MAGNETIC ENTROPY AND MAGNETIC HEAT CAPACITY NEAR THE FIRST-ORDER FERROMAGNETIC TO PARAMAGNETIC PHASE TRANSITION

MUKHERJEE, P. K.

Department of Physics, Government College of Engineering and Textile Technology, West Bengal, India.
e-mail: huda.aqeel[at]uomosul.edu.iq

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Abstract. The continuous development of magnetization below the transition point is the characterization of the second order ferromagnetic (FM) phase to paramagnetic (PM) phase transition (FM-PM). The discontinuous change in magnetization along the hysteresis path is the characterization of the first order FM-PM phase transition. The manganites with the highest FM-PM transition temperature undergo a conventional second order phase transition, whereas for the lower FM-PM transition temperature manganites, the FM-PM phase transition is first order. In the presence of an external magnetic field, the first order FM-PM transition shifts towards the higher temperature while the width of thermal hysteresis in magnetization decreases gradually and the transition becomes second-order. The magnetic entropy and magnetic heat capacity near the first-order ferromagnetic to paramagnetic phase transition are discussed using Landau theory. The magnetic entropy and magnetic heat capacity are calculated near the phase transition. The theoretical results are discussed by piloting figures. We show that negative values of the magnetic entropy and positive values of magnetic heat capacity in the ferromagnetic phase increase with the increase of the magnetic field.

Keywords: *ferromagnetic, paramagnetic, entropy, heat capacity, phase transition*

Introduction

In general, the transition from the ordered ferromagnetic (FM) phase to the disordered paramagnetic (PM) phase transition (FM-PM) is second-order. This is characterized by the continuous development of magnetization below the transition point. But in some systems, the FM-PM phase transition often demonstrates the discontinuous change in magnetization along the hysteresis path. It has been observed that manganites with the highest FM-PM transition temperature undergo a conventional second-order phase transition, whereas the lower FM-PM transition temperature manganites, the FM-PM phase transition is first order (Tomioka et al., 2009; Ghosh et al., 1998). It has been found that the change of first-order to second-order FM-PM phase transition depends on various external conditions (Mukherjee et al., 2018; Mydeen et al., 2008; Sarkar et al., 2009a, 2009b, 2008; Belevtsev et al., 2006; Amaral et al., 2003; Kim et al., 2002; Alexandrov and Bratkovsky, 1999; Das and Ghosh, 1983; Imry and Wortis, 1979). In the presence of an external magnetic field, the first-order FM-PM transition shifts towards the higher temperature while the width of thermal hysteresis in magnetization decreases gradually and the transition becomes second-order.

Kim et al. (2002) studied the doping dependence of the FM-PM transition and observed the tricritical behavior of the FM-PM transition. Amaral et al. (2003) studied the magnetization of manganite using Landau theory. They observed the first order character of the FM-PM transition with the existence of hysteresis. Belevtsev et al. (2006) studied ultrasonic properties of near the FM-PM transition and measured temperature dependences of longitudinal and transverse sound velocities for different magnetic fields. They observed the first order as well as second order character of the FM-PM transition as the applied field changes. Mydeen et al. (2008) studied the effect of hydrostatic pressure of $Sm_{0.52}Sr_{0.48}MnO_3$. They found that the nature of the FM-PM transition changes from discontinuous to continuous as pressure changes. Sarkar et al. (2008) experimentally studied the magnetic field dependence of the order of the FM-PM transition in $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal and observed the tricritical point. Sarkar et al. (2009b) studied the magnetic field, hydrostatic pressure, and doping dependence of the order of the FM-PM transition in $Sm_{0.52}Sr_{0.48}MnO_3$ single crystal and observed the change in the character of FM-PM transition within the framework of the formation of polarons.

Sarkar et al. (2009a) studied the hydrostatic pressure dependence of FM-PM transition in a $(Sm_{0.7}Nd_{0.3})_{0.5}Sr_{0.48}MnO_3$ single crystal and observed the change of the character of the transition from first order to second order transition. Imry and Wortis (1979) studied the effect of random quenched impurities on the FM-PM transition. They discussed criterion for the appearance of rounding due to local fluctuations in thermodynamic phase. Das and Ghosh (1993) theoretically calculated the pressure dependent thermal hysteresis near the first order FMPM transition. Alexandrov and Bratkovsky (1999) studied the carrier density collapse and colossal magnetoresistance in doped manganites to test the first order or second order character of the FM-PM transition. Mukherjee et al. (2018) studied the effect of external magnetic field, pressure and chemical substitution on the nature of the FM-PM transition in manganites. They observed that the first order FM-PM transition becomes second order at the tricritical point under external perturbations.

Change in the magnetic entropy and magnetic specific heat capacity is another interesting topic in the order-disorder transition in magnetic systems. Bishwas and Poddar (2016) experimentally studied the magnetic entropy and magnetic heat capacity across the order-disorder transitions in ferrimagnetic Fe3Se4 nanorods and observed a pronounced anomaly in the heat capacity at the Curie temperature. Palacios et al. (2015) experimentally studied the magnetocaloric effect of $Ni_{50}CoMn_{36}Sn_{13}$ by calorimetric technique by measuring the magnetic entropy and magnetic specific heat capacity. Kapusta et al. (2018) also studied the magnetocaloric properties of the Co@Au system by heat capacity measurement and finally examined the system in terms of isothermal magnetic entropy change. On the theoretical modeling side, Takahashi and Nakano (2004) theoretically calculated the magnetic entropy and magnetic heat capacity of itinerant electron ferromagnets based on the spin fluctuation mechanism. Their results cover a wide range of temperatures and external field strength. Van Dijk (2021) evaluated the field exponent for the magnetic entropy change near the first and second order of the FM-PM phase transition using Landau theory. The purpose of the present work is to evaluate the analytic expression of the magnetic entropy and magnetic heat capacity near the first-order FM-PM phase transition using Landau theory analysis.

Theory

The magnetic free energy density in terms of the magnetization M in the presence of external magnetic field H can be written as:

$$F = F_0 + \frac{1}{2}AM^2 - \frac{1}{4}BM^4 + \frac{1}{6}CM^6 - HM \qquad \text{Eq. (1)}$$

Where; F_0 free energy density of paramagnetic phase. The coefficient A can be assumed as A=*a*(T-T*) where a is a positive constant and T^* is the virtual transition temperature. The coefficients B and C assumed to be temperature-independent. We assume C>0 for the stability of the free energy, The free energy density (1) describes a first-order FM-PM phase transition for B>0 and H=0 while the transition is second-order for B<0. However, for H≠0, the transition becomes second-order even for B>0. The free energy density (1) shows that M=0 can never be a solution of H≠0, which means that an induced magnetization is observed in the paramagnetic phase. Minimization of Eq. (1) with respect to M can be expressed as:

$$AM - BM^3 + CM^3 - H = 0 \qquad \text{Eq. (2)}$$

Solving Eq. (2) will show the variation of M with temperature T and magnetic field H. The magnetic entropy in the ferromagnetic phase can be calculated from the expression S=-∂F/∂T as:

$$S(H,T) = -\frac{aB}{4C}\left[1 + \sqrt{1 - \frac{4AC}{B^2}}\right] + \frac{aA}{2B}\left(1 - \frac{4AC}{B^2}\right)^{-1/2}$$
$$-Ha\sqrt{\frac{C}{2B^3}}\left[\left(1 - \frac{4AC}{B^2}\right) + \left(1 - \frac{4AC}{B^2}\right)^{3/2}\right]^{-1/2} \qquad \text{Eq. (3)}$$

The magnetic entropy in the paramagnetic phase can be expressed as:

$$S_p(H,T) = -\frac{3H^2}{2a(T - T^*)^2} - H \qquad \text{Eq. (4)}$$

The magnetic heat capacity in the ferromagnetic phase can be calculated from the expression C_P=-T (∂^2 F)/(∂T^2) as:

$$C_P^f(H,T) = T\left[\frac{a^2}{B}\left(1 - \frac{4AC}{B^2}\right)^{-\frac{1}{2}} + \frac{a^3C}{B^3}(T - T^*)\left(1 - \frac{4AC}{B^2}\right)^{-\frac{3}{2}}\right.$$
$$\left. + H\frac{a^2C^{3/2}}{\sqrt{2}B^{7/2}}\left(2 + 3\left(1 - \frac{4AC}{B^2}\right)^{\frac{1}{2}}\right)\right] \times \left[\left(1 - \frac{4AC}{B^2}\right) + \left(1 - \frac{4AC}{B^2}\right)^{\frac{3}{2}}\right]^{-3/2} \qquad \text{Eq. (5)}$$

The magnetic heat capacity in the paramagnetic phase can be expressed as:

$$C_P^p(H,T) = \frac{3H^2T}{a(T - T^*)^3} \qquad \text{Eq. (6)}$$

The background heat capacity in the paramagnetic phase for zero fields can be expressed as:

$$C_P^p = b_1 + c_1(T - T^*) + d_1(T - T^*)^2 \qquad \text{Eq. (7)}$$

Here b_1 is a positive constant and c_1 and d_1 are negative constants.

Materials and Methods

Landau theory of phase transition has been used to calculate the magnetic entropy and magnetic heat capacity of ferromagnetic materials exhibit first order FM-PM phase transition. The theory is applicable for all manganites materials. The analytical and numerical methods have been used to discuss the theoretical results. Theoretical results have been discussed by plotting figures using Fortran 77 and Xmgrace software.

Results and Discussion

The author discusses the results by plotting magnetic entropy and magnetic heat capacity as a function of magnetic field and temperature. The magnetic entropy as a function of temperature in the ferromagnetic phase of the first-order FM-PM phase transition is shown in *Figure 1* and *Figure 2* respectively. This is done using Eq. (3). The author choose the parameter values a=0.5, B=2.2, and C=4.0. *Figure 1* shows the variation of magnetic entropy with temperature for three different values of the magnetic fields. The increase of the negative values of magnetic entropy with a magnetic field is clearly observed in the ferromagnetic phase of the first-order FM-PM phase transition. Further, the negative magnetic entropy decreases with temperature as indicated in *Figure 1*. *Figure 2* shows the variation of magnetic entropy with a magnetic field at a constant temperature. *Figure 2* also shows the increase of negative values of magnetic entropy with a magnetic field in the ferromagnetic phase of the first-order FM-PM phase transition. In order to show the variation of magnetic heat capacity with temperature, the author use Eq. (5) to Eq. (7). *Figure 3* (Eq. (5) shows the variation of the magnetic heat capacity in the ferromagnetic phase with temperature for three different values of the magnetic field. The increase of magnetic heat capacity with the magnetic field is clearly observed in *Figure 3*. To show the variation of magnetic heat capacity near the first-order FM-PM phase transition we have plotted Eq. (5) to Eq. (7) in *Figure 4*. *Figure 4* shows a clear indication of an increase in magnetic heat capacity with the magnetic field near the FM-PM phase transition. Thus it is clear that from *Figure 1* to *Figure 4*, both the magnetic entropy and magnetic heat capacity increase with magnetic field in the ferromagnetic phase of the first order FM-PM phase transition. The above results agree with the experimental results of magnetic systems (Kapusta et al., 2018; Bishwas and Poddar, 2016; Palacios et al., 2015; Takahashi and Nakano, 2014). The qualitative agreement between the theoretical results and various experimental results show the validity of the Landau theory of phase transition of the FM-PM phase transition.

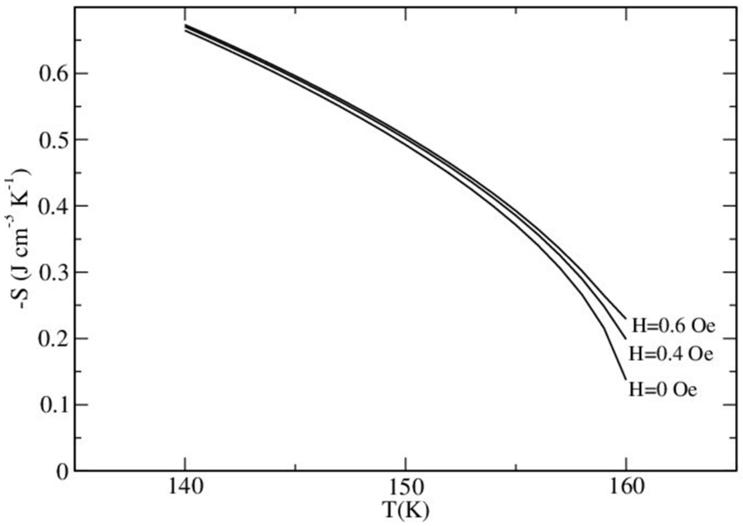

Figure 1. *Temperature dependence of magnetic entropy for different values of magnetic field in the ferromagnetic phase of the FM-PM phase transition.*

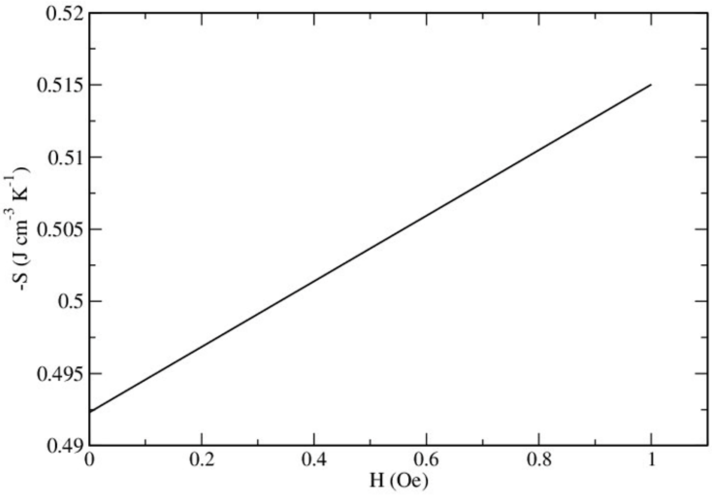

Figure 2. *Magnetic field dependence of entropy for fixed temperature in the ferromagnetic phase of the FM-PM phase transition.*

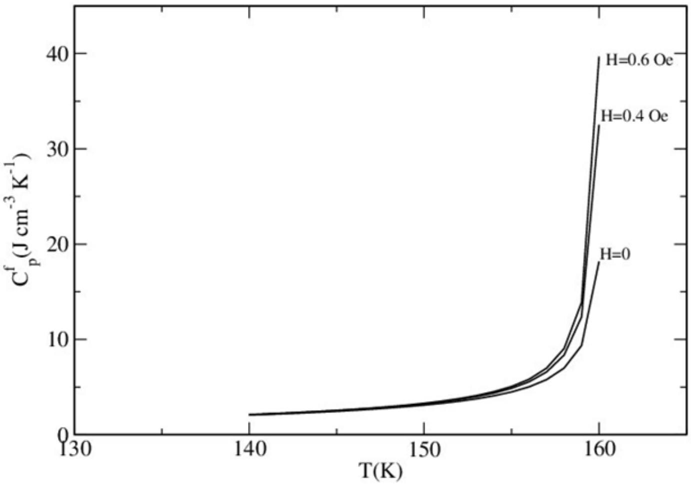

Figure 3. *Temperature dependence of magnetic heat capacity for different values of the magnetic field in the ferromagnetic phase of the FM-PM phase transition.*

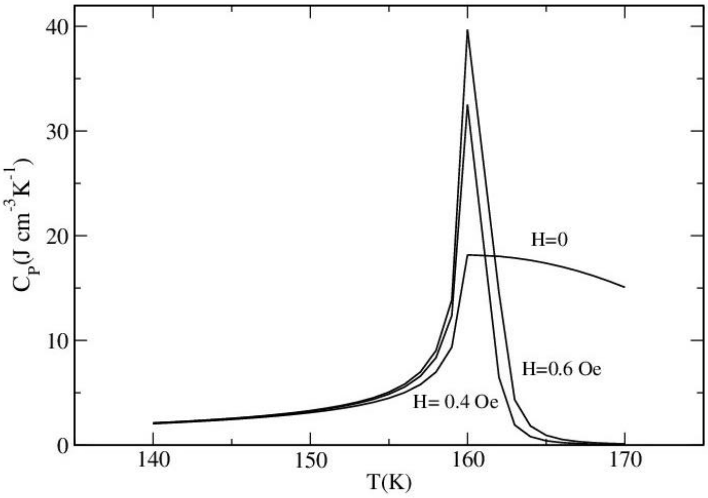

Figure 4. *Temperature dependence of heat capacity for different values of the magnetic field of the FM-PM phase transition.*

Conclusion

The author has discussed the magnetic entropy and magnetic heat capacity near the first-order PM phase transition based on Landau theory. The analytical expressions of the magnetic entropy and magnetic heat capacity are calculated. In the presence of a magnetic field, negative values of the magnetic entropy and the positive values of the magnetic heat capacity increase near the first-order FM-PM phase transition. The magnetic entropy increases with the temperature and magnetic fields. The magnetic heat capacity also increases with the temperature and magnetic fields. Our results qualitatively agree with experimental results (Kapusta et al., 2018; Bishwas and Poddar, 2016; Palacios et al., 2015; Takahashi and Nakano, 2014).

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Conflict of interest

The author declares no conflict of interest, financial or otherwise.

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