Field and Temperature induced magnetic transition in Gd_5Sn_4, a giant magnetocaloric material

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Gd_5Sn_4 exhibits a giant magnetocaloric effect comparable to that reported in the $Gd_5(Si, Ge)_4$ system. The giant magnetocaloric effect is associated with a first-order change that occurs at ∼82 K in zero field, and can be reversed by the application of an external field of a few Tesla. ^{119}Sn Mössbauer spectroscopy shows that this material is magnetically inhomogeneous over a wide range of temperatures and fields.

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I. INTRODUCTION

The discovery of a giant magnetocaloric response in $Gd_5Si_2Ge_2$ [1] has revived interest in both rare-earth/Si-group alloys [2,3] and various manganese-based compounds [4] in a search for materials for use as magnetic refrigerants. A critical requirement for any potential magnetocaloric material is a large change of magnetic entropy (S_{mag}) in an accessible magnetic field. Assuming that the system remains in equilibrium (or at least quasi-static conditions apply), then the magnetic entropy can be obtained from magnetisation data through the Maxwell relation [1,5]:

$$(\partial S_{mag}/\partial B)_T \;=\; (\partial\sigma/\partial T)_B$$

where T is the absolute temperature, B is the applied magnetic field and σ is the magnetisation. This implies that a large magnetic entropy change, ΔS_{mag}, requires a strongly temperature dependent magnetisation. This in turn leads us to seek first-order magnetic transitions where the magnetisation is lost more abruptly than at a more conventional continuous transition. Furthermore, in order to maximise the magnetisation change, it is essential to have a large magnetisation in the ordered state. Alloys rich in gadolinium or manganese are therefore popular choices.

Following a survey of the $Gd_5Si_xSn_{4-x}$ system [6], we identified Gd_5Sn_4 as a candidate giant magnetocaloric material. Unfortunately, the high absorption cross section of natural gadolinium presents a severe barrier to neutron diffraction studies, so that a direct magnetic and structural study is not possible. We have therefore turned to ^{119}Sn Mössbauer spectroscopy to obtain both magnetic and structural information on a local scale.

We present here a combination of magnetisation and ^{119}Sn Mössbauer spectroscopy that confirms that Gd_5Sn_4 undergoes a first-order magnetic transition at 82 K (in zero field). An applied field causes the transition to move to higher temperatures at ∼3.5 K/T, and the change can be driven by both temperature and field. In addition, the ^{119}Sn Mössbauer spectra provide direct evidence that the system is magnetically inhomogeneous over a wide range of temperatures and fields. Finally, Gd_5Sn_4 exhibits a giant magnetocaloric effect that is comparable to that seen in the $Gd_5Si_xGe_{4-x}$ [3].

II. EXPERIMENTAL METHODS

Samples were prepared in a tri-arc furnace with a base pressure of better than 6×10^{-7} mbar. Stoichiometric amounts of the pure elements (Gd (99.9%) and Sn (99.99%) [7]) were melted several times under pure (less than 1 ppm impurity) Argon to ensure homogeneity. The alloy is air-sensitive, tending to segregate into metallic tin and gadolinium oxide on exposure to air for a few hours. All sample handling was therefore carried out under argon in a glove box.

Powder x-ray diffraction measurements were made using Cu K_α radiation. Analysis showed that Gd_5Sn_4 adopts the Pnma orthorhombic Sm_5Ge_4−type structure at room temperature, with a = 8.047(3)Å, b = 15.545(5)Å and c = 8.199(3)Å [6]. Basic magnetic characterisation was carried out on a commercial susceptometer/magnetometer at temperatures from 5 K to 300 K. AC susceptibility (χ_{ac}) measurements were made with a driving field of 1 mT at 137 Hz. Magnetisation measurements were made in fields of up to 9 Tesla.

Mössbauer spectra were obtained using a 370 MBq ^{119m}Sn $BaSnO_3$ source. For the zero-field runs, temperatures between 9 K and room temperature were achieved using a vibration-isolated closed-cycle refrigerator. This spectrometer was operated in constant-acceleration mode and calibrated against a 99.99% α−Fe foil using a ^{57}Co source. The applied field spectra were obtained using a superconducting split solenoid with the field axis vertical and the $\gamma-$beam horizontal. This system was operated in sine-mode and was calibrated using a He/Ne laser interferometer. All spectra were fitted using a conventional non-linear least-squares minimisation routine that allowed for a combination of Lorentzian lines from sharp components and a Gaussian field distribution for the disordered component.

III. RESULTS

The 5 K magnetisation curve in Fig. 1 shows that Gd_5Sn_4 is ferromagnetic and yields an average moment of 6.8 μ_B/Gd. Two features are apparent in the χ_{ac} data shown in the inset to Fig. 1: the large step at ∼80 K reflects the transition from the high magnetisation ordered form to the non-magnetic form. The magnetic transition of a monoclinic Gd_5Sn_4 impurity at ∼130 K [6] accounts for the second feature in the χ_{ac} data. These assignments are confirmed below using ^{119}Sn Mössbauer spectroscopy.

The spectrum of Gd_5Sn_4 at 9 K [6] is dominated by two well-split magnetic sextets that account for about 86% of the total absorbed area. At 30.99(1) T and 38.55(2) T, the hyperfine fields (B_{hf}) are remarkably large, indicating that the tin is coordinated by ferromagnetically ordered Gd moments. There are three tin sites in the orthorhombic structure ($4c_1$, $4c_2$, and 8d) and analysis of the coordination suggests that the hyperfine fields at the $4c_2$ and 8d sites should be similar and smaller than that at the $4c_1$ site [6]. This pairing leads us to expect a 3:1 area ratio, in perfect agreement with the 2.94(8):1 that is observed.

An additional weakly magnetic component, accounting for about 11% of the total area at 9 K, could be fitted as a Gaussian distribution of hyperfine fields ($< B_{hf} > \sim$ 16.5 T). The parameters of this component are close to those of the monoclinic form found in $Gd_5Si_xSn_{4-x}$ for $0.6 < x < 1.4$ [6]. Finally, there is a weak, broad singlet (∼3% of the area). The parameters of these three components were found to be stable from sample to sample, however the relative contributions varied by several percent, perhaps reflecting an incomplete transformation on cooling as a result of stresses, differing cooling rates or minor compositional variations.

On warming from 9 K to 80 K (Fig. 2), the central component becomes more prominent, at the expense of, but coexisting with, the sharp sextets (similar changes are seen later in the applied field spectra), indicating a gradual temperature driven conversion from a magnetic to a non-magnetic form. This behaviour provides direct confirmation that the material is magnetically inhomogeneous, with strongly and weakly magnetic phases coexisting from 9 K to ∼90 K, a result that has previously only been inferred indirectly from magnetisation studies of the related $Gd_5Si_{1.5}Ge_{2.5}$ [8]. An approximate fit to the temperature dependence of B_{hf} for the two sharp sextets up to 80 K suggests an ordering temperature of about 200 K. However, the gradual decline in hyperfine field is interrupted above 80 K: the sharp magnetic components disappear abruptly, to be replaced by the central non-magnetic component, as the material transforms to its non-magnetic form. As Fig. 3 shows, this loss of the magnetic components occurs at a temperature well below that at which the hyperfine fields would extrapolate to zero, confirming that the 82 K feature in the χ_{ac} data is associated with a significant magnetic transformation. As the spectral parameters of the sharp components below 82 K are identical to those seen for the orthorhombic form found in $Gd_5Si_xSn_{4-x}$ for x>1.5 [6], and the x-ray structure at room temperature is also orthorhombic, it appears likely that if the magnetic transition is associated with a change in crystal structure, then that change may be between two closely related orthorhombic forms, as seen for $Gd_5Si_{0.4}Ge_{3.6}$ [9]. The Gaussian-broadened spectral component is unaffected by the 82 K event, and continues to exhibit a hyperfine field up to ∼130 K. This component accounts for the upper feature in the χ_{ac} data in Fig. 1.

Magnetisation curves obtained above the magnetic transition of 82 K (Fig. 4) show that even here, a large magnetisation is obtained, but that it appears abruptly above a minimum field that increases with temperature. Similar behaviour has been seen in the $Gd_5(Si, Ge)_4$ system [10,11], however there are two important differences: (i) the saturated magnetisation in Gd_5Sn_4 appears to fall more slowly with temperature, and (ii) the magnetisation in the non-magnetic state is significantly lower here than in the $Gd_5(Si, Ge)_4$ system. These differences combine to yield a much larger change in magnetisation between the two states at a given temperature, and thus we expect a larger magnetocaloric response.

Fig. 5 shows the results of applying the Maxwell relation to the magnetisation data. As is typical in first-order transitions, once a field sufficient to complete the transition is applied, a plateau in $\Delta S_{mag}(T)$ is obtained. Larger field changes simply increase the width of the plateau but do not affect its height as they cannot cause any further entropy change [12]. At ∼35 J/kg-K, the plateau value is close to some of the best giant magnetocaloric responses reported for the $Gd_5Si_xGe_{4-x}$ system [3], suggesting that Gd_5Sn_4 may have significant potential as a giant magnetocaloric material.

In order to demonstrate that the step in the magnetisation curves evident in Fig. 4 which leads to the large magnetocaloric signal in Fig. 5 is indeed associated with the magnetic transformation observed on heating, we need to show that an externally applied field can reverse the collapse of the magnetic component seen in the spectra in Fig. 2.

This reversal is shown in Fig. 6. At 90 K, the transformation to the non-magnetic state is essentially complete and the spectrum is dominated by the central, non-magnetic feature, with a small (∼15%) contribution from the disordered, weakly magnetic monoclinic phase. By 3.25 T the presence of the sharp well-split pair of sextets is clearly evident, and their area increases rapidly at the expense of the central feature as the field increases. This behaviour is the exact reverse of the collapse seen on heating through 80 K in Fig. 2. Furthermore, when the magnetic fraction in the Mössbauer spectra is plotted *vs.* the applied field (Fig. 7) it closely follows the magnetisation obtained at the same temperature. As with the temperature driven transformation, the field driven conversion is associated with a broad, magnetically inhomogeneous co-existence region, which at 90 K spans fields from ∼2 T to ∼4 T.

Finally, if we plot the hyperfine fields of the two sextets *vs.* the applied field we obtain a slope of -1.00 ± 0.25 T/T, consistent with ferromagnetic order in the highly magnetic phase. When these fields are extrapolated back to zero applied field they are nicely consistent with the temperature dependence observed below the transformation in zero field (solid points in Fig. 3), confirming that the applied field does indeed reverse the thermally driven magnetic transformation, and it restores the low-temperature ferromagnetic form.

IV. CONCLUSIONS

Gd_5Sn_4 exhibits a large magnetocaloric effect associated with a first-order magnetic transformation at 82 K. ^{119}Sn Mössbauer spectroscopy confirms that there is a first-order transition between 80 and 85 K and that the step in the magnetisation curves observed above the transition is due to a reversal of the change by the applied field. The data also provide direct confirmation that this material is magnetically inhomogeneous over a wide range of temperatures (9–130 K) and fields (2–4 T at 90 K). Low-temperature x-ray diffraction data are now needed to determine whether there is a change in structure associated with the magnetic transition.

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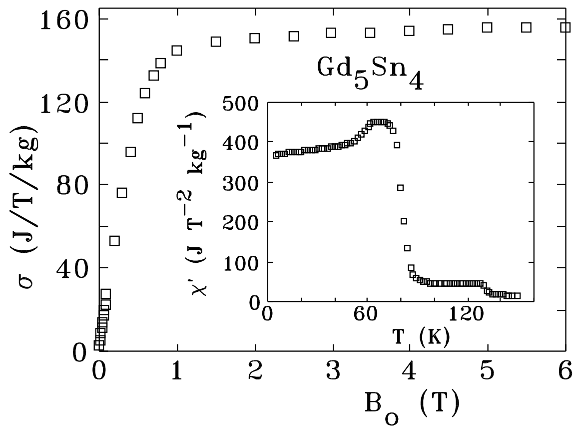

FIG. 1. Magnetisation of Gd_5Sn_4 at 5 K. Inset: χ_{ac} vs. T data showing two features at ∼80 K and ∼130 K.

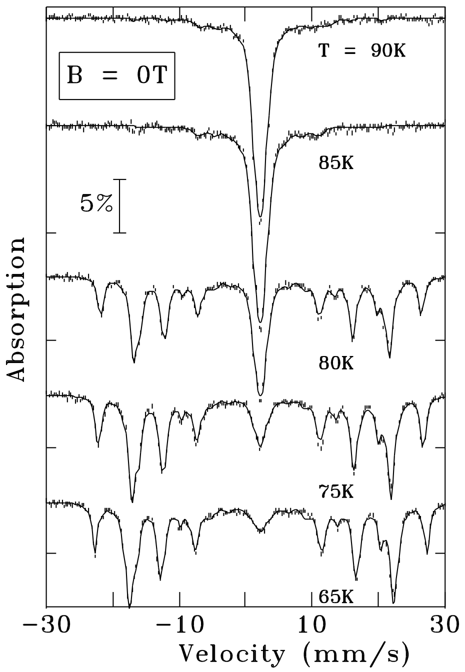

FIG. 2. [119]Sn Mössbauer spectra of Gd_5Sn_4 at several temperatures. This sample shows an abrupt transition to a non-magnetic state above 80 K as the sharp sextets disappear.

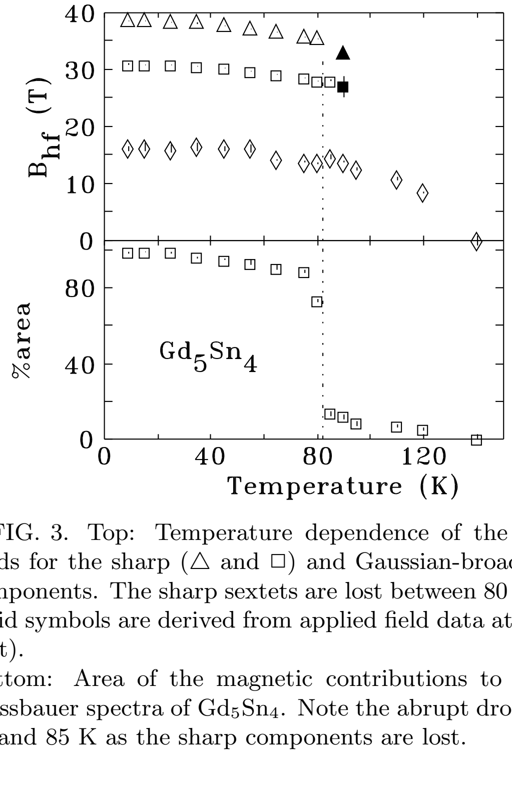

FIG. 3. Top: Temperature dependence of the hyperfine fields for the sharp (△ and □) and Gaussian-broadened (◇) components. The sharp sextets are lost between 80 and 85 K. Solid symbols are derived from applied field data at 90 K (see text).
Bottom: Area of the magnetic contributions to the [119]Sn Mössbauer spectra of Gd_5Sn_4. Note the abrupt drop between 80 and 85 K as the sharp components are lost.

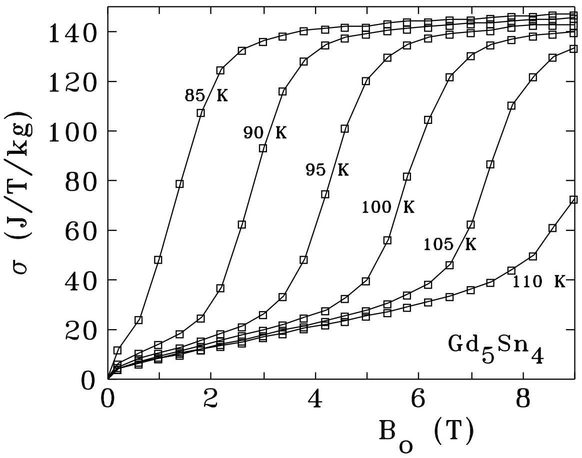

FIG. 4. Magnetisation curves taken above the ∼80 K transition showing the abrupt increase in magnetisation typically associated with the giant magnetocaloric effect.

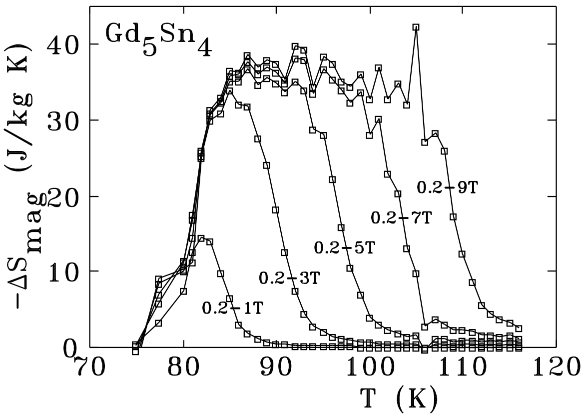

FIG. 5. Magnetic entropy change obtained from magnetisation curves through the Maxwell relation. Data are for decreasing fields and show a large plateau value between 85 K and 110 K.

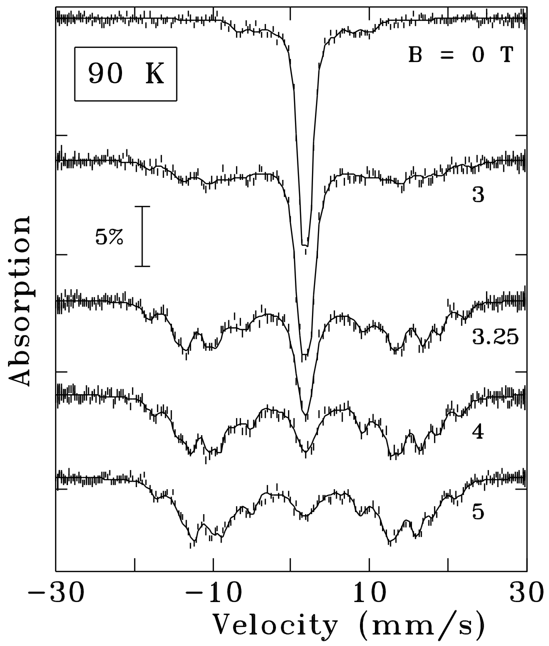

FIG. 6. ^{119}Sn Mössbauer spectra of Gd_5Sn_4 at 90 K in several applied fields. Note the restoration of the magnetic phase in fields above 3 T.

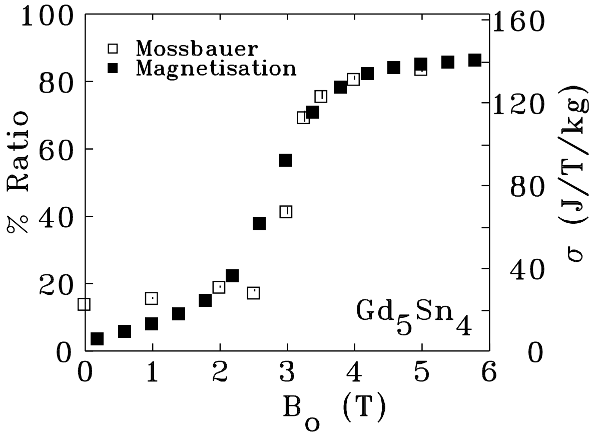

FIG. 7. Area of the magnetic components (open symbols) as a function of applied field at 90 K compared with magnetisation data (solid symbols) at the same temperature.