Exploring Phase Transitions in Chromium
PHY 300 - Junior Phyics Laboratory

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1   Introduction

A phase transition in a material is when it changes from one state or phase of matter to another. These exhibit starkly different physical and chemical properties. Chromium, the material whose phase change is investigated in this experiment, changes its magnetic properties above a certain temperature. The temperature of this phase change, the latent heat of the transition and the coefficient of thermal expansion of chromium is calculated with the aid of volume and strain measurements using a strain gage.

2   Theoretical Background

2.1   First and Second Order Phase Transitions

A first order transition is one in which there is a discontinuity in the first derivative of the Gibbs free energy. Second order transitions are continuous in the first derivative of the Gibbs free energy but discontinuous in the second. Common first order transitions include melting, boiling and condensation and an example of a second order transition is the order-disorder transition in metal alloys such as CuZn.

$$G = H - TS \qquad H = U + PV$$

$$G = U + PV - TS$$

$$dG = dU + V\,dP + P\,dV - T\,dS - S\,dT$$

$$dU = T\,dS - P\,dV$$

$$dG = T\,dS - P\,dV + V\,dP + P\,dV - T\,dS - S\,dT$$

$$dG = V\,dP - S\,dT \tag{1}$$

The first derivative is shown in Equation 1, and as is clear the material must show a discontinuity in the derivative with respect to volume and pressure for it to be discontinuous. The Gibbs free energy is the maximum amount of non-expansion work that can be extracted from a system. In our experiment

2.2   Clausius Clapeyron Equation

This equation is a way of characterizing the a discontinuous phase transition between two phases of matter. In effect it gives the slope of the line (the coexistence curve) that separates the two phases in a P vs T graph. The equation is shown after its derivation in Equation 2.

$$ds = \frac{\partial s}{\partial V}dV + \frac{\partial s}{\partial T}dT = \frac{\partial P}{\partial T}dV$$

$$\frac{\partial s}{\partial T}dT = 0$$

$$\frac{\partial s}{\partial V}dV = \frac{\partial P}{\partial T}dV$$

$$\frac{\Delta s}{\Delta V} \approx \frac{\partial P}{\partial T}$$

$$\Delta s = \frac{\Delta H}{T}$$

$$\frac{\partial P}{\partial T} = \frac{\Delta H}{T\Delta V} \tag{2}$$

2.3 Phase Transitions in Chromium

Chromium encounters a phase transition at the Neel Temperature of Chromium [1]. This is a first order transition. The chromium below the Neel temperature (TN) has its atoms in an anti-parallel alignment which gives it antiferromagnetic properties. After crossing the Neel temperature atomic alignment becomes random resulting in an increase in volume and a change from antiferromagnetic behavior to paramagnetic behavior. The transition can be observed by observing either of these transitions. We have chosen to see look for discontinuous changes in volume to indentify TN.

3 Experimental Techniques

3.1 Measuring the change in Volume

We are using the increase in volume of the Chromium cube to identify the phase transition and so we can use a strain gage to find the strain ($\Delta L/L$) of the chromium and use Equations 3 and 4 to obtain the change in volume. The strain gage is model number LY11 and has a base resistance of 120 Ohms. It was directly glued to the material using adhesives and bonding pads. Strain gage specifications can be found on [2].

3.2 Electronics

During transition the strain gage records a very small change in its resistance. To be able to accurately read this increase in resistance we attach the strain gage to a Wheatstone Bridge connected to an Instrumentation Amplifier (AD 624, with gain value of 500) as shown in Figure 1. A modified bridge equation is given in Equation 3 which was used to calculate the change in the resistance of the gage.
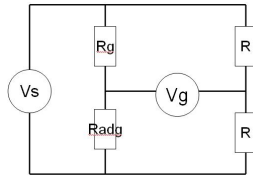

Figure 1: Wheatstone bridge.

$$Rg = R\frac{2Vg + Vs}{Vs - 2Vg} \tag{3}$$

3.3 Temperature Measurements

A pre-calibrated thermocouple directly connected to the Data Acquisition board (DAQ) was used to measure temperature. It was a J-type thermocouple and was taped onto the chromium piece.

4   Experimental Method

The experimental setup is shown in Figure 2. Care was taken to heat the sample slowly so that results would be easier to analyze. The heater was kept on low and the Chromium kept on sand which was kept on a glass plate which was placed on a heater to ensure slow heating. A fan was used to cool the chromium between experiments but care was taken to close all nearby fans while readings were being taken. Heating was turned on and data acquired in LabView. Temperature was changed from room temperature to 45-50 C. This took around 30-45 minutes.
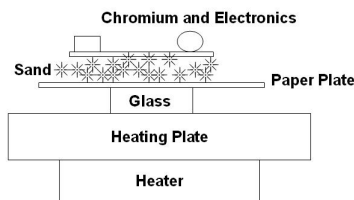

Figure 2: Experimental Setup with intruments to ensure slow steady heating

5   Results and Analysis

5.1   Identifying the Neel Temperature

The Neel temperature of chromium was deduced by looking for discontinuities in the volume obtained by the experiment. We observe the Neel temperature to be $37.38 + 273.15 = 310.53$ K, which is very close to the accepted value of 312 K [1]. A magnified portion of the Resistance vs Temperature curve near Tn is displayed in Figure 3. The red circles signify the extent of volume expansion that we considered was a result of the phase change.
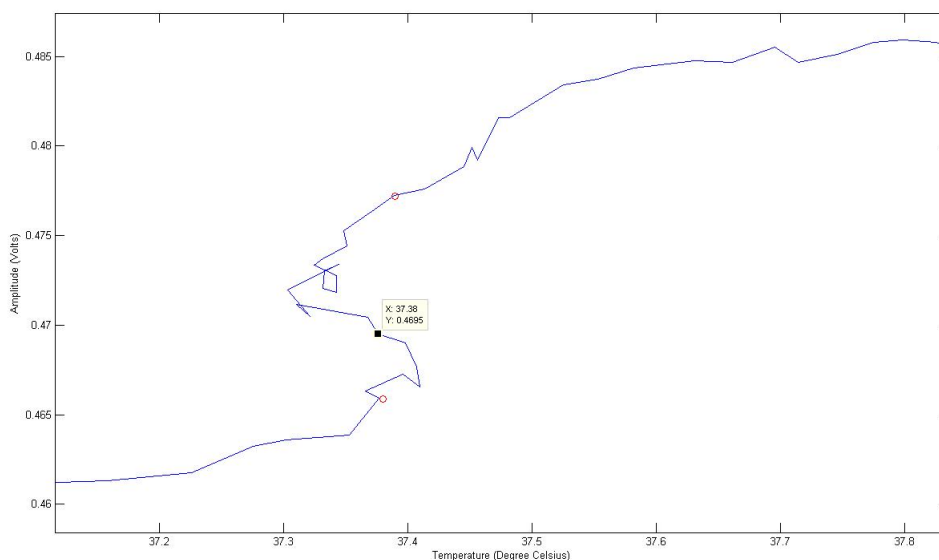

Figure 3: Discontinuity in the Volume of Chromium at T = 310.53 K.

5.2 Latent Heat of Chromium

We will calculate the latent heat of chromium using the Clausius Clapeyron equation (2).

5.2.1 Calculating the Strain

The change in the voltage drop across the strain gage is read of from the graph at the two red points and come out to be: Vg1 = 0.4659/500 V and Vg2 = 0.4772/500 V. This was put into the Wheatstone Equation to get

$$Rg1 = 120.3269 \quad Rg2 = 120.3349 \quad \Delta R = 0.0080\ Ohms$$

The output resistance of the strain gage is related to the strain by Equation 4, where F is the gage factor which was 2 for our strain gage. R is taken to be the lower value of Rg (Rg1).

$$Strain = \frac{\Delta L}{L} = \frac{\Delta R}{FR} = \frac{0.008}{2 \times 120.3269} = 3.324 \times 10^{-5} \tag{4}$$

5.2.2 Calculating the Change in Volume

The density of Chromium is 7.19g/cm and the mass of the sample was 8.6g. Hence,

$$Volume = \frac{mass}{density} = \frac{8.6}{7.19} = 1.196 \times 10^{-6} m^3$$

The change in volume can be related to the strain by Equation 5.

$$V = L^3$$

$$\frac{\Delta V}{\Delta L} = 3L^2$$

$$\frac{\Delta V}{V} = 3\frac{\Delta L}{L}$$

$$\Delta V = \frac{3V\Delta L}{L} = 3 \times 3.324 \times 10^{-5} \times 1.196 \times 10^{-6} = 1.193 \times 10^{-10} m^3 \tag{5}$$

5.2.3 Latent Heat

As derived earlier the latent heat can be calculated using the Clausius-Clapeyron Equation. We take $\frac{dP}{dT} = -7.692 \times 10^6 K/Pa$ from [4].

$$L = T\Delta V \frac{dP}{dT} = 310.53K \times 1.193 \times 10^{-10} m^3 \times 7.6923 \times 10^{-6} K/Pa = 0.2850J$$

There are 8.6/52 = 0.165 moles of chromium in our chromium sample. Therefore the molar latent heat is

$$\frac{0.2850}{0.165} = 1.72J/mol$$

The published value for the latent heat of chromium is 1.10 ± 0.10 J/mol according to [1] and 1.97 J/mol according to [3]. Our value lies between both these measurements.

5.3 Coefficient of Thermal Expansion of Chromium

The coefficient of thermal expansion is the increase in volume of material due to heating, as shown in Equation 6. The coefficient was calculated for chromium before and after the Neel temperature. It was calculated with the help of the Resistance vs Temperature which is displayed in Figure 3. The expansion of the steel of the strain gage effects the effective strain, the relationship given in Equation 7. And so the gradient of the red lines marked in Figure 3 were used to calculate the coefficient with the help of solely Equation 8.

$$\beta c = \frac{1}{V}\frac{\partial V}{\partial T} = \frac{1}{V}\frac{\Delta V}{\Delta T} \qquad (6)$$

$$\frac{\Delta L/L}{\Delta T} = \frac{\alpha}{F} + |\beta s - \beta c| \qquad (7)$$

$$\beta c = \beta s - \frac{\Delta L/L}{\Delta T} + \frac{\alpha}{F} \qquad (8)$$

$\alpha = 6.25 \times 10^{-10} K^{-1}$ and is the temperature coefficient of resistance of the strain gage. This is very low because we do not want the increase in resistance of the strain gage due to heating to interfere with the increase in resistance due to expansion which is what we are interested in. F = 2 and is the gage factor for our gage. $\beta s = 16.6 \times 10^{-6} K^{-1}$ and is the coefficient of thermal expansion of the steel strain gage.

Before phase change for $\Delta T = 1.51K$

$$Rg1 = 120.3157 \quad Rg2 = 120.3242 \quad \Delta R = 0.0085$$

$$\frac{\Delta L}{L} = 0.5 \times \frac{0.0085}{120.3157} = 3.5 \times 10^{-5}$$

$$\beta c = 1.66 \times 10^{-5} - \frac{3.5 \times 10^{-5}}{1.51} - \frac{6.25 \times 10^{-10}}{2} = -0.66 \times \mu m/mK$$

After phase change for $\Delta T = 2.51K$

$$Rg3 = 120.3431 \quad Rg4 = 120.358 \quad \Delta R = 0.015$$

$$\frac{\Delta L}{L} = 0.5 \times \frac{0.015}{120.3431} = 6.2 \times 10^{-5}$$

$$\beta c = 1.66 \times 10^{-5} - \frac{6.2 \times 10^{-5}}{2.51} - \frac{6.25 \times 10^{-10}}{2} = -0.81 \times \mu m/mK$$

The published values of the thermal expansion of chromium are $\approx 4.9 \mu m/mK$ [4]. Are calculated values are of the same order however are negative. Chromium is known to expand due to heating.

5.4 Change in Entropy at Neel Temperature

6 Error Analysis

Taking stock of error is hard work in this experiment as there are so many variables and alot of intermeidiate steps to the final results. One must identify the dominating error and give priority in controlling and measuring it along with keeping a weary watch on the other errors. One of the major sources of error is the reading of resistance. We measure a very minute change in voltage of the order of 10^{-2} volts. This had been amplified by a factor of 500 and so actual voltage changes are very minute. Therefore taking accurate voltage measurements can greatly increase the accuracy of the calculations. This can be done in several ways. Our strain gage had a room temperature resistance of 120 Ohms. A higher base resistance of 300 - 500 Ohms or greater will help increase accuracy as then the ΔR that corresponds to the same change in strain will be larger due to the larger R in the denominator. It is also possible to attach multiple strain gages to the chromium and this in effect does the same thing. Adjusting Radj can also help take better voltage measurements as a small deviation from 0 can be more accuratly measured than a tiny deviation from say 2V. The error in ΔR creeps into all calculations as it is the basis for calculating the strain.
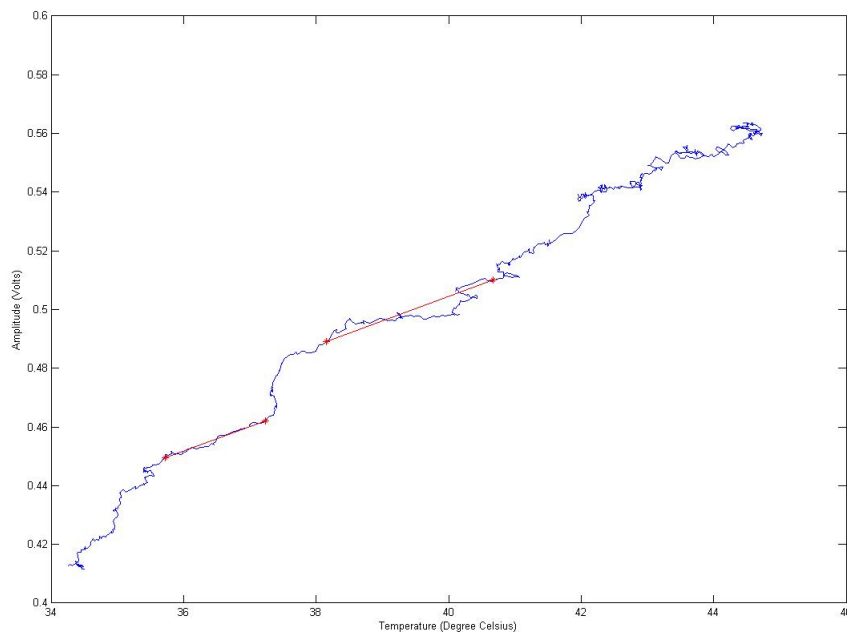
Figure 4: Complete curve for the expansion of chromium due to heating

Constant and slow heating allows us to intepret results better. The graphs that were obtained had very unsteady readings and other temperatures may be mistaken for the Neel temperature as heating might have been faster in some regions. The block should be insulated to some extent for example with a cover that traps air around the chromium block. This will help take care of unexpected cooling as which happened during our transition and at other places in the curve.

There is a intrumental error in the temperature readings but the thermocouple uncertainty of 55 μ Volts/ C is several orders smaller than the other errors. The experimental apparatus was remade with another chromium block of a similar size and the weight of this block might have been different. This has not been taken into account.

7 Conclusion

We obtained the Neel temperature of chromium (310.53 K) which varies by only 0.3 % from the published value of 311.5 K. We further calculated the latent heat of chromium by the Clausius Clapeyron equation and it came to be 1.725J/mol. This was further away, 36 % of, from the published value of 1.10 J / mol. We also calculated the coefficient for thermal expansion for chromium to be $-0.66 \times \mu m/mK$ below the Neel temperature and $-0.81 \times \mu m/mK$ above the Neel temperature. While these values are close to the accepted value they are negative which we cannot explain. Moreover, strain gages seem to be prone to error with regard to voltage measurements due to the minor change in the voltage that has to be measured. This report lacks the sufficient quantitative error analysis.

References

[1] G Benediktsson , H U Astrom and K V Rao, "Calorimetric studies of the order of magnetic phase transitions in Cr and some Cr alloys at the Neel point", J. Phys. F: Metal Phys., Vol. 5. October 1975

[2] Kyowa Electronic Instruments, Strain Gages, technical information avaialable at http://www.kyowa-ei.co.jp/english/products/gages/index.htm.

[3] N.H. Sze and G.T. Meaden, "Latent heat of chromium due to the first-order transition at the Nel point" N.H. Sze*, Physics Letters A, Volume 35, Issue 5, 28 June 1971, Pages 329-330

[4] http://en.wikipedia.org/wiki/Chromium Extracted 7 Dec 2010