

Phase transition of chromium and electron diffraction

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Abstract

This study examines the magnetoelastic phase transition of chromium, specifically the transition from antiferromagnetism to paramagnetism at Néel temperature. This study examines the relationship between magnetic reordering and volumetric changes using direct volume measurements. The experiment explores the relationship between magnetic properties and structural transformations by precisely manipulating environmental parameters, including temperature. This experiment contributes to a better understanding of phase transitions, material effects, and physics instrumentation. The calculated results are within the error range. Errors have been discussed and addressed.

Keywords

Chromium–Phase transition–Néel’s temperature

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Objectives

- To study the phase transition of Chromium at Néel’s temperature.

1. Introduction

In physics, phase transition is a phenomena when a state of medium transitions into another state of medium owing to change in environmental conditions. Phase transition can

also occur within solid when the magnetic ordering of the materials change. Transition of naphthalene balls and sublimating in the atmosphere is an example of phase transition. Similarly, chromium is a metal that exists in BCC lattice structure and undergoes a phase transition at a characteristic temperature called **Néel’s temperature** that changes the magnetic properties of the metal. The chromium metal, which is anti-ferromagnetic at room temperature transitions into paramagnetic material above the Néel’s temperature. The theory of the phase transition is given in section 1.1.

1.1 Phase transitions

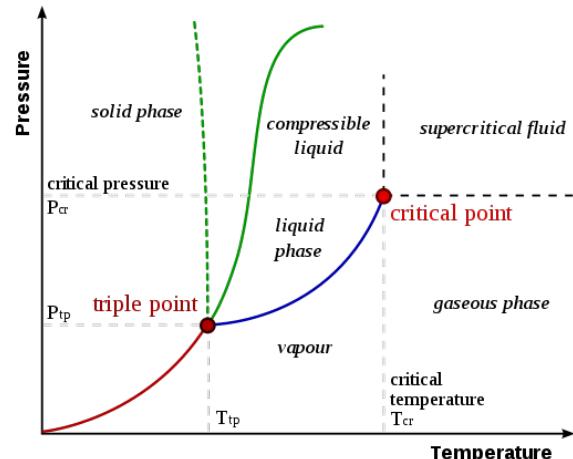


Figure 1. Triple point

Phases are a state of matter whose properties vary smoothly with respect to thermodynamic variables. Clarke et.al.^[1] described phase as an entity of material that system that is uniform in chemical composition and physical state. Phase transitions phenomena occurs when there is a macroscopic change in a macroscopic thermodynamic quantity by changing an

environmental variable infinitesimally. This phenomena is peculiar and leads to singularities in the system. The phase transitions can be classified based on their order of transitions. To define the order, knowing the notion of order parameter is important. Bagchi^[2] defines the order parameter of a system is a physical quantity so chosen that it is 0 before the phase transition and non zero after the phase transition or vice-versa. For example, change in density can be defined as an order parameter near the transition temperature for water. The idea of how phase transitions occur can be explained through the evolution of the order parameters.

1.1.1 Ehrenfest classification

Ehrenfest classified phase transitions with respect to the derivatives of the free energies with changing different thermodynamic variables and order parameters. A n th order of phase transition is one in which the n th derivative of the free energy with respect to the order parameter or other thermodynamic variables shows discontinuity^[3]. The main reason a system undergoes a phase transition is to minimize its free energies. The stability of the materials can be determined using the second derivative of the macroscopic variable. For example, Gibbs free energy is a concave function of pressure and temperature while the Helmholtz free energy is a convex function of volume while a concave function of pressure. Metastability, hysteresis and nucleation are some of the important properties of phase transitions. In first order phase transitions, there exist a meta stable state where the free energy has a local minima. For example, amorphous ice is an example of meta stable state of water near freezing temperature. Hysteresis and nucleation are other properties of phase transitions as discussed by Yuri^[4]. The physics of phase transition can be studied what happens near the phase transition point. Thus, Landau expanded the thermodynamic quantities near the phase transition using the order parameter.

1.1.2 Landau Theory

Landau expanded the free energies as:

$$F^{(n)} = F_0 + \alpha\eta + A(T)\eta^2 + \beta(T)\eta^3 + \dots \quad (1)$$

Since the free energy is minimized, the 2nd term $F^{(2)} = \alpha\eta$ goes to 0. Since, $(\frac{\partial F}{\partial \eta})_{\eta=0} = 0$ gives $\alpha = 0$. Thus, the free energy equation simplifies to:

$$F^{(n)} = F_0 + A(T)\eta^2 + C\eta^4 + \dots \quad (2)$$

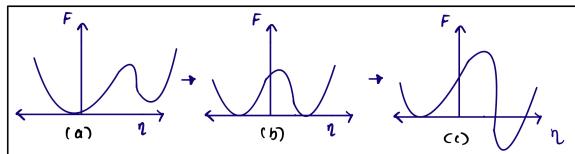


Figure 2. 1st order phase transition

In case of 1st order transition, since η is small, the expansion is truncated to 3rd order and the properties are studied. Due to presence of η^3 term, we see an asymmetry in the system. Thus, this leads to a metastable state near the transition points

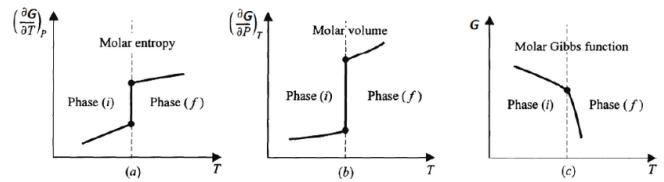


Figure 3. First order phase transitions

as shown in figure . In fig 2(b), we observe coherence and there is a separation between the two states due to nucleation. Thus, first order transitions are not spontaneous, which can also be realized from Golstone theorem which states that there shall exist a low energy excitation state of the system when a symmetry is spontaneously broken. In case of second order phase transitions there is an inherent symmetry that can be observed from eq(2). Taking upto order 4 term and minimizing, we can arrive at the equations that give critical exponents a basic definition. For example, solving for lowest energy from eq(2):

$$\eta = 0, \pm \sqrt{\frac{a(T_c - T)}{2C}} \quad (3)$$

where T_c is the critical temperature and $\frac{1}{2}$ is the critical exponent.

When a phase transition occurs, it does not occur simultaneously for all atoms/molecules of the system. Thus, there may be differences in the states that lead to differences in the surface tensions. This can lead to extra energy terms in the Landau theory, incorporating the surface tensions and nucleations. Thus, finally the Ginsberg - Landau theory is proposed and is given by:

$$F^{(n)} = F_0 + \alpha\eta + A(T)\eta^2 + \beta(T)\eta^3 + \dots + k \int dr (\nabla \eta(r))^2 \quad (4)$$

In case of phase transition of Cr, it is a 1st order process and can be studied by observing the volumetric change with respect to change in temperature. At room temperature, the chromium is anti-ferromagnetic. When it reaches the Néel temperature, it loses its anti-ferromagnetic properties and becomes paramagnetic owing to thermal agitations and high collisions among the electrons. Since there is an inherent change in the magnetic moments, the crystal structure often shifts to accommodate for the change in the system. Thus, we observe a drastic change in the volume of the sample at Néel temperature. This can be measured using a strain gauge.

1.2 Thermodynamics of phase transition

When a phase transition is observed, it is accompanied by minimization of free energies. The Gibbs free energy is given

by:

$$G = H - TS \quad (5)$$

When the process is reversible, the variables can be changed infinitesimally and thus the equation becomes:

$$dG = Vdp - SdT \quad (6)$$

From this, the expressions for entropy and volume can be extracted as:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad (7)$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T \quad (8)$$

From equations 7 and 8, we can see that at first order phase transitions, we have the following phenomena:

- The molar entropy and molar volume change at the phase transition.
- The first-order derivatives of the Gibbs function with respect to temperature and pressure change discontinuously, as shown in fig 3.

Since it is not feasible to measure the entropy change, often observing volumetric change is preferred. This is done using the strain gauge.

1.2.1 Clausius-Clapeyron Equations

The Clausius-Clapeyron Equations give a relationship between pressure and temperature near the phase boundaries. The line separating two phases is known as a co-existence curve. Along the coexistence curve, the Gibbs free energy is constant. In case of melting of ice, the slope of the phase boundaries is given by the equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{L}{T\Delta V} \quad (9)$$

where L is the latent heat and H is the enthalpy. Since $dT = 0$ and $dP = 0$, we see discontinuity in entropy and volume at near the phase transitions. There are two important points in a phase transition graph, namely the triple point and the critical points. The triple point of water is the combination of pressure, temperature at which all states of water, namely ice, water and vapours exist simultaneously. The critical point on a P-T graph is the point beyond which the substance is indistinguishable between liquid and gaseous states. In other words, once can change from one phase to another without involving a phase transition.

1.3 Experimental setup

The experiment uses the following components:

- Chromium sample

- LT11 strain gauge
- K type thermocouple (Metravi)
- Silicon oil
- Exp Eyes setup
- Heater
- IC : LT1024, OP07
- Connecting wires / breadboard
- Power supply
- Laptop

A heater was designed in the workshop with a slot to put in Chromium sample with dimensions 12.87mm x 12.87mm. Thin double sided tape was used to stick the sample to the heater and the K-type thermocouple was attached to the surface of the sample and sealed using aluminium tape. This was then dipped into the silicon oil for even heat transfer to the sample from the heater.

2. Experimentation

2.1 Volume measurements

The volume is measured using the strain gauge. The LT11 strain gauge is made of steel and is attached to the surface of the sample. As the sample expands, it also expands the attached strain gauge. This change in its geometry leads change in the resistance of the strain gauge. Thus, a change in the resistance of the strain gauge is observed per unit change in length. The change in length due to the change in magnetic order can be given by the equations:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (10)$$

$$TdS = C_p dT - V\beta dP \quad (11)$$

where $C_p = T\left(\frac{\partial S}{\partial T}\right)_P$ is the heat capacity at constant pressure. When a phase transition occurs, the change in pressure and temperature are 0, so $dT = dP = 0$. Thus, near transition, we find discontinuous change in volume since $C_p \rightarrow 0$ and $\beta \rightarrow 0$. The strain gauge is connected with the chromium sample using adhesives and bonding pads. So, a change in length of chromium is directly proportional to the change in length of the strain gauge and thus to the change in the resistance of the strain gauge. The volume expansivity and the linear expansivity are related by the equation:

$$\beta = \frac{3}{V} \frac{\Delta L}{L} \quad (12)$$

The gage factor of a strain gauge is defined as the fractional change of resistance per fractional change of length. Mathematically:

$$F = \frac{\Delta R}{R} / \frac{\Delta L}{L} \quad (13)$$

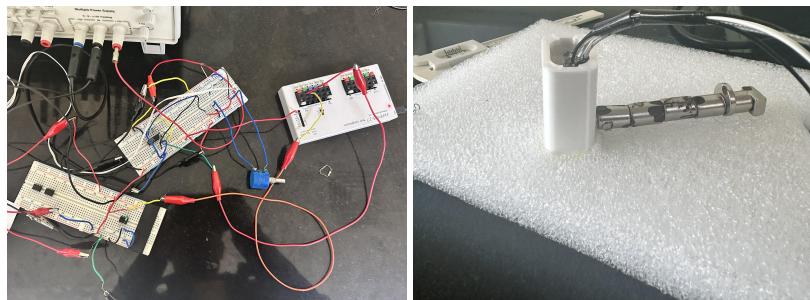


Figure 4. Experimental setup

2.2 Temperature measurements

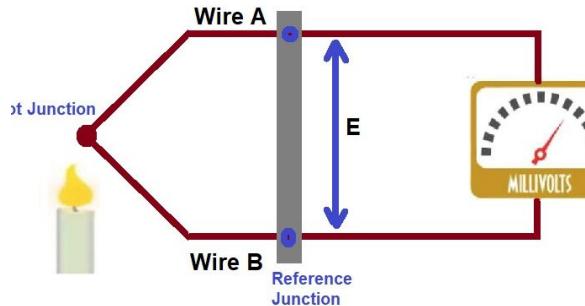


Figure 5. Thermocouple schematics

A K type thermocouple is used to measure the temperature change of the sample. The thermocouple is attached to the sample in order to get accurate measurements. Thermocouples work on the concept of Seebeck effect. Seebeck effect is a phenomena in which temperature difference between two dissimilar metals/semiconductors produces a voltage difference between the two metals. This happens as the electrons in the hotter region move towards the cooler region, creating a potential difference and thus, a current. The K type thermocouple uses nickel and chromium in its positive leg and nickel and aluminium in the negative leg. The seebeck coefficient of a thermocouple is the change in its voltage per unit temperature change in kelvins. It is $40 \mu\text{V}$ for the K type thermocouple. The thermocouple is attached to the sample using a glass slide and then aluminium tape for good conductivity of heat. The voltage is measured on Expeyes-17 at intervals of 1 seconds and the change in temperature is noted using the seebeck coefficient and knowledge of the room temperature. The system here uses a silicon oil medium so that heat transfer takes place at faster rates and the system is evenly heated.

2.3 Thermal expansion

The strain gauge uses semiconductors and steel for measuring the strains. This results in formation of strain per unit change in the temperature. The induced strain per unit change in temperature is given by:

$$\frac{\Delta L}{L \Delta T} = \frac{\alpha}{F} + (\beta_s - \beta_c) \quad (14)$$

where α is the temperature coefficient of resistance, F is the gauge factor, β_s and β_c are coefficient of thermal expansion

of strain gauge and chromium sample respectively. Ideally, specific equipments are required to study the change of strain in the strain gauge. In our case, we use a wheatstone bridge to study the change of resistance in the sample.

2.4 Wheatstone bridge

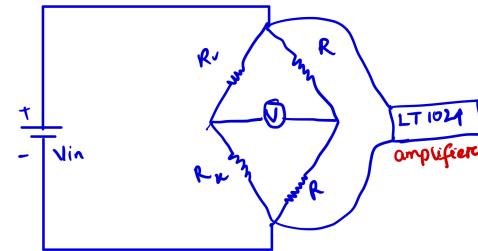


Figure 6. Wheatstone bridge schematics

Wheatstone bridge is a special arrangement of resistances arranged in such a manner that if any three resistances are known, then we have a knowledge of the fourth resistance. It works on the principle of null detection that is the ratio of resistance is equal and the net flow of current in the circuit is 0. The schematics for the wheatstone bridge is shown in fig . The equilibrium is achieved when:

$$\frac{R}{R_v} = \frac{R}{R_{sg}} \quad (15)$$

If initial values of all the resistances are known, the change in one of the resistances can be found by measuring the voltage across the bridge. Due to change in resistance, the bridge becomes unbalanced and using the Kirchoff's laws, we can get the following relation:

$$V_g = V_{in} \left(\frac{R_v}{R_v + R_{sg}} - \frac{R}{2R} \right) \quad (16)$$

where $R_1 = R_2 = R = 56.2$ ohms, R_v is the variable resistance which is found to be 121.7 ohms at room temperature. The R_{sg} is the resistance of the strain gauge. Thus, when there is change in the R_{sg} , due to increase in temperature and strain, we can obtain the values continuously by measuring the output voltage V_g . The resistance of the strain gauge is given by:

$$R_{sg} = R_v \left(\frac{2V_g + V_{in}}{V_{in} - 2V_g} \right) \quad (17)$$

An increase in voltage leads to an increase in the resistnace. Thus, the resistance of the strain gauge increases with increasing the temperature, which also corresponds to the volume expansion. Hence, at neels temperature, we shall see a kink near the Neel's temperature in voltage / resistance vs temperature graph.

2.5 LT 1024 amplifier

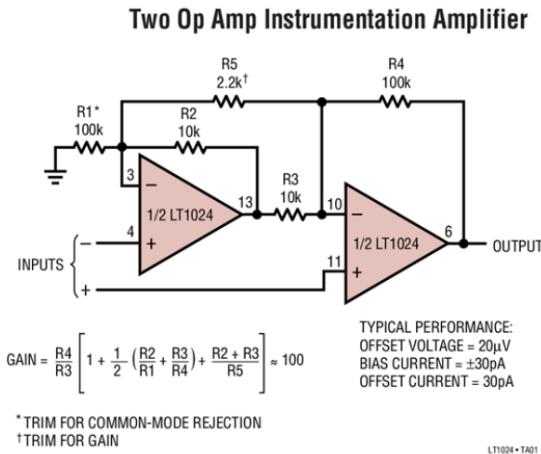


Figure 7. LT1024 instrumentation amplifier schematics.

The LT1024 is a dual, matched, low-noise operational amplifier that balances high performance and cost-effectiveness, making it ideal for instrument amplifiers. Features include low offset voltage, bias current, and drift, as well as high common-mode rejection ratio, power supply rejection ratio, and voltage gain. In this experiment, we use the LT1024 to create an amplifier that detects the potential difference between the two arms of the Wheatstone bridge while also capturing strain gauge resistance changes.

2.6 Data acquisition

In order to get continuous data for V-T characteristics, ExpEyes -17 was used to get record data every at interval of every 1 second. Initially, the voltage output from the thermocouple and the wheatstone bridge were low. Thus, amplifiers were used to get the get the amplified voltage outputs. The OP07 amplifier was used to amplify the signal from the thermocouple by 991 times while the signal from the wheatstone bridge was amplified by 112 times using LT1024 instrumetnation amplifier. The OP07 and LT1024 are low noise amplifiers that are good at detecting signals low low amplitude without adding much to the noises. The schematics for the LT1024 is given in fig 6. This allowed to take data in more than 2.5mV ranges which is the least count for ExpEyes. Thus, the readings were taken by increasing the temperature and measuring the voltage every 1 second for 900 seconds, for a heating - cooling process. The code used is attached:

```
import eyes17.eyes
p = eyes17.eyes.open()
import threading
import time

def observation(counter):
    x=[]
    y=[]
    A = 1
    while counter!=900:
        print(counter)
        time.sleep(1)
        counter= counter + 1
        A = p.get_voltage('A2')
        B = p.get_voltage('A3')
        x.append(A)
        print(A,B)
        y.append(B)
    return x,y
filename = "dataset15feb_4.csv"
X = []
Y = []
X,Y = observation(0)
with open(filename,'w') as f:
    f.write('Voltage_thermocouple, Voltage_wheatstone\n')
    for i in range(len(X)):
        f.write(f'{X[i]},{Y[i]}\n')
```

Figure 8. Code for data reading.

This allowed us to get a csv file with voltage from the thermocouple and the voltage from the wheatstone bridge. The thermocouple voltage was renormalized to get 0 at room temperature and the change of temperature was measured through change in voltage divided by the amplified seebeck coefficient, which was 0.03964. i.e,

$$\Delta T = \frac{\Delta V}{S} \quad (18)$$

where S is the seebeck coefficient. Thus, this temperature was added to the room temperature to get the temperature of the sample. Next, the plot between voltage and temperature was plotted. This, gives us a curve that is related to voltage by constants, so, a kink in the V-T graph would give us kink in the Volume - T graph and a first derivative discontinuity and hence, would denote the trasition temperature, called the Neel's temperature.

2.7 Issues faced and resolved

The first issue faced was with the sample holder. It was a glass jar, with oil in it. The jar was too big and it took a long while to heat up. Also, while measuring the fields, it caused issues. Thus, a new holder was made to hold the sample perpendicular and fixed while also reducing the volume of oil used for faster heating. The picture of the same can be seen in fig(4). This solved our issue of slow heating and erroraneous field measurements. Another issue faced was the low voltage readings. These were solved by using LT1024 and OP07 amplifiers. These helped to get the readings using ExpEyes 17 which has least count of 2.5mV. The data acquisition had to be interaced with ExpEyes, which had some hurdles which were solved over time. The next problem was measuring the field at which the transition vanishes, which was resolved using the new sample holder, although we still could not achieve precise values.

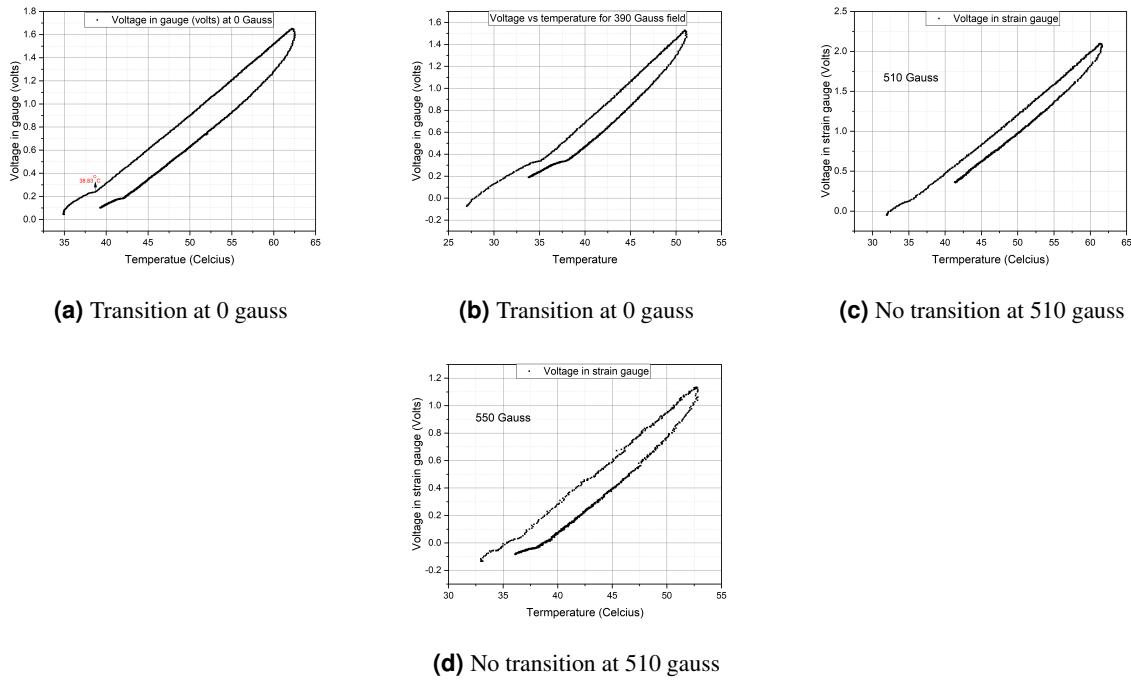


Figure 9. V-T graph for various magnetic fields

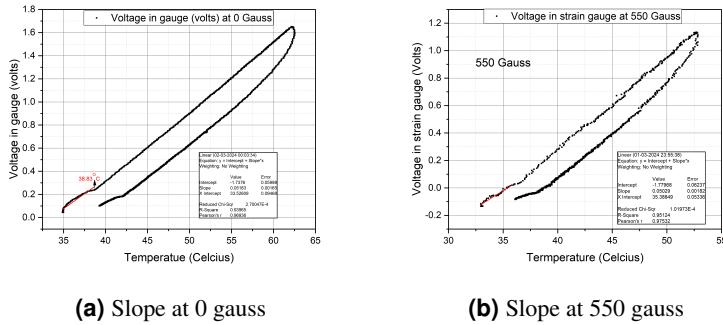


Figure 10. V-T graph with slopes.

3. Observations and calculations

The observations were made using the setup. Initially, the phase transition was studied at 0 net magnetic field. This allowed us to find the Neel's temperature of Chromium sample. Since there is transition of Cr from AFM to FM, we see a transition. In presence of adequate magnetic field, there was no transition, which has a lower threshold of 510 gauss, as shown in fig(9d).

From 10b and 10a, we find the slope:

$$m_0 = 0.05183 \pm 0.00165$$

$$m_{550} = 0.05029 \pm 0.00182$$

The units of slope are voltage / kelvin. We take 0 gauss and 550 gauss cases to calculate various other parameters of the readings. From eq 13 and eq 14, we can get the fractional expansions to get the different values:

- $\beta_c(0) = 4.654 \times 10^{-6} \text{ K}^{-1}$
- $\alpha_{cr}(0) = 1.695 \times 10^{-6} \text{ K}^{-1}$
- $\beta_c(550) = 4.084 \times 10^{-6} \text{ K}^{-1}$
- $\alpha_{cr}(550) = 2.265 \times 10^{-6} \text{ K}^{-1}$

Here, $\alpha = 0.00045 \text{ (1/K)}$, $F = 120 \text{ ohms}$ and $\beta_s = 2.6 \times 10^{-6} \text{ (1/k)}$.

3.1 Error Analysis

Calibration, electrical noise, signal drift, thermal contact, hysteresis, signal averaging, environmental factors, data analysis, and instrumentation limitations all have the potential to cause errors. The data tables presented at the end of the table are used to plot the graphs to get slope errors in β and α . Thus, we get:

$$\delta\beta_c(0) = 0.34 \times 10^{-7} \text{ K}^{-1}$$

$$\begin{aligned}\delta\alpha_{cr}(0) &= 0.23 \times 10^{-8} \text{ K}^{-1} \\ \delta\beta_c(550) &= 0.56 \times 10^{-7} \text{ K}^{-1} \\ \delta\alpha_{cr}(550) &= 0.28 \times 10^{-7} \text{ K}^{-1}\end{aligned}$$

Error in slopes for the V-T curves are given in the inset of the graphs and are all within 10% error range.

4. Results

- The Slopes for the V-T curves : $\sim 0.05183 \text{ V/K}$ with the largest error of ± 0.00165 which is acceptable and comes within the 10% error range.
- $\beta_c(0) = 4.654 \times 10^{-6} \text{ K}^{-1} \pm 0.34 \times 10^{-7} \text{ K}^{-1}$
- $\alpha_{cr}(0) = 1.695 \times 10^{-6} \text{ K}^{-1} \pm 0.23 \times 10^{-7} \text{ K}^{-1}$
- $\beta_c(550) = 4.084 \times 10^{-6} \text{ K}^{-1} \pm 0.56 \times 10^{-7} \text{ K}^{-1}$
- $\alpha_{cr}(550) = 2.265 \times 10^{-6} \text{ K}^{-1} \pm 0.28 \times 10^{-7} \text{ K}^{-1}$

5. Discussion and conclusion

In this experiment, the transition of chromium metal with change in temperature was measured and its theoretical aspects were studied. We saw that there was sudden increase in the voltage at the Neel's temperature. This was within 10% error bar of measurements. The sample was heated to higher voltages and then when the sample was cooled, we saw a decrease in the volume of the volume of the sample, and hence a hysteresis. But, this is counter intuitive since there shall be residual behaviour in the system and the sample shall be elongated compared to normal sample at the room temperature. Interestingly, we also see transition in the reverse process. But this is achieved at a different temperature. These two observations need further investigation. Further, we observed that the transition of AFM - PM vanishes after applying a threshold field, beyond which we see no transition. For the sample, this was found to be between 510 - 550 Gauss. Although due to limitations in measuring the magnetic field the exact field could not be noted.

The slope of the V vs T graph was analysed, and it was found to be consistent with pre-transition antiferromagnetic behaviour in both magnetic fields and without. As observed from data, saturation at specific temperatures can lead to limitations in semiconductor strain gauges, which are common in temperature-sensitive materials..The error analysis discussed the calculated thermal expansion coefficient for chromium, which was close to theoretical values (10^{-6}), while also addressing experimental limitations. Overall, the experiment was a success and the properties of Cr along with phase transitions were studied.

phase transitions of the solid state (iupac recommendations 1994). *Pure and Applied Chemistry*, 66(3):577–594, January 1994.

- [2] Biman Bagchi. *Statistical Mechanics for Chemistry and Materials Science*. CRC Press, 7 2018.
 - [3] Gregg Jaeger. The ehrenfest classification of phase transitions: Introduction and evolution. *Archive for History of Exact Sciences*, 53(1):51–81, May 1998.
 - [4] Yuri Mnyukh. Hysteresis and nucleation in condensed matter, 2011.
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References

- [1] J. B. Clarke, J. W. Hastie, L. H. E. Kihlborg, R. Metselaar, and M. M. Thackeray. Definitions of terms relating to