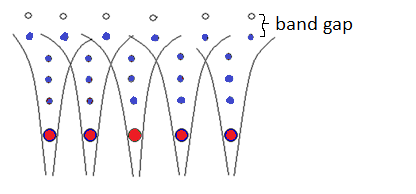
**Electron – Crystal Excitations**

Here’s the periodic table from before,

Table

Description automatically generated

So the basic story is...undoped semiconductors, like Ge say, would look like this.



They have a band gap. Now say we dope with As, which has one more valence electron than Ge. The additional valence electron will typically occupy an energy level (called the donor level) just below the main conduction band. And thus at relatively low T’s they will readily populate the conduction band. So these impurities are called n-type, because they donate negative charges to the conduction band.

Chart, diagram

Description automatically generated

Another possibility is to dope with impurities with fewer valence electrons, like Ga.

Chart, diagram

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Then the extra-valence level of the impurity will often take an energy level just above the valence of the main set of atoms (Ge in our example). This energy level is called the acceptor level. Then a Ge electron will/can jump into extra valence level of the impurity (when T > 0), creating a hole in the main valence band. Because this will create an effective (+) charge in the valence, these types of SC’s are called p-type. Let’s be a little more thorough. So let’s look at the band structure of Ge,

Diagram

Description automatically generated

The valence band is the fourth one up from the bottom, and the conduction band is the fifth one. We can see that Ge has a direct band gap at the center of the BZ (Γ).

**n-type semiconductors**

And let’s reconsider the n-type impurities, like As. In the leftward configuration, can see that As forms the covalent bonds that the other Ge’s want, but has one electron left over. The four valence electrons (as well as its inner core electrons) surrounding As do not quite cancel out As’s entire nuclear charge. There is one unmatched proton left over. And so we basically have a Ge crystal lattice structure with one leftover proton and one leftover electron (we’ll call this the donor electron). Thus As’s donor electron will feel the crystal potential plus the potential of As’s extra proton.

Chart, bubble chart

Description automatically generated

The eigenstate of this donor electron would basically just be a Hydrogen atom ground state, if the H atom were in free space. But the effective H atom is sitting in a crystal lattice with N Ge nuclei and equal/opposite negative charge of valence electrons roaming (somewhat) the lattice. So basically the Hilbert space out of which the H-atom could construct its ground state would be the conduction band and higher. Near the minimum, εc, the conduction band can be treated as a free band with renormalized mass, m\*. And so we would think that the GS of our donor electron would be (see Quantum Mechanics/Time-Independent/H-atom file for that formula for its ground state):



(where d stands for donor state, because it can donate electrons to the conduction band) But we also have to take account of the fact that other mobile electrons will screen the H nucleus’s force on the donor electron, reducing its potential V → V/εr, where εr = ε/ε0. I’m assuming this screening is coming from electrons partially populating the conduction band, or holes populating the valence band (this can happen only at higher T’s though) as filled bands cannot conduct and hence cannot screen? Anyway, so then we could write:



Apparently m\* ~ m/10, and εr ~ 10 as well. So the donor electron will sit below the conduction band by about 0.1eV perhaps. I’m going to draw pictures of different possible configurations. For the n-type impurities, we may represent the conduction band and donor levels just below. And then we have the crystal lattice with effective (+)proton, and (-)electron impurities.

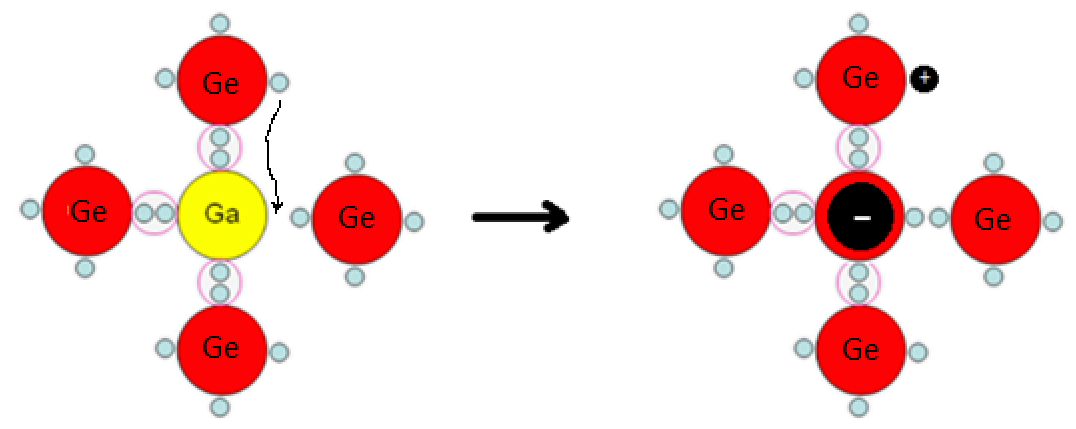
A picture containing chart

Description automatically generated

On the left, all the (-)electrons are bound to the (+)protons, and we can represent this bound state as comprising one electron (and one hole) filling the donor level. And the energy of this state is, we’re saying, E1 = 3εd. In the middle diagram we illustrate the possibility of having two electrons orbit a single proton, tantamount to putting two electrons in a donor level. Having two electrons orbiting the same proton, and therefore in such close proximity, would be prohibitively energetic, though; so the energy of this state would be quite high, and ruled out. But the energy of this state would be E2 = εd + ∞. And in the last diagram, we illustrate the possibiliy of two donor electrons being liberated into the conduction band (by absorbing some energy of course), leaving just one electron filling a donor level. The energy of this state would be E3 = 2εc + εd. And note this satisfies work-energy equation kind of thing as E3 – E1 = 2εc - 2εd = 2(εc-εd) = 2[13.6eV·m\*/mεr], which is twice the binding energy of two electrons. So remember the energy of the donor band, disregarding double occupancies, is obtained by multiplying the number of occupancies by εd.

**p-type semiconductors**

Now let’s reconsider the p-type impurities, like Ga. When Ga sits in Ge’s place, it can’t form all the covalent bonds that the Ge’s would like as it has one less valence electron than Ge. I think at this point (we can pretend that) one of the nearby valence electrons might drop down and fill the spot. This will make the Ga overall net negatively charged though, and it will also open up a hole in the Ge where the electron left. So we get something like this on the right.



So now we have a similar problem as before, just with signs reversed. And we’d like to work out the energy level of the hole (we’ll call it the acceptor hole) orbiting the ‘anti-proton’, within the crystal lattice. This is also a hydrogenic state, but comprised of free hole states, which would come from the valence band, as this is the first free band which can be populated with holes (hole energy increases as we go down – see Metals/Free Day/Electrons/Excitations/Properties of States file). The valence band can be approximated as a free band with an effective mass m\*, and there would be screening which would reduce the potential energy between the central electron and hole by factor of εr. So we could say the energy of this ‘acceptor’ state is:



So we expect the acceptor state to sit about 0.1eV above the valence band. Another way to see that it’s above the valence band is that if it were below the valence band, then an electron from the valence band would drop into the acceptor level immediately, creating a hole in the valence band, and allowing the valence band to conduct. But as it is, it requires energy (thermal or otherwise) to populate the acceptor bands. Basically it requires energy to liberate the hole from its bound state with the electron, and allow the hole to travel through the band. So the acceptor level must be above the valence band. We can draw a similar picture for the acceptor guys.

A picture containing diagram

Description automatically generated

On the left, all the (+)holes are bound to the (-)electrons (in the nucleus), and we can represent this bound state as comprising one hole (and one electron) filling the acceptor level. We can represent the energy of this state as E1 = 3εa. In the middle diagram we illustrate the possibility of having two holes orbit a single (-)electron, tantamount to putting two holes in an acceptor level. And we’ll note the rightmost (-)electron in the middle diagram has no holes orbiting it, which is tantamount to having captured two electrons (one electron in the nucleus, and another electron which has canceled out the hole that was orbitting it). But analogous to the corresponding donor diagram, having two holes orbit the same electron would be prohibitively energetic, due to the Coulomb repulsion between the holes, and so forbidden on energetic grounds. And we could represent the energy of this state as E2 = 3εa + ∞. In the last diagram, we illustrate the possibility of two acceptor holes being liberated down into the valence band (by absorbing some energy of course), leaving just one hole filling an acceptor level. Could alternately think of this as liberating two electrons from the valence band into the acceptor band. And we could write the energy of this state as: E3 = 5εa - 2εv. And this follows the work energy equation too because E3 – E1 = (5εa - 2εv) - 3εa = 2(εa – εv) = 2[13.6eV·m\*/mεr], which is, like last time, twice the binding energy of two electrons (or holes, depending on how you want to think of it). So remember that the energy of the acceptor band, disregarding double hole occupancies, is obtained by multiplying the number of electrons by εa.

One last remark: it seems if the valence band, w/o p-type impurities, comprised 2N electrons, that it must now comprise 2N-Np electrons, where Np is the number of p-type impurities. But if if we represented the valence band that way, then it would have to be conducting, due to holes in it? Or maybe the holes would be pinned within the lattice, due to fact that they’re bound? In any event, least the states that are defined via the diagram above can be put into a 1-1 correspondence with those diagrammatically defined at the top of the page (showing the atoms and the Coulomb potential wells, etc.), and the conductive properties of corresponding states is the same.

So for future reference, let’s remember,



**Appendix**

Trying to make more sense of working out the ground state of H atom in crystal lattice. Well w/o the crystal lattice, the ground state is roughly Gaussian in position space. So in momentum space eigenstate of H it would be the same:



If we put H atom in a really wide box, of width L0, it stands to reason that eigenstate would be:



since if L0 is large enough, the atom shouldn’t notice its confinement. But then say we adiabatically decrease L0 to L. Then what should the ψ(n) be. It would seem that its projection onto the nth state shouldn’t change as L is varied. And that we should have:



So maybe that’s As in a box. And one would imagine we could do the same thing for As in a finite potential well. So basically we just form the unconfined H ground state in terms of the free |k> states. And then we replace with periodic states|k(L0)> in a very wide box. And then we can replace these with smaller box states |k(L)>. Another way to say it,



And so the same kind of thing happens for our H in the lattice. In this case our free |k(L0)> adiabatically turn into |k(L)> of the crystall lattice (in the first free band, which is the conduction band – that part needs more explanation).