

Temperature Dependence of the Energy Gap of Semiconductors in the Low-Temperature Limit

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The temperature dependence of the electronic states and energy gaps of semiconductors is an old but still important experimental and theoretical topic. Remarkably, extant results do not clarify the asymptotic $T \rightarrow 0$ behavior. Recent breakthroughs in the spectroscopy of enriched ^{28}Si allow us to measure changes in the band gap over the liquid ^4He temperature range with an astounding precision of one part in 10^8 , revealing a $T^{4.0 \pm 0.2}$ decrease with increasing T . This is in excellent agreement with a theoretical argument predicting an exponent of 4. This power law should apply, in the low temperature limit, to the temperature dependence of the energies of all electronic states in semiconductors and insulators.

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Introduction.—The first reports on the measured temperature dependence of electronic excitation energies (energy gaps) date back to 1930 [1]. In this work it was assumed, on the basis of the few experimental points available, that the observed excitation gaps E_g depend linearly on temperature all the way down to $T = 0$. A decrease of dE_g/dT at lower temperature leading to a value of this slope that tends to zero for $T \rightarrow 0$ is already implicit in the early theoretical treatments [2,3]. The flood of experimental data on semiconductors that appeared after the invention of the transistor [4] definitely established the vanishing of dE_g/dT for $T \rightarrow 0$.

In a much cited paper, Varshni [5] suggested the empirical law for $E_g(T)$:

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

giving as a justification only the facts that it reproduced the linear behavior observed and calculated at high T [1,2] and, moreover, it led at low T to an asymptotic behavior like T^2 , which Varshni incorrectly claimed it followed from the theories in [1,2]. In 1955 Antončik [6] introduced a term $DE_g(T)$ that was fundamentally tied to the self-energy terms calculated in [1,2] and thus could not be neglected even though most theoretical work prior to 1983 evaluated either the self-energy terms or the Debye-Waller terms introduced in [6] but not both simultaneously. A number of full quantitative calculations of $E_g(T)$, based on realistic models of the electron-phonon interaction, have appeared since then [7–9], but none of them allows us to reach reliable conclusions on the asymptotic behavior for $T \rightarrow 0$ because of the limited number of points that had to be used to simplify the rather complicated \mathbf{k} -space integration. A few other parametrized expressions have also been used. They involve either a finite number (1 or 2) of Bose-Einstein terms,

which have a clear physical meaning [10], or complicated algebraic expressions, such as the one in [11], which leads to the asymptotic dependence for $T \rightarrow 0$,

$$E_g(T) = E_0 - AT^p, \quad (2)$$

where p is an adjustable parameter. Fits to $E_g(T)$ for a large number of materials, discussed in [11] lead to values of p between 2 and 3.3 (unfortunately no error bars are given).

The work in [11], however, demonstrates the inability of a few Bose-Einstein terms to reproduce the asymptotic behavior for $T \rightarrow 0$ (see also Fig. 4 in [10]). It is easy to show that the T^2 behavior suggested in [5] is theoretically incorrect and to demonstrate that the asymptotic behavior predicted by theory is $\sim T^4$. The argument can be made without using any equations, simply on the basis of Debye's model of the asymptotic behavior of the specific heat [12], which is exact in the $T \rightarrow 0$ limit. The integral leading to the total phonon energy in the Debye model has an asymptotic behavior like T^4 (i.e., T^3 for its derivative, the specific heat). The expression for the gap renormalization due to electron-phonon interaction is similar [7], except for the presence in the integrand of a matrix element of that interaction squared divided by the frequency (the latter term arises from the square of the phonon amplitude). A factor of ω (i.e., the energy of a phonon) must also be removed from the integrand in Debye's expression for the vibrational energy vs T in order to calculate the gap renormalization. The key point is that the electron-phonon matrix element must vanish for $\omega \rightarrow 0$ in the case of acoustic phonons since, in this limit, the acoustic phonons represent a uniform translation of the crystal. Hence, the first term in the expansion of the matrix element vs ω is proportional to ω . We must thus square this term and divide it by ω in order to convert the expression for the total energy of the phonons into the

corresponding behavior for the gap renormalization in the $T \rightarrow 0$ limit. This results in a factor of ω^3 in the integrand, like that found for the Debye energy. Correspondingly, T^4 is obtained for the asymptotic behavior of the gap. We have not yet mentioned a possible contribution to the temperature dependence of the band gap energy due to the thermal expansion of the lattice, which in the low temperature limit would also be expected to vary as T^4 . This contribution is expected to be negligible in the $T \rightarrow 0$ limit, because unlike the electron-phonon interaction, the linear thermal expansion coefficient of Si undergoes two sign reversals at low T , one near 120 K and the other near 17 K, resulting in a very small expansion coefficient in the temperature region of interest here [13]. Even in the high temperature region, the thermal expansion effect makes only a small ($\sim 10\%$) contribution to the temperature dependence of the band gap energy [10,14].

Experiment.—An earlier study of the no-phonon photoluminescence (PL) transitions of the bound excitons associated with the residual shallow donor P and acceptor B in a sample of highly isotopically pure ^{28}Si (isotopic purity 99.896%) revealed that in this sample the lines were much sharper than ever observed in the closest to perfect natural Si, and were, in fact, beyond the instrumental resolution of the best commercially available apparatus [15]. It was predicted that the actual linewidths of these transitions, which occur at $\sim 9280\text{ cm}^{-1}$, just below the Si band gap, would be less than 0.005 cm^{-1} in isotopically pure material. The sample used in the present study is similar to the one used in that first PL study, but enriched to a ^{28}Si content of 99.94%, and with somewhat lower residual B and P concentrations than the earlier sample. The present sample was used in a recent study [16] which demonstrated that many of the midinfrared donor and acceptor absorption transitions are also much sharper in isotopically pure Si than in the best samples having the natural isotopic composition.

In order to investigate the true linewidths of the shallow bound exciton transitions in ^{28}Si , we have constructed a novel apparatus for examining the bound exciton absorption spectrum, using a single frequency laser, and monitoring the very weak absorption by detecting the TO-phonon replica luminescence of the bound excitons. Such photoluminescence excitation (PLE) spectroscopy had been demonstrated earlier for shallow bound excitons in natural Si, but using a multimode laser source [17]. In the present apparatus, the laser oscillator is a diode-pumped Yb-doped fiber laser using distributed feedback (Koheras A/S, Birkerød, Denmark), which can be temperature tuned over the bound exciton absorption region. The $\sim 5\text{ mW}$ oscillator output, which has a sub-MHz linewidth, was amplified to $\sim 500\text{ mW}$ using a commercial Yb-doped fiber amplifier (Keopsys S.A., Lannion, France). The laser frequency was continuously monitored using a wave meter (Burleigh WA 1500, Exfo, Vanier, Canada) having an accuracy of one part in 10^7 . By aver-

aging 100 readings of the wave meter, a frequency reproducibility of $\pm 2\text{ MHz}$ at $\sim 278.2\text{ THz}$ (i.e., $< 10^{-8}$ in relative terms) was obtained.

The sample was mounted completely free in liquid He, so as to avoid any strains. The excitation laser beam illuminated the sample after passing through a $\sim 10\text{ nm}$ wide bandpass filter centered on the no-phonon bound exciton energy region. It should be emphasized that while the excitation power was high, only a tiny fraction of this is actually absorbed due to the very low oscillator strength of the bound exciton transitions in Si. The resulting bound exciton luminescence signal was passed through a double 0.75 m monochromator set to the TO-phonon replica luminescence energy, and was detected using a liquid nitrogen cooled InGaAs photovoltaic detector. The double monochromator acted only to reject the scattered laser light—its spectral resolution of $\sim 1\text{ meV}$ passed the luminescence of all the TO-replica bound exciton transitions (which are in any case unresolved due to phonon broadening).

In order to investigate the shift in the transition energies (and thus, as justified in the following section, the shift of the band gap) with temperature, the laser was locked onto the center of the strongest PLE component of the B bound exciton multiplet (corresponding to the PL line at $\sim 9280.95\text{ cm}^{-1}$ in Fig. 2 of Ref. [15]). This was done by a small modulation of the laser frequency, achieved by applying a sinusoidal modulation to the laser diode drive current, thus modulating the instantaneous fiber temperature, and, correspondingly, the laser frequency. The resulting small modulation of the PLE signal intensity was synchronously detected using a lock-in amplifier, generating a feedback signal, which changed the fiber laser temperature so as to keep the frequency centered exactly on the B bound exciton PLE line. The sample temperature was assumed to be identical to that of the liquid He bath in its immediate vicinity, which was monitored using a calibrated Ge resistance thermometer (Lakeshore GR-200A-100, Westerville, OH). It must be remembered that significant thermal gradients can exist in the liquid He above the lambda point. The He vapor pressure over the liquid He was also continuously monitored with a precision manometer, and controlled with a constant pressure regulator.

Since, as we shall see, the hydrostatic pressure at the sample position was an important parameter, the hydrostatic pressure resulting from the height of the liquid He above the sample is also significant. In order to keep this constant (the volume of liquid He is reduced by $\sim 50\%$ in pumping down from 4.2 to $\sim 1.3\text{ K}$), the measurements were performed as the He bath slowly warmed up, after an initial pump down to the lowest achievable temperature.

Results and discussion.—We begin by justifying the assumption that the shift in the shallow bound exciton transition energy accurately reflects the shift in the band gap energy, which is often made in measuring changes in

band gap with temperature, pressure, average isotopic composition, etc. While it is true that one would in principle expect some change of the exciton binding energy (measured relative to the band gap energy) as a function of temperature or other perturbations, to the best of our knowledge no such shift has ever been reported for shallow bound excitons in Si. In the hydrogenic approximation, such shifts in the exciton binding energy would come about from the temperature dependence of the dielectric constant and effective masses. Closely related to this, small shifts in boron acceptor and phosphorus donor binding energies have, indeed, been reported between ^{28}Si and ^{30}Si , but the size of these shifts relative to the impurity binding energies was equal to or less than the size of the band gap shift between ^{28}Si and ^{30}Si relative to the Si band gap energy [18]. Thus, ignoring a possible temperature dependence of the exciton binding energy in determining the change in band gap energy is expected to introduce an error of at most the ratio between the exciton binding energy (~ 20 meV) and the band gap energy (~ 1170 meV), or 2%.

The measured frequency of the strongest B bound exciton PLE transition as a function of temperature between 1.28 and 4.8 K, with the He vapor pressure in equilibrium with the liquid at each temperature, is shown in Fig. 1 as the solid circles. It is interesting to note that even these raw data are fitted remarkably well by a T^4 temperature dependence. However, the dominant component of the energy shift seen in Fig. 1 is not directly a temperature effect, but rather a hydrostatic pressure effect, since in covering the temperature range of Fig. 1 we are also changing the hydrostatic pressure acting on the sample by ~ 1.7 bars. From the known [19] value of the hydrostatic pressure shift of the Si indirect band gap at $T = 10$ K, -1.44 $\mu\text{eV}/\text{bar}$ (~ 348 MHz/bar), we see that most of the shift seen in Fig. 1 should result from this hydrostatic pressure effect. We have directly verified this hydrostatic pressure shift, by starting with the He liquid and vapor in equilibrium just above the lambda point, and then quickly increasing the He vapor pressure to the pressure corresponding to our highest temperature point. Before the liquid He can warm appreciably, the frequency of the transition quickly jumps to the point indicated by the open circle in Fig. 1 due to the change in hydrostatic pressure. Thus, ΔE_P represents the hydrostatic energy shift under these conditions, and ΔE_T represents the temperature-dependent shift between the temperature of the starting point of the pressure jump measurement and the highest temperature point. From this we obtain a hydrostatic shift of 368 ± 20 MHz/bar, in good agreement with the earlier value. Note that this hydrostatic pressure coefficient is not expected to have a strong temperature dependence, and even the room temperature value of 341 ± 15 MHz/bar [20] is the same with experimental error.

We use our observed value of the hydrostatic pressure coefficient, together with the measured He vapor pressure

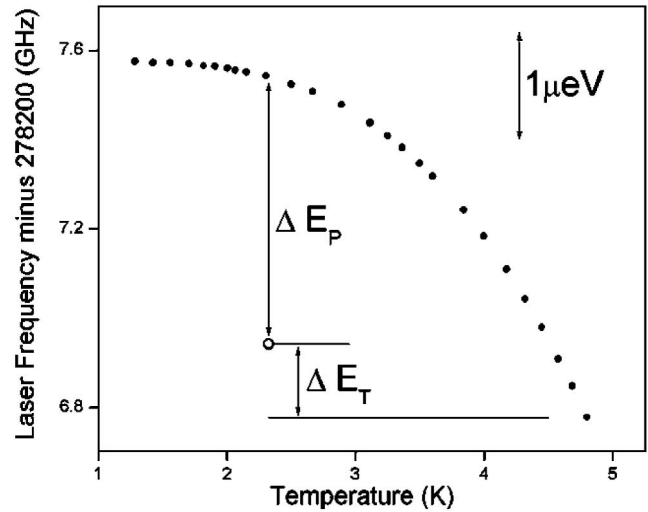


FIG. 1. The solid circles show the measured frequency of the strongest PLE component of the boron bound exciton non-phonon multiplet as a function of the He bath temperature near the sample, with the He vapor pressure in equilibrium with the liquid. Any sample heating above the bath temperature is expected to be negligible. The two vertical segments marked ΔE_P and ΔE_T , together with the open data point, refer to the pressure jump experiment described in the text. Here ΔE_P is the pressure induced change in frequency in going from $T = 2.32$ K, $P = 0.071$ bar to $T = 2.32$ K, $P = 1.684$ bars (the open data point), while ΔE_T is the temperature induced change in going from the latter point to $T = 4.80$ K, $P = 1.684$ bars. The vertical line in the upper right hand corner indicates $1 \mu\text{eV}$.

at each point, to subtract the hydrostatic contribution from the total energy shift, leaving only the temperature-dependent term (we note that using the slightly smaller previous values given above for the pressure correction results in no perceptible change in our results). These zero-pressure temperature-dependent band gap shifts were fitted to the form $E_T(T) = E(0) - AT^p$ using a non-linear least-squares fitting routine, with $E(0)$, A , and p as adjustable fit parameters. The value of the exponent p obtained from the fits was weakly dependent on the range of temperatures used for the fit. If only the nine lowest temperature data points were used, an exponent of 4.1 was obtained, while using the lowest 19 data points ($T < 4$ K) gave an exponent of 3.9 and using all 26 data points resulted in $p = 3.6$.

The results are best visualized in a log-log plot, as shown in Fig. 2, a plot of $\ln(\Delta E_T)$ vs $\ln(T)$, where $\Delta E_T = E(0) -$ measured $E_T(T)$, and the extrapolated ($T = 0$ and pressure = 0) energy of the transition, $E(0)$, is 278 207.5756 GHz. Below ~ 4 K, the data agree very well with the line having a slope of 4. Above 4 K, the data begin to show a decreasing exponent, with slope near 3.6 for the highest temperature points. The T^4 form predicted earlier is, of course, valid only in the low temperature limit, since it is well known that in the high temperature limit the band gap decreases linearly with

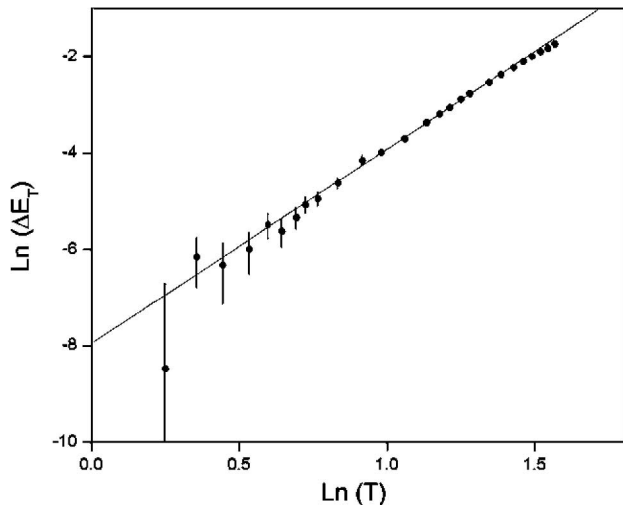


FIG. 2. The natural logarithm of ΔE_T , the temperature-dependent component of the observed shift in band gap energy (in GHz), calculated at zero pressure, relative to the asymptotic $T = 0$ value is plotted vs the natural logarithm of the temperature (in K). The straight line has a slope of exactly 4.

increasing temperature. Thus, Fig. 2 both demonstrates the predicted T^4 behavior at low temperatures and shows that the low temperature limit for this physical property of Si corresponds to $T \leq 4$ K.

The fit, and the data shown in Fig. 2, also provide us with a value for the prefactor A in the observed $E_g(T) = E(0) - AT^p$ behavior of the band gap in the low temperature limit, namely, $\sim 3.5 \times 10^{-4}$ GHz K $^{-4}$. Unfortunately, this prefactor is not as readily calculated as that in the T^3 Debye heat capacity in the $T \rightarrow 0$ limit, since the band gap renormalization integral over ω involves the square of the electron-phonon matrix element. Our asymptotic T^4 result comes from a simple argument that this matrix element should vary as ω in the limit of small ω . If one made the extreme assumption that the matrix element remained linear for all ω , then one could connect the prefactor A with the high temperature linear shift of the band gap with temperature, but this assumption cannot be justified. A proper calculation of the prefactor A would involve a detailed calculation of the matrix element as a function of ω (and branch), which is beyond the scope of this Letter.

Conclusions.—We have presented a simple and quite general argument showing that the electronic band gaps of semiconductors should vary as T^4 in the low temperature limit. We have experimentally demonstrated this behavior for the indirect band gap of Si, using the extremely narrow bound exciton transitions recently discovered [14,15] in isotopically pure Si, together with a new apparatus for performing PLE measurements with unprecedented precision. The same measurements also clearly show the hydrostatic pressure induced changes in the Si band gap due to remarkably small changes in ambient pressure.

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