Scaling analysis of the magnetocaloric effect in Gd$_5$Si$_2$Ge$_{1.9}$X$_{0.1}$ ($X=$Al, Cu, Ga, Mn, Fe, Co)

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**Abstract**

The field dependence of the magnetic entropy change has been studied for a series of doped Gd$_5$Si$_2$Ge$_2$ alloys, which possess a magnetic phase transition that is either entirely second order or a combination of primarily second-order mixed to a very minor degree with a first-order transition arising from a magneto-structural phase change. By analyzing the field scaling of the refrigerant capacity as well as of the reference temperatures used for constructing a universal scaling curve, a procedure for estimating the values of the critical exponents for the alloys was developed. For the cases where the transition is entirely second order, the results obtained from this procedure are comparable to the values obtained from the Kouvel–Fisher method. For the case of Fe-doped alloys which partially possess a first-order phase change, the Kouvel–Fisher method is inapplicable. However, their critical exponents determined by our developed procedure can be used to estimate the Curie temperature of the orthorhombic majority phase.

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1. Introduction

During the last decade magnetic cooling, based on the magnetocaloric effect (MCE), has been the focus of an increasing number of studies [1–5], due mainly to its potential for near-room temperature magnetic refrigeration applications [6]. Compared to conventional vapor-compression systems, magnetic refrigeration can be a very efficient and environmentally friendly technology [1–5], since it does not require the use of either ozone depleting CFCs or lead to the emission of greenhouse gases. The MCE of any magnetic material is generally found to peak near magnetic transitions occurring in the material as the temperature is varied. Generally, first-order magneto-structural transitions give rise to abrupt changes in the magnetization, whereas in second-order transitions changes in the magnetization with temperature are more gradual. In the milli Kelvin (mK) regime, paramagnetic salts have been used for decades to reach these temperatures by the MCE effect in cryostats at research laboratories. Broadly speaking, magnetocaloric materials fall into the following two material classes: one class displaying moderate size MCE values over a large temperature range resulting from second-order magnetic phase transitions and a second class generally displaying large MCE values over a smaller temperature range resulting from first-order magneto-structural phase transitions [7]. The Gd$_5$Ge$_5$Si$_2$ compound belongs to this latter class of materials. In this compound, its large (‘giant’) MCE is associated with a field-induced magneto-structural phase transition, involving a reversible monoclinic-to-orthorhombic crystal structure change. For comparison of refrigerant materials, one needs a better understanding of the connection between the characteristics of the MCE (e.g., peak magnitude, width, and peak temperature) and the magnetic phase transitions in that material. There is also interest in using the equations of state of a material at a transition to describe that material’s magneto-thermal behavior. The critical parameters from such equations of state are particularly useful in such a calculation [8,9]. One should also keep in mind that MCE values are not the only figure of merit for a magnetic refrigeration material. The magnitude of the magnetic hysteresis of that material upon cycling the field is also an important parameter [5]. It is a negative factor which limits the usefulness of a material’s MCE.

Most recently, the study of materials whose magnetocaloric response is associated with the presence of more than one magnetic phase has become important. This contribution of multiple magnetic phases to the magnetocaloric response can be due to two reasons: (a) the presence of magnetic transitions in the different magnetic phases coexisting throughout the whole temperature range of interest [10] and (b) the transformation from one crystal phase into another crystal structure having a different magnetic state within the temperature range of interest. This latter case applies to the Gd$_5$Si$_2$Ge$_2$ compound, whose large magnetocaloric effect is directly related to a magneto-structural
transformation. In order to use critical phenomena methods for the prediction of material properties, the transitions being
analyzed must not be interrupted by a second transition before
the first transition is completed. For instance, the determination
of the Curie temperature of the ferromagnetic orthorhombic (low
temperature) phase in the Gd$_5$Si$_2$Ge$_2$ compound is tricky since it
transforms by a first-order transformation into a monoclinic
phase before the Curie temperature is reached. However, the
existence of two coupled transitions opens interesting questions
regarding the ability of any data analysis method to extract
information for each of the transitions separately. Ideally, if the
hidden second-order phase transition, which would have been
indicated by a Curie temperature, can be fully described by using
any specific technique (like the one which is proposed in this
paper), one might be able to deconvolute the contributions of the
different transitions to the magnetocaloric effect. This paper is an
initial approach to characterizing a second-order phase transition
when there is a minor contribution from a small amount of
material undergoing a first-order phase transition overlapped on
it. The complete deconvolution of the contributions of coupled
first and second-order phase transitions is still an open question
and is beyond the scope of this paper.

For the case of the Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ family of compounds, some
authors have recently used Arrott–Noakes (A–N) plot extrapola-
tions [11] to make predictions of Curie temperatures which are
consistent with predictions made from their phase diagram [12].
However, the values of the critical exponents which are obtained
from these A–N plot temperature extrapolations are quite different
from the values obtained for other magnetic materials using more
usual techniques. The reason for the anomalous values for the
Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ compounds is that their A–N plots are approxi-
mately linear (within experimental error and in a limited tem-
perature range), even for large variations of the critical exponents.
Therefore, there is a large uncertainty in finding the optimal
values of the exponents which provide the best linearity for the
curves. Consequently, temperature extrapolations of the A–N plots
may also be circumspect. The usual and more accurate procedures
[13] cannot be used in this case since the magnetic phase being
studied is no longer present when the temperature of that
material reaches its Curie temperature.

An alternative approach is to suppress the magneto-structural
transition by proper doping as was done for the case of the
Gd$_5$Si$_2$Ge$_2$ compound [14,15]. In the undoped compound, the low
temperature phase is orthorhombic and it transforms to a mono-
clinic phase at temperatures above 270 K. However, in the
Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$$_{1.9}$X$_{0.1}$ doped alloy (with X=Al, Cu, Ga, Mn, Fe, Co) the
monoclinic phase is entirely suppressed in the case of the first
four of these metal additives, and is mostly suppressed in the
cases of the latter two of these additives. Suppressing the forma-
tion of the monoclinic phase also results in suppressing the
magneto-structural transition that is present in the undoped
compound since there is no monoclinic phase to transform into an
orthorhombic structure upon application of a field. This suppres-
sion greatly reduces both the thermal and magnetic hysteresis,
while at the same time increases the refrigerant capacity relative
to that of the undoped compound. Also, for the purpose of the
present study, doping allows us to experimentally determine the
Curie temperature of the orthorhombic phase since it is stabilized
to higher temperatures.

In this work we will show that scaling analysis of the magnetoc-
aloric effect with magnetic field near a transition is a promising
tool for estimating the values of the critical exponents describing
that magnetic transition. In the case of compounds with a second-
order phase transition, results are comparable to those obtained
from the more common Kouvel–Fisher (K–F) method [16]. For the
case of materials exhibiting a magneto-structural phase change,
but for which the hysteresis losses are not large, scaling analysis
of the magnetic entropy change can also be used to estimate the
critical exponents of the vanishing phase together with its Curie
temperature. Therefore, the Al-, Cu-, Ga-, and Mn-doped alloy
samples, in which the phase transition is purely second order, will
be used as a demonstration of the applicability of this procedure
to estimate the critical exponents; the Fe-doped material, which
possesses a small amount of hysteresis from the presence of a
minor amount of monoclinic phase above the transition tempera-
ture, will be used to test the feasibility of this new procedure to
determine the Curie temperature of the orthorhombic phase.

2. Experimental

The Gd$_5$Si$_2$Ge$_{1.9}$X$_{0.1}$ doped alloy samples (with X=Al, Cu, Ga,
Mn, Fe, Co) in the present study were all prepared by arc melting
the appropriate amounts of the component elements, using a
water-cooled copper hearth in an argon atmosphere under
ambient pressure after previously evacuating the preparation
chamber to a vacuum of $10^{-6}$ Pa. The purity of the starting
constituents was 99.9% mass fraction or better. After melting the
sample three times, turning the button upside down between
melts, the samples were homogenized at 1300 °C for 1 h in a
vacuum of $10^{-6}$ Pa and then furnace cooled. Additional details
about the structure, microstructure, and composition of each alloy
sample are given elsewhere [14,15].

The magnetic measurements on the alloy samples were
performed by SQUID magnetometry up to a maximum applied
field of 5 T. The magnetic entropy change ($\Delta S_M$) due to the
application of a magnetic field has been evaluated from integrat-
ing the temperature ($T$) and field ($H$) dependent magnetization
($M$) curves:

$$\Delta S_M = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH.$$  \hspace{1cm} (1)

A phenomenological universal curve relating $\Delta S_M$ to $H$ and $T$
can be constructed by: [17] (1) normalizing all the $\Delta S_M(T,H)$
curves to their respective maximum value $\Delta S_M^0$ (e.g., $\Delta S' = \Delta S_M(T)/\Delta S_M^0$) and (2) rescaling the temperature axis above and below the Curie
temperature, $T_C$, as

$$\theta = \theta_1 = (T - T_C)/(T_T - T_C),$$

where the reference point $T_T$ is selected as that corresponding to a
certain fraction of $\Delta S_M^0$. The particular choice of that $\Delta S_M^0$ fraction
has no relevance in the actual construction of the universal curve,
as it implies only a proportionality constant. Throughout this
work, the reference temperatures have been selected according to
the relation $\Delta S_M(T) = 0.6\Delta S_M^0$; justification for constructing
the universal curve with such parameters has recently been published
[9]. In some experimental cases the material departs from ideal
behavior and it is necessary to use two well separated reference
temperatures, $T_1$ and $T_2$, to construct the universal curve: [18]

$$\theta = \theta_2 = \begin{cases} 
(T - T_C)/(T_1 - T_C); & T \leq T_C \\
(T - T_C)/(T_2 - T_C); & T > T_C
\end{cases}$$ \hspace{1cm} (3)

Determination of the critical exponents, $\beta$ and $\gamma$, using the
Kouvel–Fisher (K–F) method has been accomplished by computing
values for $M_0(T)$ and $\gamma_0(T)$, respectively, from the intercepts of
various isothermal magnetization vs. field curves on the ordinate
(for temperatures below the Curie temperature) and abscissa (for
temperatures above the Curie temperature) of the Arrrott–Noakes
plot (i.e. the plot of $M^2$ vs. $(H/M)^\gamma$). Once the $M_0(T)$ and $\gamma_0(T)$
curves have been constructed, two additional parameter data sets, \( X(T) \) and \( Y(T) \), may be determined:

\[
X(T) = \frac{1}{\gamma} \left( T - T_c \right) \frac{d\beta}{dT}^{-1} = (T - T_c)/\gamma \tag{4}
\]

\[
Y(T) = \frac{1}{\beta} \left( T - T_c \right) \frac{d\gamma}{dT}^{-1} = (T - T_c)/\beta \tag{5}
\]

In the critical region, both \( X(T) \) and \( Y(T) \) should be linear, with slopes which give the values of the critical exponents, and intercepts of the temperature axis which correspond to the Curie temperature. The values of the critical exponents can be refined by using an iterative method: once Eqs. (4) and (5) produce the temperature. The values of the critical exponents can be refined by using an iterative method: once Eqs. (4) and (5) produce the

In order to test the possibility of obtaining information about the critical exponents from the magnetic entropy change curves, we assume that the reference temperatures used for constructing the universal curve should scale with field [9], i.e.,

\[
T_r \propto H^{1/\Lambda},
\]

where \( \Lambda = \beta\delta \) is the gap exponent.  

**3. Results and discussion**

Most all so-far analyzed magnetocaloric materials which undergo a second-order magnetic phase transition have been found to exhibit a magnetic entropy change whose field dependence can be eliminated by constructing a phenomenological universal curve (see [9] and references therein). Although the procedure was initially developed for soft magnetic Fe-based amorphous alloys, it has also been successfully applied to materials ranging from single crystals to polycrystalline and amorphous samples, and from transition metal to rare-earth based materials [19]. Some exceptions have appeared, but they are not indicative of a limitation in the method; the exceptions are instead due to the samples not meeting the minimum requirements for application of the method. For example, if the experimental magnetization curves as a function of field and temperature should follow a scaling equation of state (whatever it is) in order to allow the method to work. As a consequence, if the material is not in a single domain state (for example, if the demagnetizing factor is large [20]), or if the sample consists of a combination of magnetic phases [10], the construction of a universal curve using a single reference temperature \( (\theta_s, \text{Eq. (2)}) \) fails. In these latter cases, it becomes necessary to introduce a second reference temperature \( (\theta_2, \text{Eq. (3)}) \) to correct for the distortions arising at temperatures close to the magnetic entropy change peak.

In Fig. 1 the universal curve is shown for several Gd\(_5\)Ge\(_2\)Si\(_2\) alloys displaying a second-order magnetic phase transition. The data for all four alloys collapse onto the same universal curve, indicating that their respective critical exponents should be close to one another [21].

The critical exponents (\( \beta \) and \( \gamma \)), and the Curie temperature (\( T_c \)) for the Al-, Cu-, Ga- and Mn-doped materials have been calculated using the Kouvel–Fisher method [16] as described above (the case for the Al doping is shown in Fig. 2). A third exponent, \( \delta \), has been calculated using the relation: \( \beta\delta = \beta + \gamma \). Results for this critical exponent determination are presented in Table 1, together with the literature results for pure Gd [22,23]. (Note from Table 1 there is a large dispersion in the published values, and the differences between the values of \( \delta \) directly obtained from the experimental measurements and those obtained by using the relationship between critical exponents are significant.) In all cases, the critical exponents for the doped Gd\(_5\)Si\(_2\)Ge\(_2\) compositions do not deviate too much from those for the pure Gd metal. In the cases of the Fe- and Co-doped samples, the limited presence of a first-order magneto-structural transition overlapping the majority second-order magnetic phase transition prevents the use of the K-F method for determining the critical exponents.

For the simpler case of the alloys exhibiting only a second-order transition, the K-F method for determining the critical exponents yields equivalent results to those obtained from the Arrott–Noakes (A-N) plot. This equivalency is evidenced in Fig. 3. Note, when the exponent values for Al-doping obtained from the K-F method were used to construct the A-N plot, linear magnetization curves in the high field regions were obtained, just as expected in A-N plots whose magnetization values have been properly normalized.

In order to test the possibility of obtaining information about the critical exponents from the magnetic entropy change curves, we assume that the reference temperatures used for constructing the universal curve should scale with field [9], i.e.,

\[
T_r \propto H^{1/\Lambda},
\]

where \( \Lambda = \beta\delta \) is the gap exponent.  

**Fig. 1.** Collapse of the magnetic entropy change for the Al-, Cu-, Ga- and Mn-doped Gd\(_5\)Ge\(_2\)Si\(_2\) alloys which only possess a second-order magnetic phase transition. Only a single reference temperature \( T_r \) was used. The different symbols correspond to data measured at magnetic fields ranging from 1.6 to 5 T.

**Fig. 2.** Extraction of the critical exponents and Curie temperature of the Al-doped Gd\(_5\)Ge\(_2\)Si\(_2\) alloy using the Kouvel–Fisher method as described in the text. The slopes give \( \gamma \) and \( \beta \) while the temperature axis intercepts give \( T_c \).
entropy change times the full width at half maximum of the peak, should also scale with field in the form of:

$$RC_{\text{FWHM}} \propto H^{1+\beta}.$$  \(\text{(7)}\)

This scaling law has been tested in a similar way in Fig. 5, using the exponents obtained from the K-F method. However, Figs. 4 and 5 only indicate that if the critical exponents are known, the scaling of the magnetocaloric effect can be predicted. In order to check if the reverse is true, i.e., determining the critical exponents by knowing the scaling of the magnetic entropy change, a non-linear fit of experimentally determined reference temperatures and refrigerant capacities to Eqs. (6) and (7) has been performed, respectively. From the fit of the refrigerant capacity, the exponent \(\delta\) can be obtained; the exponent \(\beta\) can be subsequently obtained from the fit of the reference temperature to Eq. (6) and finally \(\gamma\) can be computed from the relation, \(\beta \delta = \beta + \gamma\). The results of this analysis are indicated in brackets in Table 1; note the reasonable agreement between both procedures. The A-N plots performed using the critical exponents obtained from this scaling analysis of the magnetic entropy change give no appreciable differences to those obtained from the K-F exponents. For example, note the straight lines obtained in the high field region of the A-N plots for the Al-doped alloy shown in Fig. 6.

In the case of the Fe-doped Gd5Ge2Si2 alloy, the fitting analysis described above for the Al-doped Gd5Ge2Si2 alloy is not successful. A universal curve for the Fe-doped alloy cannot be constructed by using a single reference temperature (Fig. 7). This result is an indication that the field dependence of the magnetic entropy change is different below and above the temperature of the peak entropy change. The demagnetizing field, one of the possible reasons for the failure of constructing the universal curve using \(\gamma\) cannot be the source of difficulties in this case since its influence is limited to the temperature region below the transition temperature [20]. However, as can be observed in Fig. 7, the various curves of entropy change vs. \(\theta\) for the different field applications do not collapse into a single curve even in the high temperature range. Therefore, the presence of some minority monoclinic phase at high temperatures should be considered, with the first-order orthorhombic–monoclinic transition being responsible for the minor hysteresis found in the thermomagnetic curves [14]. Taking into account that the majority of the sample

<table>
<thead>
<tr>
<th>Material</th>
<th>Curie Temperature (T_c) (K)</th>
<th>(\beta)</th>
<th>(\gamma)</th>
<th>(\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Gd</td>
<td>293.3</td>
<td>0.381</td>
<td>From 1.196 to 1.24</td>
<td>Measured 3.615</td>
</tr>
<tr>
<td>Cu doping</td>
<td>295.5</td>
<td>0.38 [0.4]</td>
<td>1.15 [1.1*]</td>
<td>4.03* [3.5]</td>
</tr>
<tr>
<td>Mn doping</td>
<td>295.6</td>
<td>0.41 [0.40]</td>
<td>1.05 [1.2*]</td>
<td>3.56* [4.1]</td>
</tr>
<tr>
<td>Ga doping</td>
<td>289.5</td>
<td>0.34 [0.42]</td>
<td>1.17 [1.3*]</td>
<td>4.44* [4.1]</td>
</tr>
<tr>
<td>Al doping</td>
<td>293.5</td>
<td>0.38 [0.39]</td>
<td>1.08 [1.1*]</td>
<td>3.84* [3.8]</td>
</tr>
<tr>
<td>Fe doping</td>
<td>292</td>
<td>[0.3]</td>
<td>[0.9*]</td>
<td>[4]</td>
</tr>
</tbody>
</table>

Values for pure Gd are also quoted as a reference. Values without brackets were calculated using the Kouvel–Fisher method; square brackets indicate that the calculation was done using the scaling of the magnetocaloric effect. The values calculated using the relation \(\beta \delta = \beta + \gamma\) are marked with an asterisk.
does not undergo the structural orthorhombic–monoclinic phase transformation, but only possesses a second-order magnetic transition, construction of the universal curve using $y^2$ was attempted. Fig. 8 shows this modified construction collapses the magnetic entropy change data onto a single curve in the temperature range close to the magnetic entropy change peak. It is worth noting that the differences in both figures are restricted to the low temperature $y_0$ range in the proximity of the peak; for temperatures above the peak, both figures are identical. At temperatures well below the peak, the collapse of the curves is not achieved, even by the use of $y_2$, because the equation of state is only really valid close to the critical temperature. The fact that an appropriately scaled universal curve can be drawn describing the data implies that the main mechanism responsible for this peak is indeed the second-order magnetic phase transition of the orthorhombic phase. Therefore, the scaling analysis of these data should provide information about the critical exponents of the orthorhombic phase together with its Curie temperature. By performing the non-linear fits of the field dependence of the refrigerant capacity and the reference temperature ($T_{r1}$) to Eqs. (5) and (6), the critical exponents of that magnetic phase transition have been computed and reported in Table 1. As $T_{r1}$ may be affected by different artifacts not directly related to the magnetic transition under study, like the influence of minority magnetic phases [10] or the effect of the demagnetizing factor [20], $T_{r1}$ was used in this analysis since it is not affected by these artifacts.

The critical exponents values for the Fe-doped alloy are comparable to those of the other doped alloys, indicating that the results are plausible. The construction of the A-N plot using the critical exponents extracted from the scaling of the magnetic entropy change. The different symbols correspond to data measured at temperatures ranging from 216 K (black diamonds) to 356 K (purple triangles) at roughly 5 K intervals, and the dashed line corresponds to the curve at the predicted Curie temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
that gives rise to a field-induced magneto-structural transition in some remaining hysteresis due to the residual monoclinic phase. hombic–monoclinic transformation is mostly suppressed (despite results.

In the case of Ge1.9X0.1 (X=Al, Cu, Ga, Mn, Fe, Co) has been studied. In the case of

4. Conclusions

The feasibility of constructing the universal curve for Gd5Ge2Si2, Ge2Si0.3X0.7 (X=Al, Cu, Mn, Fe, Co) has been studied. In the case of Al, Cu, Ga and Mn, where the first-order magneto-structural transition is totally suppressed by doping, the universal curve can be constructed using a single reference temperature. In addition, all the magnetic entropy change curves for all the available compositions collapse onto the same universal curve, indicating that the critical exponents for these four alloys should be similar.

In the case of the Fe-doped Gd5Ge2Si2 material, as the orthorhombic–monoclinic transformation is mostly suppressed (despite some remaining hysteresis due to the residual monoclinic phase that gives rise to a field-induced magneto-structural transition in the vicinity of $T_c$), the universal curve can be constructed in the temperature region near the magnetic entropy change peak by using two reference temperatures. For Co-doping, the hysteresis is too large to provide meaningful results.

Studying the magnetic field dependence of the magnetic entropy change, namely of the refrigerant capacity and the reference temperature, we have developed a procedure for estimating the critical exponents of the magnetic transition. Results are consistent with those provided by the Kouvel–Fisher method in the cases where the K-F method is valid (i.e. for the Al–, Cu–, Ga– and Mn-doped material, where a purely second-order magnetic phase transition exists). In the case of Fe-doped material, although the K-F method cannot be used due to the existence of some minor monoclinic phase in the high temperature range, the estimate of the critical exponents using the scaling of the magnetic entropy change still provides plausible results and it also enables an estimation of the Curie temperature of the orthorhombic phase to be made.

Acknowledgments

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