Hemachander Subramanian
Department of Physics
NIT DGP

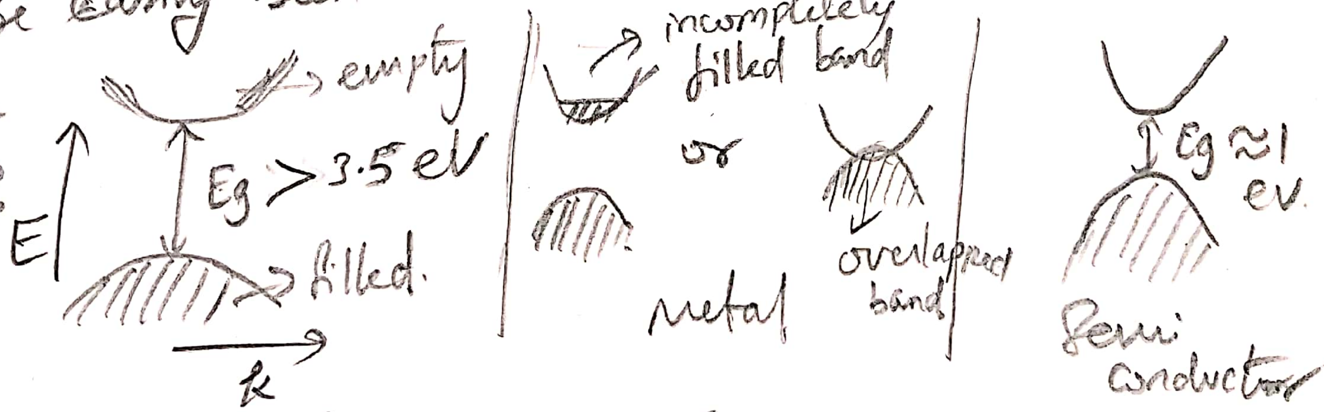
(A) A point particle is described by its position, whereas a wave is described by its wavelength. Since electrons in atoms are considered as waves, we use wavelength λ or equivalently its wave vector $k = \frac{2\pi}{\lambda}$ to describe electrons.

a.k.a momentum

Each electron in a material has a specific wave vector $\vec{k}$ & correspondingly a specific energy E. A plot of $E(\vec{k})$ as a function of $\vec{k}$ is called the band diagram or band structure of the material.

Band diagrams are extremely important in the study of materials. For example, the distinction between metals, insulators & semiconductors can be easily seen in their respective band structures.

Temperature T=0 :



As we raise the temperature of the material, e's would gain energy and move to higher energy states. In insulators there are no higher energy states available within thermal energy range.

So electrons stay in the valence band and the material does not respond (at least electronically) to raising temperature.

In metals, there are available states immediately above the states that are occupied at $T=0$. Any raise in temperature of metals boost the electrons into these unoccupied states, imparting them with energy (kinetic). Thus, these $\bar{e}$'s conduct the thermal energy / electrical energy, because of the availability of electronic states for electrons to move into.

In semiconductors, at $T=0$, the valence band is fully occupied and conduction band is empty. But as we raise the temperature, the electrons gain thermal energy and can actually move into the conduction band because conduction band states are "close-by", within about 1 eV, which is of the order of thermal energy. The number of electrons in the conduction band becomes a function of temperature, because electrons with energy E_v (top of valence band) need temperature to jump to states with energy E_c (bottom of the conduction band).

Due to the presence of the energy gap, the number of e's in the conduction band raises exponentially with temperature:

ie $n \propto e^{-E_g/k_BT}$.

This fact underlies the sensitivity of semiconductors to external perturbations (electrical, thermal, light, chemical etc). This sensitivity, in turn, makes them useful as sensors of various kinds and as amplifiers of small signals.

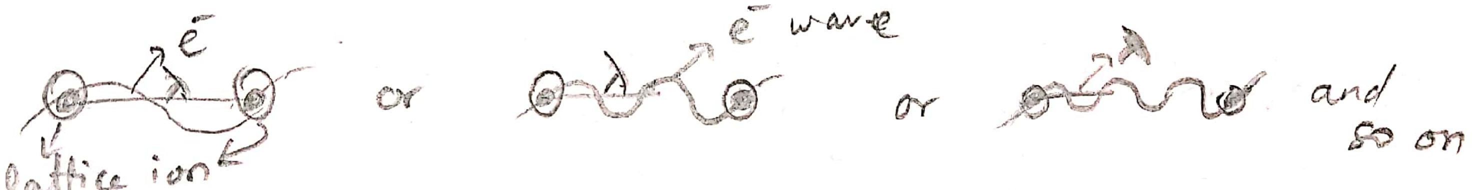
Remember that we demonstrated the sensitivity using the band-diagram of the semi-conductors, without which we could not have understood their properties.

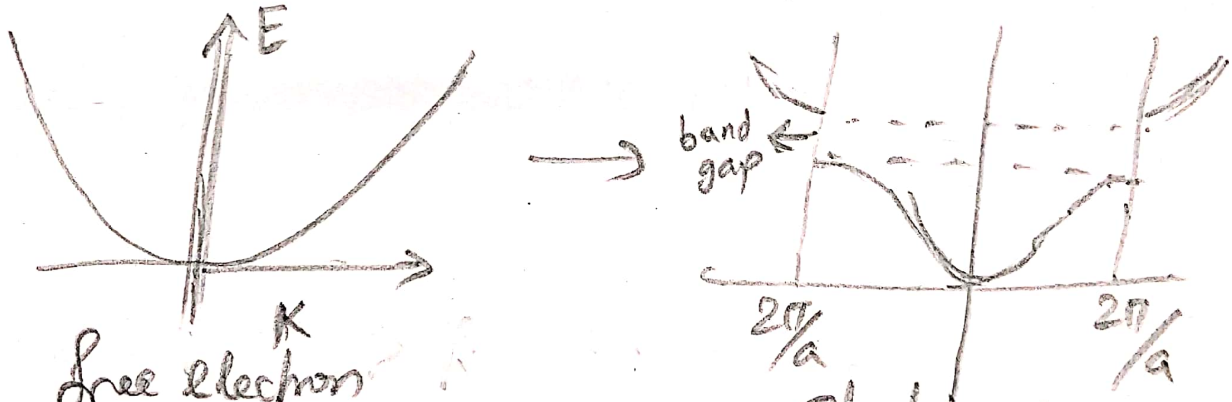
This is also the reason for negative coefficient of resistance — decrease in resistance with increase in temperature — unlike metals. As temperature increases, # of electrons increase, thereby increasing conductivity. At T=0, semiconductors behave like insulators.

Hemachander Subramanian
Department of Physics
NIT DGP

Physical meaning of Band-diagram:

As mentioned before, band diagram is a plot of energy of electrons that have a wave length of λ & $K = \frac{2\pi}{\lambda}$ in a periodic lattice. The periodic lattice perturbs the energy $E = \frac{\hbar^2 K^2}{2m}$ of free electrons, distorting the parabola significantly whenever the wavelength λ (or $K = \frac{2\pi}{\lambda}$) is equal to 'a' (lattice constant) or $a/2$, $a/3$, $a/4$, ... That is, whenever

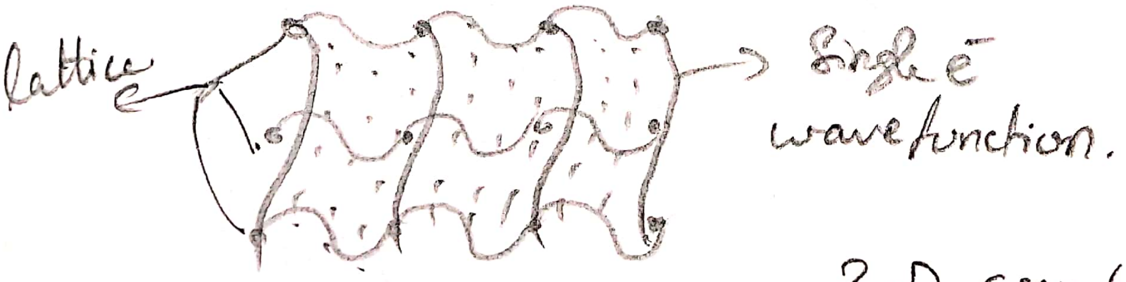




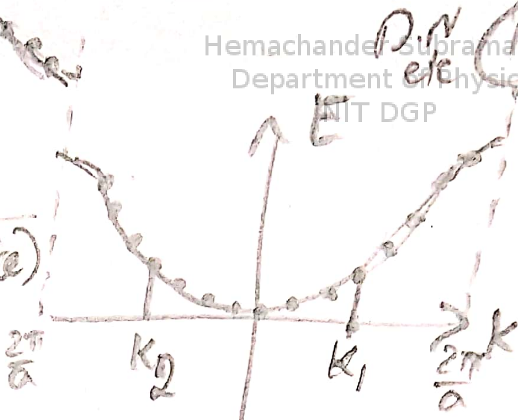
free electron band diagram

Electron in a 1-D periodic potential.

If the lattice constant is b in the y-direction, we will have a similar plot for the y direction as well.



2-D crystal

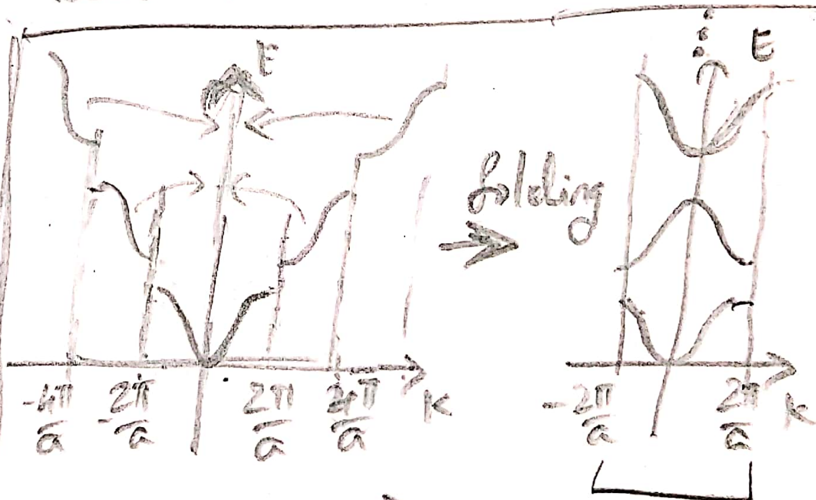


Every dot in this diagram corresponds to an electron (or, state) in the crystal. The $\bar{e}$ marked at K_1 has a wavelength of $\frac{2\pi}{K_1}$, and because K_1 is +ve, is traveling to the right in the crystal. Similarly, the $\bar{e}$ denoted by the point K_2 has a wavelength of $\frac{2\pi}{K_2}$ and is traveling left.

Thus, every point in the E-K band diagram corresponds to an $\bar{e}$, whose energy is given by its position along y-axis. [This is not precise, but helps in understanding]

In the case of Silicon or GaAs, the band diagram would look like follows:

These dots correspond to possible electrons in other zones with higher K that got mapped back to the first Brillouin zone. That's why they have higher energies.



Extended zone scheme

First Brillouin zone

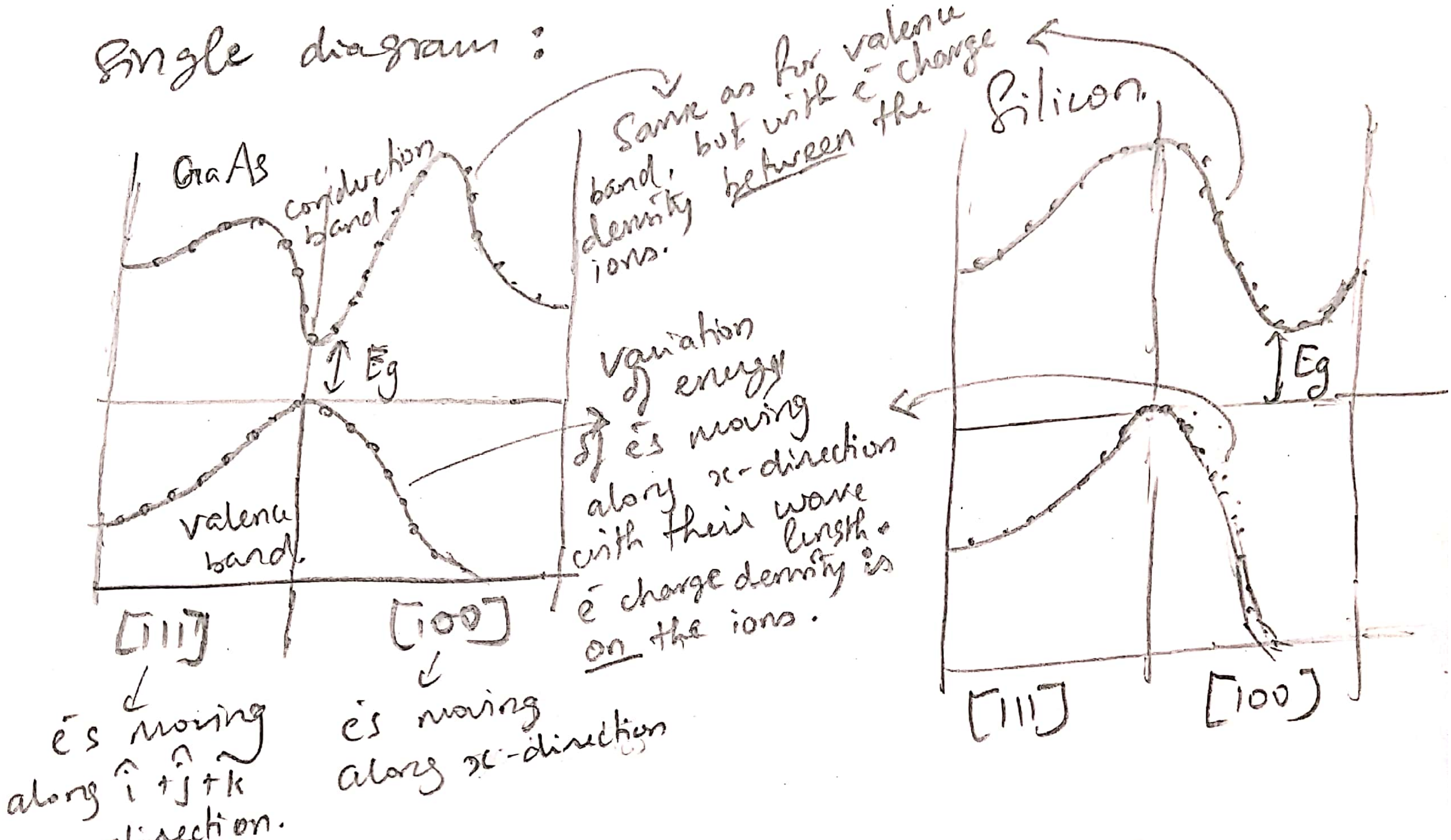
reduced zone scheme

In 1-D, the E-k band diagram is a curve. In 2-D, it is a surface. In 3-D, it becomes a volume. Visualizing such volumes (the band structures) of various materials is a career path for many a physicist! That's how important these diagrams are, in understanding material behavior.

These volumes of band structures encompass information about the energy of electrons moving in all possible directions, denoted by the vectors $\vec{k} = k_x\hat{i} + k_y\hat{j} + k_z\hat{k}$. For every $\vec{k}$ vector, there is an electron with energy $E(\vec{k})$.

If we want to look at the energy of electrons moving in a specific direction in a crystal, say [111], then we look at the energy for $\vec{k} = k_0(\hat{i}+\hat{j}+\hat{k})$ and plot E vs k_0. For [100] direction, the $\vec{k}$ vectors will be $\vec{k} = k_x\hat{i}$ and the band diagram will be E vs k_x, and so on.

It is customary to combine the E vs $\vec{k}$ diagrams along various directions into a single diagram:



In GaAs, the e's at the top of the valence band need not change their momentum ($\hbar\vec{k}$) to move to conduction band states — <u>Direct Band Gap</u>.

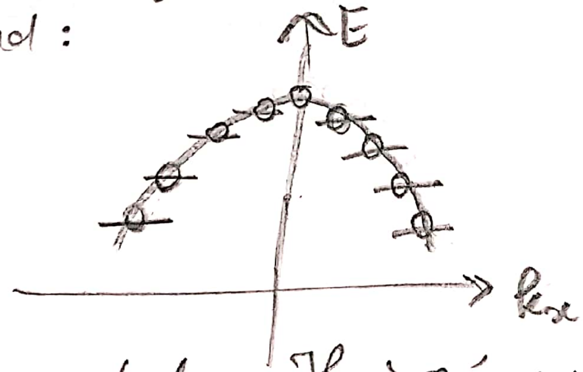
In Silicon, the e's need to lose/gain momentum to move from/to conduction band — <u>Indirect Band Gap</u>. For indirect band gap materials, the momentum needs to be conserved during transitions between valence & conduction bands. This lost/gained $\bar{e}$ momentum usually comes from the crystal lattice.

The concept of holes :-

About 100 years ago, when people measured the Hall coefficient of various semi-conductors they found that, sometimes, the sign of charge carriers were +ve. But ē's have a -ve sign. Before Quantum Mechanics & the idea of band structures were discovered, the "+ve charge carrier" problem remained unsolved.

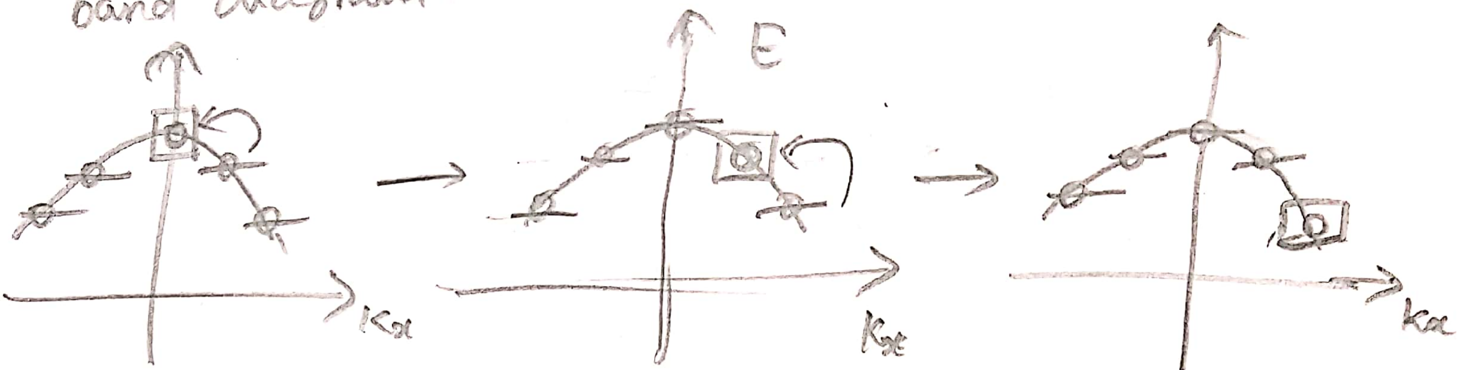
How do -vely charged ē's behave like +vely charged particles? Read on.

Holes reside in the valence band. Imagine electrons occupying the "dots" [states] on the valence band:



The dots marked with '$\ominus$' are occupied by ē's and the dot on the top 'o' is unoccupied. The ē there moved to the conduction band. Let us now apply an electric field $\vec{E}$ along the '+x' axis. In real space, ē's will move towards '-x' direction which means they will have a velocity along '-x' direction.

The e^-s will move towards '$-k_x$' direction in the band diagram.



As you can see, the unoccupied orbital/state moves towards '$+k_x$' direction, behaving as if it has a '+ve' charge. Instead of describing the jumping of multiple e^-s from different states, we can just describe the vaccancy as a particle itself.

As you know, an e^- moving in an electric field gains kinetic energy and its velocity increases..

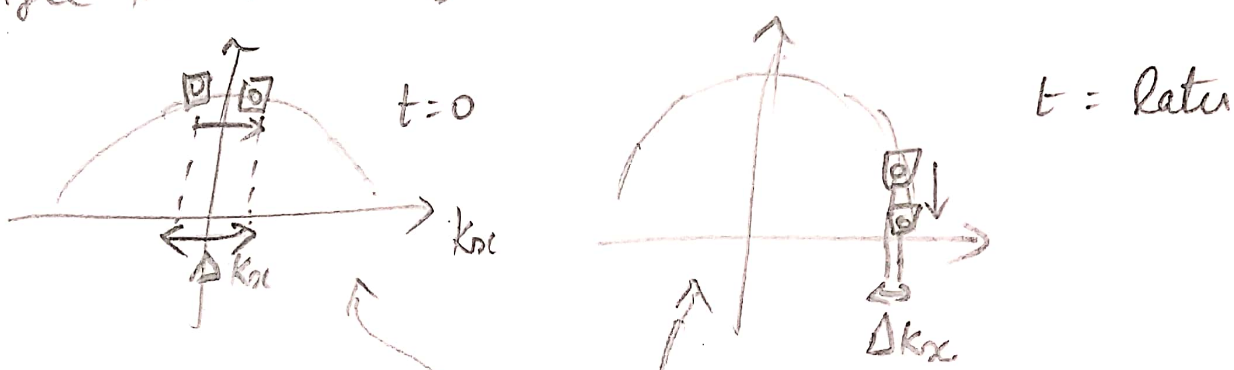
What is happening to the energy of the unoccupied state as it moves towards '$+k_x$' direction?

It's total energy decreases!

How is that possible? where is the energy imparted by the electric field going?

To the lattice.//

If you look at the graph carefully, you will see the following:



As the 'hole' moves, its "momentum" $\hbar k_x$ changes maximally initially but as it moves further along the $+k_x$ direction, the momentum does not change as much. That is, the rate of change of momentum decreases. It is as if the total force on the hole $\left[F = \frac{dp}{dt}\right]$ is decreasing and the hole is decelerating.

Is this picture correct? NO!

The k_x used in the band diagram is not the total momentum of an e^-! It is just an index. The e^- is a mixture of plane wave e^{ikx} with other reflected plane waves with higher & lower momenta. That is why k_x or $\vec{k}$ in the band diagram is called "<u>crystal momentum</u>".

The difference in behavior of e^-s & holes in an electric field [acceleration vs deceleration] differentiates them.

Holes are not just "lack" of electrons. Their behavior is entirely different from that of e^-s. And this arises directly from the band structure. There really are two "species" of carriers in semiconductors.

All of this intuitive picture can be neatly encapsulated in a few lines of mathematics:

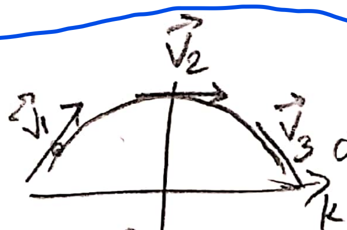
We know, for free electrons,

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m} \quad \therefore \quad \frac{dE}{dk} = \frac{\hbar^2}{m} \cdot k$$

$$\frac{dE}{dk} = \frac{\hbar}{m} \cdot \hbar k = \frac{\hbar}{m} \cdot p = \hbar \cdot v(\vec{k})$$

$\therefore$ velocity of the free e^- is

$$\boxed{\vec{V}(\vec{k}) = \frac{1}{\hbar} \cdot \frac{dE}{d\vec{k}}}$$

In the 

diagram, as the hole moves from left to right in an electric field, its velocity is +ve initially $(\vec{V}_1)$, becomes zero $(\vec{V}_2)$ and then becomes −ve $(\vec{V}_3)$!

It is as if the hole is decelerating. (accelerating in the opp. direction) etc.
This is because the crystal field is repelling the hole more than the electric field is driving the hole. This reduces the effective force on the hole and actually reverses the effective force! This makes it decelerate.

Effective mass of hole:

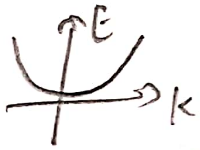
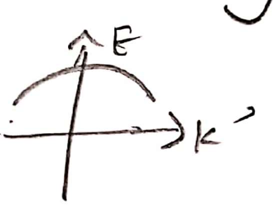
This "negative acceleration" phenomenon is captured in the variable called "effective mass" of hole. As you know, the mass of the object determines how much it accelerates under a given force. If the hole is accelerating in the opposite direction, it means $F = (-m) \cdot a$. This implies that holes have a negative mass! What physicists do is to take this -ve sign on 'm' and add it to the $F = -eE$, making $F = +eE$ and say that the "charge" is positive.

Again, mathematically, this becomes a few lines of derivation:

We start with the free electron case and generalize it to e^-s in a periodic potential.

$$\underbrace{E(\vec{k}) = \frac{\hbar^2 k^2}{2m}}_{\substack{\Downarrow \\ \text{free } e^- \text{ equation.} \\ \text{does not apply to solids.}}} \Rightarrow \frac{d^2E}{dk^2} = \frac{\hbar^2}{m}.$$

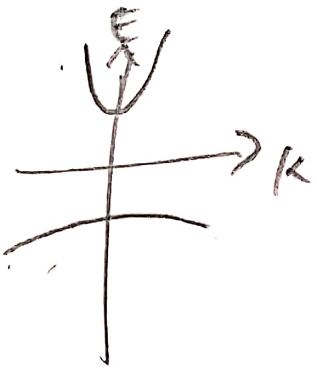
Or, $\boxed{\frac{1}{m_{eff}} = \frac{1}{\hbar^2}\frac{d^2E(\vec{k})}{dk^2}}$ → This $E(\vec{k})$ does not have to be $\frac{\hbar^2 k^2}{2m}$. It can be any function! Generalization.

For an E vs $\vec{k}$ curve that is a parabola, like , $\frac{d^2E(\vec{k})}{dk^2}$ is +ve [slope increases as $\vec{k}$ increases]. But for a E vs $\vec{k}$ curve like , the quantity $\frac{d^2E}{dk^2}$ is −ve [slope decreases with increasing $\vec{k}$]. This quantity $\frac{d^2E}{dk^2}$ measures the "curvature" of the curve, how curved it is. Thus, from the above equation, we see that the effective mass "meff" is −ve. This is precisely because the hole undergoes "negative acceleration" with an external force.

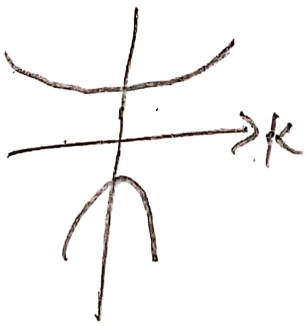
The quantity called "effective mass" tells us how holes behave in an external force – how much and in which direction they accelerate.

A curve of E vs $\vec{k}$ like  has high -ve curvature than  and hence, the holes in the former curve have lower (-ve) effective mass – which implies that small forces are enough to accelerate (in the opposite direction as that of $\bar{e}$s) the holes to higher velocities.

In general, the curvature of conduction and valence bands need not be the same. It can be



or



Thus the two species of carriers can have different effective masses and will react differently to the external applied force.