Entropy Change Calculations for Pure Gd and a Ni–Mn–Cu–Ga Heusler Alloy: Constant Field vs. Constant Temperature Experiment

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(Received February 2, 2015)

The magnetocaloric effect may be assessed indirectly by expressing it as the change in magnetic entropy in varying magnetic field, H, as the function of temperature, T. Magnetization, $M = f(T, H)$, may be experimentally acquired from a series of isothermal measurements with variable field, or from a series of constant field measurements with variable temperature. The accuracy of magnetic entropy calculation depends on the number of series in these experiments. The aim of this work is to determine how little data is sufficient to obtain accurate results of magnetic entropy change calculations, on the basis of real, magnetocaloric materials. Pure gadolinium and a Ni–Mn–Cu–Ga Heusler alloy were studied. For both materials, the magnetic entropy change and relative cooling power were calculated from both experiments, with the decreasing number of experimental data. For both materials, the constant field experiment with only 6 field values provided only a 5% error of calculations, as compared to the experiment with 100 field values. The Arrott plots were also drawn for constant field mode with 6 field values, easily indicating the order of transition. Comparison of the calculation results suggests that the constant field mode magnetization measurement may be more accurate and faster than isothermal mode.

DOI: 10.12693/APhysPolA.128.111
PACS: 75.30.Sg, 65.40.gd

1. Introduction

The magnetocaloric effect is a change in temperature of a magnetic material caused by changing its magnetic state. Its magnitude may be expressed directly by the temperature difference between two magnetic states, or indirectly, by the change in specific heat, or the change in magnetic part of entropy, when varying magnetic field is applied. Usually, the isothermal magnetic entropy change, $\Delta S_M(T)$, is calculated from the well-known Maxwell equation

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B, \tag{1}$$

where S, B, T, and M stand for entropy, magnetic field induction, temperature, and magnetisation respectively, provided the values of magnetisation vs. field and temperature, $M = f(T, H)$, are known. The smaller increment of field and temperature, the more accurate values of entropy change are obtained, since the derivation $\partial M/\partial$T is included in the calculations

$$\Delta S_M\left(T, \Delta H\right) = \mu_0 \int_{H1}^{H2} \left(\frac{\partial M\left(T, H\right)}{\partial T}\right)_H \mathrm{d}H, \tag{2}$$

where H and μ_0 are magnetic field and magnetic constant, respectively [1]. Most frequently, the $M = f(T, H)$ function is obtained from the set of isothermal measurements of magnetisation, $M = f(H)_{T=\text{const}}$. Scanning across H_1 to H_2 range should be carried out with sufficient number of H points. Such approach requires that the temperature values must be selected carefully: large T increment may be used where the effect is not expected, but in the temperature range where abrupt changes in magnetisation may occur, temperature points should be close to each other. If this condition is met, integration of $\partial M/\partial T$ along H provides accurate results. On the other hand, the $M = f(T, H)$ function may be obtained from the set of thermomagnetic curves, $M = f(T)_{H=\text{const}}$. In this case, the more H values are selected, the better result is obtained, while usually a sufficient number of T values are recorded. From mathematical viewpoint, both methods of $M = f(T, H)$ data acquisition are equally good, as long as the same set of data is obtained, on which calculations are carried out. However, this requires that the experiment is time consuming, and usually a compromise between experiment time and precision must be made. In both data acquisition modes, the insufficient number of constant T or constant H curves is detrimental to the accuracy of calculations. In this work, application of both modes of data acquisition is imitated, based on the precisely measured properties of two real materials with a significant difference in magnetocaloric behaviour: gadolinium with a smooth, second order phase transition, and a Heusler alloy, $Ni_{50}(Mn,Cu)_{25}Ga_{25}$ (atomic percent), exhibiting a sharp structural transition. The calculations were done with the decreasing number of data points in

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order to reveal the critical number of $M = f(T)_{H=\text{const}}$ or $M = f(H)_{T=\text{const}}$ curves that keep the results reliable.

2. Experimental

Samples of pure Gd and the $Ni_{50}Mn_{18.75}Cu_{6.25}Ga_{25}$ alloy, prepared by induction melting of pure elements in argon atmosphere and then homogenised at 1073 K for 48 h and slowly cooled with the furnace, with masses of 83.5 mg and 26.4 mg, respectively, were mounted to the LakeShore 7410 vibrating sample magnetometer (VSM) equipped with a cryostat, and their magnetisation vs. temperature was measured in isothermal mode. For Gd, the temperature range was from 200 to 360 K, and for the Ni–Mn–Cu–Ga alloy, the range was from 240 to 400 K. In both cases, temperature interval between isotherms was 2 K. The magnetic field induction varied from 0 to 2 T, with the step of 0.02 T. For each field step, its value was stabilised, then the magnetisation was measured 100 times and the arithmetic average was calculated. After the maximum field was reached, it was reduced to zero and next temperature was set for the measurement. From these results, the arrays of $M = f(T, B)$ were constructed in a spreadsheet. From these arrays, values of $\Delta S_M(T)$ were calculated using the formula

$$\Delta S_M(T,B) = \sum_{i=1}^{n} \frac{M_i(T_i,B) - M_{i-1}(T_{i-1},B)}{T_i - T_{i-1}} \Delta B, \quad (3)$$

where i is the number of induction of magnetic field value (for $i = 0$, $B = 0$ T) and n is the number of induction of magnetic field values, similarly to the formula (2) in [2]. As the next step, the data from the arrays were gradually removed: in one case T interval was maintained original with the increase of B interval, in another case B interval was maintained original with the increase of T interval. Such operation imitated the measurements in two modes: constant field or isothermal, with gradual reduction of available data (increase of interval between constant field values or constant temperature values). From the arrays with reduced data points number, again the values of $\Delta S_M(T)$ were calculated using (3). For the purpose of comparison of the results of calculations, the peak values of $\Delta S_M(T)$ for B change from 0 to 2 T, further bearing the $\Delta S_M^{\max}$ symbol, were used. On the basis of the calculated $\Delta S_M(T)$ dependence, relative cooling power (RCP) for B change from 0 to 2 T was calculated for each variant of dataset, using the formula

$$\text{RCP} = -\Delta S_M^{\max} \delta T^{\text{FWHM}}, \quad (4)$$

where δT^{FWHM} is the full width at half maximum of the $\Delta S_M(T)$ function.

3. Results

The dependence of magnetisation on field and temperature for both materials is visualised in Figs. 1 and 2. It is clear that the Heusler alloy exhibits an abrupt drop in magnetisation around 312 K, and for gadolinium the transition is rather smooth. This observation confirms that the studied materials are different in terms of intensity and temperature span of magnetocaloric effect.

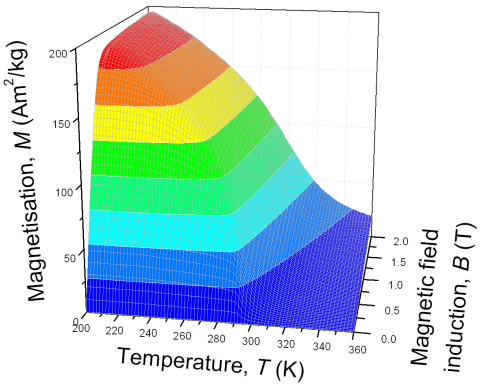

Fig. 1. Magnetisation vs. temperature and magnetic field for gadolinium.

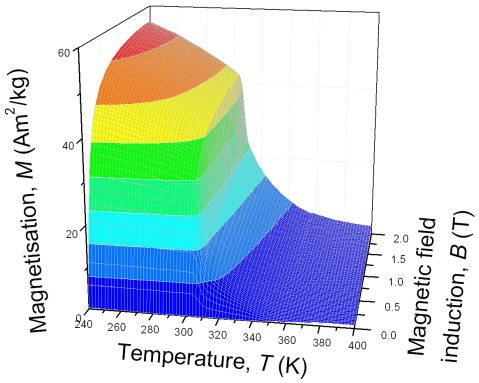

Fig. 2. Magnetisation vs. temperature and magnetic field induction for $Ni_{50}Mn_{18.25}Cu_{6.25}Ga_{25}$ alloy.

3.1. "Isothermal" mode

In the mode imitating the isothermal measurements, i.e. with continuously variable magnetic field values for the given set of temperatures, the dataset consisted of a number of magnetisation curves ($M = f(B)_{T=\text{const}}$). In these curves, there were always 100 values of B. On the basis of the full set of data, i.e. 81 temperatures, the maximum value of $\Delta S_M^{\max}$ was calculated as the reference, and was equal to -5.54 J/(kg K) for gadolinium, and -8.69 J/(kg K) for the Heusler alloy. From this dataset, magnetisation curves were gradually removed, imitating a more rough, careless experiment, i.e. when temperature interval between one curve and the next one is increased. This way, datasets with temperature intervals of 4, 6, 8, 10, 12, 14 and 16 K were created. From these datasets, the values of $\Delta S_M(T)$ were calculated. For Gd, the values of the maximum magnetic entropy change gradually decreased, dropping to -4.47 J/(kg K) for $\Delta T = 16$ K (see Fig. 3), which accounts for 20% error

from the reference value. For the Heusler alloy, the maximum magnetic entropy change values became dramatically incorrect already when $\Delta T = 4$ K: the error was of 30%, and this error increased to 65% when $\Delta T = 16$ K (see Fig. 3).

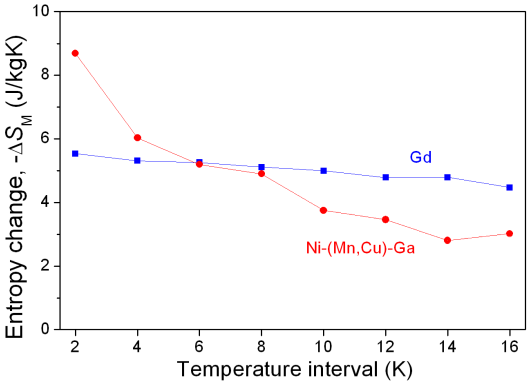

Fig. 3. Peak value of magnetic entropy change, $\Delta S_M^{\max}$, for gadolinium and $Ni_{50}Mn_{18.25}Cu_{6.25}Ga_{25}$ alloy, calculated for varying temperature interval.

The clear difference in the presented results originates from the phase transitions that undergo these materials. For the first order magnetostructural transition, from ferro- to paramagnetic phase in the Heusler alloy [3], the structure transforms in just a few K: the full width at half maximum (δT^{FWHM}) of $\Delta S_M(T)$ plot is of about 5 K. Therefore, the increase of interval between isothermal measurements simply causes that the $\partial M/\partial T$ derivative (here: $(M_i - M_{i-1})/(T_i - T_{i-1})$) is calculated incorrectly. In the case of Gd, the second order transition from ferromagnetic to paramagnetic state occurs in a wider temperature span: δT^{FWHM} equals to 40 K. Calculation of the $(M_i - M_{i-1})/(T_i - T_{i-1})$ derivative for Gd with the increasing ΔT causes a much smaller error as compared to the other studied material. However, it should be stressed that even in the case of the second order transition, doubling the temperature interval caused a 5% error in $\Delta S_M^{\max}$ assessment. This leads to an easily anticipated conclusion that in the vicinity of transition, the temperature interval must be kept as small as possible to avoid errors in the magnetocaloric effect calculations.

The relative cooling power gradually increased with the increase of temperature interval, which was the result of the δT^{FWHM} values increase (Fig. 4). It is particularly clear for the 1st order transition case: the real transition is manifested in $\Delta S_M(T)$ plot within only 5 K. Application of larger temperature step caused the apparent plot distortion and peak widening, eventually leading to the error in RCP of 50%. Such a large error in RCP results from the fact that it is the product of $\Delta S_M^{\max}$ and δT^{FWHM}, and both are affected by the errors from the limited number of source data. In all cases, there is no doubt that setting the temperature step as small as possible is key to obtain accurate results of magnetic entropy change calculations.

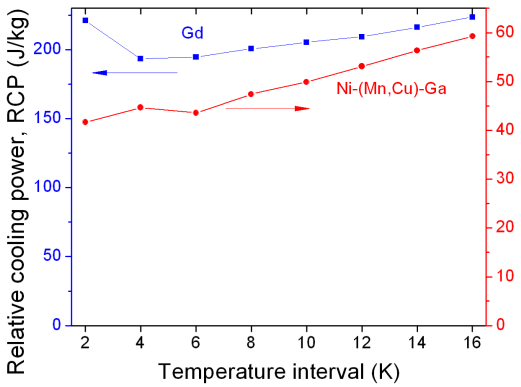

Fig. 4. Relative cooling power for gadolinium and $Ni_{50}Mn_{18.25}Cu_{6.25}Ga_{25}$ alloy, calculated for varying temperature interval.

3.2. "Constant field" mode

In the mode imitating constant field measurements, meaning recording thermomagnetic curves with constant field applied and continuously varying temperature, the dataset consisted of a number of thermomagnetic curves, $M = f(T)_{B=\mathrm{const}}$. In these curves, there were always 81 values of temperature ($\Delta T = 2$ K). On the basis of the full set of data, i.e. 100 values of field ($\Delta H = 200$ Oe), the maximum value of $\Delta S_M(T)$ was calculated as the reference. From this dataset, thermomagnetic curves were gradually removed, imitating that the interval between field values was increased. Several sets of data were created, with the number of field values: 50, 25, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2 and 1. On this basis, using formula (3), values of $\Delta S_M(T)$ were calculated and $\Delta S_M^{\max}$ were recorded. For gadolinium, the reduction of number of curves taken to calculation from 100 to 10 did not affect the values of magnetic entropy change. Further reduction of number of field values caused a gradual reduction of the calculated $\Delta S_M^{\max}$ (see Fig. 5). However, if the number of field values was 6 or more, the error was not larger than 5% of the reference value, and for 8 or more field values, the error was under 2%, which is sufficient to consider the measurement accurate. Even better result was observed for the Heusler alloy: all the obtained values of $\Delta S_M^{\max}$ were within 5% error, regardless of the number of fields (Fig. 5). These results, obtained for two studied materials, differing in the magnetic behaviour, indicate that it is not necessary to run an experiment with a large number of field values, and only 6 fields is a sufficient number to stay in a 5% error margin. Such error may be acceptable considering that other errors emerging from the experimental techniques are claimed to be in the 5–10% range [1].

For the relative cooling power calculation, in the constant field mode, the error caused by a limited number of data is insignificant unless the number of field values is below six, see Fig. 6. If this condition is met, the error in RCP assessment is better than 7%. Still, the error in RCP is larger that that of $\Delta S_M^{\max}$, see the argument in "isothermal" mode section.

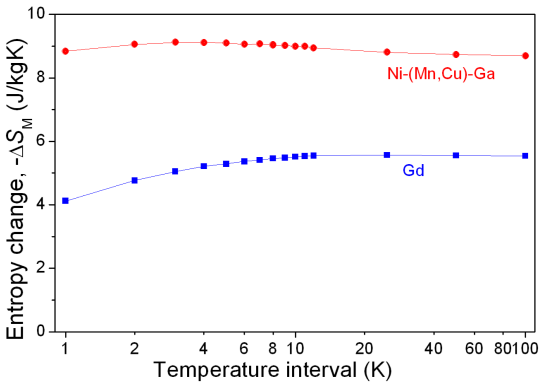

Fig. 5. Peak value of magnetic entropy change, $\Delta S_M^{\max}$, for gadolinium and $Ni_{50}Mn_{18.25}Cu_{6.25}Ga_{25}$ alloy, calculated for varying number of magnetic field values.

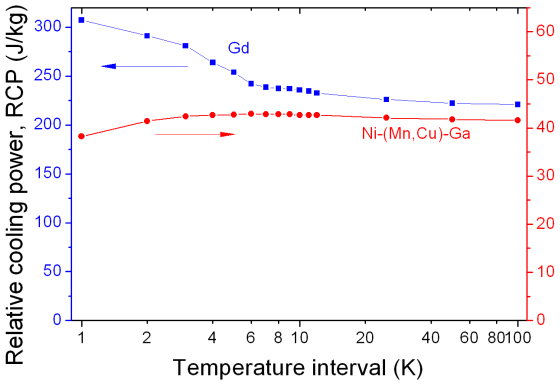

Fig. 6. Relative cooling power for gadolinium and $Ni_{50}Mn_{18.25}Cu_{6.25}Ga_{25}$ alloy, calculated for varying number of magnetic field values.

From the $M = f(T, H)$ values Arrott plots may be drawn, with the H/M as abscissa and M^2 as ordinate. The shape of these plots indicates the order of the phase transition: straight, parallel lines are typical of 2nd order transitions, whereas the distorted, convex and concave ones suggest a magnetostructural, 1st order transition. A large number of field values allows drawing a set of nearly continuous lines. However, densely drawn data points are unnecessary. Figures 7 and 8 present the Arrott plots of both materials studied herein, drawn with the data obtained in the constant field mode, with only 6 values of magnetic field. Clearly, the lines between the data points are sufficient to lead eyes and easily determine the type of phase transition that takes place in the material, and, in the case of the material that undergoes the transition of 2nd order, it is possible to assess the Curie temperature. This, again, proves that small number of magnetic field values, together with good temperature resolution, obtained with the use of constant field mode, is an efficient way to prepare the set of data points from which meaningful conclusions may be drawn.

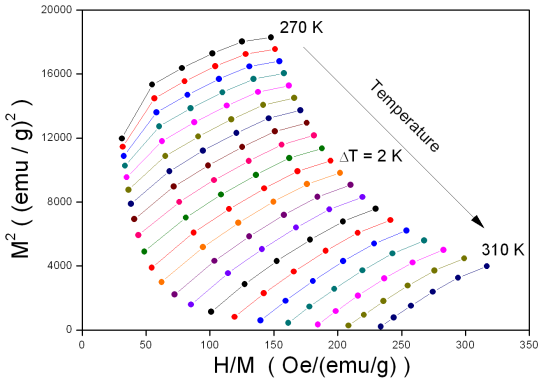

Fig. 7. Arrott plot for gadolinium, markers indicate only the 6 selected magnetic field values.

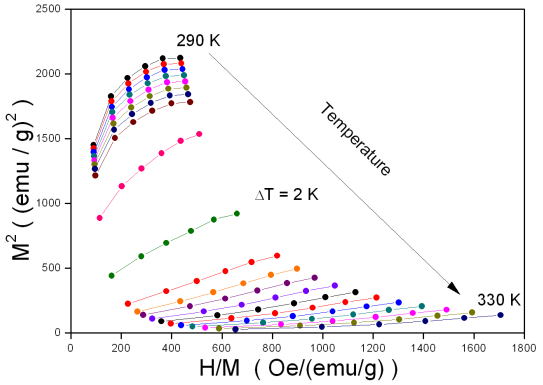

Fig. 8. Arrott plot for $Ni_{50}Mn_{18.25}Cu_{6.25}Ga_{25}$ alloy, markers indicate only the 6 selected magnetic field values.

On the ground of the above presented experiment it may be suggested that constant field measurement offers more benefits than isothermal measurement. The constant field mode requires that only 6 to 8 $M = f(T)_{H=\text{const}}$ curves must be recorded, as compared to 20 to 30 $M = f(H)_{T=\text{const}}$ curves in isothermal mode. As the constant field mode measurement is carried out with continuously changing temperature, recording of magnetisation with 1 or 2 K interval is usually possible. Such small temperature interval enables accurate calculation of $\partial M/\partial T$ derivative, which, in turn, is very important for precise calculation of magnetic entropy change and, subsequently, relative cooling power. Small temperature interval allows easy identification of temperature of the magnetocaloric effect. In addition, the order of phase transition may be easily determined from constant field experiment.

4. Conclusions

In this work, two different approaches of magnetisation vs. temperature and field data acquisition were presented from the viewpoint of accuracy of calculation of magnetic entropy change due to magnetocaloric effect. Mag-

netic properties of two dissimilar materials, with smooth, 2nd order phase transition (Gd) and sharp, 1st order phase transition (Ni–(Mn,Cu)–Ga alloy), were measured. It was found that measurement of $M = f(T, H)$ dependence in constant field mode, with only 6 values of field, is sufficient to keep the error of calculated magnetic entropy change within 5%, regardless of the material. The constant field mode measurements may also improve the temperature resolution of the magnetocaloric effect examination as compared to isothermal measurements with arbitrary temperature selection.

Acknowledgments

This work was supported by the project No. UDA-POIG.01.03.01-00-058/08-00 granted by the Polish Ministry of Science and Higher Education within the Operation Programme Innovative Economy.

References

[1] V.K. Pecharsky, K.A. Gschneidner Jr., *J. Magn. Magn. Mater.* **200**, 44 (1999).

[2] E. Brück, *J. Phys. D Appl. Phys.* **38**, R381 (2005).

[3] S. Stadler, M. Khan, J. Mitchell, N. Ali, A.M. Gomes, I. Dubenko, A.Y. Takeuchi, A.P. Guimarães, *Appl. Phys Lett.* **88**, 192511 (2006).