Hall effect in Bismuth

Table 5.1 illustrates the curious Hall effect in Bismuth: If we make the apparently reasonable assumption that every Bi atom contributes to the metallic state with 5 valence electrons, the Hall constant $R_H = -1/(ne)$ is several orders of magnitude higher than expected. A possible explanation for this could be that the electron concentration n is for some reason much lower and this is also the case. This note explains this in more detail and it also gives a good illustration of the electron counting arguments that we have used in the text in order to determine if a solid is a metal or a semiconductor.

Bi atoms have 5 valence electrons, two s electrons and 3 p electrons. The bulk crystal structure of Bi is a bit complicated but for us the only important thing is that there are two atoms per unit cell. This makes 10 electrons per unit cell. Since this is an even number, Bi could technically be a semiconductor but we need to keep in mind that having an even number of valence electrons per unit cell is only a necessary criterion for having a semiconductor. It is not sufficient. In the case of Bi, we have an electronic situation that is very close to being a semiconductor - but not quite.

This is illustrate in Figure 1(a) which shows the band structure of Bi. The two lowest bands can be viewed as s-derived. The are well separated from the higher p-type bands and fully occupied by the 4 s electrons in the unit cell. this leaves 6 p electrons which could exactly fill three more bands. A superficial look on the band structure appears to confirm this. When zooming in as schematically done in Figure 1(b), however, we see that the upper "valence band" crosses the Fermi energy the T point of the Brillouin zone whereas the lowest "conduction band" drops below the Fermi energy at the L point. The valence band is thus almost completely filled apart from a very small concentration of holes and the conduction band is completely empty apart from a very small concentration of electrons. The total electron and hole concentration must the the same, of course, so that the Bi remains charge neutral. An impressive illustration of the small carrier concentration is shown in density of states shown Figure 1(c). At first glance the density of states appears to go to zero near the Fermi energy such that a gap is formed. But this is so only superficially. The density of states does not actually go to zero. It is just very small.

The effect on the Hall constant can now be seen qualitatively from the expression for the Hall effect in the presence of both holes and electrons (see Problem 7.6)

$$R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(p\mu_h + n\mu_e)^2}. \tag{1}$$

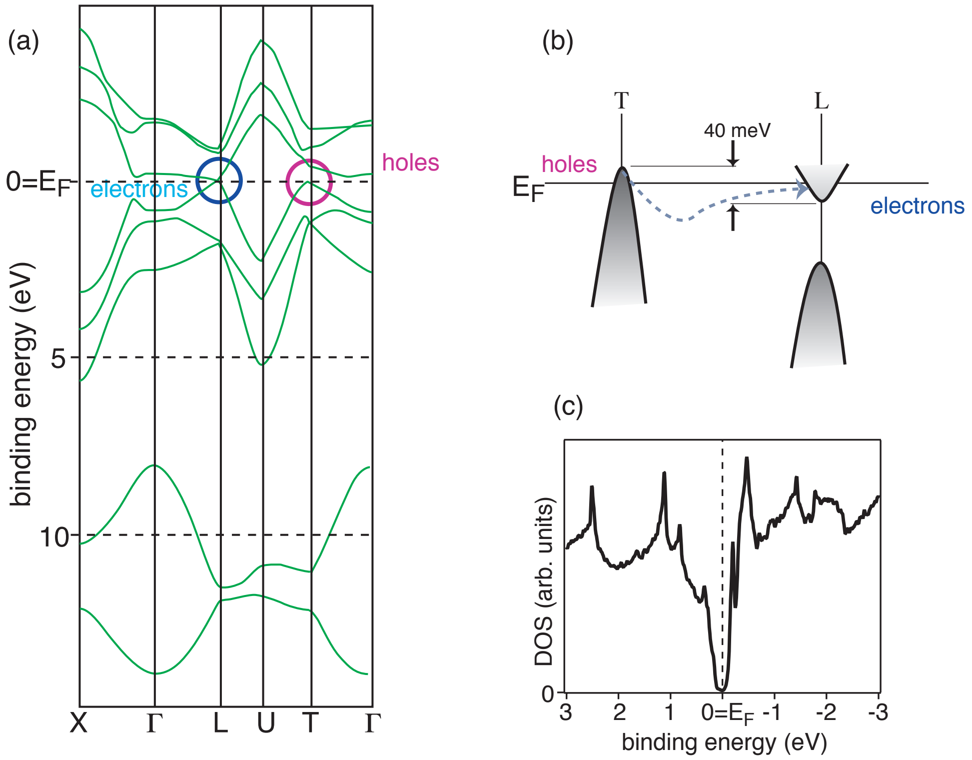

Figure 1: Electronic structure of Bismuth. (a) Bulk band dispersion in different directions of the Brillouin zone (b) Schematic band structure of the bands crossing the Fermi energy. (c) Density of states.

Here we simplify this by assuming that $n = p$ so that

$$R_H = \frac{\mu_h^2 - \mu_e^2}{en(\mu_h + \mu_e)^2}. \tag{2}$$

This expression does not only contain the electron (or hole) concentration but also the mobilities. In any event, both n and p are very small such that the denominator is small, too, giving rise to a high R_H. This effect would, however, disappear for equal electron and hole mobilities because this would lead to a vanishing numerator.