^{119}Sn Mössbauer study of the giant magnetocaloric compound: Gd_5Sn_4

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Abstract. Gd_5Sn_4 exhibits remarkably large transfered hyperfine fields at the two tin-sites (36.6 T and 29.4 T) at 12 K. The alloy undergoes a first-order structural change from a ferromagnetic to non-magnetic form at 82 K. The transition can be reversed by the application of a magnetic field indicating that the structural and magnetic properties of this system are intimately related.

Keywords: Tin, Gadolinium, Structure, Magnetocaloric effect

1. Introduction

The recent discovery of a giant magnetocaloric response in $Gd_5Si_2Ge_2$ [?] has revived interest in rare-earth/Si-group alloys. The structural [?] and zero-field magnetic [?] phase diagrams for $Gd_5Si_xGe_{4-x}$ have been published and $R_5Si_xGe_{4-x}$ ternary compounds with other rare-earths are being investigated [?].

In the $Gd_5Si_xGe_{4-x}$ giant magnetocaloric materials, the magnetic transition is accompanied by, or possibly driven by, a first order structural phase transition from orthorhombic to monoclinic [?]. It is crucial, therefore, to determine the structural as well as magnetic phase diagrams for these compounds. Unfortunately, the high absorption cross section of natural Gadolinium presents a severe barrier to neutron diffraction studies. We have therefore turned to Mössbauer spectroscopy as providing both magnetic and structural information on a local scale.

In this paper, we report the results of a combined high-field magnetisation and ^{119}Sn Mössbauer study of Gd_5Sn_4. Our motivation was twofold. First, if the Sn-based ternary 5:4 compounds exhibit the same giant magnetocaloric effect as the Si/Ge containing alloys, then they will do so at a lower temperature. This may permit a wider operating temperature range by combining several alloys. Second, one can use ^{119}Sn Mössbauer spectroscopy to investigate the magnetic and chemical environment of each crystallographically inequivalent Sn atom.

2. Experimental Methods

The sample was prepared in a tri-arc furnace using stoichiometric amounts of Gd (99.9%) and Sn (99.99%). The alloy was air-sensitive, tending to segregate into metallic tin and gadolinium oxide on exposure to air for a few hours. All sample handling was therefore performed under argon in a glove box.

Powder x-ray diffraction measurements were made using Cu K_α radiation. Magnetisation measurements were carried out on a commercial susceptometer/magnetometer in fields of up to 9 Tesla.

Mössbauer measurements were made on a constant-acceleration spectrometer using a 74 MBq ^{119m}Sn $BaSnO_3$ source and a vibration-isolated closed-cycle refrigerator. Spectra were fitted using a conventional non-linear least-squares minimisation routine. The spectrometer was calibrated against a 99.99% $\alpha-$Fe foil.

3. Results and Discussion

Cu K_α x-ray diffraction showed that the sample was single-phased, and that the alloy adopted the Pnma orthorhombic Sm_5Sn_4-type structure. AC susceptibility showed evidence for two magnetic transitions in Gd_5Sn_4. The largest change is associated with the event at 82 K, however there is also a weaker pedestal that disappears at 137 K. Such behaviour might suggest an impurity phase is present, however none was detected by x-ray diffraction. High-field magnetisation showed the alloy to be ferromagnetic at 5 K with an average Gd moment of $6.5\mu_B$.

The room temperature Mössbauer spectrum of Gd_5Sn_4 consists of a single sharp line at +1.9 mm/s, consistent with the alloy being single-phased. By contrast, the spectrum at 12 K is far more complex. Fig. **??**) shows that the 12 K pattern is dominated by two well-split magnetic sextets that account for about 70% of the total absorbed area. In addition, there is a singlet with an isomer shift of +2.4 mm/s. With these primary features subtracted, an additional component is visible. This could be fitted as the sum of two Gaussian distributions of hyperfine fields, and accounted for about 25% of the total area. The hyperfine fields at the tin sites in the two sharp sextets are remarkably large, being 29.4 T and 36.6 T. These fields are both larger than the 28 T reported for Gd_5Sn_3 [**?**]. The area ratio for these sites is 2.5:1, somewhat lower than the 3:1 ratio expected from the ($4c_2$ + 8d):($4c_1$) pairing derived from the structural analysis. However the field ratio (1.24:1) is very close to the 5:4 expected when the nearest Gd neighbours were counted.

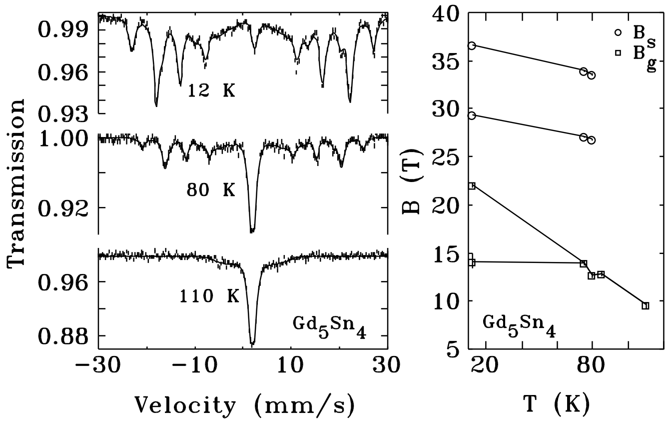

Figure 1. Left: ^{119}Sn Mössbauer spectra of Gd_5Sn_4. There is an abrupt transition to a non-magnetic state above 80 K as the sharp sextets disappear.
Right: Temperature dependence of the hyperfine fields for the sharp (B_s) and Gaussian-broadened (B_g) components. The sharp sextets are clearly lost above 80 K.

The temperature dependence of the spectra (Fig. **??**) provides clear evidence for a thermally driven change in structure. While the hyperfine field at each of the two sharp sextets changes only slowly on heating, their area declines rapidly, at the expense of the central feature. By 80 K, the two fields are 34 T and 27 T, however the area fraction of this component is down to 45%, and at 85 K it is gone entirely. The loss of the sharp magnetic component clearly corresponds to the main feature in the AC susceptibility data. Inspection of the spectrum at 110 K shows that a broad magnetic component with an average field of $\sim$13 T is still present and it is this contribution and its ultimate disappearance at 140 K that provides the pedestal in the AC susceptibility data. The progressive structural change evident on cooling explains why the sample can appear single-phased in RT x-ray diffraction, while exhibiting mixed-phase behaviour at 12 K.

The abrupt transition from a magnetically ordered form to a non-magnetic structure on heating is precisely the behaviour required for a giant magnetocaloric effect. In order to demonstrate that the magnetic and structural changes are coupled, we have made magnetisation measurements at temperatures just above the structural change to the non-magnetic form. As Fig. **??** shows, fields of a few Tesla are sufficient to reverse the change and restore a highly magnetic form. The field required to reverse the magnetic$\rightarrow$non-magnetic change increases rapidly with temperature, and by 110 K ($\sim$30 K above the zero-field transition temperature) a field of 8 Tesla is required to restore the magnetic state.

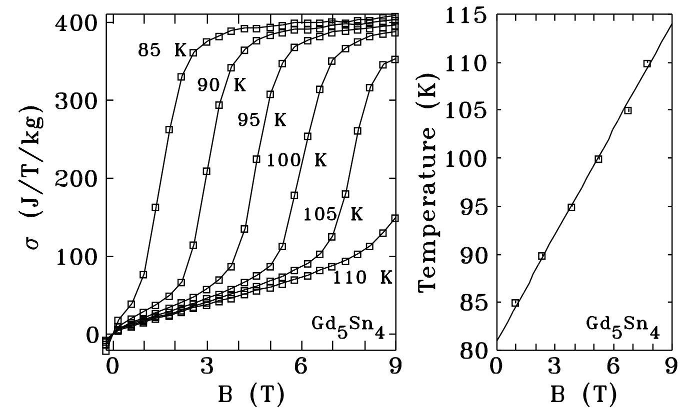

Figure 2. Left: Magnetisation curves for Gd_5Sn_4 at several temperatures above the structural transformation. The sample exhibits an abrupt transition back to a high-magnetisation state in an applied field. Right: Field dependence of the non-magnetic to magnetic transition temperature for Gd_5Sn_4.

4. Conclusions

^{119}Sn Mössbauer spectroscopy shows remarkably large transfered hyperfine fields at the Sn sites Gd_5Sn_4 at 12 K. The alloy exhibits a first-order structural change from a ferromagnetic to non-magnetic form at 82 K. The transition can be suppressed by the application of a magnetic field indicating that the structural and magnetic properties of this system are intimately related. The transition is expected to be associated with a giant magnetocaloric effect.

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