**Thermal Equilibrium Properties**

Guess I’ll look at a few things. The first thing we need is the thermal occupancy of the bands,

**Thermal Occupancy**

So let’s consider again one of those band diagrams, say of Carbon.

Diagram

Description automatically generated

At T = 0, the valence bands are full, and the conduction bands are empty. For non-zero T, some electrons from the valence bands will begin to populate the conduction bands. We’d like to know how many, so that we can calculate the thermodynamic properties of our semiconductor. The band populations are governed by the chemical potential, μ, which, for a fixed number of electrons, is a function of temperature μ = μ(T). So we’d like to work out what μ is. Turns out, at T = 0, μ is directly half way in between the two bands, and increases as T goes up. But we’ll see that in a bit.

Diagram, engineering drawing

Description automatically generated

So let’s presume we have some density of states function ρv(ε) for the valence bands, and ρc(ε) for the conduction bands. We’ll recall we found in the Excitations file that these were, to the extent that we can approximate the energy spectra as ellipsoidal near the band extrema,



where ε0 = εc/v is the bottom/top of the conduction/valence bands respectively. Then the number of electrons in these bands ought to be:



(-∞ and +∞ are just shorthand for the lower and upper limits of those bands) Now of course,



Now we make a convenient approximation. We said that μ(T=0) starts off in the middle of the band gap, which sounds reasonable for now. And if so, then μ-εv and εc-μ are around 1eV, but the thermal energy kBT is around (1.38×10-23 J/K)(300K)/(1.6×10-19J/eV) ~ 10-21/10-19 eV = 0.03eV. Should highlight this,



So that means β(ε-μ) is large and positive or large and negative, and so we approximate,



(Taylor series on last one) Filling this into our occupation number equations, we have:



The first term is the number of spaces in the valence bands that can be filled. And so the second term is the number of holes in the valence bands. If we denote the number of holes as pv(T), then we can write:



As for the conduction bands, we have:



So altogether, we’ve got,



Note this formula, especially for nc(T), makes good sense if we just recall that the classical thermal occupation number of particles in the grand canonical ensemble is proportional to e-β(ε-μ). And then just treat the holes as having a kind of ‘negative temperature’. And can kind of treat the bands as flat levels with Nc(T) and Pv(T) degeneracies. If we can use the ellipsoidal density of states formula, then we can calculate the Nc, and Pv guys. For instance,



So we have,



Note if we have multiple minima/maxima in the band (as we saw we do in Si and C conduction bands), then we’d basically get Nc(T), Pc(T) for each one, and add them together to get the overall Nc(T), Pc(T). We can expect these formulas to be pretty good, even if the rest of the band beyond the extremum doesn’t have an ellipsoidal shape, since the Nc, Pv formulas contain eβε factor which damps contributions from higher/lower energies beyond the band extrema.

Now we can work out the chemical potential. We know that for any nonzero T, due to conservation of particle number, the number of electrons in the conduction band must be equal to the number of holes in the valence band. So we can say,



So we have:



and in the ellipsoidal band approximation, this comes to:



This confirms our earlier statement that at T = 0, μ lies midway between the bands. Moreover, since 1/β is on order of 0.01eV, as we saw up above, and the band gap is ~ eV, it would seem that μ will always be pretty far from the bands’ extrema. So,



And so this means that the thermal occupation numbers nc(T) and pv(T) will be pretty small. Now that we know the chemical potential, we can go back and get nc(T) and pv(T). But actually we’ll use a shortcut. Since we know that nc(T) = pv(T) (and we just spent a bunch of time working out the chemical potential which makes this so), we can say:



We’ll call the common value of nc(T) and pv(T) to be ni(T), the particle/hole density in the intrinsic semiconductor. So,



In the ellipsoidal approximation, we’ll have:



So,



To restore MKS units, looks like we need ℏ3 in the denominator. Moving on,

**Heat Capacity**

Now let’s take a look at the heat capacity of a semiconductor. We would expect the band gap to make the low T heat capacity much different than it is for the free electron gas. So we will need to know the energy expectation of our bands as a function of T. So we want,



As we saw, we can make the Boltzman approximation on these guys,



So can say,



We can add these together, and neglect the T-independent constant,



I guess I’ll fill in the ellipsoidal densities of states, to have something concrete.



Well,



So we can say,



Taking note that:



and using nc(T) = pv(T) = ni(T), this comes to:



So we can say,



And the heat capacity is c(T) = ∂ε(T)/∂T. And going to neglect 3/β in comparison to Eg. So filling in ni(T), and taking derivative,



Again can neglect 1/β in favor of Eg,



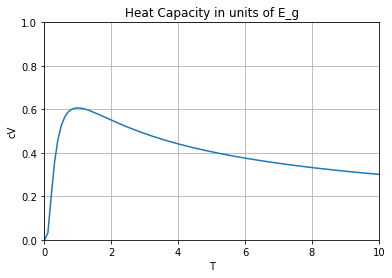
Again noting that in our approximation, we have:



we can write this as:



Shouldn’t worry about the 1/T2 as the exponentially damping afforded by e-Eg/kT will kill it, and make c(T) go to zero for small T, so the third law of thermodynamics is saved. Heat capacity looks something like this,



where the T is in units of Eg/kB. Also note that this formula won’t be true at extremely high temperatures, when μ becomes comparable to, and then exceeds εc.

**Example**

The heat capacity has a peak – a Schotky peak – characteristic of systems with large energy gaps that essentially make them two-state systems. Where is this peak?



Let’s differentiate the ln of cV(T) and find the peak of *it*, rather (of course it’s the same as the peak of cV(T)).



So we find,



Cool! Perhaps this is one way to calculate the band gap of a semiconductor. Of course this heat capacity contribution would be overlaid against all the others, so it might be hard to resolve the peak. Also, we kind of assumed kBT << Eg in our analyis, so this peak might be of dubious interest.

**Appendix**

It’s convenient to work out what Nc, Pv are at room temperature. To do that we have to restore the missing factor of ℏ in our formulas. So we need,



So in SI, these would read,



Well let’s compare to a standard value where **M**0 is a diagonal tensor of the electron mass, and T0 = 300K. Then,



So we find,



And Pc(**M**0,T0) would be the same. So then the intrinsic carrier density, at say T = 300K, and Eg = 1.12eV (that’s the band gap of Si), would be:



So Si has intrinsic carrier density,



And Si’s atomic density is around,



So we’ll note that this amounts to about 1 electron/1012 atoms. Cu has about the same atomic density, but has one carrier (electron) per atom. So can see the intrinsic carrier density of a metal vastly outweighs that of a semiconductor like Si.