THE ISOTHERMAL MAGNETOCALORIC COEFFICIENT

Tomasz Plackowski *

A simple method of in-magnetic-field calorimetric measurements is presented. It is based on commercial Peltier elements used as sensitive heat-flow meters of high thermal conductivity. In the presented experimental setup the Peltier element thermally connects the sample to a heat sink of constant temperature. Application of the magnetic field \( B \) ramp results in the sample temperature change due to magnetocaloric effect, but, due to high thermal conductivity of the Peltier element, any temperature difference is quickly thermalized. The ensuing heat flux, detected as a voltage on the Peltier element terminals, is proportional to a quantity called the isothermal magnetocaloric coefficient, \( M_T \). It could be measured quasi-continuously up to the maximum field attainable by the superconducting magnet used in the experiment (\( B_{\text{max}} \approx 13 \text{T} \) in our case). The available temperature range spans between 20 and 300 K. The obtained set of \( M_T(B) \) curves holds a valuable information on magnetic and thermodynamic properties of the matter. It is particularly useful if compared with the set of specific heat curves \( C_B(T) \) taken at constant field, which could be obtained using the very same experimental setup. Several examples of the behavior of the isothermal magnetocaloric coefficient for various magnetic (\( \text{Mn}_{0.9}\text{Co}_{0.1}\text{P} \) and \( \text{UA}_{0.97}\text{Se}_{0.03} \) single crystals) and superconducting (\( \text{YBa}_2\text{Cu}_3\text{O}_7-\delta \) single crystal and Bi2223 tape) materials are given.

**Keywords:** magnetocaloric effect, specific heat, heat-flow meters, heat-flow calorimetry

1 INTRODUCTION

Usually, the magnetocaloric coefficient (\( M_S \)) is measured at the quasi-adiabatic conditions and defined as the ratio of the sample temperature \( T \) change to the increase of the applied magnetic field \( B \):

\[
M_S = \langle \frac{dT}{dB} \rangle_{\text{S-const}},
\]

where \( S \) is entropy. However, the precise physical interpretation of the behavior of this coefficient is often impeded by the fact that both temperature and magnetic field are varying simultaneously during experiment. Therefore, in this report we present a simple method of direct studying the magnetocaloric effect at quasi-isothermal conditions. The respective isothermal magnetocaloric coefficient is defined as follows:

\[
M_T = \langle \frac{\partial Q^+}{\partial B} \rangle_{T=\text{const}},
\]

where \( \partial Q^+ \) is the heat released in the sample due to magnetocaloric effect. Thus, \( M_T \) results could be presented in function of only one thermodynamic variable as \( M_T(B) \) curves. Both coefficients are interrelated by a simple equation:

\[
M_T = M_S C_B,
\]

where \( C_B \) is specific heat measured at constant field. This relation indicates that both magnetocaloric coefficients are always of the same sign.

In terms of the entropy or the free energy \( (F) \) \( M_T \) coefficient could be expressed as follows:

\[
M_T = -T\langle \frac{\partial S}{\partial B} \rangle_T = T\langle \frac{\partial^2 F}{\partial B^2} \rangle .
\]

As seen, it is a mixed second derivative of the free energy. \( M_T \) coefficient, together with specific heat, gives the full thermodynamic information on the investigated magnetic material. Comparing their units, \( (\text{J/molK}) \) for specific heat versus \( (\text{J/molK}) \) for \( M_T \), one realizes that \( M_T \) could be regarded as a sort “magnetic” specific heat, in the sense it measures the change of the enthalpy upon increasing magnetic field. However, the direct thermodynamical relation between both quantities is not so obvious:

\[
\langle \frac{\partial C_B}{\partial B} \rangle_T = M_T/T - \langle \frac{\partial M_T}{\partial T} \rangle_B .
\]

It is worth underlying that the observed lack of the dependence of specific heat on the applied field \( \langle \frac{\partial C_B}{\partial B} \rangle_T = 0 \) does not necessarily mean no magnetocaloric effect at all. This only means that \( M_T \sim T \).

The isothermal magnetocaloric coefficient is also closely related to the molar magnetization \( M \) trough a simple formula:

\[
M_T = -T\langle \frac{\partial M}{\partial T} \rangle_B .
\]

It is worth to note, that for an ideal paramagnet, which magnetization could be described by the formula \( M = C B / T \) \( (C \) is the Curie constant) we obtain a striking result: \( M_T = M \). Of course, for more complicated materials this equality does not hold, nevertheless it underlines another feature of the \( M_T \) coefficient: it shares the same physical units \( (\text{J/mol}) \) with magnetization, so they both could be presented on the same plot.

2 EXPERIMENTS

The idea of the method is presented in the Fig. 1. The sample of temperature \( T_s \) fixed to a copper block of stabilized temperature \( T_b \) through a high-sensitivity heat-flux meter of high thermal conductivity. As the latter device we utilized a miniature commercial Peltier element based on \( \text{Bi}_2\text{Te}_3 \), for which the heat-flux \( (J_0) \) is simply proportional to the measured voltage on its terminals \( (U_P) \). If the applied magnetic field varies slowly at constant rate \( dB/dt \) then the magnetocaloric effect results in slight a
change of $T_s$ and, thus, a heat flow between sample and block. The isothermal magnetocaloric coefficient could be thus determined as (the minus sign is the result of adopted convention):

$$M_T = -j_Q/(dT/dt).$$  \hfill (7)

The same setup could be easily used to determine specific heat $C_B$. If $B$ is kept constant and temperature $T = T_b \approx T_s$ is varied slowly at constant rate $dT/dt$ then:

$$C_B = j_Q/(dT/dt).$$  \hfill (8)

The magnetocaloric measurements upon both increasing and decreasing magnetic field make it possible to study the hysteresis effects. The typical rate of 0.2 T/min gives the data density higher than 100 points/T.

In analogy, the specific heat measurements upon both cooling and heating are possible. In this case, the typical temperature drift rate of 1 K/min gives the data density higher than 20 points/K. In such experimental conditions the temperature difference $|T_s - T_b|$ usually does not exceed 10 mK, making the isothermal assumption reliable. The exception may occur in the vicinity of the first-order phase transitions, if the apparent heat capacity of the sample increases extremely high ($\delta$-shaped anomaly). Then some special corrections should be applied [1].

The method was implemented using a liquid helium cryostat with 13 T superconducting magnet and a variable temperature insert. It was proved to give reliable results in the temperature range 20 – 300 K. The high vacuum was provided by a turbomolecular pump. The size of the used Peltier elements (3.2 mm $\times$ 3.2 mm top plate, see Fig. 2) was suited for the samples of the mass of $\sim$100 mg. Two Peltier elements in two different positions were fitted in our measuring insert. One element has its surface perpendicular to the magnetic field (as in Fig. 1), the second one has its surface aligned with the field. This makes possible to simultaneously study two pieces of the same single crystal with magnetic field oriented along two different crystallographic directions.

The *sine qua non* condition for these measurements is the provision of good, stable thermal contact between Peltier element and the sample. In our case it was ensured by apolymeric glue.

The sensitivity and the heat capacity of top plates (addenda) was measured for both heat-flow meters in separate experiments with pure Cu samples in function of temperature and magnetic field. Unfortunately, the sensitivity of the Peltier elements, used as heat-flow meters, decreases with temperature and below 20 K they are no more useful. Thus, and was proved to give reliable results in the temperature range 20 – 300 K More details could be found in the description of the previous version of the heat-flow calorimetric insert [1].

The magnetocaloric measurements upon both increasing and decreasing magnetic field make it possible to
The magnetocaloric properties of its parent compound UAs have been described earlier [3]. UAs$_{0.97}$Se$_{0.03}$ is also characterized [4] by an extremely complicated magnetic phase diagram containing incommensurately ordered phase (see Fig. 4). Here, the isothermal magnetocaloric measurements were used to study the possibility of the existence of the Lifshitz point in this compound.

Fig. 6. The isothermal magnetocaloric coefficient (blue) and molar magnetization (red) for UAs$_{0.97}$Se$_{0.03}$ single crystal with the magnetic field aligned along the (100) axis ($B||a$)

The magnetocaloric $M_B(B)$ curves and respective magnetization $M(B)$ curves taken at selected temperatures for UAs$_{0.97}$Se$_{0.03}$ single crystal are shown in Fig. 6. Note the negative magnetocaloric anomaly at the AF-I-1k/FERRI-1k phase transition (Fig. 6a), the discontinuous transition between the incommensurate and FERRI-1k phase (Fig. 6b) and the behavior in the vicinity of the alleged Lifshitz point, where the paramagnetic, incommensurate and FERRI-1k phases meet together (Fig. 6c).

As a third example we present the magnetocaloric data for a high-temperature superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ (compare [7]). The data were collected just above (the black curve) and below (color curves) its critical temperature of $T_c = 88.5$ K, mainly in the reversible region (see Fig. 6). Negative values of the magnetocaloric coefficient confirm that the superconducting state has lower entropy than the normal state. The divergency observed for $B\rightarrow 0$ just below $T_c$ results from crossing the $H_{c1}$ line (the first critical field). At lower temperatures ($T \leq 86$ K) an onset of irreversibility is visible (see the inset in Fig. 7).
The problem of the magnetocaloric irreversibility in type-II superconductors was studied in detail in [8]. Here, we present an exemplary measurement for a superconducting textured Bi2223 tape oriented perpendicularly to the external magnetic field. A large hysteresis, i.e., the difference between signals for increasing and decreasing field, is visible. The hysteresis widens with the lowering temperature and closes with the increasing field. In analogy to the Bean model for the magnetization of type-II superconductors, the value of this hysteresis is simply proportional to the critical current [8]. This way, the isothermal magnetocaloric measurements offers a new method of basic characterization of superconducting materials.

4 CONCLUSIONS

The heat-flow (quasi-isothermal) calorimetry could be used to measure two different physical quantities: specific heat, \( C_B \), (upon cooling or heating), and the isothermal magnetocaloric coefficient, \( M_T \), (upon increasing or decreasing magnetic field). If commercial Peltier elements based on Bi2Te3 are used as heat-flow meters then the heat-flow rate, \( dB/dt \), (upon cooling or heating), and the isothermal magnetocaloric coefficient can be described in terms of critical current [8].

This is crucial for the reasonable interpretation. Next, \( M_T \) is the second derivative of the free energy. This causes that \( M_T \) behavior near critical point resembles that of specific heat and magnetic susceptibility and \( M_T(B) \) could be described in terms of critical exponent [5, 6]. Moreover, \( M_T \) does not contain any non-magnetic contribution, like eg phonon contribution to \( C_B \). Thus, no doubtful procedures of the background subtraction are necessary. Finally, for type-II superconductors the magnetocaloric hysteresis is a measure of their critical current value [7, 8].

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REFERENCES


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