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Direct Measurement of the Magnetocaloric Effect in $Gd_5Si_2Ge_{1.9}Ga_{0.1}$

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Abstract. Doping with some metals (Fe, Cu, Ga, Mn, Al) reduces or removes the strong thermal hysteresis in the giant magnetocaloric alloys $Gd_5(Si_xGe_{1-x})_4$. We present heat capacity and direct measurements of the isothermal entropy change, ΔS_T, and adiabatic temperature increment, ΔT_S, of $Gd_5Si_2Ge_{1.9}Ga_{0.1}$. $T_C = 293.6 \pm 0.2$ K is quite higher than in the non-substituted alloys and similar to the values in the Si rich compounds (i.e. $x > 0.5$). The results indicate that even this small addition of Ga makes the transition of second-order type, as a usual magnetic transition in the orthorhombic phase. The magnetocaloric parameters are lower than in the non-substituted compound and comparable to those for pure Gd.

1. Introduction

Since 1997, when the giant magnetocaloric effect (GMCE) was discovered in $Gd_5Si_2Ge_2$ [1], both the magnetic and structural properties of the $Gd_5(Si_xGe_{1-x})_4$ compounds have been extensively studied owing to their potential as effective refrigerants for near-room temperature magnetic cooling applications. $Gd_5Si_2Ge_2$ undergoes a temperature-induced first-order magneto-structural transition around 270 K from an orthorhombic ferromagnetic (FM) phase to a monoclinic paramagnetic one. Within a narrow temperature range above 270 K, the monoclinic phase can be converted back to the FM orthorhombic phase by applying a magnetic field, reverting back to monoclinic when the field is removed. The GMCE displayed by $Gd_5Si_2Ge_2$ is associated with the first-order magneto-structural transition. Its isothermal entropy change, ΔS_T is enhanced by the electronic and/or vibrational entropy change resulting from the structural transition from one crystal phase to the other. The main drawback of $Gd_5Si_2Ge_2$ is the thermal hysteresis of about 15 K at zero field [2] which produces large magnetic hysteresis losses, reducing the refrigeration capacity of the compound and, thus, its cooling efficiency [3]. The thermal hysteresis also imposes a rather intense threshold field of 4 T at T_C [2].

Past studies have shown that doping $Gd_5Si_2Ge_2$ with a small amount of different metal elements (Fe, Cu, Ga, Mn, Al) greatly reduces or completely eliminates the hysteretic behaviour. This is because metal doping has the effect of suppressing the first-order magneto-structural transition and shifting it to a second-order magnetic transition at a Curie temperature of about 295 K where the MCE peak of the doped material is centered [3]. Although metal doping reduces the magnitude of the MCE peak relative to that of the undoped compound, the corresponding

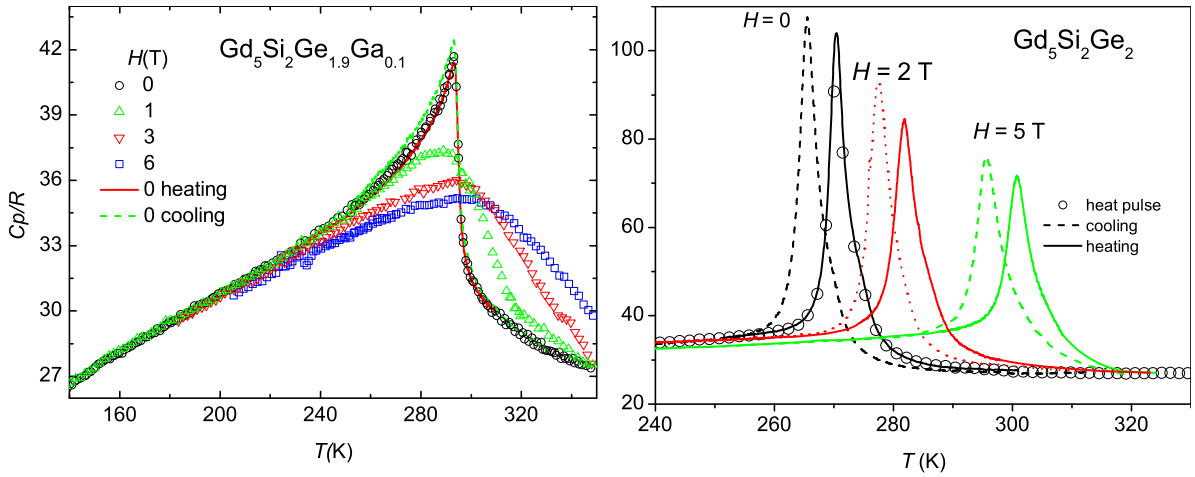

Figure 1. Left: Molar heat capacity of $Gd_5Si_2Ge_{1.9}Ga_{0.1}$ at 0, 1, 3, and 6 T, measured with the standard heat-pulse technique (symbols). Data obtained on continuous heating (solid, red line online) and cooling (dashed, green line online) at zero field. Right: Molar heat capacity of $Gd_5Si_2Ge_2$ at 0, 2, and 5 T obtained via the pulse (symbols), continuous heating (solid lines) and continuous cooling (dashed lines) techniques.

refrigeration capacity is 30-50% larger. Both the MCE peak and the refrigeration capacity had been computed from isothermal magnetization (M_T) measurements [4].

For the case of materials undergoing first-order transitions, often accompanied by the presence of large magnetic hysteresis losses, the computation of ΔS_T from magnetic measurement data via the use of the Maxwell relation can lead to large computational artifacts [5]. Moreover, the calculation using this relation can lead to non-physical values and the resulting huge errors have been quantitatively analysed [6]. In fact, in many cases the obtained MCE peak values are much higher than the corresponding values computed from either heat capacity, $C_{p,H}$, or from direct thermal measurements data [5, 6]. Moreover, the magnetization data alone cannot give the adiabatic temperature increments, ΔT_S, for a given field change.

In this work we studied the magnetocaloric properties of $Gd_5Si_2Ge_{1.9}Ga_{0.1}$ through $C_{p,H}$ (both on cooling and heating) by adiabatic calorimetry at constant field, and quasi-static direct determinations of both ΔS_T and ΔT_S for different field variations between 0 and 6 T.

2. Experimental

The Rietveldt fit of an X-ray diffraction pattern showed that the sample, in percent mass, was actually composed of 81.6% of $Gd_5Si_2Ge_{1.9}Ga_{0.1}$ (majority phase) and two minority phases: 3.7% of $GdSi_{0.5}Ge_{0.5}$ and 14.7% of $Gd_5Si_{1.5}Ge_{1.5}$. These amounts are consistent with the average atomic composition of the sample obtained with X-ray fluorescence analysis.

$C_{p,H}$ (Fig 1, left panel) was measured at $H = 0$ from 27 K up to 350 K. To obtain the absolute entropy, the experimental data have been extrapolated to 0 K, using the temperature dependence $C_{p,0} = AT+BT^3$. A lambda-type anomaly was observed with the peak at 293.6±0.2 K. $C_{p,0}$ has also been measured by continuous heating or cooling at an average rate of 1 mK/s, using a quasi-static technique previously described [7]. The heating and cooling curves coincide within temperature differences of 0.1 K. This small difference is not due to any thermal hysteresis but to the dynamics of the heat conduction through the extensive sample in this slow cooling or heating process. For fields $H = 1$, 3, and 6 T the heat capacity was measured in a limited temperature range around the transition. Under an applied field the sharp anomaly becomes

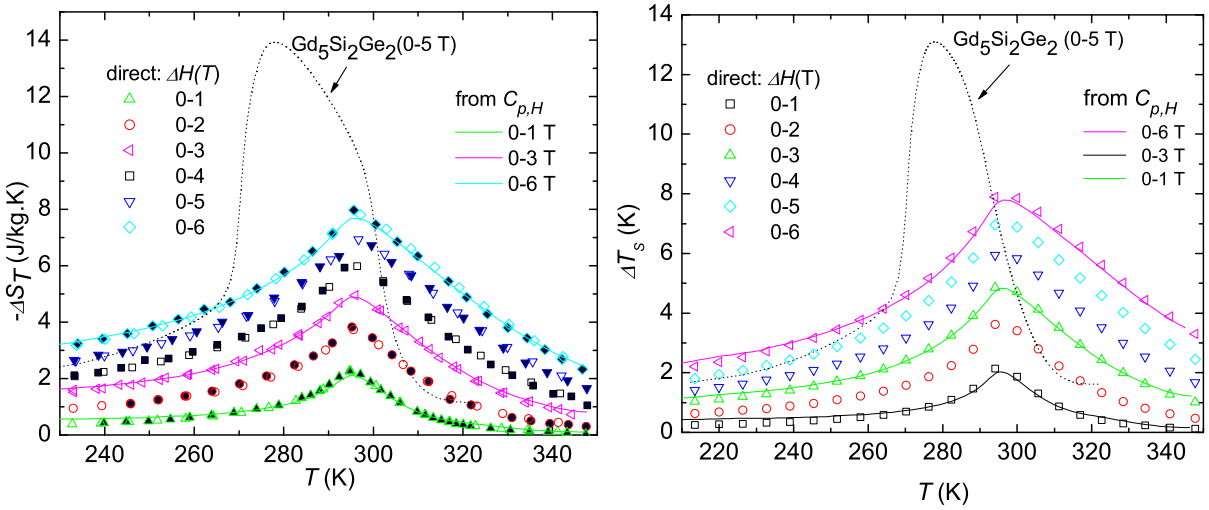

Figure 2. Magnetocaloric parameters for $Gd_5Si_2Ge_{1.9}Ga_{0.1}$ from $C_{p,H}$ (solid lines) and direct measurements (symbols). Dotted lines show data for $Gd_5Si_2Ge_2$. Left: ΔS_T. Right: ΔT_S.

rounded. These facts suggest a second-order transition. In addition, another small peak was found at 67 K, which could be ascribed to the $GdSi_{0.5}Ge_{0.5}$ minority phase [9].

For the purpose of comparison, $C_{p,H}$ of undoped $Gd_5Si_2Ge_2$ has been measured, using the same experimental set-up and procedures, and is shown in Fig. 1, right panel. These results agree with those of the literature [1] and show a clear thermal hysteresis. The anomaly has a sharp an narrow shape which can be understood as a Dirac δ due to the latent heat, but is broadened by such factors as non-homogeneous composition, field, stresses, grain size, etc. The area under the anomaly (latent heat) and the hysteresis decrease on approaching the critical field. The maxima of $C_{p,H}$ do not flatten. All these features are markedly different than those observed in the Ga-doped compound.

From $C_{p,H}$, the entropy can be computed by numerical integration using the formula

$$S(T,H) = \int_0^T \frac{C_{p,H}(T)dT}{T} \tag{1}$$

For each field $H \neq 0$ the reference for the absolute entropy has been determined from the curve at zero field, by adding the small experimental entropy difference, ΔS_T, at a fixed $T_0 > T_C$. The values of $S(T,H)$ have been obtained integrating between the limits T_0 and T. The results, $\Delta S_T = S(T,H) - S(T,0)$, are shown on the left panel of Fig. 2, whereas $\Delta T_S = T(S,H) - T(S,0)$ has been computed from the $C_{p,H}$ data using the inverse function $T(S,H)$ and is shown on the right panel of Fig. 2.

ΔS_T has also been measured directly. The procedure is based on supplying the necessary heat to keep constant the sample temperature while the field decreases from some initial value to zero. The rate of field variation is sigmoidal with a maximum of 0.01 T/s and decreasing to zero at the beginning and end of the field change. The procedure was tested with pure Gd and it yielded errors lower than 1% when compared to the corresponding results obtained from $C_{p,H}$. Compared to the literature data [10], the difference is less than 5%, probably due to either experimental errors in these values or slight differences in the state of the material. The results from the direct measurements for $Gd_5Si_2Ge_{1.9}Ga_{0.1}$ (Fig. 2) agree with those from $C_{p,H}$. The maximum $-\Delta S_{T,max} = 6.93 \pm 0.05$ J/kg·K occurs at 296.8 K for $\Delta H = 0$ to 5 T and is slightly higher than the value obtained from M_T on a similar compound, $-\Delta S_{T,max} = 6.5$ J/kg·K [11].

The temperature increment has also been measured directly when the field is increased quasi-statically and adiabatically. The entropy increment of the sample holder is computed from the initial and final temperatures using previous measurements of the empty holder. This result is used to deduce ΔT_S for the sample alone using the experimental temperature increment observed (as described in [8]). The results agree with those deduced from $C_{p,H}$ (Fig. 2, right panel).

3. Discussion

The value $-\Delta S_{T,max} = 6.93$ J/kg·K at 296.8 K for $\Delta H = 0$ to 5 T is significantly lower than that of $Gd_5Si_2Ge_2$ and occurs at a higher temperature. In fact, for $Gd_5Si_2Ge_2$ we obtained $-\Delta S_{T,max} = 13.9$ J/kg·K, which is lower than the reported value, 18.5 J/kg·K [1]. The larger value computed from M_T is most likely overestimated due to the presence of a spurious "spike", as discussed in [6]. For the Ga-doped compound, $-\Delta S_{T,max}$ can be compared with that of pure Gd metal, where $-\Delta S_{T,max} = 10$ J/kg·K. These values are even closer when they are normalised per gram-atom of Gd, $-\Delta S_{T,max} = 1.57$ J/K·Gd-gram-atom for Gd metal, and $-\Delta S_{T,max} = 1.68$ J/K·Gd-gram-atom for $Gd_5Si_2Ge_{1.9}Ga_{0.1}$, where the experimental phase percentage has been taken into account. The overall shape of $-\Delta S_T(T)$ is similar to the curves found for Gd.

All the features found in our sample, - the shape of $C_{p,0}(T)$, the absence of hysteresis, and the disappearance of the sharp peak under weak fields - suggest a second-order character of the ferromagnetic transition for our compound. From DSC data, a second-order transition was also inferred in similar Ga-doped compounds [11]. In fact, T_C occurs near the T_C values that are observed for compounds in which the monoclinic phase is not present (i.e. Si rich compounds in the 5:4 composition). The transition seems to be purely magnetic (i.e. without any structural transition). The value of $\Delta T_{S,max} = 8$ K is also lower than that obtained for the undoped compound ($\Delta T_{S,max} = 13$ K, Fig 2) and for pure Gd (11.2 K). The lower $\Delta T_{S,max}$ compared to that of pure Gd is to be expected due to the dilution effect caused by the presence of non-magnetic elements in in the Ga-doped compound.

In summary, regarding the potential of $Gd_5Si_2Ge_{1.9}Ga_{0.1}$ for magnetic cooling applications, when compared to $Gd_5Si_2Ge_2$, the former looses the GMCE feature displayed by the later material. But on the positive side, the thermal hysteresis disappears, avoiding the magnetic losses present in the undoped compound. Also the useful temperature range with relevant magnetocaloric properties broadens, producing an increase of the refrigerant capacity.

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