Level 2 lab manual:

Using the Hall Effect to Investigate Electrical Transport in a Doped Semiconductor

Summary of measurements and analysis

1.1: Calibration – determining background voltage in zero applied magnetic field.
Plot: voltage against current in zero magnetic field
Analysis: determine background correction for Hall Voltage measurements

1.2: Determining hole carrier mobility through Hall Effect measurements as a function of current and constant magnetic field
Plots: Hall voltage versus current for three different fixed values of magnetic field strength
Analysis: Make plots of drift velocity versus current using the measured data. Determine the carrier mobility μ for the p-doped germanium in either units of $cm^2 V^{-1} s^{-1}$ or $m^2 V^{-1} s^{-1}$.

1.3: Determining the density of hole carriers by Hall Voltage measurements as a function of magnetic field and constant current
Plots: Hall voltage versus magnetic field for three different fixed values of current
Analysis: determine charged carrier density n (number of holes per unit volume) in p-doped germanium in units of cm^{-3} or m^{-3}. Present values of carrier density for intrinsic germanium and for a typical metal. Estimate the percentage (by number of atoms) of p-type dopant.

1.4: Observing the transition from extrinsic to intrinsic conduction in p-type doped Ge
Plot: Hall voltage versus temperature for p-type doped Ge
Analysis: Determine the temperature where there is a transition from extrinsic to intrinsic semiconducting behaviour.

1.5: Determining the band gap of Ge (60 min) by measurements of conductivity in the high-temperature intrinsic regime
Plot: Conductivity of p-type doped germanium as a function of temperature
Analysis: Determine the intrinsic band gap of Ge using the conductivity measurements in the high-temperature intrinsic region identified in Experiment 2.1.

Glossary of terms

J – current density (A/m^2)

I – current (A)

A – cross sectional area through which current flows (m^2)

q – carrier charge (C)

σ – electrical conductivity ($\Omega^{-1}m^{-1}$)

ρ – electrical resistivity (Ωm)

R – electrical resistance (Ω)

v_d = drift velocity of free carriers (m/s)

μ – carrier mobility ($cm^2V^{-1}s^{-1}$ or $m^2V^{-1}s^{-1}$). Subscripted e or h for electrons and holes respectively).

ε – applied electric field (V/m). Note that the symbol, E, is used to denote energy in this manual.

$D(E)$ – Density of energy states per unit volume ($eV^{-1}m^{-3}$)

$f(E)$ – Fermi Dirac distribution function (unitless)

E_F – Fermi level (eV)

ΔE_g – energy band gap between valence and conduction band (eV)

n –number of free carriers per unit volume, known as 'carrier concentration' or 'carrier density' (cm^{-3} or m^{-3})

n_e – total number of free electrons per unit volume (cm^{-3} or m^{-3})

n_h - total number of free holes per unit volume (cm^{-3} or m^{-3})

n_i – number of thermally generated electrons or holes per unit volume ($n_i = n_e = n_h$ in intrinsic semiconductor)

N_A – the number of acceptor dopant atoms per unit volume (m^{-3})

$\underline{B}$ – applied magnetic flux density (T)

$\underline{F_B} = q\left(\underline{v_d} \times \underline{B}\right)$ - Lorentz force due to magnetic field acting on a moving charge carrier

V_H – the Hall voltage developed due to applied magnetic field (V)

R_H – the Hall coefficient, $R_H = n^{-1}q^{-1}$ ($m^{-3}C^{-1}$)

d, w – geometric lengths of germanium slab used in experiment (mm)

V_{drop} – voltage supplied to drive current I across germanium slab (V)

U_{A1}, U_{B1}– voltage inputs on the Cassy sensor

I_{A1} – current input on the Cassy sensor

Purpose of the experiment

Historically, in the early 1800s, it was recognised that resistance and conductance were physically measurable quantities that could be obtained from simple measurements of current and voltage. However, the fact that different sized samples gave different resistances led to the understanding that there must be an underlying material property that is independent of geometry and related to the current-carrying capabilities of the sample i.e. the resistivity (or conductivity). Following this, at the turn of the 20th century, classical models were developed to try and explain the physical processes underpinning electrical transport in solids for the first time. However, it was only with the development of quantum mechanics that a holistic description of transport in insulators, semiconductors and metals could be developed to a satisfactory degree. This approach involves the use of 'carrier density' and 'carrier mobility' as key physical parameters for describing electrical transport properties.

The purpose of this experiment is to appreciate the key role that electronic energy band structure has in determining the electrical transport properties of semiconducting materials and the roles played by carrier density and mobility in conductivity measurements. Applied magnetic fields will be used to quantify transport properties in a doped semiconductor via the Hall Effect (Edwin Hall, 1879). Historically, the Hall Effect is important in that it was used to demonstrate experimentally the existence of positively charged hole based conduction, not explainable by classical theories. In semiconductor industry, the Hall Effect proved to be a vital tool for quantifying carrier mobilities and densities, which are critical functional characteristics for semiconductor devices such as the modern electronic transistor (Shockley, Bardeen & Brattain, Nobel Prize 1956). Today's experiments will involve measurements of carrier mobilities and densities in p-type doped germanium as well as investigating the impact of carrier statistics on electrical transport at elevated temperatures.

Introduction

When an electric field is applied to a crystalline solid a current may flow, i.e. a movement of charge through unit area per unit time. The current density J passing through an area A can be expressed as:

$$J = I/A = qnv_d,$$

Where: q is the carrier charge, n is the number of charge carriers per unit volume, called 'carrier density' or 'concentration', and v_d is the 'drift velocity', the average velocity the charge carriers move with under the influence of the applied field. Any further progress requires some physical theory of scattering. A useful model results from the simple assumption that the scattering randomizes the electron's velocity and acts as a frictional force acting opposite to the motion. A semiclassical analysis gives a drift velocity that is proportional to ε:

$$|v_d| = \mu|\varepsilon|,$$

where the constant of proportionality, μ, is the carrier 'mobility' and is a measure of how quickly a charge carrier moves under an applied field. Note that n and μ are expected to have some form of temperature dependence. The current density J can then be expressed (with temperature dependencies highlighted):

$$J(T) = qn(T)\mu(T)\varepsilon = \sigma(T)\varepsilon,$$

This is a restatement of Ohm's Law with the proportionality constant σ being the temperature-dependent electrical conductivity (units $\Omega^{-1}m^{-1}$). The resistivity $\rho(T)$ is defined simply as the inverse of the conductivity and has units of Ωm.

Take a moment to acknowledge that, when a voltage is applied to a material, the size of the current that flows is determined not only by the number of charge carriers per unit volume but also their how fast they can move under the applied field (i.e. their mobility). Critically, the quantities $n(T)$ and $\mu(T)$ can vary strongly from one material to the next and this accounts for the broad variation of electrical transport behaviour seen in crystalline solids. The origin of electrical resistance is fundamentally due to electron scattering and this is captured in the behaviour of $\mu(T)$ which necessarily requires a theory for scattering of free carriers (e.g. by thermally vibrating ions, impurities). Predictive theories for the values of $n(T)$ require a quantum mechanical theory of electronic band structure and the use of thermal statistics.

In elemental metals, the temperature variation of $n(T)$ is negligible and, over a broad range of temperature, the temperature dependence of mobility $\mu(T)$ due to electron scattering by thermal vibrations primarily determines electrical conductivity as a function of temperature.

By contrast, in <u>pure</u> ('inrinsic') semiconductors, the magnitude of conductivity is largely determined by the temperature dependence of the carrier density $n(T)$ (the number of carriers per unit volume available to contribute to conduction). To appreciate why this is the case requires development of the quantum mechanically derived energy band structure combined with the thermodynamics of how electrons fill quantum states according to Fermi-Dirac statistics (see background information).

Some relevant background theory and explanatory figures is included at the end of this document and it is worth reading through it to become familiar with some of the main ideas.

Temperature dependence of electrical conductivity in an intrinsic (i.e. elementally pure) semiconductor

In all solids, electron scattering processes from impurities and lattice vibrations will affect the mobility μ and thereby contribute to some degree to the measured resistivity. However, the defining difference between metals and semiconductors is the creation of free carriers in the latter through pair-production as temperature is increased. Noting that the magnitude of electrical conductivity also depends on the carrier density $n(T)$, it turns out that this strong (exponential) dependence of free carrier density on temperature is the key determining factor for conductivity in elemental semiconducting materials. In elemental metals, $n(T)$ does not vary much with temperature (no pair production mechanism) and the temperature dependence of resistivity is determined by that of the carrier mobility.

To estimate the total density of free carriers at a given temperature in an intrinsic semiconductor, it is necessary to integrate the product of the density of states function $D(E)$ and the Fermi-Dirac function $f(E)$ over the energy interval occupied by electrons in the partially-filled conduction band:

$$n(T) = \int D(E)f(E)dE$$

At sufficiently high temperatures, in the "classical limit", the Fermi-Dirac function approximates as the Maxwell-Boltzmann distribution:

$$f(E) = \frac{1}{1 + e^{\left(\frac{E-E_F}{k_B T}\right)}} \approx \frac{1}{e^{\left(\frac{E-E_F}{k_B T}\right)}},$$

Where E is electron energy, E_F is the Fermi level, k_B is the Boltzmann constant. Assuming a parabolic shaped conduction band ($E \propto k^2$) for estimating the density of states, and after some working out, the integral for $n(T)$ gives an expression for the number of electrons/holes as:

$$n_i(T) = N_{eff} e^{\left(-\frac{\Delta E_g}{2k_B T}\right)},$$

where N_{eff} is approximated as a material dependent constant known as the 'effective density of states'. For a given temperature, there are both n_i electrons and n_i holes (i.e. $n_i = n_e = n_h$). Note that the number of intrinsic carriers per unit volume depends <u>exponentially</u> on both the size of the energy band gap ΔE_g and on the temperature T. Importantly, the carrier density increases exponentially as temperature is increased, a consequence of the thermal distribution assumed. The same number of holes will be left behind in the lower energy band where the electrons originated, and these will also contribute to current flow independently.

The conductivity of a semiconductor is given by the sum of the electronic and hole contributions:
$$\sigma(T) = e n_e(T) \mu_e(T) + e n_h(T) \mu_h(T) = 2 e n_i(T)(\mu_e(T) + \mu_h(T)).$$

If the temperature variation of the mobility is approximated as constant, we therefore find that:
$$\sigma(T) \propto e^{\left(-\frac{\Delta E_g}{2k_B T}\right)},$$

i.e. the conductivity is expected to increase exponentially as temperature is increased in a semiconductor.

This leads to an expectation that the measured semiconductor resistance $R(T)$ will decrease exponentially with increasing temperature:

$$R(T) = A e^{\left(\frac{\Delta E_g}{2k_B T}\right)},$$

where A is a weakly temperature dependent pre-factor that can be assumed to be constant.

Semiconductor doping

In pure elemental semiconductors, the thermal generation of electron-hole pairs with increasing temperature leads to an exponential decrease in resistivity as temperature is increased, due to the increased number of free carriers available to conduct electricity. In this 'intrinsic' mechanism of charged carrier generation, thermally excited bonding electrons become delocalised and leave behind positively charged vacancies in the bonding structure (electron 'holes'). Both carriers can contribute independently to conduction and they are always equal in number in a pure semiconductor. However, the transport properties of semiconductors can be radically altered through 'doping', whereby various amounts of impurities are introduced into the semiconductor crystal that have a different valence than the host. In this case, a small percentage of atoms in the germanium crystal lattice are replaced with a carefully selected impurity species, such as e.g., arsenic as shown in Figure 1a. Ge atoms share four bonding electrons with nearest neighbour atoms, whereas in arsenic, atoms typically share five. Arsenic atoms substituted into a germanium lattice are forced to contribute four electrons for crystal bonding but therefore have one electron left over that remains only loosely bound. The energy of this electron is ~ 0.01 eV below the conduction band (Figure 2a) and easily receives that amount of energy from random thermal motions of the ions and is promoted into the conduction band to become a free carrier (compared to thermally produced electron-hole pairs which require an energy input comparable to the width of the band-gap). The impurity in this case is known as a *donor* because it can give up (i.e. donate) a negative carrier to the

crystal. A crystal of germanium grown from melt which has a very small amount of arsenic added will have arsenic atoms distributed evenly throughout the crystal and have a certain density of negative carriers built-in as a result. The germanium is then said to be 'doped'. At room temperature, all of the donor sites will be ionised (i.e. all donor electrons available for conduction) and the transport properties will be determined by the dopant species carrier type i.e. n-type in this case. In this regime of conduction the germanium is described as an *extrinsic semiconductor*.

On the other hand, it is also possible to dope the germanium crystal with an impurity that only has three outer electrons available for bonding, such as aluminium, shown in Figure 1b. In this case, the aluminium atom is one electron short of that required for the ideal bonding configuration. Again, the energy requirement to promote a nearby germanium valence electron into this spot is small compared to the energy gap (Figure 2b). Thermal agitations are sufficient to supply this energy such that the aluminium atom obtains an extra electron. The vacated germanium valence state becomes a positively charged hole which drifts away from the impurity ion, leaving the electron trapped at the impurity site. Just like for intrinsic hole conduction, the sequential process of electrons travelling from neighbouring sites to occupy a vacancy (hole) constitutes the motion of a positively charged free carrier. An impurity atom which creates a hole in this way is called an 'acceptor' (because it 'accepts' an electron). A germanium crystal grown from melt with a small amount of impurity (e.g. aluminium) will have a certain number of positive hole carriers built-in as a result. At modest temperatures, all of the acceptor sites will be ionised (meaning all the holes associated with impurity atoms are available for conduction) and the extrinsic transport properties will be determined by the acceptor holes i.e. the doped germanium behaves as a p-type semiconductor.

In short, the electrical transport behaviour of the material can be controlled by selecting a dopant species that provides an excess of electrons (n-type donor doping) or a deficit (p-type acceptor doping). At room temperature, the number of ionised donor/acceptor sites will vastly outnumber the intrinsic thermally generated carrier population such that the overall transport properties will be determined by the dopant species carrier type i.e. n- or p-type. You can show that this is the case by noting that the number density of intrinsic carriers at room temperature in pure elemental germanium is $n_i \sim 2x10^{13} \ cm^{-3}$ and estimating how many holes become available if even only 1 in 10^6 atoms is replaced with an p-type donor (atomic density of Ge is $\sim 4x10^{22} \ cm^{-3}$). At room temperature, it is reasonable to assume that all donor atoms are ionised and give up their carrier for conduction. This is known as the 'extrinsic' regime since the electrical transport properties are almost completely determined by carriers originating from dopant atoms.
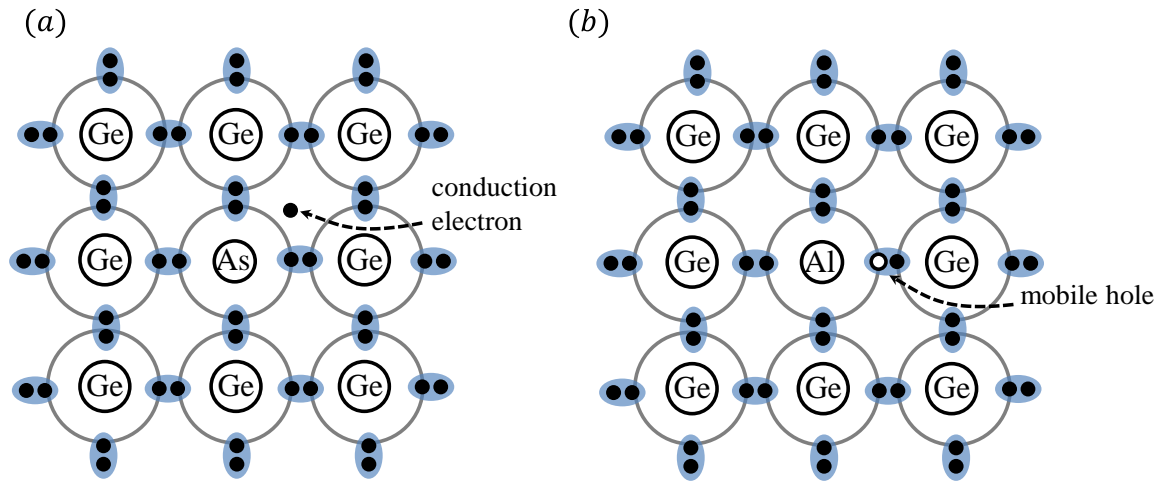
Figure 1: *Simplified schematic of an arsenic dopant atom present in the germanium lattice. Arsenic has five electrons available for bonding but since only four are required for bonding with germanium, the extra electron becomes free for conduction. (b) Analogous case for an aluminium atom inserted into the germanium lattice. Aluminium is one electron short of the required quota for bonding and therefore leaves a mobile hole.*
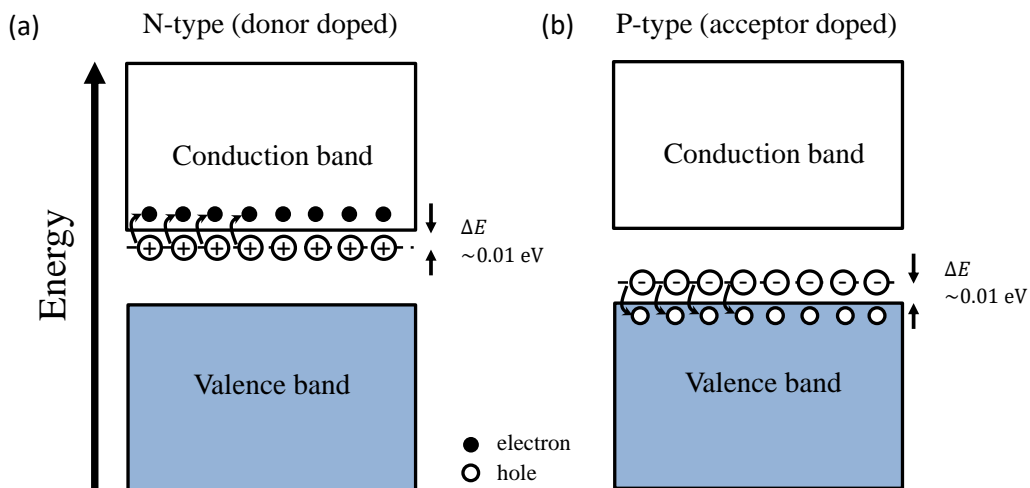

Figure 2: *Schematic energy band diagrams for a (a) donor- or (b) acceptor-doped semiconductor. The horizontal axis k-vector information has been omitted for simplicity. In (a) the energy level of the added impurity electron orbitals lies just below (~ 0.01eV) the conduction band edge. Ionisation of the impurity atoms occurs easily at room temperature contributing free electron carriers to the conduction band. (b) In this case, the impurity atoms create vacant energy levels just above the valence band. At room temperature electrons can be promoted into these levels, leaving positive hole carriers in the valence band that contribute to conduction.*

Hall Effect measurements of transport properties in a doped semiconductor: Introduction and theory

The Hall effect is an important experimental method for determining the microscopic parameters of charge transport in metals and doped semiconductors. It can be used to determine the polarity of charge carriers and, if the geometry of the sample is well known, the number density of charge carriers and mobility (a measure of how easily charged particles move through the material).

Hall effect measurements involve the application of a magnetic field ($\underline{B}$) perpendicular to the direction of current flow in a semiconductor (or metal) sample. Physically, the Hall effect arises due to the 'Lorentz force' that deflects moving charge carriers in a magnetic field. The Hall Effect manifests as a potential difference (V_H) between the faces perpendicular to *both* the direction of current flow and applied B-field.
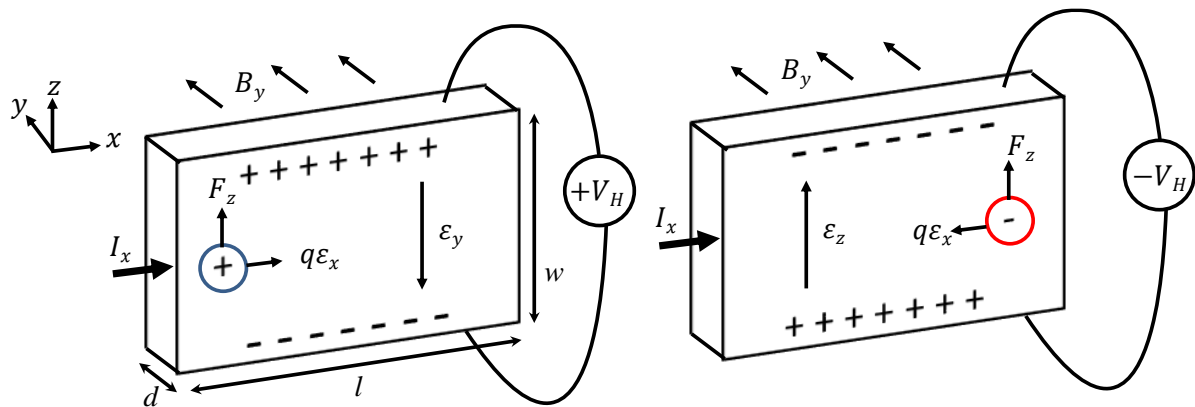

Figure 3: Schematic Hall Effect in a slab of material with current flowing left-to-right mediated by (a) positive charge-carriers and (b) negative carriers. A potential difference develops across the top-faces and can be detected with a voltmeter and used to determine the majority charge carrier polarity in the sample.

Consider a non-magnetic rectangular slab of material as shown in Figure3 of dimensions *l = 20 mm*, *w* = 10 mm and *d* = 1 mm. An electric field $\underline{\varepsilon}$ is applied parallel to the long-axis exerting a force $\underline{F_E} = q\underline{\varepsilon}$ on charge carriers and leads to a current flow. A magnetic field $\underline{B}$ is then applied perpendicular to the slab causing charge-carriers travelling with drift velocity $\underline{v}_d$ to be deflected sideways by the Lorentz force. The deflecting force acts in a direction normal to the current and magnetic field and is determined using a right-hand rule:

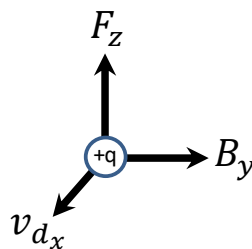$$\underline{F_B} = q(\underline{v}_d \times \underline{B}). \qquad [1]$$

Figure 4: Vector relationship between $\underline{F}, \underline{v}_d$ and $\underline{B}$ in a right-hand system.

When $\underline{v}_d$ and $\underline{B}$ are oriented along perpendicular axes, such as in Figure 4, we can write the direct product:

$$F_{B_z} = qv_{d_x}B_y. \quad [2]$$

The deflection due to the magnetic Lorentz force causes charge carriers to become accumulated on one face and therefore produces a deficit on the opposing face. This leads to development of an electric force that exactly counterbalances the magnetic Lorentz force. In the steady-state:

$$q\varepsilon_z = qv_{d_x}B_y, \quad [3]$$

Expressing E_z in terms of the so-called 'Hall potential' V_H:

$$V_H/w = v_{d_x}B_y, \quad [4]$$

$$V_H = wv_{d_x}B_y. \quad [5]$$

Knowing the cross-sectional area of our slab $A = dw$, the current flowing through the slab is:

$$I_x = J_xA = nqv_{d_x}dw, \quad [6]$$

$$\therefore V_H = \frac{I_xB_y}{nqd}. \quad [7]$$

Notice that the Hall voltage is predicted to be directly proportional to both the magnetic flux density (B_y) and the current supplied (I_x). These proportionalities will be tested as part of today's experiment.

Knowing the magnitude of the applied current and magnetic field, measurement of the Hall voltage therefore allows the carrier density 'n' to be determined from Eq.7.

The use of the Hall voltage for diagnosing the carrier-charge sign can be appreciated by recalling that a current travelling from left to right can in principle be comprised of either positive carriers (e.g. holes) moving left-to-right or negative carriers (e.g. electrons) travelling right-to-left. Note that this means simple current measurements alone are unable to reveal the carrier type. However, when a magnetic field is applied, both carrier types are deflected in the same direction leading to a potential difference V_H of opposite sign (Figure 3). You should convince yourself of this by looking at the Lorentz Force expression, equation [2], upon necessary reversal of signs of both carrier charge q *and* the velocity v_{d_x} when considering electron-mediated transport as opposed to the positive-charge mediated case for currents travelling the same direction.

Another crucial parameter for characterising charge transport is the carrier mobility. Mobility is defined through $|\mu| = v_d/|\varepsilon|$, and is a measure of how easily the charged carriers move through the material under the influence of an applied electric field (in a classical picture determined by the mean free path between scattering events). Using equation [5] above, the carrier drift velocity v_{dx} can be expressed:

$$v_{d_x} = \frac{V_H}{wB_z} \quad [10]$$

And expressing ε_x in terms of the potential-drop across the long-axis i.e., as V_{drop}/l, we can write the mobility as:

$$\mu = \frac{v_{d_x}}{\varepsilon_x} = \frac{v_{d_x}l}{V_{drop}} = \frac{V_Hl}{wB_yV_{drop}} \quad [11]$$

Therefore, the carrier mobility can also be determined by experimental measurement of the Hall voltage, when the magnetic-flux density and voltage required to drive a current through the Ge-element are known.

EXPERIMENTAL SETUP

The Hall-effect module will be used to measure the Hall voltage (V_H) and electrical conductivity (σ) of a semiconductor element on a plug-in board as a function of temperature (T) (Figure 5). The semiconductor element wired to the board is a rectangular slab of p-type doped germanium. The module provides an adjustable current-source allowing the cross-current (I) through the semiconductor element to be varied while the Hall voltage is measured. The voltage drop (V_{drop}) required to drive the desired current through the semiconductor element can also be measured.

The semiconductor element is located between the pole-pieces of an electromagnet and the magnetic-flux density (B) can be measured using the supplied Hall sensor placed in front of the crystal element.

A resistive heater built-in to the semiconductor chip allows the temperature of the crystal to be increased. A thermocouple mounted near the crystal provides a voltage output that is proportional to the crystal temperature.

For today's experiment, the Hall-Effect module has already been mounted for you with the Ge-chip positioned between the magnet pole pieces. The magnet has been wired to the power source such that the magnetic-field strength can be adjusted by the current amplitude of the source output.
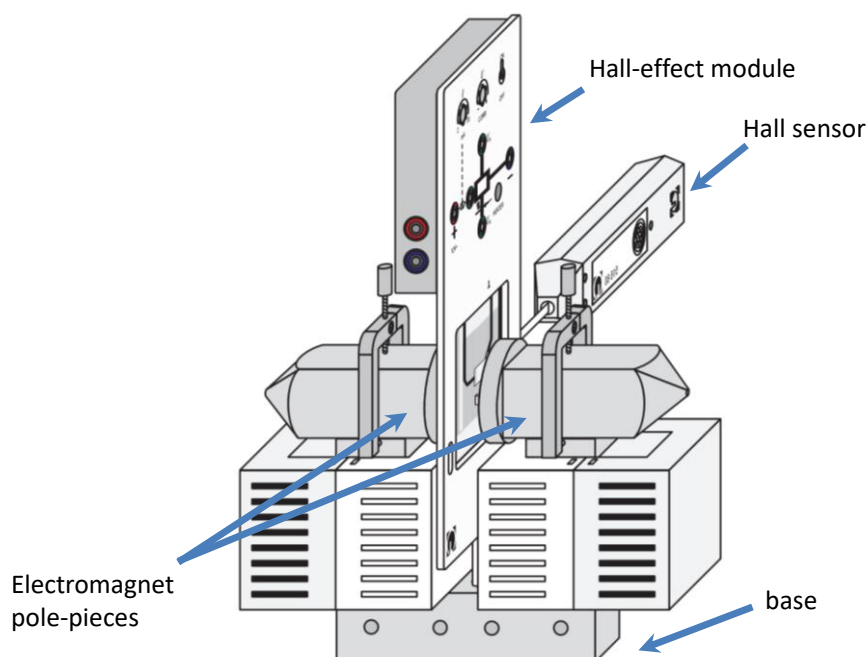

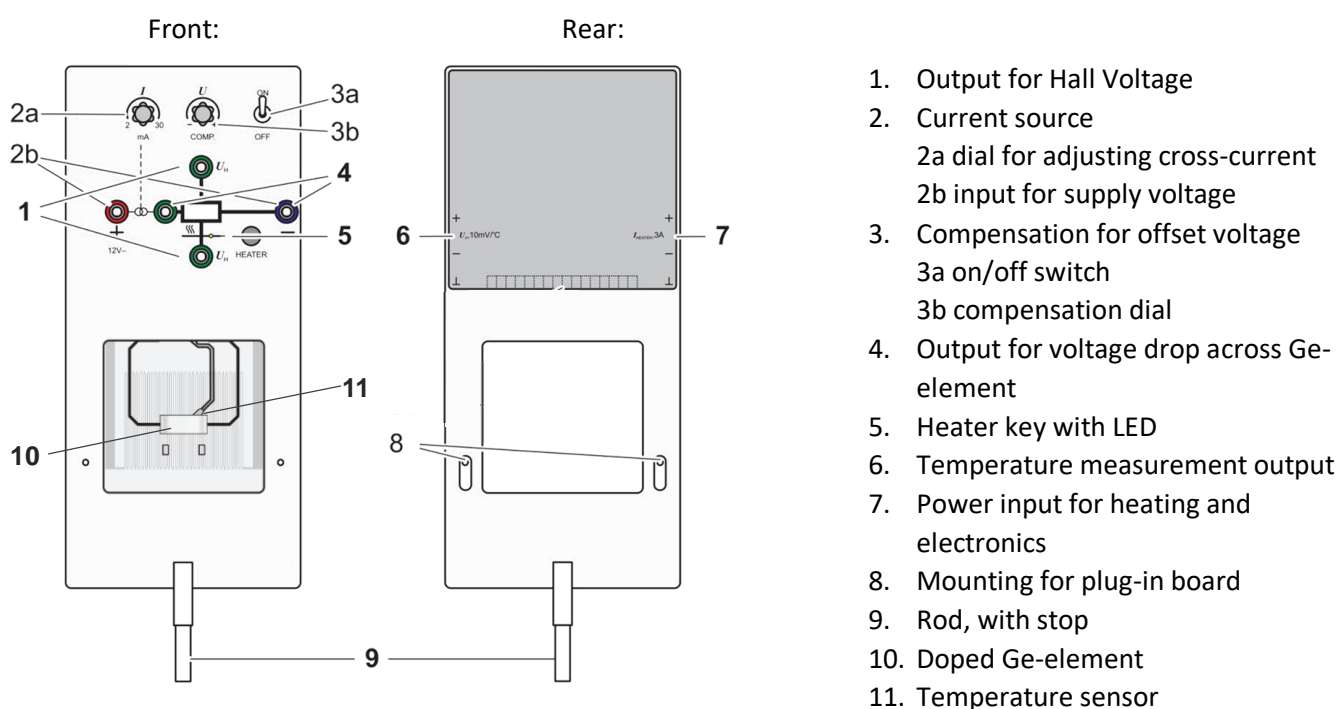**Figure 5:** *Side-on schematic of Hall Effect setup*

HALL-EFFECT MODULE:

Front: Rear:

1. Output for Hall Voltage
2. Current source
   2a dial for adjusting cross-current
   2b input for supply voltage
3. Compensation for offset voltage
   3a on/off switch
   3b compensation dial
4. Output for voltage drop across Ge-element
5. Heater key with LED
6. Temperature measurement output
7. Power input for heating and electronics
8. Mounting for plug-in board
9. Rod, with stop
10. Doped Ge-element
11. Temperature sensor

Figure 6: *Front-on view of the Hall-effect module with Ge-board*

EXPERIMENTS

Experiment 1.1: Calibration – determining background voltage in zero applied magnetic field (15 min)

In the ideal case, no potential difference should be detected across the transverse electrodes (labelled '1' in Figure 6) when the cross-current is applied since the electrodes are oriented perpendicular to the current (i.e. the electrodes should lie along an equipotential plane). However, in reality the transverse electrodes are not perfectly oriented and minor misalignment can lead to a small 'offset' potential (V_{offset}) that develops whenever the cross-current is applied *even in the absence of an applied magnetic field* (i.e. when no Hall Effect is anticipated). Since this potential difference is not associated with the Hall effect we need to measure it so that it can be removed when later making Hall voltage measurements in non-zero magnetic fields. A diagram schematically illustrating the electrode misalignment is included in the appendix.

Setup

- The Hall-Effect circuit-board has already been mounted for you in its holder positioned between a pair of electromagnet pole pieces.
- Connect the terminals of the transverse voltage output to input B terminals of the Cassy Sensor as shown in Figure 7 below. This will allow the transverse voltage to be monitored using Cassy Lab software.

- On the Hall Effect board turn the cross-current control dial fully left (see '2a' in Figure 6) and turn the compensation toggle switch to 'off'.
- In order to supply the cross-current, 12 V must be supplied to the cross-current terminals on the Hall module. The Cassy sensor has a voltage output that can be used for this purpose. Firstly, on the Cassy Sensor turn the voltage output dial (labelled '0 V … 16 V' at the bottom) all the way to the left stop. As shown in Figure 7, connect the voltage output terminals (labelled 'S') to the cross-current inputs on the Hall module as indicated. Before proceeding again check that the voltage output is connected to the *outer two* terminals for the cross-current supply (coloured red and blue, ask a demonstrator if unsure).
- Connect a multimeter *in parallel* to the Cassy Sensor voltage output. Operate the multimeter as a voltmeter in the Volt range. On the Cassy Sensor, turn the output voltage dial to the right to increase the voltage control until 12.0 V is readout. Once set, you will not have to adjust this dial for the remainder of today's experiment. A current (~2 mA) will now be flowing through the doped-Ge piece with and can be increased to 30mA by turning the cross-current dial on the Hall module to the right. Keep the cross-current dial turned fully to the left when not making measurements (driving larger currents for extended periods can cause Joule heating of the Ge piece that can adversely affect your measurements).
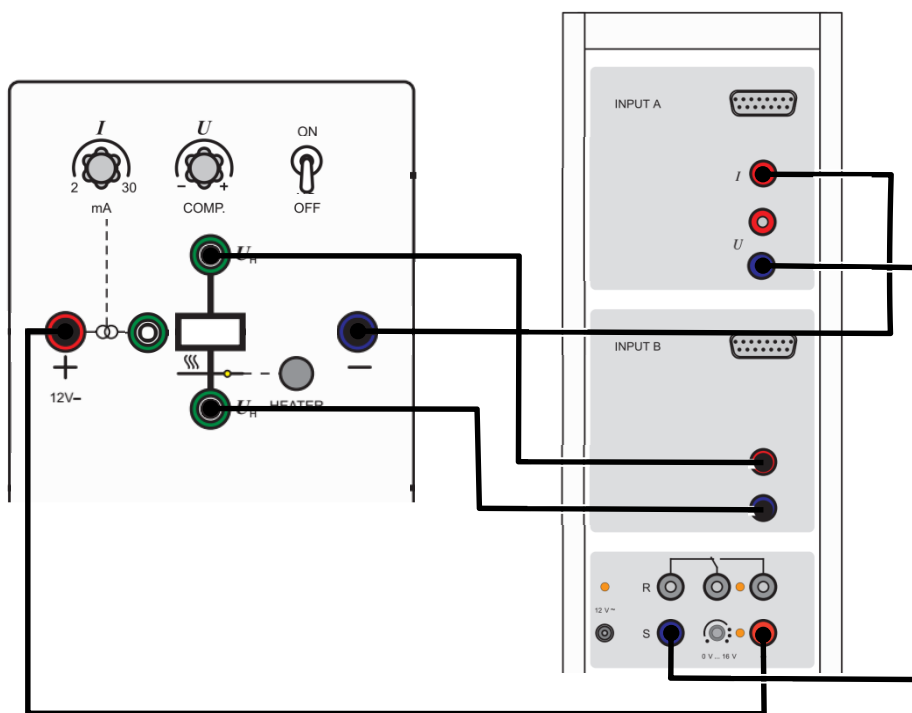

Figure 7: *Wiring diagram for experiment 2.1*

Setting up Cassy Lab for measurement of voltage vs. current:
- Open Cassy Lab on your computer from the desktop.
- A panel should appear prompting you to select the inputs you want to measure. Click on the corresponding inputs for channel A (I_{A1}) and channel B respectively. They should light up to indicate they have been activated, then click 'close'.
- In the 'settings' panel in the top-right of window locate the 'Current I_{A1}' setting (through hierarchy 'CASSYs $\rightarrow$ Sensor-CASSY 2 $\rightarrow$ Input A1 (left) $\rightarrow$ Current I_{A1}').

- Click the 'automatic' check-box option for the ammeter measurement range and select 'Averaged values' with an averaging time of '100 ms'. Choose 'origin' as 'left'. You should notice that the real-time current read-out panel now shows greater decimal point precision.
- Similarly for the 'Voltage U$_{B1}$' setting , select 'automatic' for the voltmeter range and 'Averaged values' with an averaging time of '100 ms'. For 'origin' choose 'left'.
- Under the 'Recording' settings select 'manual'
- We require a plot of transverse voltage (V) against Current (I) with $B = 0$ in order to determine the background potential difference.
    - In the 'settings' panel navigate to 'Displays → Standard'. Click on one of the plots and delete it using the 'delete' option that appears below.
    - Select the remaining plot and choose 'U$_{B1}$' on the y-axis and 'I$_{A1}$' on the x-axis. Under 'Style' choose to plot 'Values'.

Making the measurements:

1. Again, make sure the 'compensating voltage' switch is turned 'off' on the Hall effect module.
2. Check that, the cross-current dial on the Hall Effect board is turned to the left stop. A current reading of ~2 mA should register on the onscreen ammeter.
3. With no magnetic field applied, manually collect measurements of voltage (V_{offset}) for several different values of drive current, I.
    - Record the offset-voltage as a function of current from 2 to 30 mA.
    - Decide upon a suitable current interval for creating the plot.
    - Measurements can be made by clicking 'F9' or by clicking the 'single measurement' icon from the top-row menu.
4. Either copy & paste the current/voltage values from the left-hand table into an Excel spreadsheet or export them as text file (File → Save As → << *set file type to .txt and save as "filename.txt" with the suffix* >>)
5. Plot a graph of offset voltage vs current. Remember to save the spreadsheet on your QUB student drive.
    - Then obtain a linear fit to determine an equation that can be used to calculate the compensation voltage for any value of drive current
6. You may notice that the offset voltage is so small as to be sub-resolution for voltmeter measurement (~0.1 mV). This indicates the electrodes are well-aligned and that no correction will be required for Hall voltage measurements in experiments 2.2 and 2.3.

Experiment 1.2: Determining hole carrier mobility through Hall Effect measurements as a function of current and constant magnetic field (30 min)

You are now going to measure the Hall voltage as a function of current for an applied magnetic-field of fixed magnitude and use the plots to determine the room-temperature mobility of mobile holes in p-doped germanium. The electromagnet has already been wired to a power source for you and a magnetic field will be established when a current is supplied to the magnet coils.

Measuring the B-field magnitude:

- The Hall sensor, oriented as shown in the inset below, can be used to measure the B-field magnitude between the electromagnet pole pieces. It has already been connected to the port labelled 'A' on the Cassy sensor for you.

- Click the [icon] icon along the top-row menu to display the active Cassy sensor channels. Click the icon corresponding to the Hall probe serial input and then click 'close'. A panel should appear displaying a real-time readout of B-field magnitude in units of Tesla.

- In the 'Settings' panel, hierarchy 'CASSYs → Sensor-CASSY 2 → Input A1 (Combination B probe) → Magn. flux density B_{A1} (tang.), select 'automatic' for the range. With the Hall probe positioned away from the gap between the pole-pieces click the '→ 0 ←' icon to zero the background readout.

- Position the Hall sensor (the chip located at the tip-end of the green support) between the pole pieces and in front of the Hall module as close to the Ge plate as possible. Be careful with positioning the Hall sensor as it is delicate and easily broken.

Hall sensor tip

Ge-element

- Turn on the power supply unit connected to the electromagnet and ensure the 'output on/off' green LED is off. Ensure the master/slave controls are set to 'normal' operation. Turn the current knob all the way to the left-stop and the voltage knob all the way to the right-stop. Now, press the 'output on/off' button and increase the current up to 5 A using the current control knob. You should see the Cassy Lab B-field magnitude readout increase to somewhere in the region of 70 – 100 mT at 5 A.
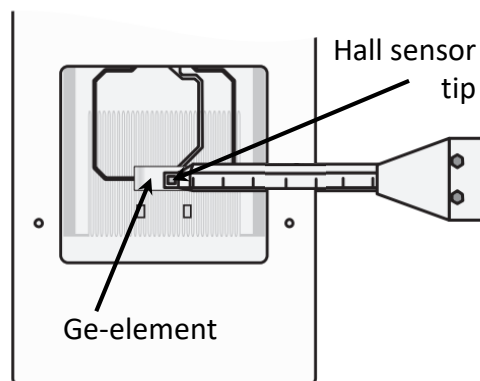
Measuring Hall voltage vs current (constant magnetic field)
The aim here is to measure V_H as a function of I for fixed values of B. From these data you will determine the carrier drift velocity, v_d and hence the carrier mobility, μ.
1. Set a constant value of B with the current source set to 5 A.
2. Setup the graph display to plot Hall voltage (U_{B1}) against I_D (I_{A1}) with 'Manual' recording. In the 'Style' settings remember to choose 'Values'. Delete any unnecessary plots from the list.
3. In the graph area right-click the axes to set the limits (note that the max current you should drive is 30 mA and the offset voltage is expected in the range of several mV). You can also adjust the axes limits during/after the experiment.
4. Decide on a suitable increment for current and plot measurements of the voltage as a function of cross-current in CassyLab. The current value is adjusted using the cross-current

dial (see '2a' in Figure 6) on the Hall Effect module. Remember to record the value of magnetic flux-density, B.

  o Once the experiment is complete turn the cross-current dial on the Hall Effect board all the way to the left.

5. Repeat step 4 for an additional two different fixed values of B-field, taking voltage readings at the same current values for each dataset.

6. Import the measured values into an Excel spreadsheet and note down the value of B for each dataset.

Analysis:

  o Plot the corrected Hall voltage by taking the measured value of V_H and removing the appropriate offset voltage (if required) for each value of I as determined using your best-fit equation from calibration exercise 2.1.

  o For each value of B, plot the corrected Hall voltage (V_H) vs cross-current (I).

  o You can use equation [10] to obtain values for v_d as a function of I from your V_H vs. I trends. How do you think the three v_d vs I plots will compare for the different background values of B? Plot v_d against I for the three B-field datasets and see.

  o Now use equation [11] to estimate an average value for the mobility, μ (in units of cm^{2}V^{-1}s^{-1}), using each of your averaged values for v_d. To evaluate equation [11] you will need to determine the voltage-drop, V_{drop}, required to drive the cross-current. This can be determined using Ohm's Law ($V_{drop} = IR$) where the resistance value for your Ge-element can be found from Table 1 in the appendix and using the unique identifier code etched into the back of the Ge-chip.

Experiment 1.3: Determining the density of hole carriers by Hall Voltage measurements as a function of magnetic field and constant current (30 min)

You are now going to measure the Hall voltage as a function of magnetic field for a fixed applied current. The plots will then be used to determine the room-temperature number density of holes in doped germanium.

1. Start a new sheet in Cassy Lab by clicking the ☐ icon from the top-row menu icons.
2. In the Cassy Lab settings change the graph display to plot Hall voltage (U_{B1}) against magnetic flux density (B_{A1}). In the 'style' settings remember to choose 'Values'.
3. Set the graph axes limits to appropriate values (a suitable upper limit for the voltage axis is ~20 mV)
4. Turn on the output of the power source to the cross-current and electromagnet. Fix the cross-current value at 30 mA
5. Measure and record the Hall voltage values as a function of magnetic field with the current fixed at 30 mA. Vary the magnetic field from zero to maximum using the current knob on the power source. Do not exceed 5 A on the magnet power supply.
6. Repeat step 5 for an additional two values of I.
7. When the experiment is finished turn off the output on the power source.
8. Calculate and plot the corrected V_H vs B-field for each value of I. If necessary, the correction will be a constant background voltage removed from each fixed value of I, determined using your equation determined from calibration exercise 2.1.

Analysis:

- Perform a linear fit with the intercept value set to zero. Use the linear fit and equation [7] to determine the hole carrier density n_h (note q = 1.6 x 10^{-19} C). Remember that the number density of carriers has units of either m^{-3} or cm^{-3} and depending on which unit you will choose there will be six orders of magnitude difference in the reported value. Hence, make sure to quote the relevant units for your calculation!
- To give your estimate for n some context, find the intrinsic carrier density values online for intrinsic germanium and a good metal (e.g. sodium) and compare these with your estimate of n_h for p-doped germanium.
- Determine the relative number of dopant atoms expressed as a percentage of the number of Ge atoms (Ge has an atomic density of 4.5x10^{22} cm^{-2}). You can assume all dopant atoms are ionised at room temperature.

Part 2: Observing the transition from extrinsic to intrinsic conduction in a p-type doped semiconductor through Hall Effect measurements (60 min)

In this part you will use Hall voltage measurements to reveal the temperature dependence of transport behaviour in doped semiconductors. You will look at the special case of a p-doped germanium crystal where the carrier type primarily responsible for current flow can be seen to change polarity as temperature is raised (even though the current direction remains the same throughout). In other words, within a certain temperature range, current is seen to be mediated primarily by positively charged holes whereas in a different temperature range the current is mediated mainly by free electrons. To make the necessary measurements, the Hall Effect module comes installed with a heater that heats the Ge element up to ~ 165°C. This allows the Hall voltage and conductivity to be measured as a function of temperature.

Temperature behaviour of doped semiconductor transport

In order to understand how the Hall voltage is expected to change with temperature in a doped semiconductor, we must consider the net conductivity, $\sigma(T)$, of the material under measurement:

$$\sigma(T) = \sigma_e(T) + \sigma_h(T),$$
$$\sigma(T) = en_e(T)\mu_e(T) + en_h(T)\mu_h(T) \qquad [12]$$

where 'e' subscripted terms refer to free electron carriers and 'h' subscripted terms refer to positive hole carriers. Note that the carrier concentrations (n_e and n_h) and mobilities (μ_e and μ_h) depend on temperature and that these can have different functional forms that depend on the sample doping.

We are now going to use the energy-band diagram for acceptor-doped germanium to rationalise the expected transport behaviour as a function of temperature, see Figure 8 below. As previously discussed, free carriers can be made available for conduction through either of two processes, i.e., by thermally generated electron-hole pairs (referred by the label n_i below) or through impurity doping. The competition between these two processes is largely responsible for determining the temperature dependence of the transport behaviour.

In the 'extrinsic' temperature range, T is only large enough to ionise all N_A of the dopant atoms in the semiconductor (*c.f.* ~ 0.01 eV required for ionisation compared to ~ 1 eV required for thermal carrier generation). The number of thermally generated carriers from Ge atoms is therefore negligible compared to the fixed number (N_A) of dopant carriers. This is the normal operating region for solid-state devices. For acceptor-doped germanium, the transport will be therefore be determined by the fixed number of dopant holes (predetermined by the concentration of acceptor dopant atoms). The only change in $\sigma(T)$ in this temperature range will be a decrease due to changes in the mobilities, however this variation is small and we can approximate $\sigma(T)$ to be constant in this regime.

As temperature is increased further, increased thermal excitation of electrons across the band-gap (i.e. creation of electron-hole pairs on germanium lattice sites) starts to become significant since this contribution increases *exponentially* with temperature (while the number of dopant hole carriers remains fixed). Therefore, beyond some critical temperature, the thermally generated carrier population (n_i) will exceed the fixed number of carriers originating from impurity dopant sites, such that $n_i >> N_A$. In this regime, the number density of mobile electrons and holes are approximately

equal (the dopant hole population is negligible by comparison) and is referred to as the 'intrinsic' temperature region (Figure 8e). A subtle, but very important, point here is that it is any difference in *mobility* between the electrons and holes that becomes the key factor in determining the majority carrier-type of the measured current. In germanium, electrons move almost twice as fast as holes ($\mu_e \approx 2\mu_h$) under an applied field, hence, in this temperature regime, conduction behaviour is seen to be n-type. This is consistent with the case seen in pure germanium, where $n_e = n_h$ at all temperatures, and transport is seen to be n-type.

In short, as temperature is increased above room temperature, a transition from p-type dopant mediated 'extrinsic' conduction to n-type 'intrinsic' mediated conduction is expected to be observed in the p-type doped Ge sample. This behaviour should also then be reflected in the behaviour of the Hall voltage with temperature. So, how do you think this transition will affect the measured Hall Voltage?
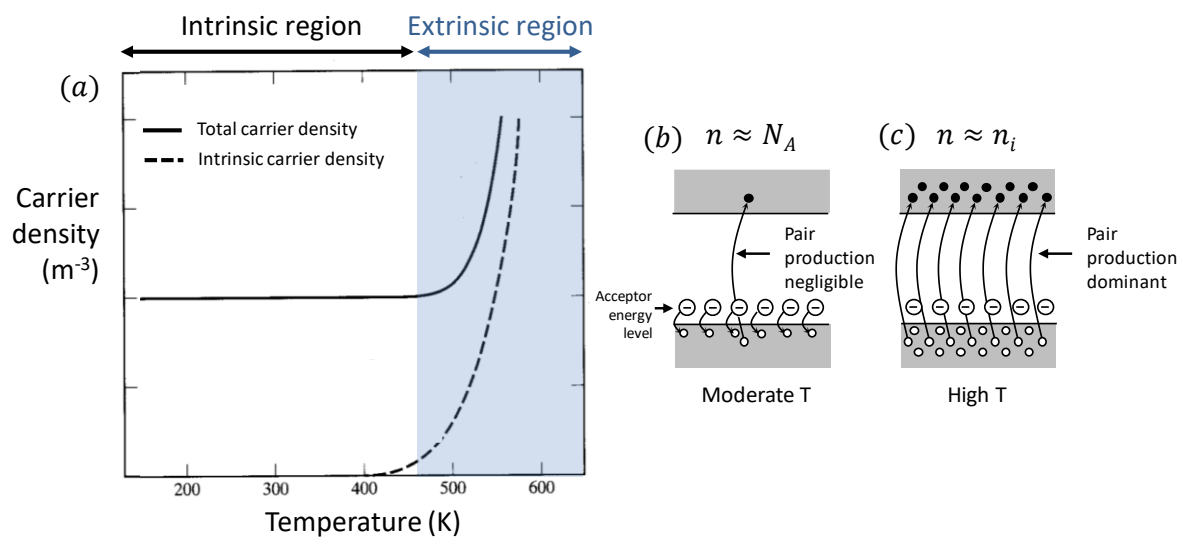

Figure 8: (a) *Typical temperature dependence of the total carrier density vs temperature in a p-type doped semiconductor. At room temperature (300 K) all of the dopant ions are ionised and the total carrier density is constant since the number of thermally generated carriers is negligible. As temperature is increased, the thermally generated 'intrinsic' carrier density (dashed line) becomes important. Notice that it only becomes significant well above room temperature. (b),(c) Explanation using a simplified energy-band picture.*

Experiment 1.4: Observing the transition from extrinsic to intrinsic conduction in p-type doped Ge

1. The wiring diagram for this experiment is shown in Figure 9 below. First, disconnect the multimeter from the Cassy Sensor voltage outputs. Remove the cross-current leads from Input A of the Cassy Sensor and plug them into the supplied multimeter (to be operated as an ammeter). Use the 'mA' and 'COM' inputs. Set the multimeter to the mA measurement range.

2. This part of the experiment utilises the heater built-in to the Hall Effect board. Connect the set of output terminals of the dc power supply (the pair not being used to power the magnet) to the heater inputs on the left-hand side of the Hall Effect board (inputs labelled 'I_{HEATER}' on the rear, see Figure 6). Connect the thermocouple readout terminals on the right-hand side of the board (labelled 'U_ϑ' on the rear) to Input A on the Cassy Sensor as a voltage input.

   Double check that the power supply is connected to the left-hand inputs as supplying voltage to the readout terminals will damage the equipment, ask a demonstrator if unsure

   Turn on the power supply and set it to 15 V (make sure current knob is fully turned to the right before increasing the voltage setting from zero).

3. Turn on the magnet power supply and set it to 5 A. The Cassy Sensor voltage output is used to supply 12 V to the cross-current inputs as before. Make sure the cross-current dial on the Hall Effect board is turned all the way left for now (to minimise Joule heating of the Ge piece when not measuring).

4. For monitoring temperature, we require Input A on the Cassy Sensor to behave as a thermocouple voltage readout. In Cassy Lab software navigate through the 'settings' panel to 'CASSYs → Sensor-CASSY 2 → Input A1 (left)' and activate 'Voltage U_{A1}'. Choose 'automatic' for range and select 'Averaged' values. Under 'recording' choose 'automatic' with a measurement time of 6000 s and check 'meas. Condition' and enter the text: abs delta UA1>=0.01 so that the resistance is measured each time a temperature interval of 1°C has elapsed.

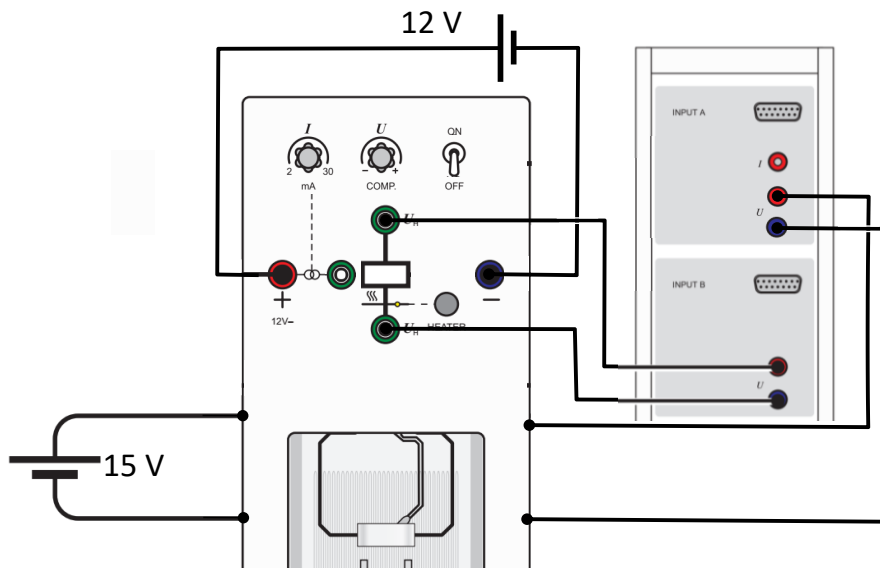**Figure 9:** *Wiring diagram for experiment 2.4*

5. The temperature in $^{\circ}$C can be determined simply as T= $100(U_{A1})$ (where U_{A1} has units of volts). Check that the onscreen voltmeter readout for U_{A1} displays a voltage corresponding to room temperature (note that the voltmeter only gives a reading when the 15V is being delivered to the electronics board).

6. In the 'displays' option setup two plots to be shown onscreen, Hall voltage vs. temperature (U_{B1} vs. U_{A1}) and temperature vs. time (U_{A1} vs. t). You will need to uncheck the box 'Same x-axis for all curves on this display' to configure the x-axes of the plots independently. Choose 'Style' as 'values' only for each plot. You should now see that you can toggle between the different y-axes of your plot and the x-axis changes accordingly.

7. Set the y-axis scale on the U_{B1} vs. U_{A1} plot from -10 mV to 30 mV and the x-axis from 0.25 V to 1.8 V. Set the y-axis scale on the U_{A1} vs. t plot from 0.25 V to 1.6 V and the x-axis from 0 s to 600s initially.

8. Set I_D = 30 mA using the cross-current dial on the Hall module.

9. Read this step and step 10 completely before carrying out the instructions: In order to measure the Hall voltage (U_{B1}) as a function of temperature (via the thermocouple voltage U_{A1}) all that has to be done is to press the button labelled 'Heater' on the Hall Effect board. When activated, the heater ramps up the temperature automatically to 167°C and then cools down in ambient conditions. Before moving on, perform a quick check that the graphing settings have been set correctly.

10. To carry out the actual measurement, first start data recording (press F9) and then press the 'Heater' button on the Hall Effect board. It takes ~ 90 s to heat up to the maximum temperature and ~ 25 min to cool back down to room temperature. The automatic data collection settings used mean the Hall voltage will be measured during both the heating and cooling cycles. You can stop data collection when the measurement is complete. Turn the power source output off and turn the cross-current dial to the left-stop.

11. Show your V_H vs. T plot to a demonstrator to verify it has the correct form before proceeding with the following analysis.

12. Copy the data values from the left-hand panel and save them in an Excel spreadsheet along with the cross-current value and magnetic field strength.

13. Plot V_H as a function of T. In acceptor-doped Ge there is expected to be a transition from positive hole-mediated conduction (extrinsic region) to negative electron-mediated conduction (intrinsic region), as shown in Figure 8. What do you expect to see happen to the value of the Hall-voltage as this transition occurs as a function of temperature? In your V_H vs. T plot you should be able to identify and label these 'extrinsic' and 'intrinsic' regimes. If the extrinsic-to-intrinsic transition is not seen to occur, you may have to repeat the measurement with zero magnetic field in order to obtain the temperature-dependent background signal so that it can be removed from your $V_H(T)$ trend.

Experiment 1.5: Determining the band gap of Ge by measurements of conductivity in the high-temperature intrinsic regime (60 min)

To further validate if the doped-Ge indeed behaves equivalently to undoped 'intrinsic' Ge at high-temperature, we would expect that exponential carrier statistics dominate the electrical transport in this regime, as in a pure semiconductor. At high enough temperature, the resistance should therefore start to decrease and follow the exponential relationship as seen for intrinsic semiconductors:

$$R(T) = Ae^{\left(\frac{\Delta E}{2k_bT}\right)}, \qquad [13]$$

where A is a constant, ΔE is the intrinsic band gap, k_b is Boltzmann's constant, and T is temperature. Furthermore, if the exponential relationship is valid for doped germanium in some high temperature region, then an estimate for germanium's band gap can be extracted from the $R(T)$ trend and compared to the literature value. You will measure $R(T)$ by monitoring the voltage required to drive a fixed amplitude cross-current (since $V(T) \propto R(T)$ by Ohm's Law) through the Ge element as a function of temperature. The magnetic field will not be required for this experiment so it can be turned off.

1. After making sure the measured values for experiment 2.4 have been saved in a separate Excel spreadsheet, clear the plotting area by clicking the 'delete measurements' button along the top-row menu icons.
2. Before proceeding, ensure the power source output is turned off and the cross-current dial is turned all the way to the left stop. Remove the leads connected to the Hall voltage outputs on the board. Re-attach the leads as shown in Figure 10 (below) for measurement of the voltage-drop across the Ge element. The other ends of the leads should already be in Input B of Cassy Sensor for voltage measurement.
3. Turn on the power source output and measure the potential drop V_{drop} (readout U$_{B1}$ on Cassylab) required to drive the cross-current across the Ge element as a function of temperature (T) for $I = 30\ mA$. Set the scale for U$_{B1}$ to $0 - 2.5\ V$. The current powering the magnetic field can be reduced to zero amps for this experiment.

Analysis:

- Convert V_{drop} to resistance (R) using Ohm's law, $R = \frac{V_{drop}}{I}$
- Then create an 'Arrhenius plot' of $log_e R$ against $1/T$ (in units of K^{-1}).
- Using the extrinsic-intrinsic transition temperature as determined in section 2.4 as a guide, identify the intrinsic region and perform a linear fit on this region alone. In this region, resistance should be decreasing as temperature is increased due to the effect of thermal carrier generation
- Take the logarithm of Eq. [13] in a way so that the gradient of your linear fit can be used to determine an estimate of the band gap ΔE. Give your answer in units of eV and compare with a literature value.
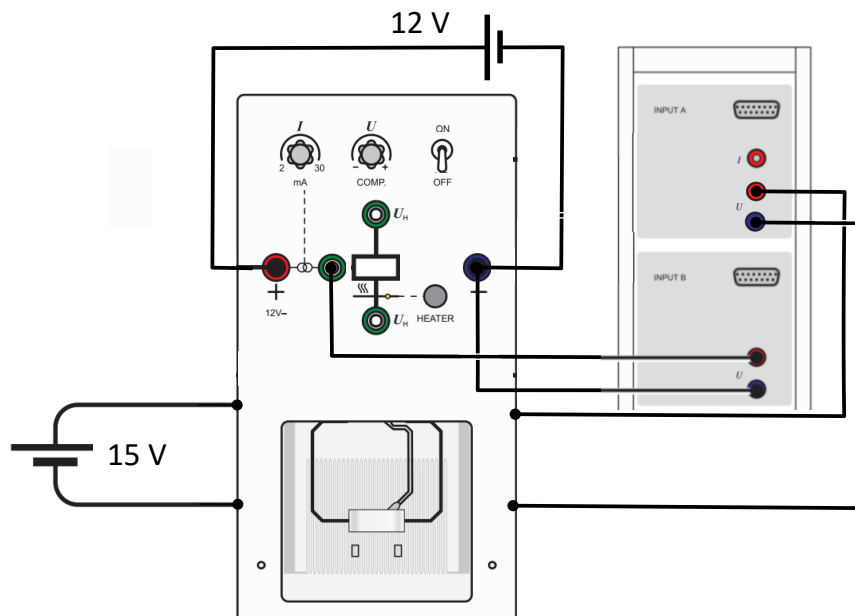

Figure 10: *Wiring diagram for experiment 2.5*

Appendix:

Table of resistance values for Ge-chip:

GE-CHIP NUMBER	QUOTED RESISTANCE	GE-CHIP NUMBER	QUOTED RESISTANCE
0310	59.4 Ω	0587	56.7 Ω
0484	49.7 Ω	0584	58.7 Ω
0485	41.9 Ω	0586	54.7 Ω
0487	53.1 Ω		
0490	50.7 Ω		
0492	54.7 Ω		
0493	54.5 Ω		

Background material: Quantum approaches to describing conduction

The free electron gas

A good starting point for explaining metallic conductivity, as it turns out, is to consider the metal as a gas of free electrons moving through a constant lattice potential (set to zero for convenience). This is basically a particle-in-a-box scenario where the sides of the confining potential correspond to the macroscopic surfaces of the metal. The time independent Schroedinger equation in one dimension for a free electron can then be expressed with the kinetic energy component only:

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2},$$

Where ψ is the electron wavefunction, m is the electron mass and E is the total electron energy. An electron wave function of the following oscillatory form is a solution:

$$\psi = \frac{1}{V}e^{ik_n x},$$

where V is the volume in which the electron is confined (a length in 1D), k is the wavevector defined as $k_n = 2\pi/\lambda_n$, and $\lambda_n = 2L/n$ where n is the primary quantum number. Substituting this solution into the Schroedinger equation above allows the very important relationship between electron energy (E) and wavevector (k) to be determined:

$$E_k = \frac{\hbar k_n^2}{2m}.$$

Figure S1 shows the wavefunction solutions for a 1D well and the associated energy/wavevector relationship. As L is increased in size, the k-vector solutions become closer spaced (since $\Delta k \propto 1/L$) until they almost form a continuum (solid line, Figure S1b); this is the scenario envisaged for a macroscopic solid. Considering periodic boundary conditions on the electron wave confined to the solid, and extending the analysis to 3D, shows that electrons have wavevectors that are determined by the quantum numbers n_x, n_y, n_z as follows:

$$k = (k_x, k_y, k_z) = \left(\frac{2\pi}{L}n_x, \frac{2\pi}{L}n_y, \frac{2\pi}{L}n_z\right),$$

where L is the length of the macroscopic dimensions of the metal and is equal to the number of ions N multiplied by the lattice constant a. These three quantised components of the wavevector almost completely characterise each free electron in the metal. Pauli's exclusion principle states that only two electrons (of opposite spin) can have the same wavevector. Therefore, only two electrons can occupy the lowest energy $k = 0$ levels and the rest of the electrons must occupy higher energy levels. This is an important result not expected classically.
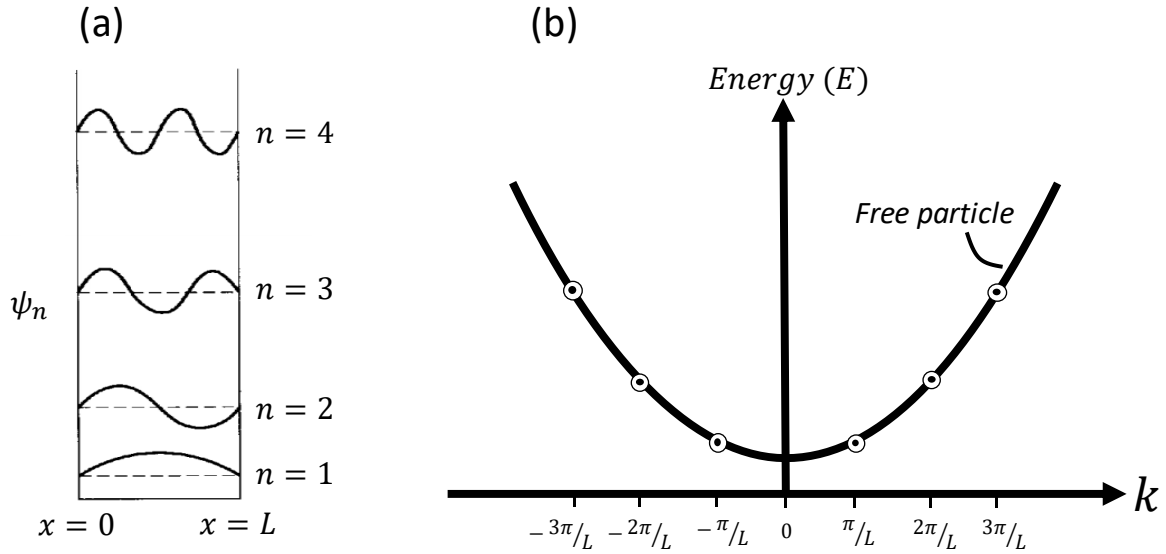
Figure S1: *(a) Spatial visualisation of wavefunctions for a particle trapped in an infinitely deep one-dimensional potential well of width L. The first four quantised energy levels are shown. (b) Allowed infinite-well energy levels versus wavevector (k) plotted as dots. As $L \rightarrow \infty$, the density of points is seen to increase, such that a quasi-continuous quadratic $E - k$ relationship is obtained in the free-particle limit.*

Electron propagation in a periodic lattice

In the free electron gas model, the potential energy term in the Schroedinger equation was set to zero and hence the electrons in the solid were not affected by the periodic array of positive ions that make up the crystal lattice. This is clearly unrealistic as the attractive Coulombic forces between electrons and positive ions should lead to a *periodic* array of potential wells (i.e. a rapidly varying potential on the atomic scale) which affect electron motion.

It is known from the theory of wave propagation in discrete structures that when a wave passes through a perfectly periodic lattice it propagates indefinitely without scattering (i.e. without losses). The effect of the atoms in the lattice is to absorb a proportion of energy from the wave and radiate it back so that the net result is that the wave continues without change in either direction and intensity, although the velocity of propagation is modified. This process is the also expected to occur for an electron wave travelling through the periodic ion array of a crystal, except that in this case we are dealing with a matter wave. By analogy to the propagation of X-rays incident upon a crystal lattice (L2 lab experiment), a special case is then expected where destructive interference between forward and reverse propagating waves prevents energy being propagated through the lattice (i.e. Bragg reflection). A similar scenario arises for electron wave propagation through a crystal lattice and is responsible for the emergence of electronic energy 'band-gaps', and following this, the prediction of insulating and semi-conducting electrical behaviour.

The 1D Schroedinger equation must now be expressed with a potential function $U_c(x)$ which has the periodicity 'a' of the crystal lattice:

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U_c(x)$$

The mathematical treatment of the problem was a triumph of Felix Bloch (Nobel prize, 1952), who in his own words puts it: "*…that the main problem was to explain how the electrons could sneak by all the ions in a metal…By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation.*" Such 'Bloch wave' solutions have the form:

$$\psi(x) = e^{ikx}u_k(x),$$

where $u_k(x)$ is a function with the period, a, of the lattice.

Substitution of $\psi(x)$ into Schroedinger's equation above (with a suitably approximated form for the perioidic potential) allows a new electron energy-wavevector $(E - k)$ relationship to be obtained, with the result that the quadratic relation previously derived for the free-electron picture is radically altered (see Figure S2). The $E - k$ diagram is no longer a continuous function and certain $E(k)$ values are not allowed: electron energy bands (regions in which energies exist) and band-gaps (regions in which energies are forbidden) form.
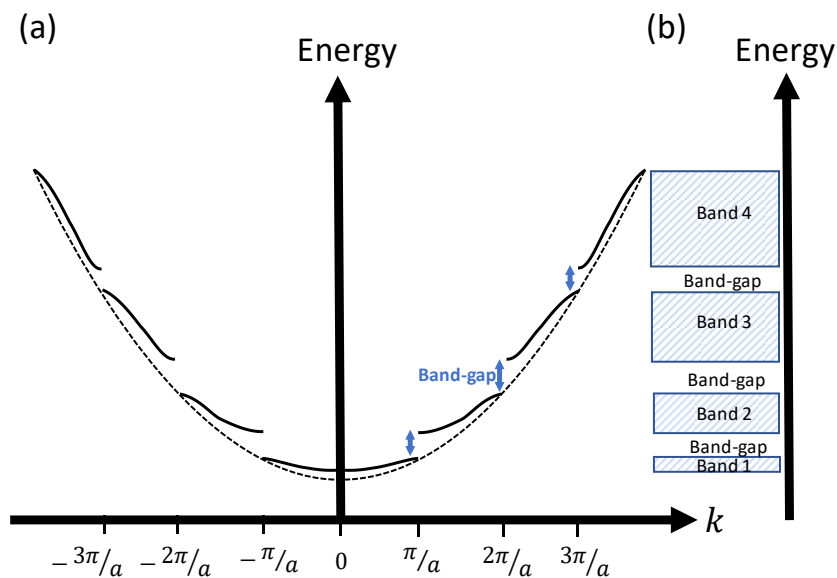

Figure S2: *(a) When the effect of the periodic lattice potential is taken into account the original parabolic form of the function found for the free-electron gas (dashed curve) is altered such that distinct regions of allowed energies appear (solid lines). These allowed energies are termed bands and energy regions in which k-states are forbidden are called band-gaps. This plot is called the 'extended zone' scheme. (c) In cases where we are only interested in the energy values of the bands, but not in the associated wavevector states, it is sufficient to plot just the energy axis alone.*

Metals, semiconductors and insulators

So far, we have rationalised the existence of energy band structure; in other words, the set of electron energies that in principle are allowed to exist in the solid and their associated wavevectors. However, determining *which* specific states that are occupied by the electrons requires a thermodynamics based rationale. Since electrons follow Fermi-Dirac statistics, two electrons of opposite spin fill each k-state, meaning that sequentially higher energy levels from the lowest energy up are filled until all electrons are accounted for. The highest filled energy state at zero Kelvin

is called the **Fermi Energy (E_F)** and the position of the Fermi level has a profound impact on the anticipated conduction behaviour.

If the states in the highest energy populated band are only <u>partially filled</u> with electrons, the Fermi energy at zero kelvin is located at the highest filled energy level and the solid is categorised as a **metal** (Figure S3(a)).

If all the states in the highest populated energy band are completely <u>filled</u> with electrons, the Fermi energy is located at the midpoint of the bandgap and the material behaves as a **semiconductor** (Figure S3(b) around room temperature if the band-gap is approximately ~1 eV. If the energy bandgap is significantly larger than ~1 eV, the material is usually categorised as an **insulator**.
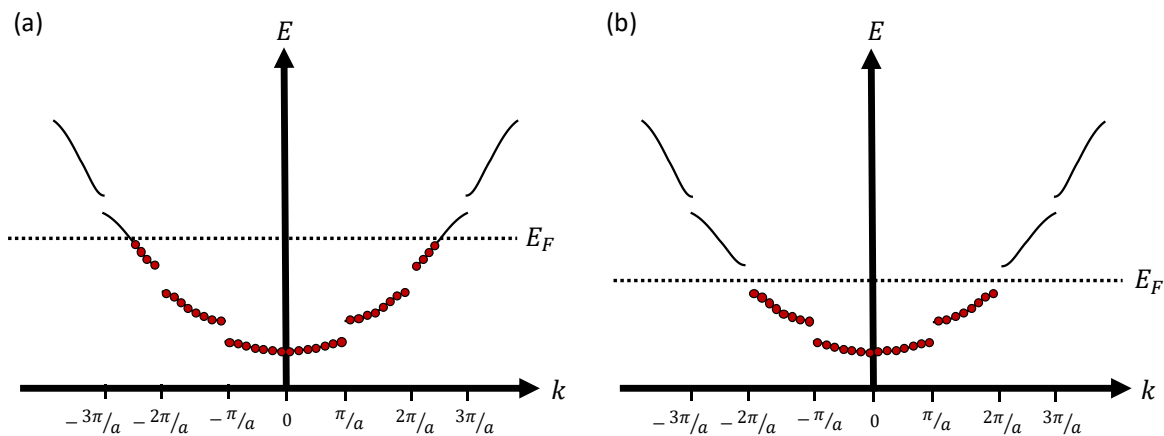

Figure S3: *The Fermi-Dirac distribution (not plotted) expresses the electron occupancy of different states as a function of energy of those states. If we plot the occupied states at zero Kelvin on an $E - k$ diagram (red filled circles) then the highest occupied state (the Fermi energy ,E_F) might lie be within an energy band (a) or within a band-gap region (b). The difference between (a) and (b) in terms of conduction is profound – (a) will be metallic, while (b) will be a semiconductor or an insulator depending on the size of the bandgap and the temperature.*

Partially filled band: metals

Consider the case where all electrons are accommodated in energy levels resulting in a partially-filled energy band (i.e. empty states of higher energy are still available in the same band) such as in Figure S4(a). The current contributed by an electron in a state k is the electronic charge times the velocity of that electron. In the absence of applied field, electron k-vectors are symmetrically distributed positive and negative and no net current flows, as expected. Under the action of an applied electric field E (Figure S4(b)), electronic states with k-vector aligned with the field direction become increased in energy by an amount $\sim q\Delta V$ (ΔV is the typical change in electron potential between scattering events), which is typically an amount of energy orders of magnitude smaller than E_F. The effect of altering the relative energies of $E - k$ states, that would have been equivalent in the absence of applied field, is that some electrons can now lower their energy by changing their wavevector and adopting a new quantum state. However, due to the Pauli exclusion principle, electrons occupying states deep within the valence band cannot move into different energy states since these are already fully occupied by electrons. The only electrons that can move into different

energy states, and therefore change k-vector, are those that occupy the top levels. These electrons move into lower energy vacant states with k-vectors in the reverse direction (Figure S4(c)). Overall, application of a small electric field unbalances the population of wavevectors such that the sum of their velocities as a population is no longer zero and a net current flows. The electrons contributing to this current are called 'n-type' carriers, due to their negative charge.
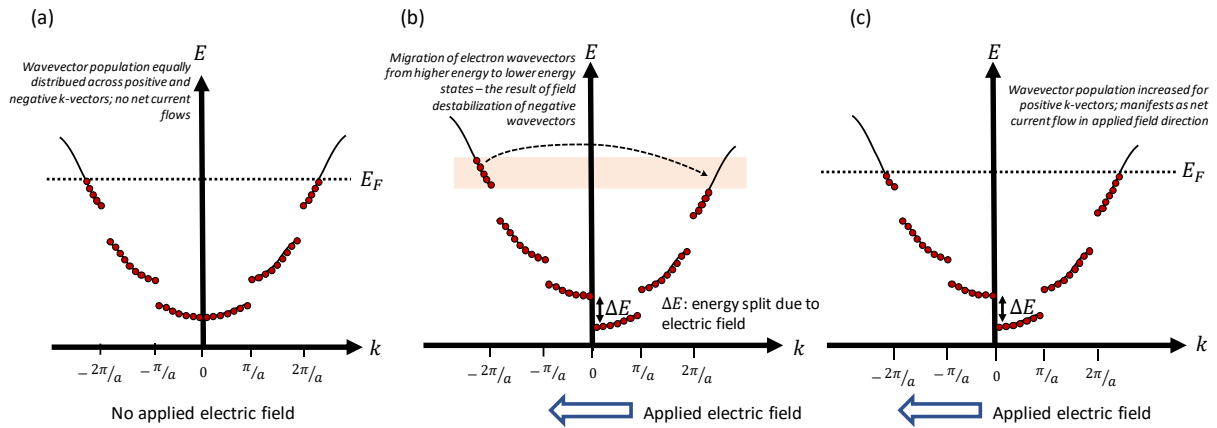

Figure S4: *(a) The highest occupied energy level in a metal lies in a partially filled band. Under no externally applied electric field the population of electron wavevectors (red points) are equally distributed in all directions and no current flows. (b) The effect of an applied field is to increase the energy of electron waves with k-vector aligned with the field and decrease the energy of those with k-vector anti-aligned. For electrons close to the Fermi energy, there is now the possibility to lower their energy by changing wavevector state into lower energy unoccupied states in the reverse direction (that were previously higher in energy before field application) (c). A net non-zero wavevector results and manifests as a current flow.*

Completely filled band: semiconductors (and insulators)

In semiconductors and insulators, when an electric field is applied, the same relative increase of the energy of electronic states with k-vectors parallel to the applied field occurs, as seen for metals. However, the fact that the energy band is filled with electrons is a crucial difference. Now, however, there are no positive k unoccupied energy states with lower energy available and so, although the energy of negative k states has increased, there is no mechanism by which electron energy lowering can occur (Figure S5). No migration of states from negative to positive wavevectors is possible; no imbalance in the wavevector population occurs and so the sum of all the wavevector velocities of all the individual electrons remains zero and no current flows. In other words, totally filled bands to not contribute to the charge-transport process. In this case, the material does not conduct any electrical current and is an **insulator**. This, at least, is the situation at a temperature of zero Kelvin. However, at finite temperature, the electron occupation of energy bands in insulators can change – thermal energy ($\sim kT$) can allow some electrons to vacate the higher energy states in one energy band and occupy the lowest energy states in a higher energy band. This process was not anticipated for the case of metals. In this higher band, the electrons have many unoccupied states with similar energies to which they can migrate and so mobilities can be high, even if the absolute numbers of free charge carriers are very low. If temperature allows this slight redistribution of electrons into a higher-energy band, then the material is no longer an insulator and is, instead, a **semiconductor**.
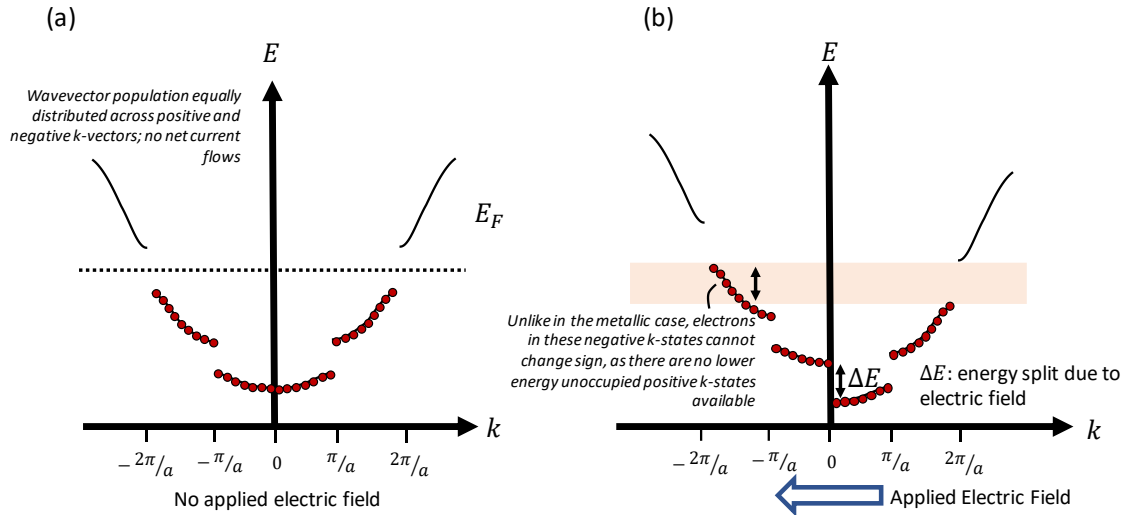
Figure S5: *(a) The highest occupied energy level in a semiconductor lies within a full band. Under no externally applied electric field the population of electron wavevectors are equally distributed in all directions (red points) and no current flows. (b) Again, an applied field increases the energy of electron waves with k-vector aligned with the field and decreases the energy of those with k-vector anti-aligned. However, in this semiconductor/insulator, there are no lower energy positive k-states that are unoccupied. Therefore, at zero Kelvin at least, no change in the adopted wavevector state occurs and the distribution of k-vectors remains the same in all directions. In other words, no current flows.*

In a semiconductor, when an electron is excited across the band-gap it also leaves behind a vacant quantum state in the lower-energy band (Figure S6). The lower energy band is then 'nearly-filled' with electrons and these electrons can now redistribute among the vacant states under an applied field to generate a current. An alternative view, although not perhaps immediately intuitive, is that the unoccupied quantum states can be shown to behave under an applied E-field as though they are occupied by positively charged particles. The positive charge carriers near the top of the nearly-full band are called 'holes' and, importantly, their motion under an applied field constitutes a *real* current that can be measured. Thus, when an electron is excited from the valence band to the conduction band, *two* mobile charge carriers are created: the electron ($-q_e$) and the hole ($+q_e$) it leaves behind in the lower-energy band. A highly simplified real-space visualisation of how holes move through the crystal lattice is illustrated in Figure S7: under the influence of an electric field, an electron occupying a neighbouring site can spatially transfer into the 'hole' but this now leaves a 'hole' at the atomic site where it moved from, and so on. In this respect, the hole responds to electric fields like a real particle with positive charge and can even be attributed an effective mass. Because of their positive charge, holes are categorised as *p-type carriers* and travel in the opposite spatial direction to an electron under an applied field. The existence of positively charged holes can be experimentally verified using the Hall Effect (session 2 experiment). In fact, so-called 'anomalous' Hall Effect measurements which indicated positive carrier mediated conduction in certain metals (e.g. tungsten) remained an enigma for some time, since p-type conduction could not be explained by simple classical models of electronic conduction.
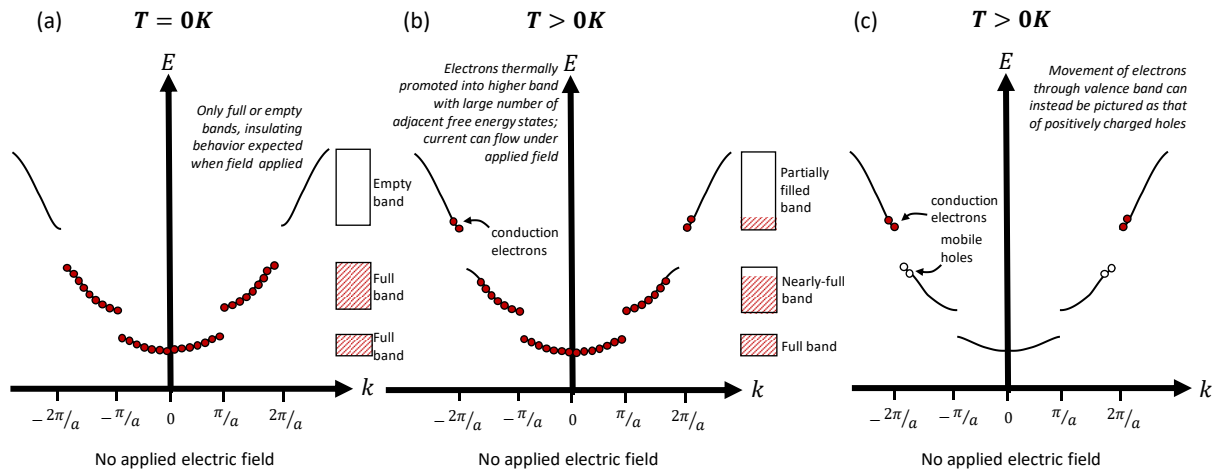
Figure S6 *(a) $E - k$ diagram for an insulator/semiconductor at zero Kelvin; no current is expected to flow when a field is applied as discussed in Figure S4. (b) At finite temperature the electron occupation of bands can change – thermal energy causes some electrons to vacate the states at the top of the lower energy band and occupy states at the bottom of the higher energy band that was previously empty. In this higher energy band, electrons have many states with similar energies that they can migrate into, so mobilities can be high even if the absolute number of carriers is low. If the band gap is small enough that temperature allows this slight redistribution of electrons into higher energy bands, then the material is no longer an insulator and is a semiconductor. (c) Redistribution of electrons among now-vacant k-states in the lower energy band can also constitute a contribution to current flow under applied field. This can be equivalently pictured as the migration of positively charged electron-holes to different energy states and is more convenient than to track than the behaviour of the large electron population in the nearly-full lower band.*
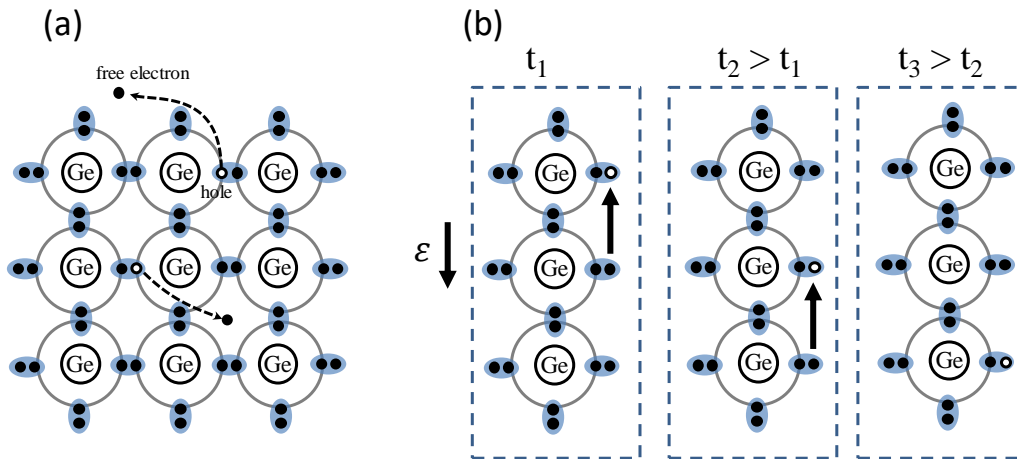

Figure S7: *(a) Simplified real-space schematic of electron-hole pair creation in a germanium crystal lattice. Thermal agitation causes an electron to become a free carrier, leaving behind a vacancy called a hole, which also behaves as a free carrier. The hole moves through the crystal under the influence of an applied field, consistent with that of a positive particle. (b) Schematic diagram showing how a positively charged hole moves through the crystal by sequential 'hopping' of electrons across lattice sites to fill in the hole. The movement of the hole generates a current in the same direction as the applied field, ε. 't' denotes time elapsed.*