

Thermal Physics Project: Analysis of Cu_3Au across OD transition.

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Abstract

Cu_3Au has an OD transition from $L1_2$ to fcc structure at 673 K. Heat capacity and temperature measurements have been used to calculate the entropy change of the compound from 595 K to 680 K to give a value of $\Delta s = 0.39$ (5) R and an excess entropy of mixing value of $\Delta s_{\text{excess}} = -0.17$ (5) R. At high temperatures, Cu_3Au becomes more disordered and eventually behaves as though it has the same random distribution as an ideal gas.

1 Introduction

This report aims to analyse the experimental measurements taken from Benisek & Dachs (BD) [1]. In the article, the authors investigated the specific molar heat capacity of Cu_3Au as it varied with temperature. This report focuses on the order-disorder (OD) transition around 680 K. Cu_3Au is a standard example of OD transitions and has been studied extensively [2], [3],[4],[5]. OD transitions are the process with which the distribution of atoms in an ordered state then changes to a disordered state or vice versa [6].

2 Theory

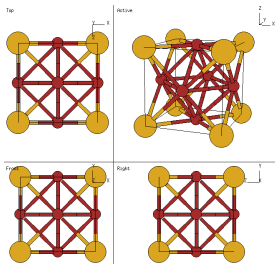


Figure 1: Image showing $L1_2$ structure of Cu_3Au . Found in [7].

At the critical temperature, $T_c = 673\text{K}$ (this temperature is labeled in figures 3 and 4) the OD transition occurs. This OD transition changes the distribution of the copper and gold atoms in the compound. Cu_3Au has an ordered $L1_2$ structure (seen in figure 1) then changes to a disordered fcc structure (seen in figure 2) after T_c . This change in structure comes with a change in volume, which is related to the magnitude of the entropy change[8].

BD states that below 500 K, Cu_3Au has no configurational entropy due to the ordered $L1_2$ structure[1]. Therefore, the entropy rise (and heat capacity rise) is due to the OD transition of $L1_2$ to fcc structure. The entropy change is due to the combination of configurational and vibrational entropy. Entropy tells us the microscopic degrees of freedom but can not be measured directly. However, isobaric heat capacity (c_P) can be measured easily by

heating up a sample and measuring the temperature rise, with constant pressure. This translates to $c_P(t) = (\frac{\partial q}{\partial t})_P = (\frac{\partial h}{\partial t})_P$, where "q" is the heat element per mole and Δh is the molar enthalpy change associated with the applied heat. Entropy change can be calculated by [9]:

$$\Delta s = s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_P}{T} dT \quad (1)$$

BD explains that in Cu_3Au there is excess heat capacity and excess vibrational entropy of mixing [1]. Equation 2, details the entropy of mixing for an ideal gas [9]. The Neumann-Kopp law states that the specific heat capacity of a compound can be calculated by adding up all the constituents specific heat multiplied by the mass fraction of that constituent [11], shown in equation 3 where N is the number of constituent elements and f is the molar fraction .

$$\Delta s_{mix} = -R(\chi_1 \ln \chi_1 + \chi_2 \ln \chi_2) \quad (2)$$

$$C = \sum_{i=1}^N C_i f_i \quad (3)$$

In Cu_3Au , $\chi_{Cu} = 0.75$ and $\chi_{Au} = 0.25$ so equation 2 gives an estimated value of Δs of 0.56 R. Equation 2 assumes that each components entropy contribution is solely due to its molar fraction χ . In reality there are many ways where entropy can deviate from this value.

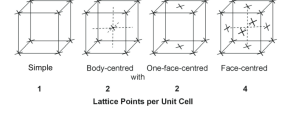


Figure 2: Simple diagram of lattice structures including face-centered cubic (fcc). From [10].

3 Methods

3.1 Plotting Figures

To produce figures 3 and 4, data for the project was taken from [1], and code (see section 6) was written to plot these figures. The code plots the raw data of specific heat against temperature (figure 3a) and then plots the specific heat per temperature against temperature (figure 3b). Once the integration bounds were found, the code then plotted the zoomed-in figure 4 that plots only the data within the integration bounds. Section 3.2 explains the choice of integration bounds.

3.2 Entropy Calculation

Equation 1 explains the entropy calculation. As computer code can not integrate physically, as temperature increments are not infinitely small, an approximation needed to be made. This is explained by equation 4 [12].

$$\int_a^b f(x) dx \approx \sum_{i=a}^b f(x_i) \Delta x_i, \Delta x_i = x_{i+1} - x_i \quad (4)$$

Where $x_i = T_i$ and $f(x_i) = (\frac{c_P}{T})_i$. "a" and "b" are the integration bounds, $595 \leq T \leq 680$ K. This range was used because in figure 4 the specific heat per temperature at $T = 595$

K and $T = 680$ K is about the same. This meant that the approximate integration would be accurate in that range, and that there could be a horizontal line drawn between the temperature bounds that would act as a zero line for the entropy calculation.

3.3 Uncertainty Calculations

The uncertainty in the temperature measurement was given as an equation in the data-set provided in [1]:

$$\sigma_T = 0.01T + 9 \times 10^{-7}T^2 \quad (5)$$

Uncertainty in specific molar heat per kelvin was calculated as a combination of the original uncertainty in specific molar heat capacity and the uncertainty in temperature:

$$\sigma_{c_p} = c_p[-0.198 + 9.4 \times 10^{-4}T - 9.2 \times 10^{-7}T^2] \quad (6)$$

$$\sigma_{\frac{c_p}{T}} = \frac{c_p}{T} \sqrt{\left(\frac{\sigma_{c_p}}{c_p}\right)^2 + \left(\frac{\sigma_T}{T}\right)^2} \quad (7)$$

Uncertainty in the molar entropy change was calculated by:

$$\sigma_{s_i} = s_i \sqrt{\left(\frac{\sigma_{\frac{c_p}{T}}}{\frac{c_p}{T}}\right)^2 + \left(\frac{\sigma_T}{T}\right)^2} \quad (8)$$

$$\sigma_s^2 = \sum_{i=1}^N \sigma_{s_i}^2 \quad (9)$$

Where s_i is the molar entropy change element from equation 4.

4 Results

The calculated value for the molar entropy change over the temperature range of 595 K to 680 K was $\Delta s = 0.39$ (5) R. This value agrees with that of the BD value at the same temperature [1]. Relating the calculated entropy to the theoretical entropy of mixing from section 2, there is a difference of $\Delta s = -0.17$ (5) R, where this entropy change is the excess entropy of mixing. For a disordered state, such as Cu_3Au after the OD transition, there ideally should be no difference between the random distribution shown in equation 2 and the fcc structure.

5 Conclusion

This report has stated and explained the calculated entropy change of Cu_3Au across the OD transition and how this value relates to the ideal entropy of mixing due to the final disordered state. The excess entropy value calculated was slightly inaccurate to BD as the authors measured the entropy to 800 K [1]. However, the value measured shows that increasing temperature in Cu_3Au will disorder the system more. Bringing the excess entropy of mixing to 0, meaning at high temperatures Cu_3Au behaves as an ideal gas, from an entropic point of view. More specific heat capacity measurements to this temperature and above could greatly improve on this value and give better insight into how Cu_3Au behaves at incredibly high temperatures.

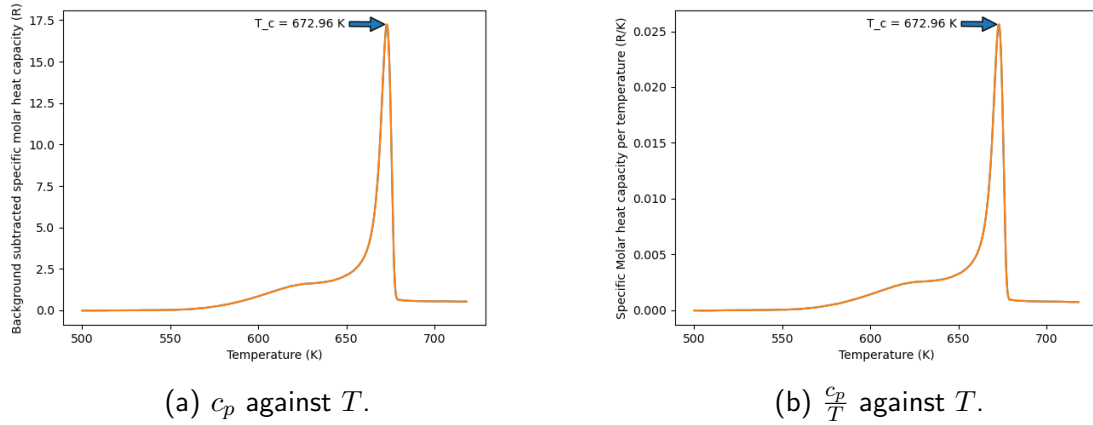


Figure 3: Plots showing specific heat capacity (R) against temperature (K) (a) and specific heat capacity per temperature (R/K) against temperature (K) (b). Plot also shows the critical temperature at the peak of the $\frac{c_p}{T}$ curve, $T_c = 672.96$ K.

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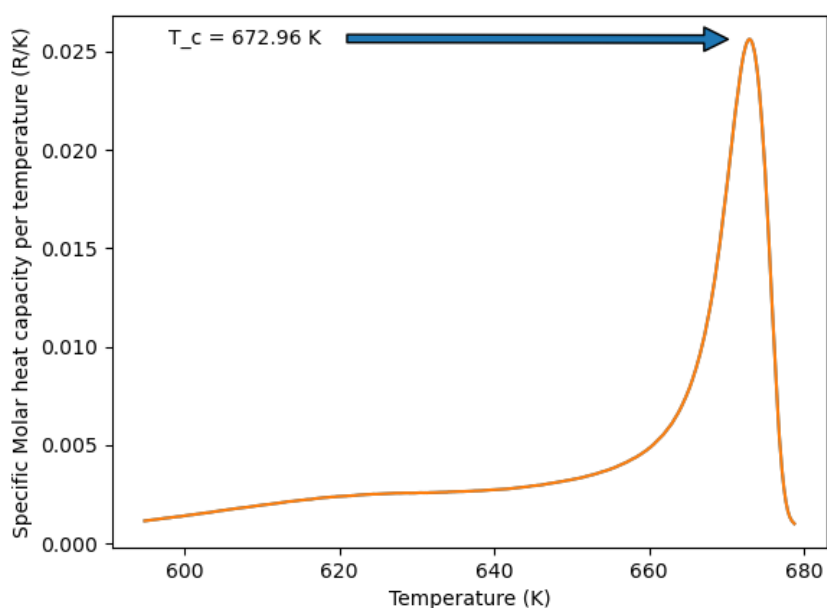


Figure 4: Plot showing specific molar heat capacity per temperature against temperature. Temperature range specific to the integration bounds of the entropy calculation. Also shows critical temperature at 672.96 K.

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6 Appendix

Code to plot graphs, estimate entropy change and estimate uncertainty from <https://github.com/hanson-0504/Thermodynamics-Project.git>.