# Uppsala University

## Department of Physics and Astronomy

### Division of Materials Theory

### Degree Project C in Physics, 15hp

---

# Quantum statistics and the magnetocaloric effect

---

*Author:*
Anna Sandberg

*Supervisor:*
Anders Bergman

*Subject reader:*
Oscar Grånäs

July 6, 2020

## Abstract

Caloric materials show prospect in replacing the function of vapor-compression systems in todays cooling devices, resulting in more energy efficient cooling and eliminating the need for refrigerents which contribute to climate change. This project has focused on magnetocaloric materials, which experience changes in temperature when exposed to magnetic fields. A step to finding viable materials is developing realistic simulations. To this end, this project has investigated if the calculated magnetocaloric effect is impacted by the choice of statistic. Three systems have been studied, bcc Fe, FeRh and $Fe_2P$, using Monte Carlo simulations. The results have shown differences in the calculated entropy change depending on the statistic of choice. The quantum statistics have shown a $\Delta S = 0$ below the phase transition, unlike the classical statistics. At the phase tranisitions quantum statistics resulted in either similar or smaller values for the calculated change in entropy.

## Sammanfattning

Kaloriska material har potential att i framtiden ersätta funktionen hos ångkomprimeringssystem i dagens kylapparater, vilket i sin tur kan leda till mer energieffektiv kylning samt eliminerar behovet av kylmedier som bidrar till klimatförändringen. I detta projekt ligger fokus på magnetokaloriska material, vilka erfar temperaturförändringar då de utsätts för magnetfält. Ett steg mot att hitta gångbara material är att utveckla realistiska simulationer. För detta ändamål undersöktes huruvida den beräknade magnetokaloriska effekten påverkas av valet av statistik. Tre system studerades, bcc Fe, FeRh samt $Fe_2P$, med hjälp av Monte Carlo simulationer. Resultaten visade skillnader i den beräknade entropiförändringen beroende på valet av statistik. För kvantstatistiken var $\Delta S = 0$ för temperaturer under fasövergångerna, vilket skiljde sig från de klassiska resultaten. Vid fasövergångarna gav kvantstatistiken liknande eller mindre värden för den beräknade entropiförändringen.

# Contents

# 1   Introduction

Climate change is a cumbersome load to carry. The hunt for technologies that will reduce the emission of greenhouse gases is a search overarching many areas of science. One part of the solution might be caloric materials, replacing the function of todays vapor-compression systems in cooling devices. Cooling devices today, such as refrigerators and air conditioners, consume a large amount of electricity worldwide and when they are used up and thrown away, most of the refrigerants leak out into the atmosphere causing an even stronger greenhouse effect than carbon dioxide [1]. Caloric materials experience a temperature change when subjected to changes in magnetic field, electric field or pressure. This make them promising candidates for future cooling applications. Caloric materials can be divided into three groups, mechanocaloric, electrocaloric and magnetocaloric. The first category responds to either being stretched (elastocaloric) or changes in pressure (barocaloric). The electrocaloric effect is driven by electric fields and the magnetocaloric effect (MCE) is in turn driven by magnetic fields [2]. In this project the focus is going to lie on the last category.

An important tool in the search for efficient and inexpensive magnetocaloric materials is simulations. It is then essential that the results of these simulations are as close to experimental results as possible. Magnetocaloric materials show a large field-dependent entropy change at their magnetic phase transition. When researching magnetocaloric materials, the entropy, or rather the change in entropy, is therefore of great interest. Recent works have investigated how calculated thermodynamical measurables of a spin system are affected by the statistics that are used in the numerical method [3]. It has been shown that using quantum statistics instead of classical can have a great impact on the calculated thermodynamical measurables. This project is going to elaborate on this and aim to answer the question; does the choice of statistic affect the calculated MCE, i.e. the field-dependent entropy change at the magnetic phase transition?

# 2 Theory

In this section the necessary theory will be presented, starting off with some fundamentals of thermodynamics that will be of use later on in this section when discussing the magnetocaloric effect. In order to understand how the simulations are done and what role the statistics play, this section will also include some statistical mechanics as well as a bit of theory on Monte Carlo simulations. To this end, there will also be a part discussing the Heisenberg spin Hamiltonian along with a brief explanation of magnons.

## 2.1 Thermodynamics

Thermodynamics is a branch of physics which relates the thermal properties of a system to each other and is used widely in physics as well as engineering. It was developed in the nineteenth century mainly because of a rising interest in heat engines [4]. Thermodynamics describes the relationships between macroscopic properties of a system such as for example volume V, temperature T, pressure P and entropy S. These can be either extensive, e.g. volume V, or intensive, e.g. temperature T. In thermodynamics there are four laws which describe the fundamental behaviour of processes in a system. The zeroth law states that if you have two systems that each respectively are in thermal equillibrium with a third system, they must also be in equillibrium with each other. The first law of thermodynamics says that energy must be conserved, i.e. energy can be transformed from one form to another but can neither be created nor destroyed. The second law states that you can not have a process where the only outcome is that heat has been transferred from a cooler system to a hotter system. Finally, the third law states that for a perfect crystal, entropy has to vanish as the temperature goes to zero [5].

The following four equations play an important roll within thermodynamics and are called the Maxwell relations [6]. Here they describe the relationship between the temperature, volume, pressure and temperature of a system.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{1}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{3}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \tag{4}$$

The first relation, eq. (1), is derived from the following central equation in thermodynamics [6]

$$dU = TdS - PdV \tag{5}$$

where U is the internal energy. The remaining Maxwell relations can be derived from similar equations for the enthalpy, the Helmholtz function and the Gibbs function [6].

From eq. (5), one can derive the following expression for the heat capacity at constant volume [6].

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{6}$$

The heat capacity is a useful quantity that describes how much heat a system can absorb with respect to temperature change.

For a magnetic system the Maxwell relations can be expressed in terms of the temperature T, the external magnetic field H, the entropy S and the magnetization M [7].

$$\left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M \tag{7}$$

$$\left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H \tag{8}$$

5

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \tag{9}$$

$$\left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_M \tag{10}$$

Similarly, here the first Maxwell relation is derived from the internal energy U, see eq. (11), and the other three relations are derived from the enthalpy, the Helmholtz function and the Gibbs function expressed in terms of S,T,H and M [7].

$$dU = TdS + HdM \tag{11}$$

From eq. (11) one can also derive the heat capacity at constant external magnetic field.

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H \tag{12}$$

Similar expressions can be found for the heat capacity at constant pressure or magnetization. This expression for the heat capacity can be written more generally as

$$C_x = \left(\frac{\partial U}{\partial T}\right)_x = T\left(\frac{\partial S}{\partial T}\right)_x \tag{13}$$

where $x$ is a quantity which is held constant, e.g. external magnetic field H and magnetization M respectively for a magnetic system.

Lastly, the entropy S of a magnetic system can be considered to be function of the temperature T and the external magnetic field H, assuming that the pressure is constant [8]. This is expressed in the following differential:

$$dS = \left(\frac{\partial S}{\partial T}\right)_H dT + \left(\frac{\partial S}{\partial H}\right)_T dH \tag{14}$$

Equations (12), (13) and (14) will be useful later on when discussing the theory behind the magnetocaloric effect.

## 2.2 Statistical mechanics

Statistical mechanics is used to describe complicated many-body problems from a stochastical viewpoint. When studying a macroscopical system such as a piece of metal or a litre of gas, the system includes way too many particles to be able to solve the equations of motion. Instead one can use statistical mechanics in order to solve the problem. The energies of the particles in the system are then assumed to follow a probability distribution. The statistics used are usually classical statistics, i.e. Boltzmann distribution, or quantum statistics, i.e. Bose-Einstein and Fermi-Dirac distributions.

### 2.2.1 Classical statistics

Classical statistics utilizes the Boltzmann distibution, where the probability of finding a particle with energy $E_i$ is proportional to

$$p_i \propto e^{-E_i/k_B T} \tag{15}$$

Here $k_B$ is the Boltzmann constant and T is the temperature. Classical statistics usually work well under "normal" conditions, when the pressure is high enough and the energy of the particles is high. For lower energies and lower pressure it does not work as well, since quantum mechanical effects then have a larger impact.

### 2.2.2 Quantum statistics

In quantum statistics two different distributions are used depending on the type of particles. For fermions the Fermi-Dirac distribution is used. Fermions are particles with half-integer spin and are subject to the Pauli exclusion principle. This means that two identical fermions can not occupy the same exact state. The other type of statistics is the Bose-Einstein distribution,

$$n_i = \frac{1}{\exp\left((E_i - \mu)/k_B T\right) - 1} \tag{16}$$

where $E_i$ is the energy, $\mu$ is the chemical potential, $k_B$ is the Boltzmann constant and T is the temperature. The Bose-Einstein distribution is used for bosons, which are particles with integer spin. The Pauli exclusion principle does not apply to bosons. At high temperatures, i.e. for $\exp(E/k_B T) >> 1$, both Bose-Einstein and Fermi-Dirac statistics are reduced to Boltzmann

7

statistics. The reason that Bose-Einstein will be used here rather than Fermi-Dirac is that magnons, which are discussed in section 2.5, are bosons.

## 2.3   The magnetocaloric effect

The magnetocaloric effect is a physical phenomena in which a material can be cooled or heated by applying, removing or varying a magnetic field. The first scientific report on the topic was published in 1917 by P. Weiss and A. Pickard, who had performed experiments on nickel [9]. In order to understand this effect we are going to start with looking at the entropy in a solid.

The entropy can be divided into three parts, magnetic, lattice and electronic. If a magnetic field is applied isothermally to a system which is ferromagnetic or paramagnetic, the magnetic part of the entropy will decrease. This is because the magnetic moments line up and become more ordered. Since the effect of the magnetic field on the lattice and electronic parts are neglible in comparison to the magnetic part, the total entropy of the system decreases. If thereafter the magnetic field is removed adiabatically, the temperature of the system will decrease. This is due to the fact that the temperature is the only free variable, see eq.(14), and since the total entropy is conserved and the removal of the field will cause the magnetic part of the entropy to increase, the temperature must then decrease. The system is now cooler than it was in the beginning.
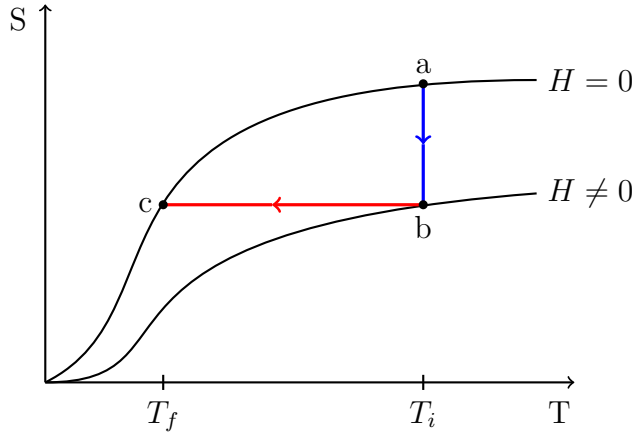


Figure 1:   Graph showing the entropy in respect to the temperature for the magnetocaloric effect. The system starts in $a$ with temperature $T_i$. From $a$ to $b$ an magnetic field is applied isothermally. The magnetic field is then removed adiabatically from b to $c$. The system now has a temperature $T_f$ which is lower than the initial temperature.

8

The same process can be performed on an antiferromagnetic system, which instead will result in an increase in temperature. This is because the applied magnetic field will cause the system to be less ordered and the entropy will then be higher. This is called the inverse magnetocaloric effect [10].

By rearranging and integrating eq.(12) we find that the entropy can be calculated as

$$S(T, H) = S_0 + \int_0^T \frac{C_H(T', H)}{T'} dT' \tag{17}$$

where $S_0$ is an integration constant that usually can be set to zero since the third law of thermodynamics states that the entropy has to vanish when the temperature is zero. The field induced entropy change can then be calculated as

$$\Delta S(T, 0 \rightarrow H) = S(T, H) - S(T, 0) = \int_0^T \frac{C_H(T', H) - C_H(T', 0)}{T'} dT' \tag{18}$$

The heat capacity can be written as the derivative of the internal energy U, as in eq.(13). The expression for the entropy will then be

$$S(T, H) = \int_0^T \frac{1}{T'} \left( \frac{\partial U}{\partial T'} \right)_H dT' \tag{19}$$

The entropy change induced by the magnetic field can then be written as

$$\Delta S(T, 0 \rightarrow H) = \int_0^T \frac{1}{T'} \frac{\partial U(T', H)}{\partial T'} dT' - \int_0^T \frac{1}{T'} \frac{\partial U(T', 0)}{\partial T'} dT' \tag{20}$$

Up to this point only the entropy change has been discussed. In order to calculate the actual temperature change, which is the most intersting aspect of the magnetocaloric effect, we can use the differential from earlier, see eq.(14). Since the entropy is constant, dS can be set to be zero. By also rewriting the expression using eq.(12) and eq.(9) we get the following equation:

$$0 = \frac{C_H}{T} dT + \left( \frac{\partial M}{\partial T} \right)_H dH \tag{21}$$

9

By rearranging this equation and integrating we get an expression for the temperature change due to the adiabatic removal of the magnetic field.

$$\Delta T(T, 0 \to H) = -\int_0^H \frac{T}{C_{H'}} \left( \frac{\partial M}{\partial T} \right)_{H'} dH' \tag{22}$$

This project will not look at the temperature change, eq.(22), but at the entropy change, eq.(20), since it is a good way of gauging the magnetocaloric properties of a material.
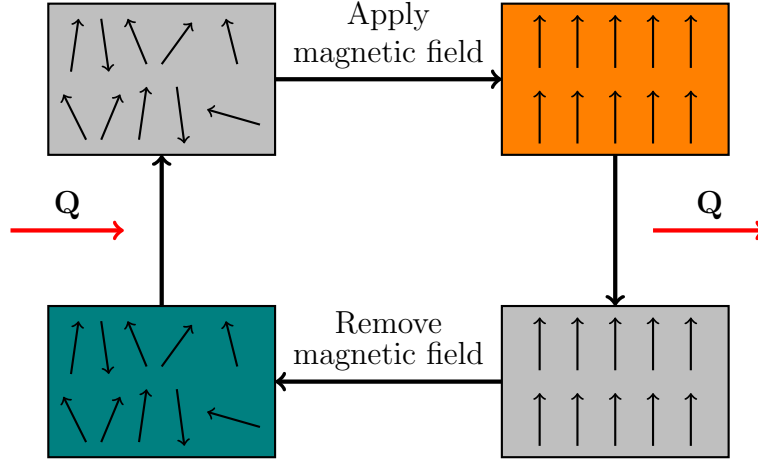


Figure 2: Illustration of how the magnetocaloric effect can be used to cool a medium. Starting in the upper left corner, a magnetic field is applied. As the magnetic moments becomes more ordered, the magnetic part of the entropy is reduced which causes the system to heat up. This heat is transferred away so that the system retains its initial temperature. The magnetic field is then removed, causing the temperature of the system to be lowered. Heat can then be transferred from e.g. a cooling coil in a refrigerator to the cold material.

## 2.4 Heisenberg spin Hamiltonian

When considering a magnetic system, the effective spin Hamiltonian can be written in the following Heisenberg form

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \mathbf{m}_i \cdot \mathbf{m}_j \tag{23}$$

where $\mathbf{m}_i$ is the atomic magnetic moment at a site $i$. $J_{ij}$ denotes the interatomic exchange parameter and describes how the energy of the system changes when rotating two magnetic moments from their initial orientation [11]. If $J_{ij}$ is positive, the moments will align themselves so that they are parallell to each other, i.e. the interaction is ferromagnetic. On the other hand, if $J_{ij}$ is negative, the interaction will be anti-ferromagnetic.

Taking magnetic fields into account, the total Hamiltonian will be as follows

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \mathbf{m}_i \cdot \mathbf{m}_j - \mathbf{H} \cdot \sum_i \mathbf{m}_i \tag{24}$$

The second term takes into consideration the interactions between the magnetic moments and an external magnetic field $\mathbf{H}$. The interatomic exchange parameters $J_{ij}$ can be calculated using DFT, density functional theory [12].

## 2.5 Magnons

Complicated many-body excitations in material physics can often be simplified using quasiparticles. Phonons, for example, are quasiparticles that can be used to describe lattice vibrations in solids. Another example are magnons, they represent the quanta of collective spin excitations.

The simplest way of explaining magnons is through the ferromagnetic spin chain. In the ferromagnetic spin chain all spins are aligned (you can also have anti-ferromagnetic spin waves, in that case, every spin in the chain is anti-parallell to its neighbours). The spins in the chain interact with each other through exchange interactions. For simplicity we can neglect all interactions except the ones from nearest neighbours. Let's also assume the

magnetic excitations can be described by the Hamiltonian from earlier [13], see equation (23).

In the ground state, all the spins in the chain are spin up. In order to reach the first excited state of the system, one spin may be flipped. To obtain the second excited state another spin is flipped and so on. The problem with this approach is that a single spin flip is not an eigenstate of the Hamiltonian. Only collective spin excitations are eigenstates of the Heisenberg Hamiltonian. Instead of simply flipping one spin, the spin flip can be 'smeared out' over the entire chain. This is called a spin wave or magnon, and is an eigenstate of the Hamiltonian [13]. Figure 3 illustrates a spin wave.
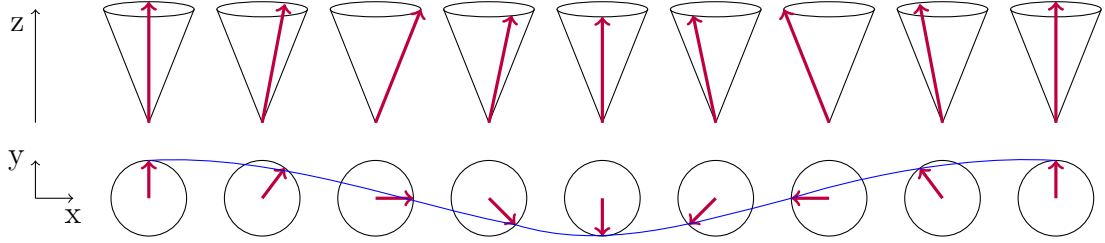


Figure 3: One spin flip is smeared over the whole chain resulting in a spin wave (magnon). The magnetic moments precess around the z-axis.

The magnon dispersion relation for a ferromagnetic spin chain can be calculated by starting from the equation of motion describing the torque on each moment in the chain [13]. The dispersion relation will then be

$$E(k) = 4\hbar JS(1 - \cos(ka)) \tag{25}$$

where J is the interatomic exchange parameter, S is the spin, k is the wavenumber and a is the lattice parameter. The dispersion relation is related to the density of states, which will be relevant when implementing the quantum statistics into the Monte Carlo simulations. The mDOS, magnon density of states, is thereby dependent on the interatomic exchange parameters $J_{ij}$ introduced in the Hamiltonian as well as the wavelength of the spin waves. When looking at a real material, the dispersion relation, and thereby the mDOS, have a more complicated behaviour. Spin waves are not the only

type of excitation that can occur in a magnetic material, there are also Stoner excitations, which are not included in this model [13].

## 2.6 Monte Carlo method

Monte Carlo methods are used to solve problems that are difficult or impossible to solve analytically. Instead of trying to solve the problem analytically they approach it stochastically. Monte Carlo methods can be used in optimization problems as well as to numerically evaluate integrals. Here we are going to focus on one Monte Carlo method, the Metropolis algorithm [14]. The Metropolis algorithm selects a configuration, e.g. a spin configuration, that minimizes the Hamiltonian of the system by the use of the following transistion probability. The transistion probability W between two states $s$ and $s'$ is then

$$W(s \rightarrow s') = \begin{cases} \exp(-\frac{\Delta E}{\eta}) & \text{if } \Delta E > 0 \\ 1 & \text{otherwise} \end{cases} \tag{26}$$

where $\eta$ is a scaling factor. Classically this $\eta$ is written as

$$\eta = k_B T \tag{27}$$

which gives us the Boltzmann distribution discussed earlier, see eq. (15). The algorithm can be modified using quantum statistics, i.e. the Bose-Einstein distribution in eq. (16), by writing the scaling factor as [3]

$$\eta(T) = \int_0^\infty \frac{E}{\exp(E/k_B T) - 1} g(E, T) dE \tag{28}$$

where g(E,T) is the mDOS, magnon density of states, for energy E of a magnon and temperature T. The former scaling factor, eq. (27), is what Metropolis et al. [14] used and is the one that usually is employed in most spin simulations. When comparing the two statistics, the only thing that will change in the simulations is this scaling factor $\eta$.

For our Heisenberg spin Hamiltonian at a given temperature T the Monte Carlo algorithm will go through the following steps [15]:

13

1. The lattice is initialized by defining a spin configuration and the energy of the system is calculated.

2. A lattice site is chosen at random.

3. The spin orientation at that site is randomized and the energy difference $\Delta E$ between the initial spin configuration $s$ and the new spin configuration $s'$ is calculated.

4. A random number r $\in$ (0,1) is generated. If r < W then $s'$ is the new reference, or else the old orientation $s$ is kept as the reference.

5. The process is reiterated from step 2 until a sufficient convergence is achieved.

# 3   Method

The simulations were performed using the UppASD simulation programme [16] running on the Tetralith cluster at the NSC (National Supercomputer Center) at Linköping University. Monte Carlo simulations were then employed in order to calculate the internal energy for the systems at given temperatures. The systems chosen for this project were bcc (body-centered cubic) Fe, FeRh and $Fe_2P$. The size of the systems were all set to be $32\times32\times32$ atoms, except for $Fe_2P$ which instead had a size of $24 \times 24 \times 24$ atoms. The simulations of the systems were first performed using the classical statistics, and were repeated for the following external magnetic fields, $H = 0, 1, 2, 3, 4, 5$ T. The Curie temperature was then extracted from the classical simulations and subsequently used in the corresponding quantum simulation. The quantum simulations were performed for the same external magnetic fields as the classical.

The result from the simulations was then used to calculate $\Delta S$ for each system and statistic respectively. The change in entropy was calculated according to eq. (20).

# 4 Results

In this section the calculated change in entropy is displayed as well as the intermediate steps, i.e. the heat capacity and the entropy. The results where calculated from Monte Carlo simulations, which employed interatomic exchange parameters $J_{ij}$ retrieved from spin density functional theory, more specifically the SPR-KKR method [17].

## 4.1 Bcc Fe

Bcc Fe was chosen as one of the systems for this project since it is a familiar example of a ferromagnetic material and is well researched. It does not have any major magnetocaloric properties. Figure 4 displays the resulting heat capacity from the classical and the quantum simulations.
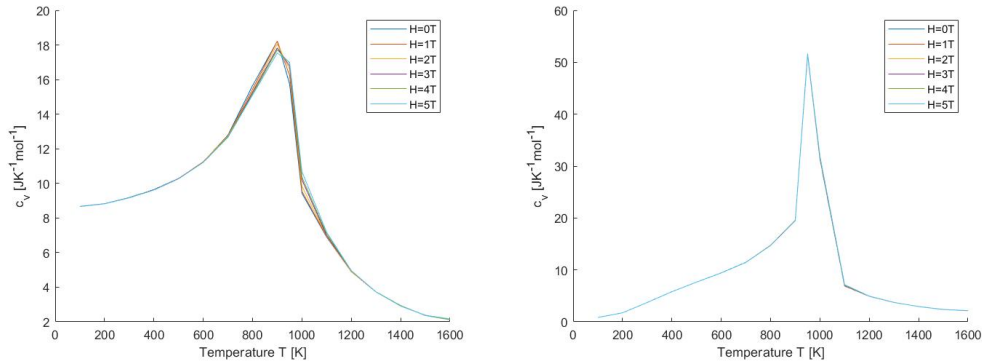


Figure 4: The heat capacity for bcc Fe. To the left, using classical statistics. To the right, using quantum statistics.

In the classical results the heat capacity is nonzero as the temperature goes towards zero, which corresponds with what we know about classical statistics. The heat capacity that was calculated using quantum statistics on the other hand is zero at $T = 0K$, which is consistent with the third law of thermodynamics. The next figure shows the calculated entropy from both statistics.
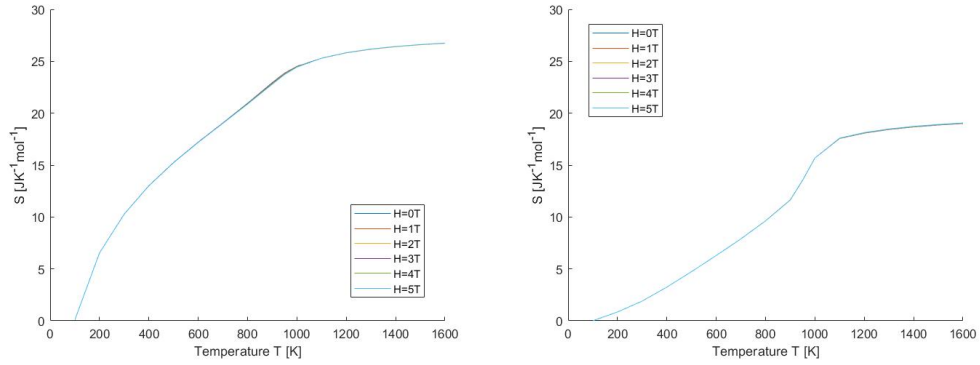
15

Figure 5: The entropy for bcc Fe. To the left, using classical statistics. To the right, using quantum statistics.

From figure 5 one can see that the main difference between between the two statistics is the behaviour of the entropy at lower temperatures. Finally, figure 6 displays the change in entropy for bcc Fe, using both statistics.
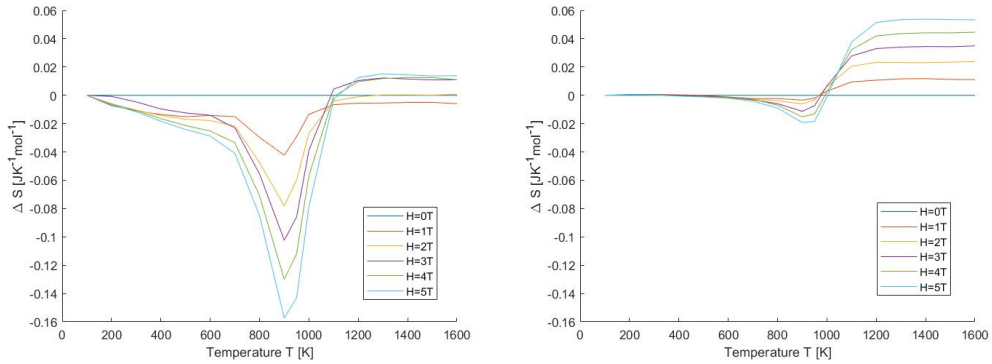


Figure 6: The change in entropy for bcc Fe. To the left, using classical statistics. To the right, using quantum statistics.

The results show several differences between the two statistics. Firstly, $\Delta S$ for lower temperatures is smaller for quantum statistics than for classical. Secondly, the entropy change at the phase transition appears to be smaller for quantum statistics than for classical, but for temperatures above the phase transition $\Delta S$ is smaller for the classical statistics than for the quantum statistics.

16

## 4.2 FeRh

FeRh was selected for this project because of it being a well-known magnetocaloric material. It is especially interesting as it experiences two phase transitions. At low temperatures it is antiferromagnetic, with increasing temperature it undergoes a AF-F (antiferromagnetic-ferromagnetic) phase transition before it reaches the Curie temperature where it becomes paramagnetic [18, 19, 20]. The following figure displays the calculated heat capacity for FeRh for each of the two statistics.
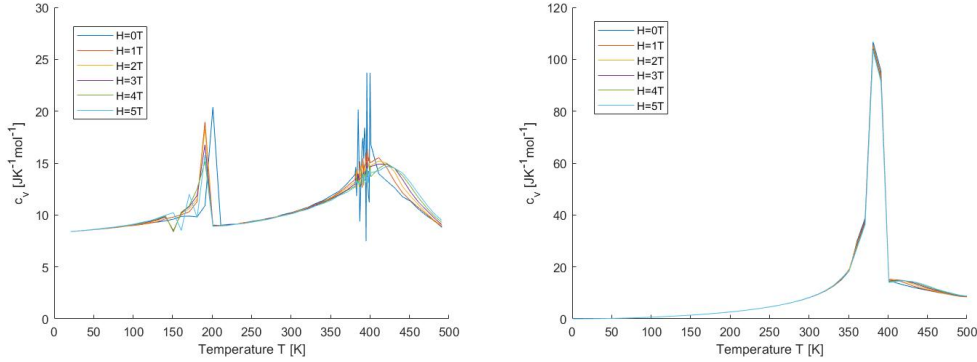


Figure 7: The heat capacity for FeRh. To the left, using classical statistics. To the right, using quantum statistics.

For the classical statistics, peaks in the heat capacity can be seen for both the AF-F phase transition and at the Curie temperature. At zero temperature the heat capacity is nonzero for the classical case and zero for the quantum case, which is consistent with what we know about the two statistics. For the quantum case there is only one peak, it might be that the peaks are so close to each other that they appear to be one peak. If one look at the change in entropy, see figure 9, the AF-F phase transition occurs closer to the Curie temperature for the quantum case. In the classical heat capacity there is some disturbance at the Curie temperature. This is due to numerical noice in the total energy, when the heat capacity is calculated as the derivative of the total energy this noice is then enhanced. Simulations are usually the most difficult at phase transitions, which can lead to disturbances such as the one in the calculated classical heat capacity. Figure 8 shows the entropy for FeRh calculated using classical and quantum statistics.
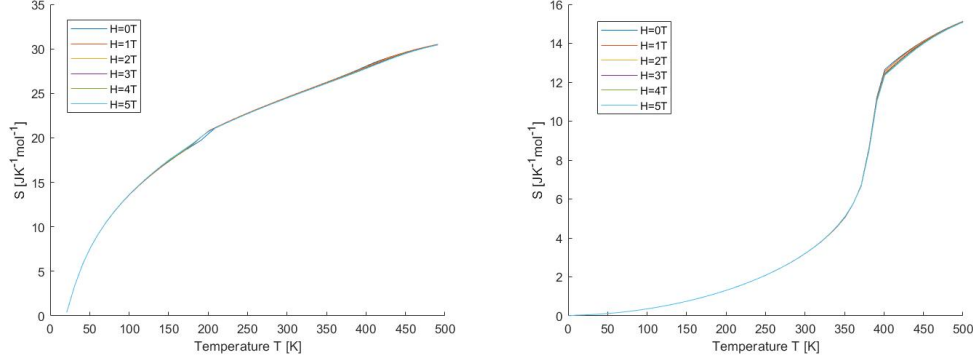
17

Figure 8: The entropy for FeRh. To the left, using classical statistics. To the right, using quantum statistics.

The behaviour of the entropy below the Curie temperature differs between the two statistics. For the quantum case the entropy goes towards zero as the temperature goes to zero, which is consistent with the third law of thermodynamics. The next figure displays the change in entropy, $\Delta$S.
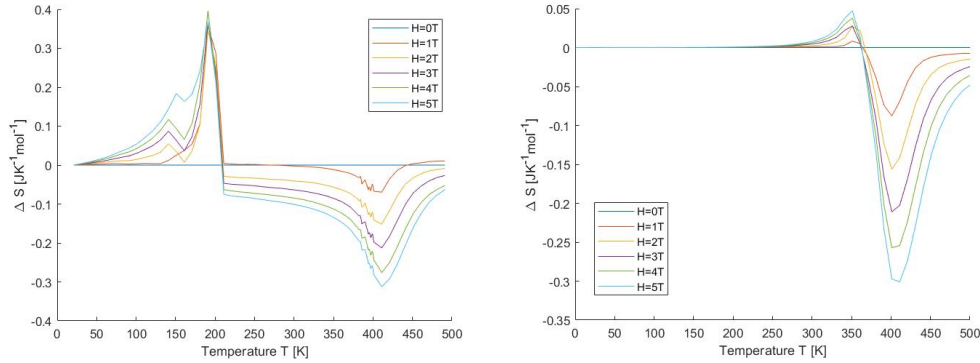


Figure 9: The change in entropy for FeRh. To the left, using classical statistics. To the right, using quantum statistics.

In figure 9 the two phase transitions in FeRh can be seen clearly for both the statistics. For the quantum statistics though, the AF-F phase transition appears at a higher temperature, closer to the phase transition at the Curie temperature. Below the AF-F phase transition $\Delta$S vanishes for the quantum

case, which is not true for the classical case. Lastly, the change in entropy at the AF-F phase transition is almost ten times larger for the classical than for the quantum case, while at the Curie temperature both statistics display similar results.
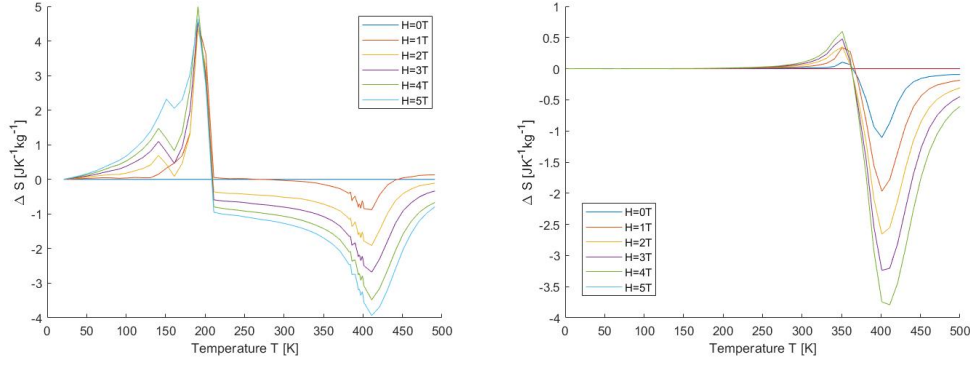


Figure 10: The change in entropy for FeRh in units of J/(K·kg). To the left, using classical statistics. To the right, using quantum statistics.

## 4.3   Fe$_2$P

Fe$_2$P was selected as one of the systems for this project since it is well known for its magnetocaloric properties [21, 22]. Figure 11 shows the calculated heat capacity for Fe$_2$P for both statistics.
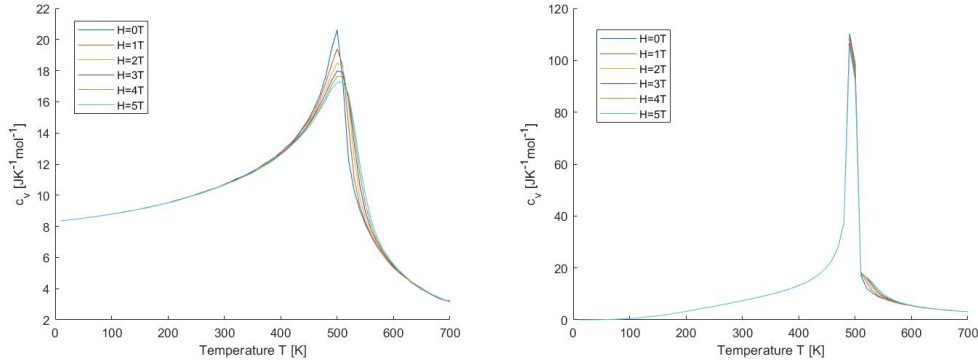


Figure 11: The heat capacity for Fe$_2$P. To the left, using classical statistics. To the right, using quantum statistics.

19

The behaviour of the calculated heat capacity is consistent with what we know about the two statistics. For the classical statistics, the heat capacity is nonzero at zero temperature, while for the quantum statistics the heat capacity goes to zero as the temperature goes to zero. Figure 12 shows the next step in the calculations, which is the entropy.
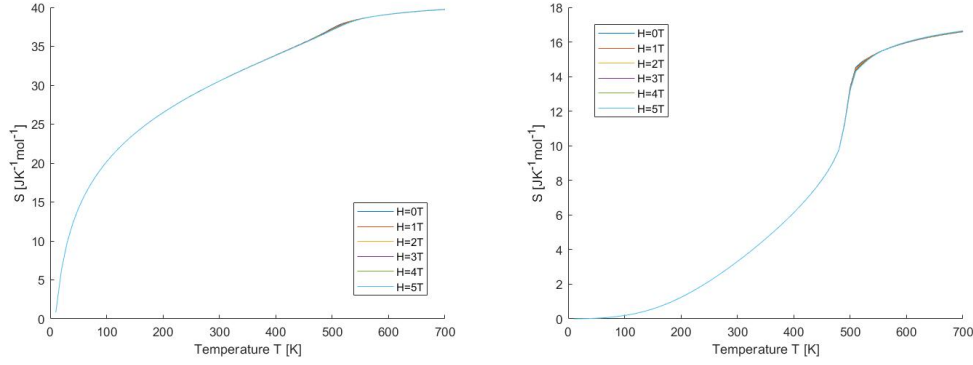


Figure 12: The entropy for $Fe_2P$. To the left, using classical statistics. To the right, using quantum statistics.

Here one can see that the behaviour of the entropy below the Curie temperature differs between the statistics. In the next figure, the change in entropy for $Fe_2P$ is shown, comparing both statistics.
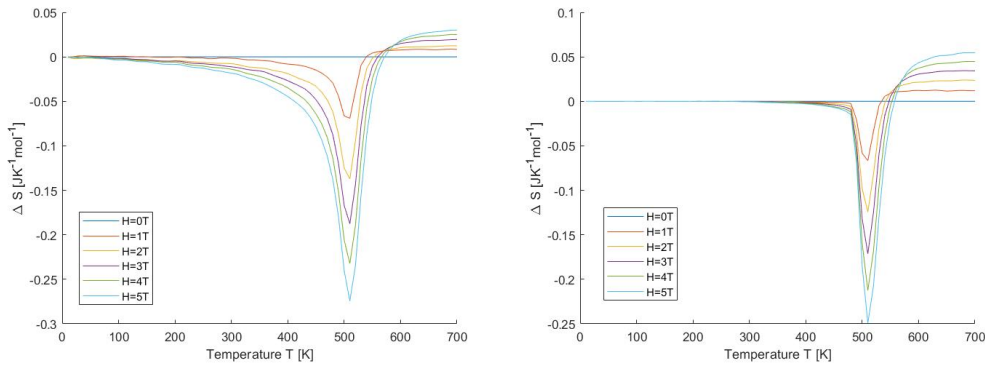


Figure 13: The change in entropy for $Fe_2P$. To the left, using classical statistics. To the right, using quantum statistics.

Below the phase transition, $\Delta$S is significantly smaller for the quantum statistics than for the classical. At the phase transition the quantum statistics shows a slightly smaller entropy change. Above the critical temperature on the other hand, the quantum statistics indicate a larger change in entropy than the classical statistics.
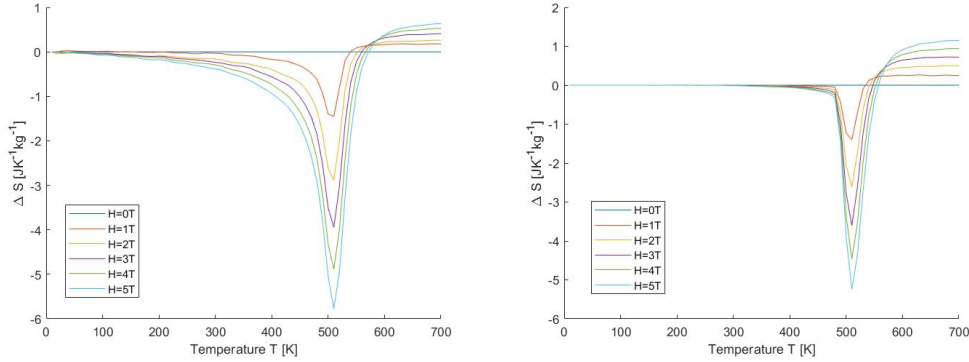


Figure 14: The change in entropy for $Fe_2P$ in units of J/(K·kg). To the left, using classical statistics. To the right, using quantum statistics.

# 5 Discussion

The aim of this project was to answer the question; does the choice of statistic affect the calculated MCE? Looking at the results in figures 6, 9 and 13 it appears that the statistic does impact the calculated change in entropy. The question that naturally follows, which perhaps is the more interesting query, is how the change in entropy is affected by the choice of statistic.

By changing from classical to quantum statistics one effectively performs a rescaling of the temperature, meaning that the activity that is spread over a larger temperature interval for the classical case is pushed away from the lower temperatures and compressed into a smaller interval for the quantum case. This can for example be seen in the calculated heat capacities, where it takes on a lower value for the quantum statistic at lower temperatures. Then at the Curie temperature the peak is substantially higher for the quantum statistic than for the classical statistic. For the change in entropy this can be seen as $\Delta$S is zero up to the phase transistion for quantum statistics, while for the classical statistics the different external magnetic fields diverge at much

lower temperatures. Above the Curie temperature the quantum statistics show a larger entropy change for bcc Fe and $Fe_2P$, while the opposite seem to be true for FeRh. The reason for this is unclear, but it might have to do with how the integration in the entropy calculation was performed.

At the phase transitions the quantum statistics showed entropy changes that were either similar or smaller to the ones calculated with classical statistics. For bcc Fe the change in entropy was almost ten times smaller for the quantum statistics than for the classical, while for $Fe_2P$ the entropy change was of the same magnitude for both statistics. For FeRh the peak at the AF-F phase transition was smaller for quantum statistics and the peaks appear at different temperatures for the two statistics. For the quantum statistics the peak has been pushed up towards the Curie temperature, which is consistent with the temperature rescaling. At the Curie temperature the quantum statistic showed a similar entropy change to the classical, it was even slightly smaller for the quantum case.

Comparing with experimental results [18, 19], both classical and quantum statistics underestimate the change in entropy for FeRh. For $\Delta H=2$ T the experiments measured a entropy change of about 17 J/(K· kg) at the AF-F phase transition, which is well above the calculated entropy changes. The quantum case underestimate the entropy change even more than the classical case. If one instead looks at the temperature at which the AF-F transition occurs, the classical statistics heavily underestimates the temperature, while the quantum statistics instead overestimates it. According to experiments [20], the AF-F phase transition occurs somewhere around 300-315 K, depending on the strength of the magnetic field. In this project the calculated Curie temperature for H=0 T was used in the quantum simulations for all external magnetic fields, even though the classical heat capacity showed different values for $T_C$ depending on the magnetic field. An extension to this project could be to use each respective calculated $T_C$ from the classical simulations for the corresponding quantum simulation, i.e. for the quantum simulation with the same external magnetic field. For $Fe_2P$ both statistics overestimate the change in entropy when compared to experimental results. According to experiments [23], the entropy change has been measured to be around 4 J/(K· kg) for H=5 T. In the same experiment the Curie temperature was measured at a temperature of about 225 K, which is substantially lower than the Curie temperature from the simulations. A possible extension to this project would be to expand and study more magnetocaloric systems to see

22

if they are impacted in the same way as this small subset. One way the results could be improved would be using more realistic interatomic exchange parameters. These determine the system and are retrieved from DFT, which was not in the scope of this project.

In this project it was assumed that the only part of the entropy that is affected by an external magnetic field is the magnetic part of the entropy. This may account for some of the differences between the results of the simulations and experiments, since the other parts also are affected by the magnetic field to some extent. Another approximation which is done is that the exchange interactions in the Hamiltonian, i.e. the interatomic exchange parameters, are assumed to be temperature independent.

# 6    References

[1] Amato, I. "In Hot Pursuit of 21st Century Cooling". *Physics.* February 20, 2020. https://physics.aps.org/articles/v13/21 (retrieved 2020-05-03)

[2] Moya, X., Kar-Narayan, S. & Mathur, N.D.,Caloric materials near ferroic phase transitions. Nature materials, 2014, vol. 13, no. 5, pp. 439-450.

[3] Bergqvist, L., Bergman, A. Realistic finite temperature simulations of magnetic systems using quantum statistics. Physical Review Materials, 2018, vol. 2, no. 1.

[4] Finn, C.B.P. *Thermal physics* Second edition. Boca Raton: CRC Press, Taylor & Francis Group, 1993. Introduction.

[5] Nationalencyklopedin, termodynamik.
http://www.ne.se.ezproxy.its.uu.se/uppslagsverk/encyklopedi/lång/termodynamik (retrieved 2020-04-14)

[6] Finn, C.B.P. *Thermal physics* Second edition. Boca Raton: CRC Press, Taylor & Francis Group, 1993. Chap. 6.

[7] Finn, C.B.P. *Thermal physics* Second edition. Boca Raton: CRC Press, Taylor & Francis Group, 1993. Chap. 8.

[8] Tishin, A.M., Spichkin, Y.I., *The magnetocaloric effect and its applications*, Institute of Physics Pub, Bristol; Philadelphia, 2003.

[9] Weiss, P., Piccard, A. Le phénomène magnétocalorique. J. Phys. Theor. Appl., 1917, vol. 7, no. 1, pp.103-109.

[10] von Ranke, P. J., N. A. de Oliveira, B. P. Alho, et al. Understanding the Inverse Magnetocaloric Effect in Antiferro- and Ferrimagnetic Arrangements. Journal of Physics: Condensed Matter, 2009, vol. 21, no. 5, pp. 056004.

[11] Eriksson, O., Bergman, A., Bergqvist, L., Hellsvik, J. *Atomistic spin dynamics: foundations and applications.* Oxford: Oxford University Press, 2017. Chap. 2.

[12] Kohn, W. Nobel Lecture: Electronic Structure of matter—wave Functions and Density Functionals. Reviews of Modern Physics, 1999, vol. 71, no. 5, pp. 1253-1266.

[13] Eriksson, O., Bergman, A., Bergqvist, L., Hellsvik, J. *Atomistic spin dynamics: foundations and applications.* Oxford: Oxford University Press, 2017. Chap. 9.

[14] Metropolis, N., Rosenbluth, A.W., Rosenbluth, M.N., Teller, A.H., Teller, E. Equation of State Calculations by Fast Computing Machines. The Journal of Chemical Physics, 1953, vol. 21, no. 6, pp. 1087-1092.

[15] Bylin, J. Best practice of extracting magnetocaloric properties in magnetic simulations. MSc Thesis, Uppsala University, Materials Theory, 2019.

[16] Uppsala Atomistic Spin Dynamics. Materials theory, Department of Physics and Astronomy, Uppsala University.
https://physics.uu.se/forskning/materialteori/pagaende-forskning/uppasd/ (retrieved 2020-05-11)

[17] Ebert, H., Mankovsky, S. Anisotropic exchange coupling in diluted magnetic semiconductors: Ab initiospin-density functional theory. Physical Review B, 2009, vol. 79, no. 4.

[18] Sandeman, K.G. Magnetocaloric materials: The search for new systems. Scripta Materialia, 2012, vol. 67, no. 6, pp. 566-571.

[19] Lewis, L.H., Marrows, C.H., Langridge, S. Coupled magnetic, structural, and electronic phase transitions in FeRh. Journal of Physics D: Applied Physics, 2016, vol. 49, no. 32, pp. 323002.

[20] Nikitin, S.A., Myalikgulyev, G., Tishin, A.M., Annaorazov, M.P., Asatryan, K.A., Tyurin, A.L. The magnetocaloric effect in $Fe_{49}Rh_{51}$ compound. Physics Letters A, 1990, vol. 148, no. 6-7, pp. 363-366.

[21] Lundgren, L., Tarmohamed, G., Beckman, O., Carlsson, B., Rundqvist, S. First Order Magnetic Phase Transition in $Fe_2P$. Physica Scripta, 1978, vol. 17, no. 1, pp. 39-48.

[22] Cedervall, J., Andersson, M.S., Delczeg-Czirjak, E.K., Iusan, D., Pereiro, M., Roy, P., Nordblad, P. Magnetocaloric effect in $Fe_2P$: Magnetic and phonon degrees of freedom. Physical Review B, 2019, vol. 99, no. 17.

[23] Caron, L., Hudl, M., Höglin, V., Dung, N.H., Gomez, C.P., Sahlberg, M., Brück, E., Andersson, Y., Nordblad, P. Magnetocrystalline anisotropy and the magnetocaloric effect in $Fe_2P$. Physical Review B, 2013, vol. 88, no. 9, pp. 094440.