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Microscopic study on magnetocaloric and electrocaloric effects near the critical point

Hitoshi Honmi *, Yoichiro Hashizume, Takashi Nakajima, Soichiro Okamura

Tokyo University of Science, 6-3-1 Niijuku, Katsushika-ku, Tokyo, 125-8585, Japan

HIGHLIGHTS

- Temperature changes are investigated in adiabatic processes near the critical points.
- Husimi–Temperley model and Slater model are applied to show the temperature changes.
- The general formalism is obtained by general representation of the free energy.
- Frustrated systems are also studied from the present aspects.

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ABSTRACT

Adiabatic temperature changes of magnetocaloric/electrocaloric effects are analytically investigated. The analytical studies are based on the microscopic statistical models such as Husimi–Temperley model and Slater model. As a result, we show the characteristic scales of the adiabatic processes correspond to microscopic parameters, namely exchange couplings and Slater energy. The scaled parameter dependence become stronger near the critical point. Furthermore, using a general Hamiltonian method, we clarify the adiabatic temperature changes depend on the relative ratio of characteristic scales. The present study may propose a useful aspect for applications.

1. Introduction

Adiabatic demagnetization is a useful way to make an ultra-cold state. The temperature decreases by vanishing the applied magnetic field. This phenomena is also called "magnetocaloric effect". In non-adiabatic process, spin states change gradually with decrease of the magnetic field. On the other hand, in adiabatic process, spin states cannot change because the magnetic field vanishes so rapidly. It is necessary to decrease the temperature of the system to conserve the total entropy. This magnetocaloric effect is enhanced near the critical point because the phase transition causes a drastic change of the entropy. Previous studies have experimentally clarified the adiabatic change of temperature as magnetocaloric effects near the critical point. For example, the maximum temperature change is 13 K in MnAs [1], while it is 15 K in $Gd_5(Si_2Ge_2)$ [2].

Obviously, the similar effect occurs on dielectric materials, that is, the temperature decreases by vanishing of electric fields to keep the state of electrical polarizations. The quantitative temperature decrease is also reported as electrocaloric effect near the critical point, namely temperature change of 11.78 K in $BaTiO_3$ thin film [3], 31 K in PMN-PT thin film [4], 12 K in $PZ_{0.95}T_{0.05}O_3$ thin film [5], 40 K in PLZT thin film [6], 45.3 K in $Pb_{0.8}Ba_{0.2}ZrO_3$ thin film [7], 12 K in P(VDF/TrFE/CFE)

* Corresponding author.
E-mail addresses: 1511082@ed.tus.ac.jp (H. Honmi), hashizume@rs.tus.ac.jp (Y. Hashizume), nakajima@rs.tus.ac.jp (T. Nakajima), sokamura@rs.kagu.tus.ac.jp (S. Okamura).

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film [8] and 12 K in P(VDF/CTFE) film [9]. These temperature changes, ΔT, are analytically studied using the thermodynamic relations;

$$\Delta T = -\int_{H_1}^{H_2} \frac{T}{C_H}\left(\frac{\partial m}{\partial T}\right) \mathrm{d}H, \tag{1}$$

or

$$\Delta T = -\int_{E_1}^{E_2} \frac{T}{C_E}\left(\frac{\partial P}{\partial T}\right) \mathrm{d}E, \tag{2}$$

where the parameters C_H and C_E denote the specific heats, and the parameters m and P denote the magnitudes of the magnetization and the electric polarization, respectively. These studies suggest the possibility of an application of ferroelectrics to cryogenic technologies and temperature controls. As shown in the previous studies, magnetocaloric/electrocaloric effects have been studied by using experimental and analytical methods. However, especially in analytical studies, phenomenological approach is mainly used to introduce the free-energy of the system, and then, it is difficult to reflect the difference of materials. For further applications, distinguishing the materials may become an important factor. In order to distinguish the difference of materials, it is necessary to describe the properties of materials by microscopic ways.

In the present study, we try to clarify the treatments of the adiabatic magnetocaloric/electrocaloric effects including phase transitions from the viewpoint of microscopic principles, and to understand the important scale to determine the temperature changes near the critical point. Here the "microstructure" or "microscopic aspects" means the lattice structure and the distribution of the interactions which controls the dynamics of the order parameters. In the aspect of statistical mechanics, there are two famous ways to treat the microscopic view points. One of them is the canonical ensemble treatment which started from the Hamiltonian $\mathcal{H}$ of the focused system. The Hamiltonian $\mathcal{H}$ generally describes such microscopic features as interactions, stochastic parameters and external fields, and then, the partition function $Z \equiv \exp[-\beta\mathcal{H}]$ (where β denotes the inverse temperature $1/k_{\mathrm{B}}T$ with the Boltzmann constant k_{B}) includes the microscopic information. The other one is the micro-canonical ensemble treatment which describes the microscopic features confining the states to the constant energy E. In both ways, we can make the microscopic discussion of the adiabatic temperature changes. At first, we apply Husimi–Temperley model to study the magnetocaloric effect. As is well known, Husimi–Temperley model is one of the simple mean-field models on which a second order phase transition occurs and is defined by Hamiltonian. Using this Hamiltonian, we show an example to obtain ΔT by canonical ensemble treatments. This analysis is included in the following section. Secondly, to study the electrocaloric effect, we study in the scheme of Slater theory which is well-known microscopic theory of the phase transitions of KH_2PO_4 (ferroelectric material) in Section 3. This is one possible example to study electrocaloric effects from microscopic viewpoints and is described by the form of microcanonical ensemble treatments. The models in Sections 2 and 3 are different distributions of each other, whereas using the policy reflected microscopic detail, we can approach microscopic temperature changes in both models. Thirdly, to study general adiabatic temperature changes, we study magnetocaloric/electrocaloric effects from the general Hamiltonian in Section 4. Summary and discussions are included in Section 5. Recently, critical research by Vdovych et al. was proposed [10]. They applied a cluster approximation for the KH_2PO_4 Hamiltonian, and numerically obtained several typical properties of KH_2PO_4. We mention the relation to this study in Section 5, and show that the fluctuation is important in conclusion.

2. Husimi–Temperley model

Here, we demonstrate a canonical ensemble treatment to analyze magnetocaloric effects based on Husimi–Temperley model which is known as a mean-field model. Of course, the adiabatic transition processes (especially the time developments) of the states cannot be treated by the canonical ensemble. Contrary to this, in the adiabatic cooling process, we assume that the microscopic time scale of the state transitions is faster than that of such macroscopic quantities as the entropy S. Actually, the previous studies [3–5,7,11] successfully explain the experimental results using the thermodynamics of equilibrium states as discussed in the Introduction. As is well known, second order phase transition occurs on the Husimi–Temperley model [12–14]. This system includes Ising spin variables $\{s_i\} = \{\pm 1\}$, the ferromagnetic interaction between spins J and the Zeeman term of magnetic field H. Thus, the Hamiltonian is defined [12–14] as

$$\mathcal{H} = -\frac{J}{2N}\sum_{i\neq j} s_i s_j - \mu_{\mathrm{B}} H \sum_i s_i. \tag{3}$$

From Eq. (3), we can obtain the partition function Z as

$$Z \simeq \exp\left\{-\frac{NJm^2}{2k_{\mathrm{B}}T} + N\ln\left[2\cosh\left(\frac{Jm}{k_{\mathrm{B}}T} + \frac{\mu_{\mathrm{B}}H}{k_{\mathrm{B}}T}\right)\right]\right\}, \tag{4}$$

using the saddle point method. The saddle point condition yields the equation of state

$$m = \tanh\left(\frac{Jm}{k_{\mathrm{B}}T} + \frac{\mu_{\mathrm{B}}H}{k_{\mathrm{B}}T}\right). \tag{5}$$