Measurement of the specific heat capacity of gadolinium

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Abstract

The specific heat capacity of gadolinium, a ferromagnetic material, was measured as a function of temperature from 14℃ to 25℃ using a relaxation method. No clear discontinuity in the heat capacity was observed that would indicate a ferromagnetic phase transition at the reference Curie temperature of gadolinium, $T_c = 292$ K [1]. The measured heat capacities were within their uncertainties of many of the values given by Griffel *et al* [2] and are on the order of $0.32\ \mathrm{J \cdot g^{-1} \cdot K^{-1}}$ and $0.24\ \mathrm{J \cdot g^{-1} \cdot K^{-1}}$ below and above the Curie temperature, respectively.

Introduction

Gadolinium is ferromagnetic below and paramagnetic above its Curie temperature [1]. As the temperature increases, the magnetization of the ferromagnetic material decreases smoothly to zero at $T = T_c$, which indicates that the ferromagnetic/paramagnetic phase transition is second-order [1] and results in a discontinuity in the heat capacity of the material [3].

The heat capacity of a material determines how its temperature changes with a given amount of heat. Neglecting temperature gradients within the material, conservation of energy relates the heat capacity of the material to the heat flux through its boundary according to [4, 5]

$$C_p \frac{dT}{dt} + K_{\text{eff}} \Delta T = P, \tag{1}$$

where C_p is the heat capacity, $\Delta T = T - T_R$ is the difference in material temperature relative to the reservoir, K_{eff} is the effective thermal conductance and P is the supplied power. Let the supplied power be a rectangle function of the form $P(t) = P_0\big(\theta(t) - \theta(t - \Delta t)\big)$, where P_0 is the power amplitude, $\theta(t)$ is the Heaviside theta function and $\Delta t > 0$ is the duration. Then the solution to Eq. 1 for the material temperature as a function of time is

$$T(t) = \frac{P_0}{K_{\text{eff}}}\big(1 - e^{-t/\tau}\big)\theta(t) + \frac{P_0}{K_{\text{eff}}}\big(e^{-(t-\Delta t)/\tau} - 1\big)\theta(t - \Delta t) + T_R, \tag{2}$$

where $\tau = \frac{C_p}{K_{\text{eff}}}$. For $t > \Delta t$, this becomes

$$T(t)_{t>\Delta t} = \Delta T_0 e^{-t/\tau} + T_R \tag{3}$$

where $\Delta T_0 = \frac{P_0}{K_{\text{eff}}}\big(e^{\Delta t/\tau} - 1\big)$. Thus, the heat capacity of the material is

$$C_p = \tau K_{\text{eff}}. \tag{4}$$

Apparatus and Methods

The gadolinium sample was wrapped with heating coils and rested on a brass post connected to the copper base (the reservoir). Under the copper base was a thermoelectric cooler (TEC) that controlled the reservoir temperature, which was monitored by a temperature sensor. The entire apparatus was covered and partially sealed to allow nitrogen gas at room temperature

to flow through and prevent condensation. Circulating water was used to stabilize the surrounding apparatus temperature at the reservoir temperature. The sample temperature was measured using a digital multimeter connected to a platinum resistance temperature detector (RTD). Figure 1 shows the apparatus configuration.

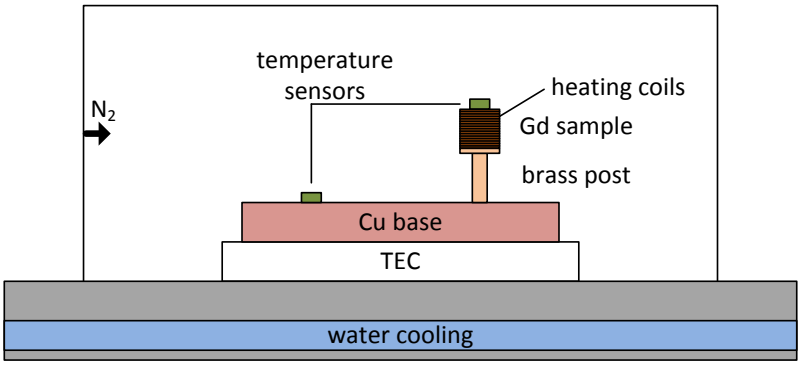

Figure 1 Gadolinium specific heat measurement apparatus (drawing not to scale). Nitrogen gas flowed through the chamber to prevent condensation, as shown on the left.

By controlling the steady state temperature of the sample in thermal equilibrium with the reservoir and then applying a short burst of heat to the sample through the resistive heating coils, the relaxation time of the sample temperature can be used to determine the heat capacity from Eq. 4. The reservoir temperature was varied from approximately 14℃ to 25℃ in 1℃ increments, allowing the sample to equilibrate with the base for several minutes before adding approximately 1 Joule of heat to the sample over a period of up to 10 seconds. This resulted in typical temperature changes on the order of 0.4℃ to 0.5℃. Using smaller heating bursts resulted in greater precision of the sample temperature due to the smaller deviation from the reservoir temperature, but this also significantly increased the uncertainties in the relaxation times. After the heat was applied, the resulting sample temperature decay was measured every 0.5 seconds until the sample re-equilibrated with the reservoir.

Results and Discussion

The relaxation time constants were determined at each reservoir temperature by fitting Eq. 3 to the measured data using orthogonal distance regression (ODR). An estimate of the uncertainty in the sample temperature is given by the ΔT_0 fit parameter, the maximum deviation of the sample temperature from the reservoir temperature. Using Eq. 4, the specific heat capacity of the gadolinium sample can be calculated by subtracting the heat capacity of the parts of the apparatus in contact with the gadolinium, the most significant of which is the brass post. Then the specific heat capacity of the gadolinium sample is

$$c_{p,\mathrm{Gd}} = \frac{\tau K_{\mathrm{eff}} - C_{p,\mathrm{b}}}{m_{\mathrm{Gd}}}, \tag{5}$$

where $C_{p,\mathrm{b}}$ is the heat capacity of the brass post, and m_{Gd} is the mass of the gadolinium. The effective thermal conductance was estimated to be $K_{\mathrm{eff}} = (5 \pm 3) \times 10^{-2}\ \mathrm{W \cdot K^{-1}}$ (see Appendix) while $C_{p,b} = (2.3 \pm 1.5) \times 10^{-2}\ \mathrm{J \cdot K^{-1}}$ and $m_{\mathrm{Gd}} = 13 \pm 1\ \mathrm{g}$.

Most of the specific heat uncertainties are due to uncertainty in the thermal conductance and heat capacity of the brass. Errors on the relaxation time constants were typically only $\delta_\tau = 1$ s, corresponding to no more than 2 percent relative error, and the mass of gadolinium had a comparatively small relative error of approximately 9 percent. Uncertainties in the actual material properties of the apparatus can lead to significant changes in the thermal conductance and apparatus heat capacity calculations (see Appendix). Additional factors that were not considered in their calculation, such as the possibility of them having temperature dependence themselves, would also impact their accuracy. Measured specific heat capacities of gadolinium are plotted as a function of temperature in Figure 2.

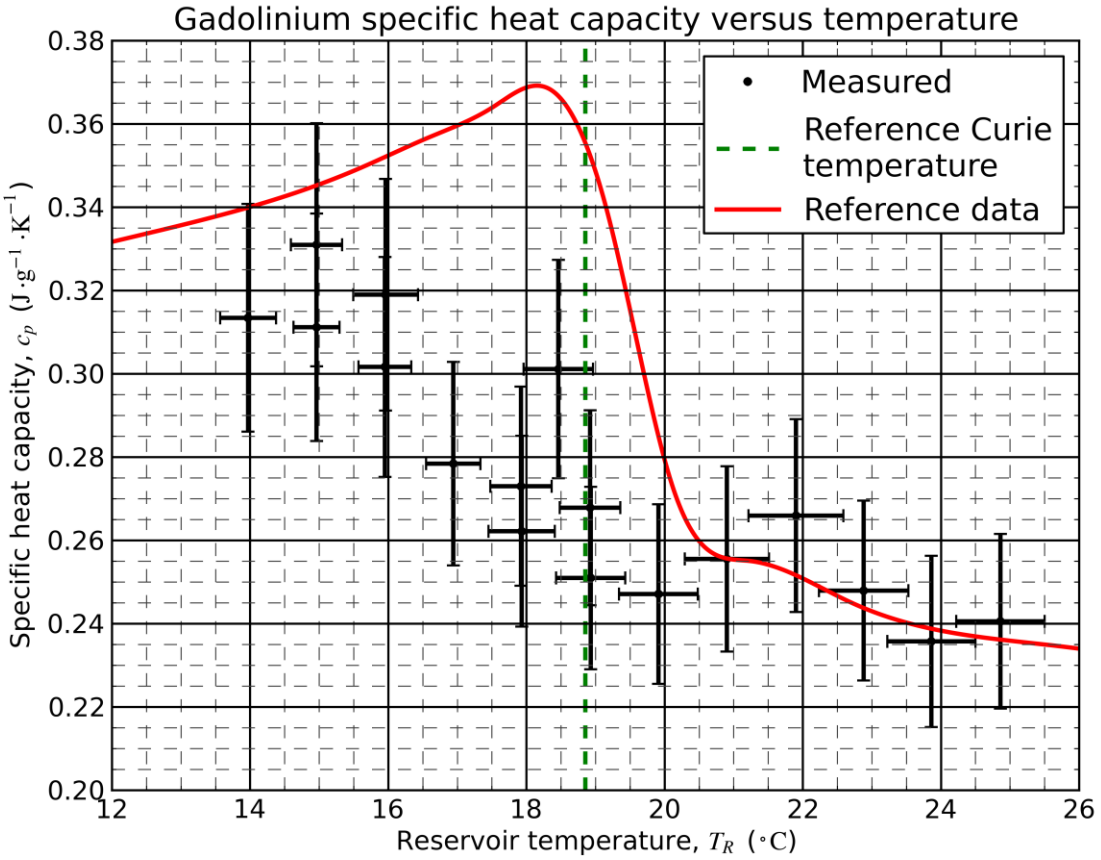

Figure 2 Measured values (black points) of the specific heat capacity of gadolinium as a function of temperature around its Curie point, shown by the green, dotted vertical line. The solid red line shows an interpolated polynomial of the reference specific heat capacity data given by Griffel *et al* [2].

We would expect the specific heats to be on the order of $0.33\,\mathrm{J \cdot g^{-1} \cdot K^{-1}}$ and $0.24\,\mathrm{J \cdot g^{-1} \cdot K^{-1}}$ below and above the Curie temperature, respectively [2]. As shown in Figure 2, many of our measurements are within their uncertainties of the reference specific heat capacities above and below the Curie temperature. However, there is no clear discontinuity in the specific heat capacity around the reference Curie temperature of $T_c = 292\,\mathrm{K}$ that would indicate a ferromagnetic phase transition. Instead, there is a gradual decreasing trend in the region where

we would expect to see the transition. This may be a result of the relatively large uncertainties in the reservoir temperature, which can produce large variations in the measured heat capacity around the transition temperature. In order to observe the transition more clearly then, smaller power bursts should be used to create the sample temperature differences around the transition temperature.

References

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Appendix: Calculation of specific heat parameters

The effective thermal conductance can be broken up into components due to radiation, convection and conduction The radiative and convection terms are given by $A\left(4\sigma\varepsilon AT_{\text{amb}}^3 + h\right)$ [5], where A is the surface area, σ is the Stefan-Boltzmann constant, ε is the emissivity, T_{amb} is the ambient temperature and h is the convective heat-transfer coefficient. For typical free gas convection, the heat transfer coefficient is $h \approx 10\ \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ [4]. The gadolinium sample has a length $L_1 = 0.9\ \text{cm} \pm 0.1\ \text{cm}$ and diameter $d_1 = 1.5 \pm 0.1\ \text{cm}$, so its surface area of the then is approximately

$$A = \frac{\pi}{4} d_2^2 + \pi d_2 L_2 = 6.0 \pm 0.4\ \text{cm}^2$$

The radiation and convection terms sum to

$$(6.0\ \text{cm}^2)(4(5.670373 \times 10^{-8}\ \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-4})(1)(300\ \text{K})^3 + 10\ \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}) = 9.7 \times 10^{-3}\ \text{W} \cdot \text{K}^{-1}$$

In comparison, the conduction term comes from heat transfer through the brass post, which has length $L_2 = 0.40 \pm 0.05\ \text{cm}$ and diameter $d_2 = 0.15 \pm 0.05\ \text{cm}$ and thermal conductivity $k = 115\ \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. Thus, the convection term contributes

$$\frac{kA_c}{L} = \frac{\pi d_2^2 k}{4L_2} = (5 \pm 3) \times 10^{-2}\ \text{W} \cdot \text{K}^{-1}$$

Therefore, conduction term is the more significant term, and $K_{\text{eff}} = (5 \pm 3) \times 10^{-2}\ \text{W} \cdot \text{K}^{-1}$. The heat capacity of the brass post can be estimated using a specific heat capacity for brass of $c_{p,\text{m}} = 0.38\ \text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ and a density of $\rho_{\text{b}} = 8.5\ \text{g} \cdot \text{cm}^{-3}$. Using the dimensions of the post the heat capacity of the brass is

$$C_{p,\text{m}} = \rho_{\text{b}} \left(\frac{\pi}{4} d_2^2 L_2\right) c_{p,\text{m}} = (2.3 \pm 1.5) \times 10^{-2}\ \text{J} \cdot \text{K}^{-1}$$

The mass of the gadolinium sample is estimated using a density of $\rho_{\mathrm{Gd}} = 7.9\ \mathrm{g \cdot cm^{-3}}$:

$$m_{\mathrm{Gd}} = \rho_{\mathrm{Gd}} \left(\frac{\pi}{4} d_1^2 L_1 \right) = 13 \pm 1\ \mathrm{g}$$