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Magnetic properties and the magnetocaloric effect in the intermetallic compound GdFeSi

M. Napoletano,[a] F. Canepa,*[a] P. Manfrinetti[a] and F. Merlo[b]

[a]*INFM e Università di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146 Genova, Italy*
[b]*Università di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, 16146 Genova, Italy*

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We report on the magnetic and magnetocaloric properties of GdFeSi, as obtained from DC magnetisation and specific heat measurements, in applied fields up to 9 Tesla and in a temperature range between 3 and 300 K. The compound orders ferromagnetically at 118 K. In the paramagnetic range it follows the Curie–Weiss law with $\mu_{eff}=8.68\ \mu_B$ and $\vartheta_c=+122$ K. At 5 K a saturation magnetic moment of 6.16 μ_B was found, while the spontaneous magnetic moment is 6.11 μ_B. From thermodynamic measurements the adiabatic temperature rise for an applied field of 9 T was $\Delta T=4.5$ K and the refrigerant capacity of the compound in the 10–160 K temperature range was calculated to be 1940 J kg^{-1}. The value is comparable with the one reported for Gd_5Ge_4 of 780 J kg^{-1} in the temperature span 10–50 K for an applied magnetic field of 5 Tesla.

1. Introduction

It is known that applying a magnetic field to a ferromagnetic material under adiabatic conditions results in spin alignment parallel to the magnetic field: this causes an increase in the magnetic order and consequently a temperature rise ΔT_{ad} due to the magnetocaloric effect. Upon removal of the magnetic field the spins become randomly oriented again and the material cools down. This effect was discovered in 1881 by Warburg[1] and was used for the first time to cool materials well below 1 K in the mid-1920's as suggested by Debye and Giauque.[2,3] This procedure known as adiabatic demagnetisation and consisting of a one step cooling process may be applied in magnetic refrigeration cycles such as Ericsson or Brayton ones providing an attractive alternative to the conventional gas compression technology. As pointed out by Pecharsky and Gschneidner[4,5] magnetic refrigeration offers several advantages such as: a high thermodynamic efficiency, due to the reversibility of the magnetocaloric effect, high energy densities, more compact devices because the working material is a solid and less pollution due to the elimination of ozone depleting chlorinated fluorocarbons (CFC). In 1997 a proof of principle apparatus[6] was designed constructed and tested at the Ames laboratories in order to show that magnetic refrigeration may be a viable alternative technology to vapour cycle compression cooling.

As a part of our current research concerning the development of new magnets for magnetic refrigeration devices[7,8] we magnetically characterised the ternary equiatomic intermetallic compound GdFeSi. Previously performed analyses[9] were extended up to higher magnetic field by DC magnetisation measurements and furthermore, the magneto-thermodynamic behaviour of the phase was analysed by measuring the heat capacity in an applied magnetic field of 9 Tesla.

2. Experimental

The compounds were prepared by melting the pure constituents (Gd 99.9 wt%, Fe 99.98 wt%, Si 99.999 wt%) in stoichiometric amounts pressed in the form of a pellet of about 4 g in a high-frequency induction furnace on a water cooled tantalum heart under an argon atmosphere. The sample was turned upside down and remelted several times in order to ensure complete homogenisation.

X-Ray powder patterns were collected by means of a Guinier camera using silicon as internal standard and indexed on the basis of the Cu_2Sb structure type, space group *P4/nmm*. The room temperature lattice constants are: $a=4.000(1)$ Å and $c=6.815(1)$ Å.

Heat capacity and DC magnetisation measurements were collected on a sample of 1.2568 g using an Oxford Maglab^{2000} system operating in the 3–300 K temperature range with applied fields up to 9 Tesla. A calibrated Cernox type thermometer from Lake Shore Cryotronics Inc. was used as a temperature sensor.

3. Results and discussion

3.1 Magnetic results

Results of magnetic measurements showing the temperature dependence and field dependence (at 5 K) of the magnetisation of GdFeSi are plotted in Fig. 1 and 2, respectively. All the experimental data were corrected for the presence of a small amount of iron (0.2 wt%) as a ferromagnetic impurity estimated from the isothermal magnetisation (up to 5 T) obtained at room temperature; it was not possible to confirm the impurity data by means of XRD diffraction due to the sensibility limit of the technique.

The change of slope in the magnetisation data indicate the occurrence of a ferromagnetic ordering near 120 K.

Above 120 K the inverse of the susceptibility exhibits a Curie–Weiss behaviour as shown in the inset of Fig. 1. The data obtained from the fit, reported as a solid line in the inset of the figure, are: $\vartheta_c=122$ K and $\mu_{eff}=8.68\ \mu_B$, slightly higher than the theoretically calculated free ion value (7.94 μ_B) and in good agreement with Welter and coworkers.[9] Isothermal magnetisation performed at 5 K (Fig. 2) saturates at 9 Tesla with a saturation magnetic moment $\mu_{gJ}=6.62\ \mu_B$ lower than the expected value (7 μ_B). By extrapolation of the high field magnetisation to zero applied field we obtain the spontaneous magnetic moment $\mu_0=6.16\ \mu_B$.

The temperature dependences of the magnetisation at low magnetic field ($\mu_0 H=0.05$ T) are shown in Fig. 3. We measured

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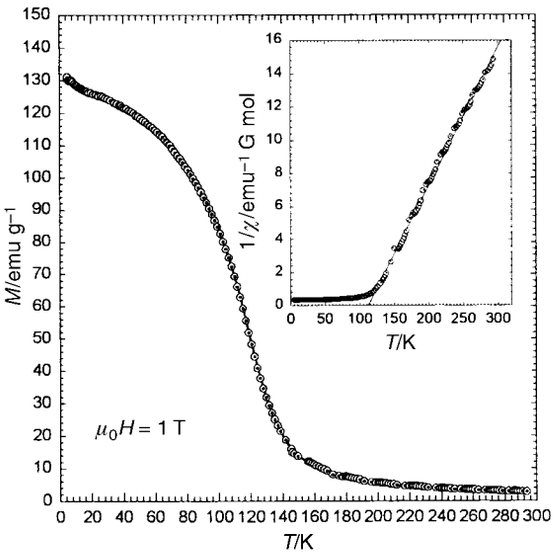

Fig. 1 Temperature dependence of magnetisation collected in a 1 Tesla field. In the inset the inverse of susceptibility is reported.

both the zero field cooled (ZFC) and the field cooled (FC) magnetisation curves with monotonically increasing temperatures. In the ZFC magnetisation the increase of the temperature supports the shift of the Bloch's walls which agree with the applied magnetic field, whereas in the FC branch the temperature rise has no particular effect on the Bloch's walls motion because the maximum order degree for that value of magnetic field has already been reached. This effect has been already reported by different authors.[10,11]

From the saturation magnetisation data no contribution of the iron atoms to the overall magnetisation was observed, therefore we could neglect the transition element–rare earth interactions and roughly estimate in the framework of the Molecular Field Theory the indirect exchange integral A_{ex} from the equation:[12]

$$\theta_p = \frac{2}{3}(g_J - 1)J(J+1)\frac{A_{ex}}{k_B}$$

where θ_p is the paramagnetic Curie temperature and g_J is the Landé factor. A_{ex}/k_B was found to be near 11 K.

3.2 Thermodynamic results

In Fig. 4 the total heat capacity of GdFeSi as a function of temperature at 0 and 9 T is shown. At $\mu_0 H = 0$ T we can notice a sharp peak corresponding to the ferromagnetic transition at

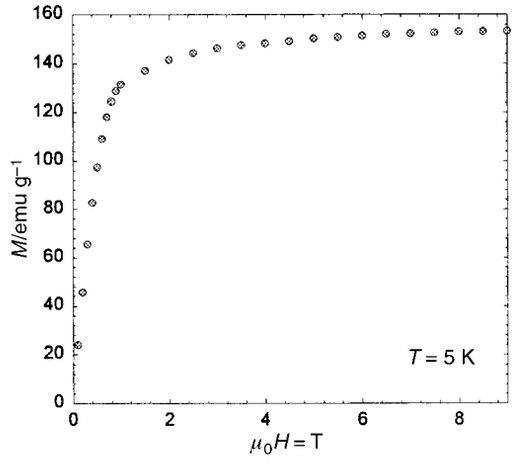

Fig. 2 Magnetisation as a function of field performed at 5 K and corrected by simple subtraction of the iron impurities contribution.

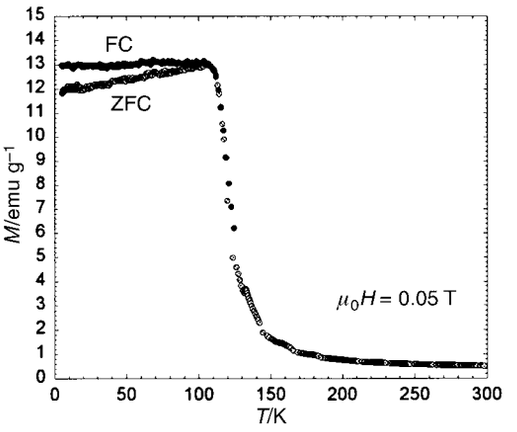

Fig. 3 Field cooled and zero field cooled thermomagnetic curves collected in an applied field of 0.05 T.

118 K which turns out to be quite different from the reported ordering temperature[5] (135 K). The mismatch between our data and the literature data may be related to the different methods employed to determine the Curie ordering temperature: in fact in ref. 5 the authors estimated the T_c value from the slope change in the thermomagnetic data while the error in the heat capacity data employed in this work may be considered not over 1%. The magnetic field application considerably broadens the peak as expected for ferromagnetic behaviour. In the inset of Fig. 4 the calculated entropy curves for the different values of applied magnetic field are reported, both of them are S shaped and increase monotonically up to 160 K. From these data the isoentropic adiabatic temperature rise ΔT_{ad} and the isothermal entropy change ΔS_{magn} were calculated (Fig. 5 and

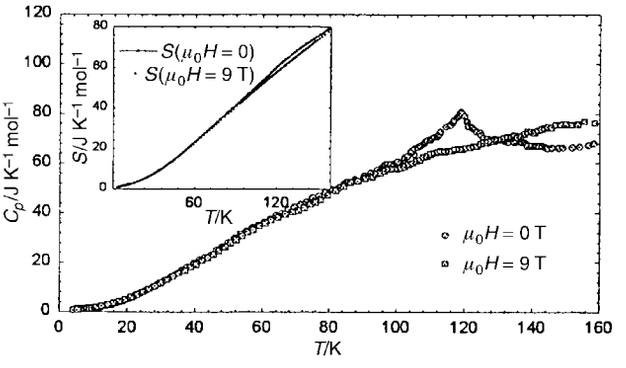

Fig. 4 Heat capacity data collected at zero and 9 T. In the inset calculated entropy curves are reported. The 9 T curve is the upper one.

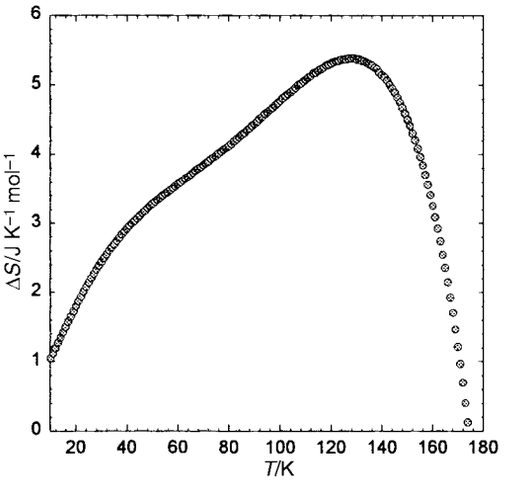

Fig. 5 Calculated entropy change and adiabatic temperature rise.

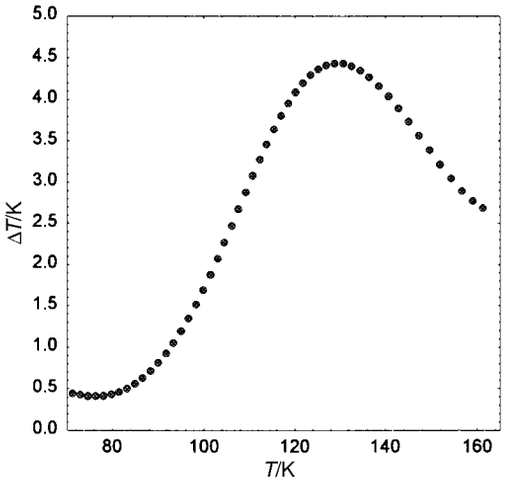

Fig. 6 Absolute temperature rise for an applied magnetic field of 9 T.

6). The entropy change and the adiabatic temperature rise maximum values were found to be 5.4 J K^{-1} mol^{-1} and 4.5 K respectively. Finally integrating ΔS_{magn} in the 10–160 K temperature range we obtained the value of the refrigerant capacity Q of the material: $Q = 1940$ J kg^{-1}. The value obtained may be compared with the values of: 780 J kg^{-1} in the compound[13] Gd_5Ge_4 (with an applied field of 5 T and in the temperature span 10–50 K), 610 J kg^{-1} in Gd_3Al_2 [14] (with an applied field of 5 T and in the temperature span 10–310 K) 610 J kg^{-1} in $GdAl_2$ [13] (with an applied field of 5 T and in the temperature span 130–185 K).

4 Conclusions

As a part of our current research for new materials for magnetic refrigeration and due to the lack of information related to the intermetallic compound GdFeSi we performed a complete magnetic and magnetocaloric characterisation of the ternary equiatomic phase. The interest in this particular compound is mainly related to the effective low cost of the constituents, which is a number one priority for a large-scale technical application of a material. From magnetisation and heat capacity measurements we have established that the ternary intermetallic compound GdFeSi undergoes a ferromagnetic transition at 118 K related to the ordering of the Gd sublattice. Moreover heat capacity measurements performed at zero and 9 Tesla allow us to obtain reliable magnetocaloric effects. Unfortunately the high magnetic field employed together with the large temperature span for the refrigerant capacity integration prevent any industrial applicability.

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