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Magnetic properties and magnetocaloric effect of Gd element under first order phase transition

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Abstract

The Bean-Rodbell model is used to study the temperature and field dependences of the magnetization M, magnetic entropy S_m, total entropy S_{total} and magnetic specific heat C_m in case of first - order phase transition in the elemental Gd system. For magnetic fields ≤ 5 T and temperature range up to 400 K, the isothermal entropy change ΔS_m and the adiabatic temperature change ΔT_{ad} are determined. For a magnetic field change of 5 T, the maximum values of ΔS_m and ΔT_{ad} are 4.599 J/mol. K and 20.1 K, respectively. As the magnetic field changes, the value of the Curie temperature T_c changes slightly. In contrast to the second-order phase transition, the maximum values of the magnetocaloric effect (MCE) for first order transition are larger. The temperature and field dependences of the magnetization, magnetic heat capacity, entropy, ΔS_m and ΔT_{ad}, in addition to Arrott-plots are indicative of first - order phase transition (FOPT).

Keywords: Bean-Rodbell model, Gd, mean field theory, magneto-volume coupling
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1. Introduction

The magnetic, magnetothermal properties and magnetocaloric effect for the element Gd have been extensively reported [1-12]. Both experimental and theoretical studied showed that Gd is a ferromagnetic element with Curie temperature around room temperature and is considered as a benchmark material for room-temperature MCE materials [11]. Few studies on the (0001) surface of Gd have been reported on presence of FOPT [5, 9]. E. P. Nobrega et al., have used

mean field approximation and Monte Carlo simulation to study the magnetocaloric effect in gadolinium [1]. M. D. Kuz'min and A. M. Tishin reported on S_{tot}, ΔS_m and ΔT_{ad} in fields up to 7T both (experimental and theoretical) [2]. The magnetic field and temperature dependences of the adiabatic temperature change were measured in single-crystalline and polycrystalline gadolinium by Spichkin et al [3]. Oroszlany et al., studied finite temperature effects on the electronic structure of the bulk and surface of gadolinium metal using first-principles calculation [4]. The magnetic phase transition in (0001) surface of Gd is found to be strongly dependent on the presence of an external magnetic field during cooling across T_c [5]. The magnetocaloric characteristics of the coarse-grained and as-consolidated nanocrystalline gadolinium metals were studied by Hong Zeng et al. [6]. Vieira et al., introduced a computationally efficient method for assessing the field-dependent entropy of magnetocaloric materials using ab-initio techniques [7]. The temperature dependence of Young's modulus and the internal friction have been measured in a high-purity gadolinium single crystal by Spichkin et al. [8].

Up to our knowledge there is no theoretical studies on FOPT in Gd. In the present work we report, using the Bean-Rodbell model, on some magnetic and MCE properties of Gd. In particular, the temperature and field dependence of magnetization, entropy, heat capacity, ΔS_m and ΔT_{ad} and the Arrott plot.

2. Model and Analysis

The Bean-Rodbell model is based on the molecular mean field approximation. The primary focus of the model is the tight relationship between the lattice spacing and the exchange interaction parameter, often known as the Curie temperature. The Curie temperature's volume change dependence can be found using [13]:

$$T_c = T_0\left[1 + \beta\left(\frac{V-V_0}{V_0}\right)\right] \quad (1)$$

In our model the magnetic system is formed by one sublattice (Gd) with angular momentum J. Under the mean field approximation with external magnetic field h_0, the magnetic state equation is :

$$M = N\mu_B g_{gd} J B_J\left[\frac{\mu_B g_{gd} JH}{k_B T}\right] \quad (2)$$

where the mean field H is:

$$H = h_0 + n_{Gd}M + dM^3 \quad (3)$$

Where g_{Gd} is Lange' g factor = 2, B_J is Brillouin function, n_{Gd} is the exchange coefficient = 780 and d is the effective magneto-elastic parameter.

The Bean- Rodbell model provided a thermodynamic description of the cubic magnetization dependency of the mean field resulting from the magnetoelastic interaction, for a single magnetic lattice d=C η [14], where C and η are:

$$C = \frac{3}{5}\left(\frac{(J+1)[(2J+1)^4-1]}{g^2J^3{\mu_B}^2[2(J+1)]^4}\right)n_{gd} \quad (4)$$

and

$$\eta = \frac{5}{2}\left(\frac{[4J(J+1)]^2 k_B K T_0 \beta^2 N}{[(2J+1)^4-1]}\right) \quad (5)$$

where N is the numbers of ions per cm^3 = $2.9 * 10^{22}$, k_B is Boltzmann constant, K is compressibility = $26 * 10^{-13} cm^2/dyne$, the critical temperature curve's slope on the cell deformation is defined by β and T_0 is the magnetic ordering temperature in the absence of deformation = 295 K.

According to the Landau theory of phase transitions, a first order magnetic phase transition i occurs when **η>1**, and second order phase transition when **η<1**.

The magnetic entropy cab be expressed as function of normalized magnetization **σ** by [15]:

$$S_m(T,H) = Ln(2J+1) - \left(\frac{1}{2a_J}\right)\left(\sigma^2 + \frac{b_J}{2}\sigma^4 + \frac{c_J}{3}\sigma^6 + \cdots\right) \quad (6)$$

where, $a_J = \frac{J+1}{3J}$,

$b_J = 0.3\frac{((J+1)^2+J^2)}{(J+1)^2}$,

and $c_J = \frac{9}{1400}\left(\frac{88(J(J+1))^2+108J(J+1)+27}{(J+1)^4}\right)$

the total entropy is the sum of the magnetic, electronic and lattice contributions :

$$S_t = S_m + S_e + S_l \quad (7)$$

The magnetic specific heat can be calculated from the magnetic entropy:

$$C_m = T\frac{\partial Sm(T,H)}{\partial T} \quad (8)$$

The MCE is well identified by two quantities: isothermal entropy change ΔS_m and adiabatic temperature change ΔT_{ad}. Entropy change can be calculated by two methods: indirect method (Maxwell relation) and direct subtraction.

$$\Delta S_m(T,\Delta H) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \quad (9)$$

$$\Delta S_m = S(T,H=0) - S(T,H\neq 0) \quad (10)$$

The adiabatic change in temperature is given by:

$$\Delta T_{ad} = -\int_0^H \frac{T}{C_{tot}(T,H)}\left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \quad (11)$$

and in case of a weak dependence on field of the quantity $\frac{T}{C_{tot}}$, close to T_c, ΔT_{ad} becomes:

$$\Delta T_{ad} \approx -\frac{T}{C_{tot}(T,H)}\int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \quad (12)$$

The nature of the phase transition is also investigated using the Arrott plots. Positive or negative (or S-shaped) slopes of M^2 vs. H/M plots indicate the presence a second or first order phase transitions respectively.

Results and Discussion

1. Magnetization

The change in magnetization as a function of temperature is shown in Figure 1. A first-order phase transition whereby M changes discontinuously at Curie temperature (T_c) is evident. the T_c of Gd in a second-order phase transition is about 298K as known [11] but in FOPT, T_c is shifted to 309K. The magnetization curves at different temperatures around T_c, and in field up to 10 T, are shown in Figure 2.

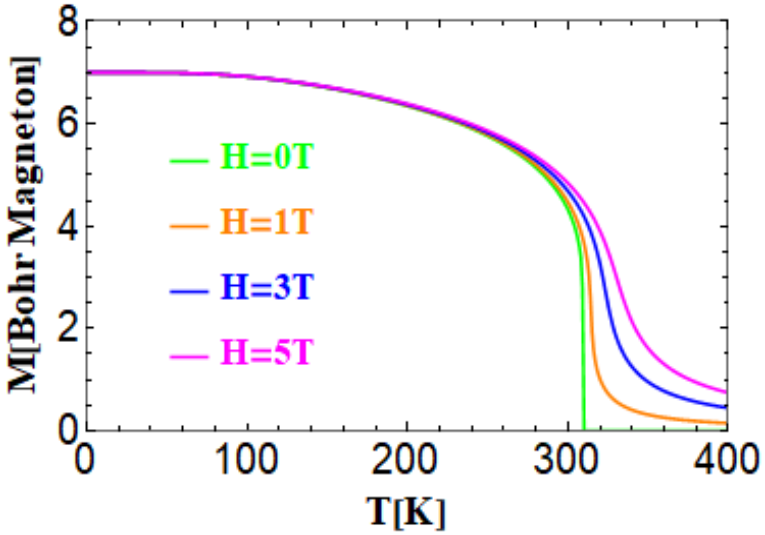

Fig.1. Magnetization vs. temperature for Gd in zero, 1, 3 and 5 T fields.

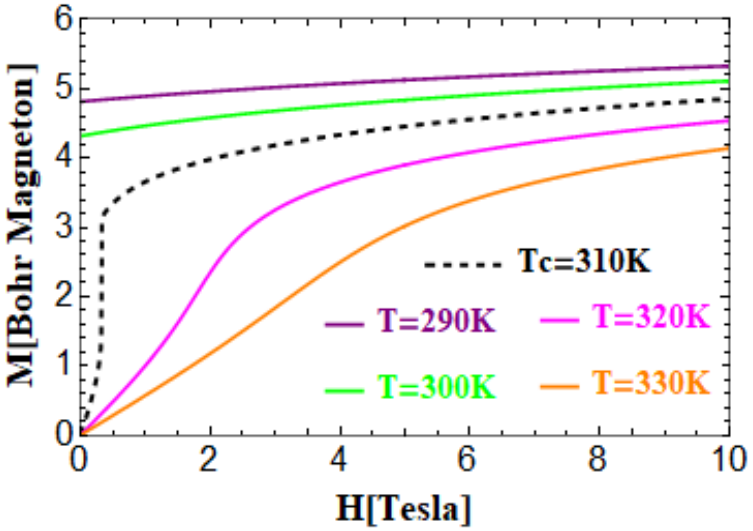

Fig 2. Isothermal magnetization M(H) of Gd calculated in the temperature range between 290 and 330 with a step of 10K.

2. Magnetic and Total Entropy

The magnetic entropy of Gd is shown in Figure 3 for various fields of 0, 1, 3 and 5T. It is evident that as temperature rises, the magnetic entropy discontinuously increases until it

reaches saturation at over 310 K. The highest magnetic entropy is in fair agreement with the theoretical value $S_m(max)= R\ Ln(2J_{Gd}+1)$, which equals 17.2. The total entropy of Gd is computed using equation (7). The latent heat, at the critical temperature, in materials with FOPT is $L=T\Delta S$ [17] . Our calculated value is 362 J/mole. (Figure 4).

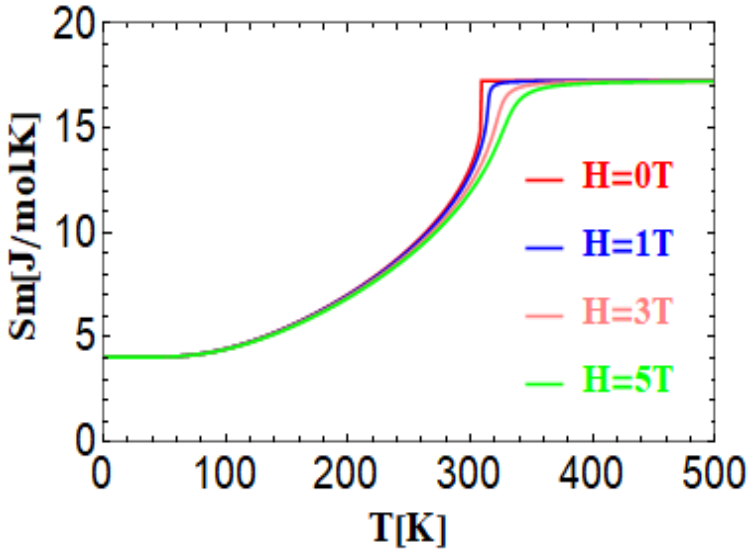

Fig 3. Magnetic entropy vs. temperature for Gd in zero, 1, 3 and 5 T fields at FOPT.

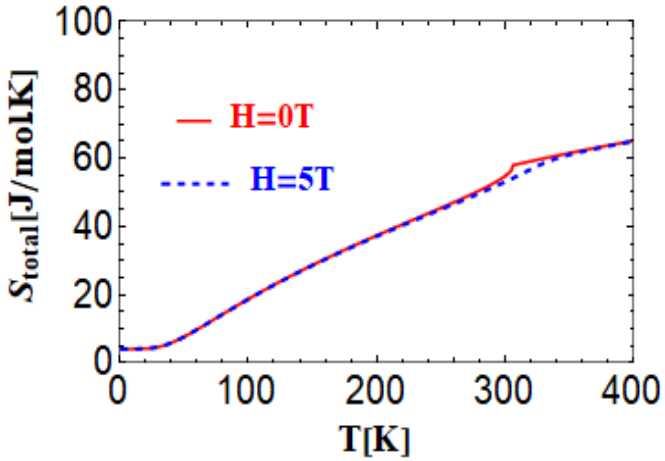

Fig 4. Total entropy vs. temperature for Gd in zero and 5 T fields at FOPT.

3. Magnetic Specific Heat

Magnetic specific heat is calculated from Eq.(8). The specific heat peaks shifts toward higher temperatures as the field increases. There is a giant magnetic heat capacity value at T_c and zero field. (Figure 5).

Table 1 shows the maximum magnetic specific heat at different fields and at the Curie temperature. We notice that the maximum values of C_m are very high compared to those in Gd in the absence of magneto-volume coupling.

Table.1: The maximum values of magnetic specific heat and the corresponding Curie temperatures at each magnetic field.

Magnetic fields H [T]	Curie temperature T_c [K]	C_m maximum value [J/mol. K]

0	309	601.14
1	314	192.24
3	322	66.79
5	327	46.60

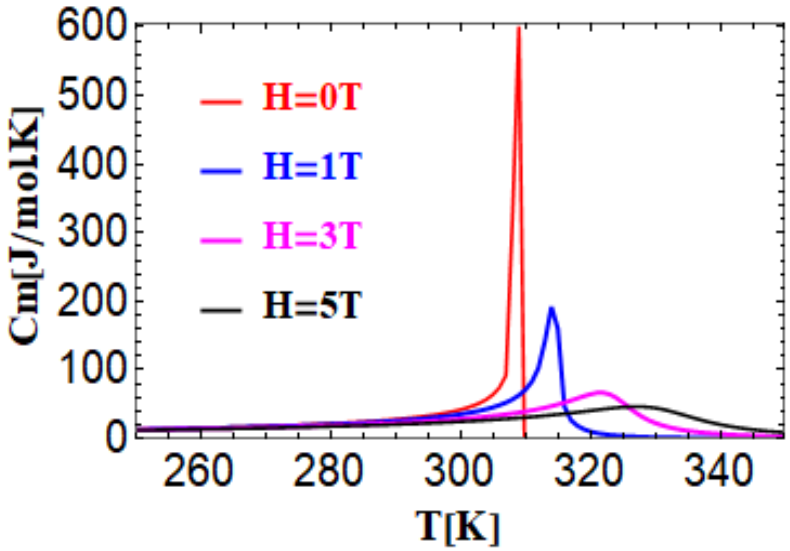

Fig 5. C_m vs. T for Gd at different fields in case of FOPT.

4. Magnetocaloric Effect

The magnetic entropy change (ΔS_m) is calculated by the direct subtraction method (Eq.10). At a first order phase transition, the features are rather different than those in case of second order transition (Figure 6).

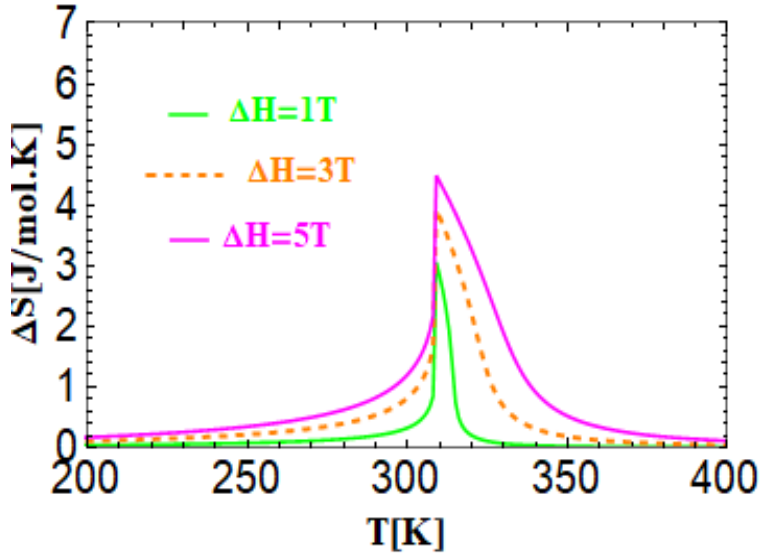

Fig 6: Magnetic entropy change ΔS_m of Gd for magnetic field changes of 1, 3, and 5 T.

We calculated the adiabatic temperature change ΔT_{ad} for magnetic field changes up to 5 T. Figure 7 displays the temperature-dependent ΔT_{ad} in different fields. For example, a temperature drop of 20 K takes place for a field change of 5 T. It is of interest to compare the values of ΔT_{ad}, for FOPT and SOPT in Gd. The data is shown in table 2.

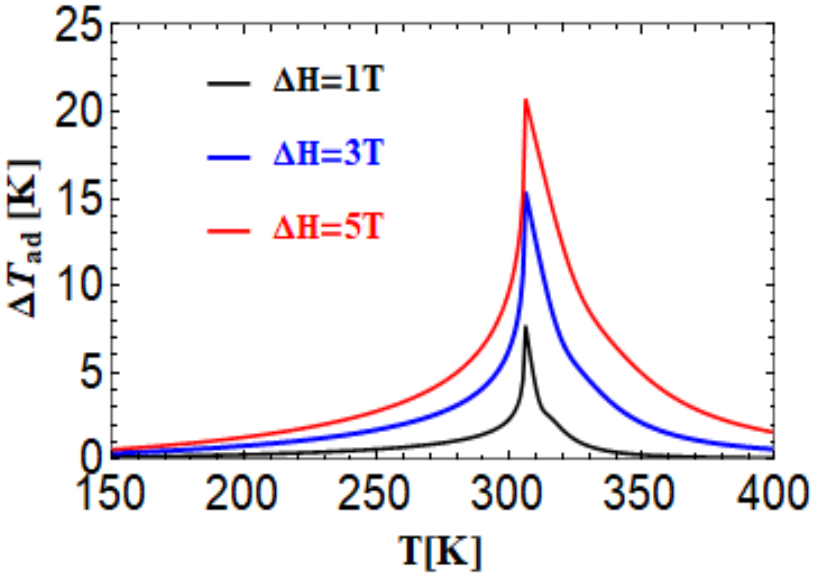

Fig 7: Adiabatic temperature change ΔT_{ad}, as a function of temperature, for field changes of 1, 3, and 5 T.

Table.2: The maximum values of ΔS_m and ΔT_{ad} of Gd element in FOPT and SOPT systems [18].

	First-order phase transition			Second-order phase transition		
ΔH [T]	**T_c [K]**	**ΔS_{max} [J/mol.K]**	**$\Delta T_{ad(max)}$ [K]**	**T_c [K]**	**ΔS_{max} [J/mol.K]**	**$\Delta T_{ad(max)}$ [K]**
1	309.3	3.13	7.68	294	~ 0.6	~ 4
3	309.35	4.04	15.39	294	-	~ 8
5	309.4	4.599	20.1	294	~ 1.5	~ 11

5. Belove- Arrott Plot

The first-order phase transition in Gd element is confirmed by negative slopes or S-shaped curves at 310 to 330K (Fig 8).

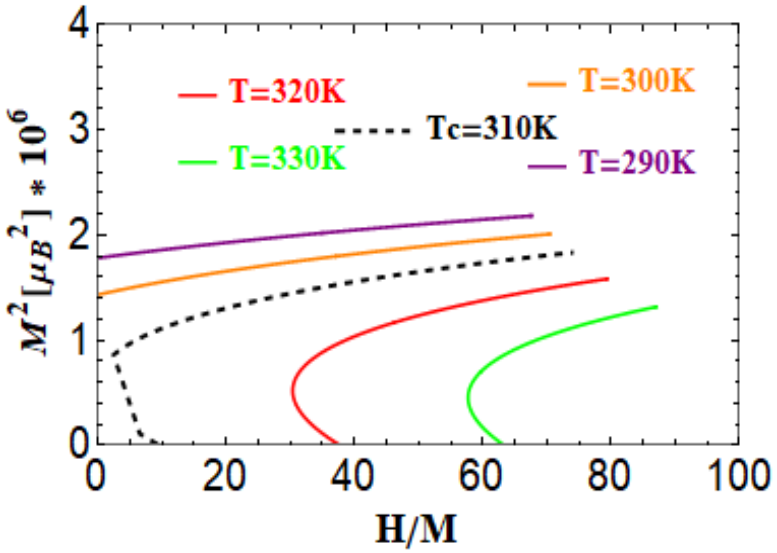

Fig 8: Belove Arrott plots, M^2 against H/M, for FOPT Gd.

6. Conclusions

We report on the isothermal and MCE quantities e.g.: M, C_m, S_m, ΔS, and ΔT_{ad} in fields up to 5T and at temperatures up to 400K, for Gd using the mean-field model with magneto-volume coupling. Taking the magneto-volume coupling into account has produced features of FOPT in the calculated quantities. The largest ΔT_{ad} is approximately 20.1 K in a 5T field change, while the largest ΔS is found to be approximately 4.599 J/mol. K, for the same field change. A comparison is given between the MCE quantities for FOPT and SOPT gadolinium. The former values are higher than the latter. It is planned to study the effect of introducing pressure and thermal expansion coefficients, in a future study.

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