Measurement of Resistivity and Determination of Band-gap using the Four-Probe method

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In this experiment, we employed the Four-Probe method, which uses four collinear probes for electrical contact, tomeasure the resistivity of Silicon, Germanium, and Aluminium samples at room temperature. Additionally, we studied the temperature variation of resistivity for Aluminium and Germanium and estimated the band gap energy of Germanium.

I. THEORY

The Four-Probe method is a widely used technique in materials science and condensed matter physics for accurate measurement of resistivity in materials. It is preferred over the conventional Two-Probe method due to its inherent advantages in minimizing errors caused by contact resistance. Four equally spaced collinear probes are used to make electrical contact with the surface of the material, with separate pairs of terminals to carry current and sense voltage. This configuration allows for precise voltage and current measurements, independent of the contact resistance, leading to more accurate and reliable resistivity measurements.

To set up a Four-Probe measurement, the probes are carefully positioned on the sample surface, to form a known probe spacing. A known current is passed through the outer probes, and the voltage drop across the inner probes is measured as shown in Fig. 1. The resistivity of the material can then be calculated using the measured voltage and current values, along with the probe spacing and geometry, following established mathematical formulas, such as the Van der Pauw method.

The Four-Probe method offers several advantages over the Two-Probe method. Firstly, it eliminates errors associated with contact resistance, which can be a significant source of inaccuracy in resistivity measurements. Secondly, it allows for precise and simultaneous voltage and current measurements, leading to improved accuracy and reproducibility. Additionally, the Four-Probe method can be used to measure resistivity in a wide range of materials, including thin films, bulk samples, and even highly resistive materials. Overall, the Four-Probe method is a reliable and widely used technique for accurate resistivity measurements in materials research and characterization.

A. Mathematical Formulation

For semi-infinite conducting material

A hemispherical equipotential surface develops at a probe when current flowing from a semi-infinite material is dispersed isotropically. The potential drop at an inner probe when two probes of different distances and opposing polarity are considered is:

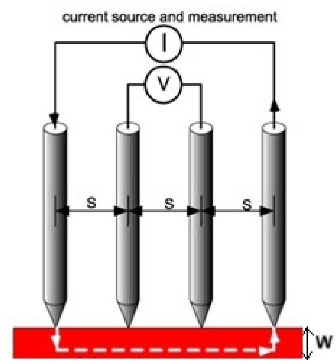

FIG. 1: Schematic of the Four-Probe setup

$$V = \frac{\rho_0 I}{2\pi}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \quad (1)$$

where ρ_0 is the resistivity, I is the current passed through the outer electrode and r_1 and r_2 is the distance from the probe 1 and probe 4 respectively. The floating potential across the inner terminals is determined by the following equation when evenly spaced probes are taken into account.

$$V = \frac{\rho_0 I}{2\pi S} \quad (2)$$

S is the probe spacing. The resistivity of the material can be calculated using the following equation:

$$\rho_0 = \frac{V}{I} 2\pi S \quad (3)$$

For thin sheet placed on a non-conducting surface

Since the thickness of the samples are small compared to the probe distance, a correction factor for it has to be applied. If the bottom surface is not conducting, then the corrected formula for resistivity will be:

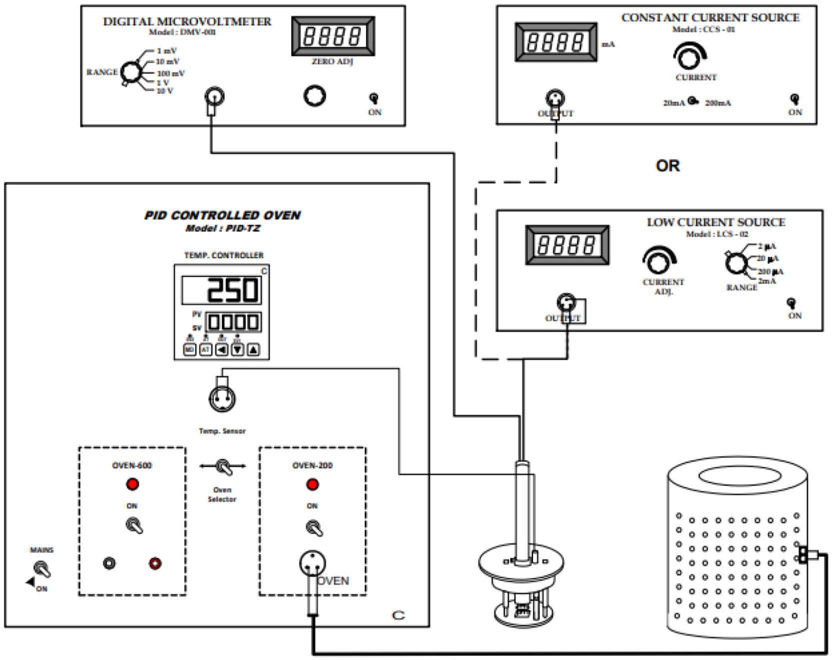

FIG. 2: Experimental setup for resistivity measurement with Four-Probe method

$$\rho = \frac{\rho_0}{G_7(W/S)} \tag{4}$$

where W is the width of the sample and $G_7(W/S)$ is the required correction factor dependent on the width-to-spacing ratio W/S, defined as follows:

$$G_7(W/S) = 1 + 4\frac{S}{W}\sum_{n=1}^{\infty} f(S,\ W,\ n) \tag{5}$$

$$f(S,\ W,\ n) = \left[\frac{1}{\sqrt{\left(\frac{S}{W}\right)^2 + n^2}} - \frac{1}{\sqrt{\left(\frac{2S}{W}\right)^2 + 4n^2}}\right] \tag{6}$$

For smaller values of $W/S(\leq 0.25)$, we can approximate the value of $G_7(W/S)$ as:

$$G_7(W/S) = \frac{2S}{W}\ln(2) \tag{7}$$

Thus, for samples where $W/S \leq 0.25$ or for sample thicknesses up to 0.5 mm, the correction factor can be directly obtained from the above equation. For the given experiment, considering $S = 2$ mm and $W = 0.5$ mm for Ge and Si and ~ 0.017 mm for Al, the correction factor is can be obtained from the above equation. Thus we get,

$$\rho = \frac{\pi}{\ln(2)} W \frac{V}{I} \tag{8}$$

B. Temperature dependence of Resistivity

The temperature dependence of resistivity varies for all three different types of materials we use.

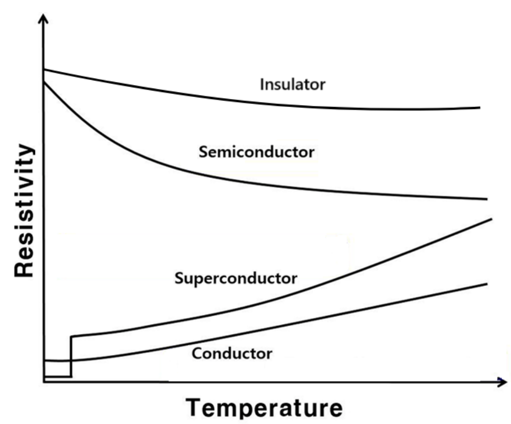

FIG. 3: A simplied plot depicting the relationship between temperature and resistivity for three types of materials

The resistance of the conductor increase with the increase in temperature because of the increased collision between electrons & vibrating lattice ions (phonons), which impede their flow and lead to resistance. The temperature coefficient of resistance of the metallic substance is positive.

In semiconductors, the numbers of free electrons in the valence band increase because of the breaking of the covalent bond at increased temperature.

Thus, more electrons from the valence band reach the conduction band. As a result, the resistance of the semi-conductor material decrease with an increase in temperature. Similarly, the resistance of the insulating material decrease with an increase in temperature (but quite slowly w.r.t. semi-conductors). Fig. 3 roughly shows the relationship between the change in the resistance and temperature rise for the three categories of material.

Relation of resistivity the band gap of a semiconductor

If E_g is the band gap energy, $k_B = 8.6 \times 10^{-5}$ eV/K is the Boltzmann constant, and T is the temperature in Kelvin,

$$E_g = 2k_B \frac{\ln(\rho)}{1/T} \tag{9}$$

where $\frac{\ln(\rho)}{1/T}$ can be determined from the slope of as appropriate $\ln(\rho)$ vs. T^{-1} plot.

II. EXPERIMENTAL SETUP

Apparatus

1. Four-Probe arrangement with spring-loaded probes
2. PID-controlled oven for temperature regulation
3. Constant current source (for both low and high current ranges)
4. Digital microvoltmeter
5. Thermocouple for temperature sensing
6. Aluminum and semiconductor samples (n-Si, n-Ge)
7. Screw Gauge

The connections were made as shown in Fig. 2 and 4. The sample was placed on a non-conducting surface, and the four probes were gently rested on the sample and tightened in position. The voltage (V) and current (I) measurements were taken from the respective digital displays.

When temperature changes were required, the sample setup was lowered into the oven chamber, and the thermocouple sensor and oven socket were connected to the PID (Proportional-Integral-Derivative) controller. After selecting the desired oven temperature (e.g., 200°C) and turning on the mains, data collection was initiated once the Present Value (PV) stabilized to the Set Value (SV) on the PID controller.

III. OBSERVATION AND CALCULATIONS

Probe distance of the setup, $S = (0.20 \pm 2\%)$ cm (fixed)

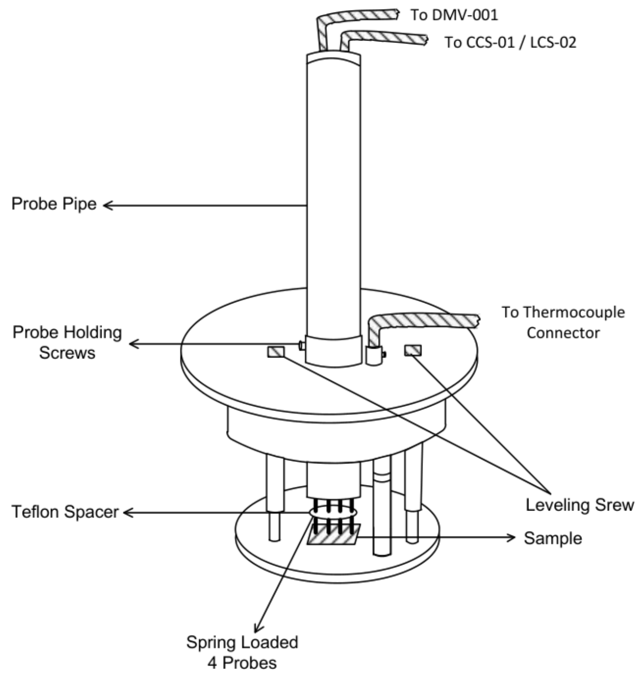

FIG. 4: The Four-Probe setup

A. Measurement of Resistivity

Table I contains the observed V-I data, using the four-probe setup, for all the three samples.

Al		n-Si		n-Ge	
I (mA)	V (mV)	I (mA)	V (mV)	I (mA)	V (V)
0.08	0.000	0.050	4.8	0.13	0.014
10.01	0.004	0.107	10.1	0.55	0.051
19.70	0.008	0.155	14.7	1.11	0.098
31.10	0.013	0.205	19.5	1.50	0.132
40.50	0.016	0.303	28.8	1.98	0.172
51.00	0.021	0.407	38.6	2.59	0.224
60.50	0.024	0.505	47.9	3.06	0.264
70.60	0.029	0.600	57.0	3.50	0.302
80.30	0.032	0.703	66.7	4.05	0.349
90.00	0.036	0.802	76.2	4.53	0.390
100.60	0.041	0.903	85.9	5.06	0.435
110.90	0.045	1.002	95.2	5.56	0.478
120.70	0.049	1.104	104.9	6.00	0.515
130.10	0.053	1.214	115.4	6.47	0.555
140.00	0.057	1.304	123.9	6.98	0.598
150.40	0.061	1.412	134.3	7.47	0.640
160.00	0.065	1.505	143.1	7.68	0.659
170.60	0.069				
180.80	0.073				
191.00	0.078				

TABLE I: V-I data for the resisvity measurement for all three samples

1. *Aluminium*

Using a screw gauge, the thickness of the given Aluminium sample was measured to be $W = 0.017$ cm.

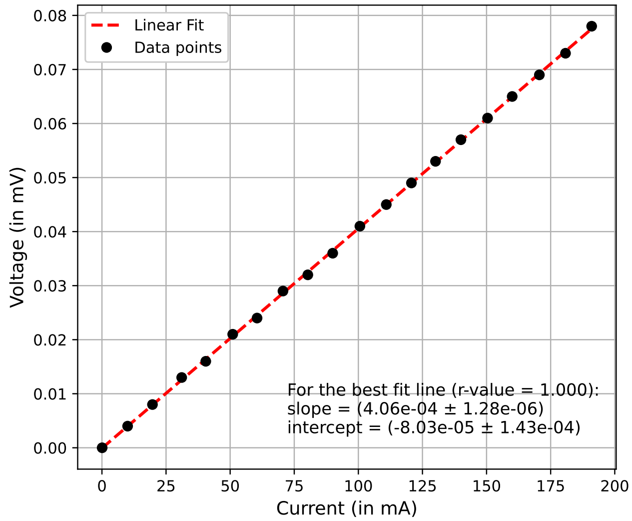

FIG. 5: V-I plot for the Aluminium sample at room temperature

Plugging the slope in Eq. 8, the resistivity at room temperature of Aluminium comes out to be $\rho = 3.131 \times 10^{-5}$ Ω cm.

2. *n-Silicon*

The thickness of the provided sample was $W = (0.05 \pm 2\%)$ cm.

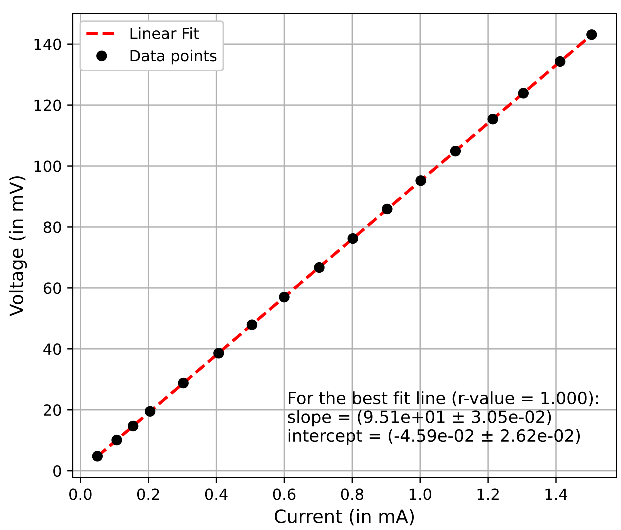

FIG. 6: V-I plot for n-Silicon at room temperature

Plugging the slope in Eq. 8, the resistivity at room temperature of n-Si comes out to be $\rho = 21.549$ Ω cm.

3. *n-Germanium*

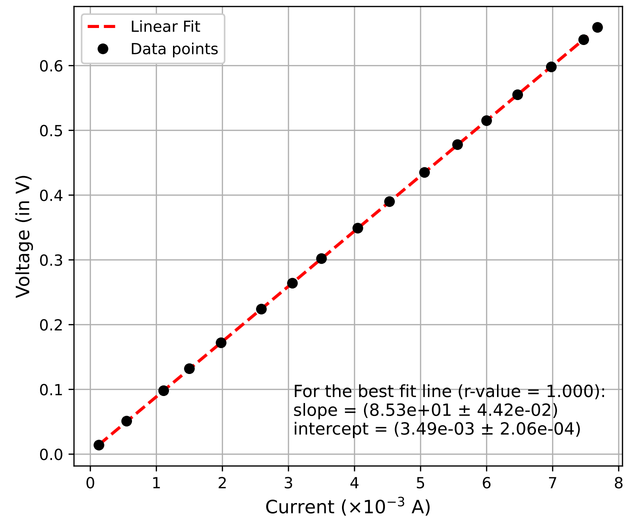

FIG. 7: V-I plot for n-Germanium at room temperature

Plugging the slope in Eq. 8, and using $W = (0.05 \pm 2\%)$ cm, the resistivity at room temperature of n-Ge comes out to be $\rho = 19.322$ Ω cm.

B. Estimation of Band-gap

1. *n-Germanium*

T (in °C)	V (V)	ρ (Ω cm)
81	0.141	14.715
82	0.138	14.402
85	0.126	13.150
90	0.108	11.271
92	0.103	10.749
97	0.091	9.497
100	0.083	8.662
105	0.073	7.618
110	0.065	6.783
115	0.057	5.949
120	0.050	5.218
125	0.045	4.696
130	0.040	4.174
135	0.036	3.757
140	0.032	3.340
145	0.029	3.026
152	0.025	2.609
155	0.024	2.505
160	0.022	2.296
165	0.020	2.087
170	0.018	1.879
175	0.016	1.670
181	0.015	1.565

TABLE II: Temperature dependence of V and subsequently ρ of the n-Ge sample at a fixed $I = 5$ mA.

Table 2 shows the observed T-V data. The error-bars are calculated with standard error propagation formulae (Section IV).

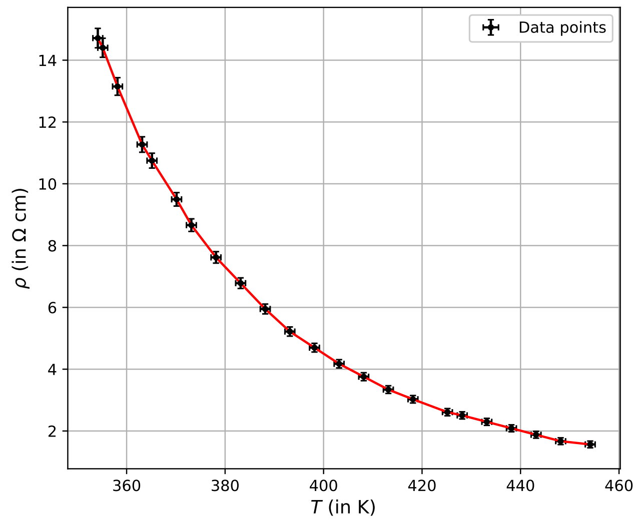

FIG. 8: ρ vs. T plot for n-Germanium for temperatures from 80°C to 180°C

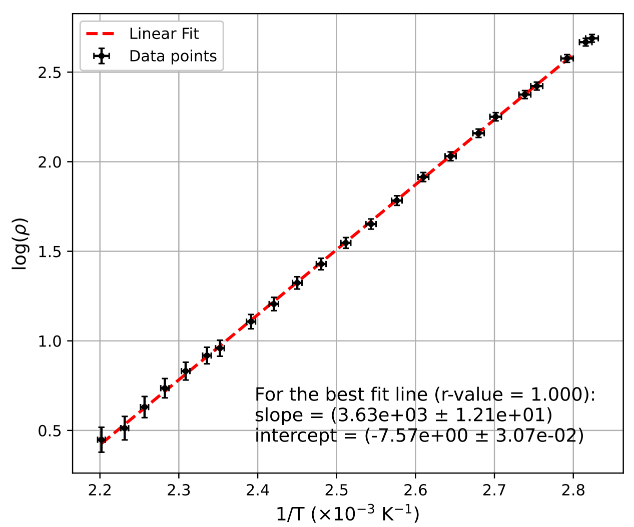

FIG. 9: $\log(\rho)$ vs. T^{-1} plot for n-Germanium for temperatures from 80°C to 180°C

From Fig. 9, we get the slope of $\log(\rho)$ vs. T^{-1} which we can substitute into Eq. 9 to get the band-gap of the given Ge sample as,

$$E_g = 2k_B \frac{\log(\rho)}{1/T} = 0.626 \text{ eV}$$

where k_B is the Boltzmann's constant $= 8.6 \times 10^{-5}$ eV/K.

2. Aluminium

Table 3 shows the observed T-V data.

T (in °C)	V (mV)	ρ ($\times 10^{-5}\,\Omega$ cm)
32	0.044	7.806
40	0.045	7.984
43	0.046	8.161
46	0.047	8.338
49	0.050	8.871
64	0.055	9.758
67	0.057	10.113
74	0.059	10.467
75	0.060	10.645
78	0.061	10.822
84	0.062	11.000
89	0.063	11.177
90	0.064	11.355

TABLE III: Temperature dependence of V and subsequently ρ of the Al sample at a fixed $I = 100$ mA.

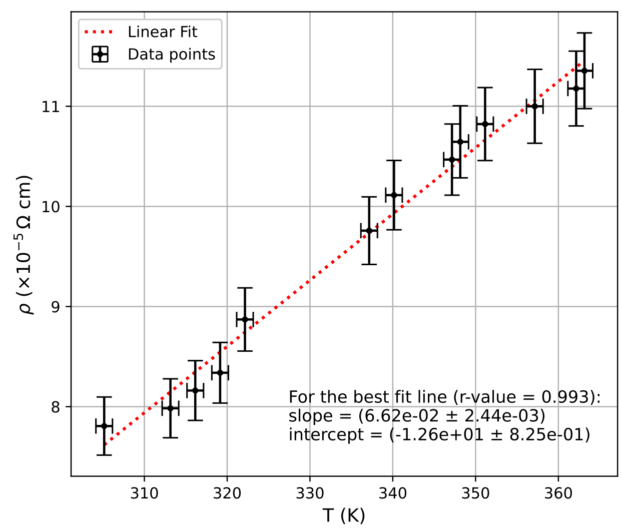

FIG. 10: ρ vs. T plot for the Aluminium sample for temperatures from 32°C to 90°C

For the temperature range used in this experiment (around 30°C to 90°C), we can theory predicts that the rise in ρ with temperature is is roughly of linear order. Using, the linear relation,

$$\rho = \rho_{T_0}[1 + \alpha(T - T_0)] \tag{10}$$
$$\text{or, } \rho = \rho_{T_0}\alpha T + \rho_{T_0}(1 - \alpha T_0)$$

and the linear fit in Fig. 10, we can approximate the temperature coefficient, α to be,

$$\alpha = \frac{\text{slope}}{\rho_{T_0}} = 8.475 \times 10^{-3} \text{ K}^{-1}$$

where $T_0 = 32°\text{C} = 304.15$ K.

IV. ERROR ANALYSIS

The error in the resistivity comes from the error of the slope of the fitted curve and the uncertainities in the thickness of the sample.

$$\frac{\Delta\rho}{\rho} = \sqrt{\left(\frac{\Delta W}{W}\right)^2 + \left(\frac{\Delta \text{slope}}{\text{slope}}\right)^2} \tag{11}$$

For the Al sample, $\Delta W = 0.001$ cm and for n-Si and n-Ge, $\Delta W/W = 2\%$. Plugging in Δslope from Figs. 5 to 7, we get

- $(\Delta\rho)_{\text{Al}} = (0.184 \times 10^{-5})\ \Omega$ cm
- $(\Delta\rho)_{\text{n-Ge}} = 0.387\ \Omega$ cm
- $(\Delta\rho)_{\text{n-Si}} = 0.431\ \Omega$ cm

For the uncertainity in E_g, we can similarly write,

$$\Delta E_g = E_g \left(\frac{\Delta \text{slope}}{\text{slope}}\right) \tag{12}$$

where the slope is the slope in the linear fit of the $\log(\rho)$ vs. T^{-1} plot. Plugging in the values, we get for the n-Ge sample, $\Delta E_g = 0.002$ eV.

The error in the temperature coefficient, α can similarly be derived using,

$$\frac{\Delta\alpha}{\alpha} = \sqrt{\left(\frac{\Delta\rho_{T_0}}{\rho_{T_0}}\right)^2 + \left(\frac{\Delta \text{slope}}{\text{slope}}\right)^2} \tag{13}$$

Using Table 3 and putting $\Delta\rho_{T_0} = 0.290\,\Omega$ cm, we get $\Delta\alpha = 0.442$ K^{-1}.

V. DISCUSSION & CONCLUSION

Our experiments utilizing the four probe method allowed us to accurately determine the resistivities of various samples, including both semiconductors and metals. Using the the variation in voltage with the applied current, we have estimated the resistivity values of the three given materials to be

- Aluminium, $\rho = (3.131 \pm 0.184) \times 10^{-5}\ \Omega$ cm
- n-Germanium, $\rho = (19.322 \pm 0.387)\ \Omega$ cm
- n-Silicon, $\rho = (21.549 \times 0.431)\ \Omega$ cm

These are close to the actual values provided by the manufacturer for n-Si ($24 \pm 1\ \Omega$ cm) and n-Ge ($18 \pm 1\ \Omega$ cm). However, there is a significant deviation in the case of Al ($2.8 \times 10^{-6}\ \Omega$ cm for pure Al), which could be due to the fact that we are using commercial-grade Al foil.

Additionally, We observed that the resistivity of semiconductors decreased with an increase in temperature, inline with theoretical predictions. We were able to calculate the band gap of a semiconductor sample through these temperature-dependent measurements, which came out to be

$$E_g = (0.626 \pm 0.002) \text{ eV}$$

This is close to the literature value of 0.680 eV. There is a round -8% deviation, which could be attributed to the fact that the band-gap varies with temperature and the literature value is defined at 303 K (30°C).

As the temperature increases, more electrons jump from the valence band to the conductance band. These electrons can now conduct the current and the conductivity increases. And hence the resistivity decreases.

We also saw that the temperature-dependence of resistivity of Aluminium metal. We saw that there was an increase in the resistivity as temperature increases, which is caused due to increased phonon scattering. We approximated a linear order fit over the temperature range used in the experiment, to estimate the temperature coefficient of Al, which came out to be $\alpha = (8.475 \pm 0.442) \times 10^{-3}$ K^{-1}. This is roughly of the order of α defined for pure Aluminium, 4.308×10^{-3} K^{-1}. There was also a large error associated with the measurements (see Fig. 10), primarily due to the error associated with the measurement of W ($\sim 7\%$).

Note that fluctuations in supply voltage, carrier injection, or impurities in the sample material could have lead to errors which were propagated to our final results. We also made assumptions about the uniformity of resistivity in our samples, which may not always hold true.

VI. PRECAUTIONS AND SOURCES OF ERROR

1. Instability in the data due to improper contact could lead to errors, so the springs should be tightened carefully.
2. Al used in the foil is commercial grade, while standard resistance is for pure Al.
3. Variation of doping or impurities in the sample could also contribute to errors.
4. Sufficient time should be given for the temperature to stabilize before noting the measurements.

[1] SPS, *Measurement of resistivity and determination band gap using Four-Probe method*, NISER (2022).

[2] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*.