, 4) it was found, to the accuracy of the experimental measurements, that the θ values corresponded to the mean frequencies θ_m of the respective acoustic and optical phonons, whereas the magnitude of the dilation term was in good agreement with that expected theoretically (5). For a single θ, the θ value was found to correspond to the mean frequency θ_m of the entire phonon spectrum.

2. Relationship between Varshni and Manoogian–Leclerc equations

Writing $\theta/2T = X$ and $\coth X = (\exp 2X + 1)/(\exp 2X - 1)$, the second term in [2] becomes $V\theta[2/(\exp 2X - 1)]$. For the case when $2X \ll 1$ we can write

$$\exp 2X = 1 + 2X + 2X^2$$

and hence

$$[3]\quad V\theta[\coth X - 1] = V\theta[1/(X + X^2)] = 2VT^2/\left(T + \frac{\theta}{2}\right)$$

With $\alpha = 2V$ and $\beta = \theta/2$ this becomes $\alpha T^2/(T + \beta)$, which is the Varshni expression. This derivation shows that the Varshni equation is a second order approximation to the second term in [2] and that it describes the vibrational part of the energy gap temperature variation only when the condition $\theta/T \ll 1$ holds. Moreover, if the Varshni equation is used to describe the complete energy gap variation, then it is implied that the effect of lattice dilation has been lumped into the electron–phonon term. Hence the significance of the α and β parameters so obtained will depend on the magnitude of the existing lattice dilation contribution.

If the Varshni equation is compared with the dynamic term of [2], a relationship between β and θ_E can be found. In the intermediate temperature region the Einstein temperature θ_E is related to the Debye temperature θ_D by the relation $\theta_E = (3/4)\theta_D$ (6). Since θ_E is equal to θ in [2], and since $\beta = \theta/2$, we have $\beta = (3/8)\theta_D$.

3. Comparison with experimental data

The main use that has been made of the Varshni equation is to analyze data for the common semiconductors such as Ge, GaAs, InAs, etc. In these cases the mean phonon energy θ_m is below 300 K and so for energy gap values above room temperature the Varshni equation can give a reasonable fit to the E_g vs. T curves. This has been shown for the case of GaAs by Thurmond (7) and Panish and Casey (8). However, as pointed out by Thurmond, the experimental scatter on the E_g values allow various combinations of α and β to be obtained. Thus Thurmond found β to be 204 ± 45 K whereas Panish and Casey fitted with $\beta = 300$ K. Manoogian (9) has shown that for GaAs $\theta_m = 297$ K, so that from the above analysis one would expect β to be 149 K. Using [2], a fit to the data published by Panish and Casey gives $\theta = 270 \pm 30$ K, which is in reasonable agreement with θ_m, and it is also found that at room temperature the dilation term contributes ~15% to the total change in E_g. Similar ranges of values can be obtained when the experimental data for Ge, Si, etc. are considered (3, 4). It is of interest to note that for the material of lowest θ_D quoted by Varshni, i.e., InAs, $\theta_D = 248$ K and Varshni obtains $\beta = 93$ K, which fits exactly to the relation $\beta = (3/8)\theta_D$ given above. This agreement implies that in InAs the dilation term must be very small.

In the case of such materials as diamond and SiC, the quoted Debye temperatures are 2220 and 1150 K, respectively. Thus all of the available energy gap data are for temperatures well below θ_D. Manoogian and Leclerc (4) have fitted the values of E_g for diamond to [2] and obtained a value of $\theta = 1355 \pm 30$ K, while the value of θ_m from the phonon spectrum is $\theta_m = 1400 \pm 60$ K. In this case the fractional contribution of the dilation term to the change in E_g is ~2%. Since the condition $\theta/T \ll 1$ does not hold for these materials, the fit of the Varshni equation to the data is poor. As indicated by Varshni it is possible to tie the equation to the experimental values at two chosen temperatures but the fit remains poor in other parts of the temperature range. Also, the values of β obtained using [1] were negative for both diamond ($\beta = -1437$ K) and SiC ($\beta = -311$ K).

A problem similar to that above has arisen when more complicated materials such as ternary and quaternary chalcopyrite compounds are considered. For the

$CuGa(Se_{1-x}S_x)_2$ alloys and for $CuGaSnSe_4$, detailed values of E_g were obtained for the temperature range 4–300 K (10, 11). Analysis with [2] gave values of θ in the region 450–750 K, but because of experimental error it was found that a good fit could be obtained to each E_g vs. T curve for a finite range of θ values. For the $CuGa(Se_{1-x}S_x)_2$ alloys, Bodnar *et al.* (12) gave phonon frequencies which provided estimates of θ_m in the range 400–550 K, in reasonable agreement with the θ values from [2]. Once again in these cases a good fit to the experimental data could not be obtained with the Varshni equation (10, 11). As in the case of diamond [1] could be tied to the experimental values at any two temperatures but it gave a poor fit at other parts of the temperature range. Fitting at the two ends of the temperature range resulted in values of β greater than 2000 K.

4. Discussion

As indicated above, fitting of the experimental curves of E_g vs. T to [1] or [2] is usually carried out for one of two reasons, (a) and (b). In case (a) it is shown by the results of Panish and Casey (8) and others that the Varshni equation can be useful. This occurs when the condition $\theta/T \ll 1$ is satisfied over most of the temperature range of interest. Usually in this case, because of the experimental scatter of the E_g vs. T data, the Varshni equation can give as good fit as the Manoogian–Leclerc equation, with fewer parameters to be determined. The main problem with [1] is to know for any given material whether the condition $\theta/T \ll 1$ is satisfied. From the examples quoted above, in the case of the chalcopyrite materials, due to the higher values of θ a good fit to the experimental data could not be obtained with the Varshni equation but it was achieved using [2]. Turning to case (b), there are obvious disadvantages in the use of the Varshni equation. Even if a good fit to the experimental data can be made, the contribution of dilation has been lumped with the vibrational term and hence the parameter values obtained will likely not indicate the correct values for the material, as is indicated above. But as has been shown previously (3, 4, 9), the fits of the Manoogian–Leclerc equation give values of θ in good agreement with θ_m of the phonon distribution for a wide range of materials. The main problem with this equation is that with more parameters to be determined an accurate set of data over the measured temperature range is needed to give a unique set of parameter values.

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