Investigation of Magnetocaloric Effects in Polycrystalline RNiAl$_4$ (R = Gd, Dy)

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Inverse magnetocaloric effects associated with magnetic transitions are observed for polycrystalline GdNiAl$_4$ and DyNiAl$_4$ via the analysis of magnetisation data. The overall behaviour is similar to that observed previously for single crystal TbNiAl$_4$, with DyNiAl$_4$ showing particular potential for magnetic cooling application because of its order-of-magnitude larger magnetic entropy change in polycrystalline form.

1. Introduction

The family of metamagnetic compounds RNiAl$_4$ (R = rare earth or Y) with orthorhombic structure (space group #63, *Cmcm*) exhibits a range of interesting magnetic behaviour. There are multiple magnetic phases as well as crystal field driven differences in behaviour for compounds containing different rare earth ions. TbNiAl$_4$ is an illustrative example. It has two phase transitions (three magnetic phases) as a function of temperature in low applied magnetic field. The Neél temperatures in zero applied magnetic field are $T_N \approx 34.0$ K and $T_{N'} \approx 28.0$ K, corresponding to phase transitions from paramagnetism to an incommensurate antiferromagnet (AF), and then to an *a*-axis aligned linear AF, respectively [1]. It also exhibits at least three magnetic phases as a function of applied magnetic field at low temperature. Coupled with the first of these magnetic field driven transitions is a large inverse (with respect to applied magnetic field) magneto-caloric effect (MCE) [2,3]. Recent neutron diffraction studies on single crystal TbNiAl$_4$, in applied magnetic fields, revealed the onset of a mixed magnetic structure including incommensurate AF order above the first field induced phase transition [4]. The inverse MCE in TbNiAl$_4$ is associated with this reordering.

There is a commonality of behaviour across this family of compounds and, in particular, multiple magnetic phases have already been observed for PrNiAl$_4$ [5], GdNiAl$_4$ [6] and DyNiAl$_4$ (this work). It is therefore reasonable to expect that MCE behaviour is not restricted to TbNiAl$_4$ and that other possibilities need to be explored. This was the motivation for the investigation of polycrystalline GdNiAl$_4$ and DyNiAl$_4$ that is reported in this paper. These particular compounds were targeted because of their large free ion R^{3+} moments and because, as for TbNiAl$_4$, they are known to exhibit multiple metamagnetic phase transitions. Magnetisation data are reported and used to estimate the magnetic entropy changes associated with isothermal field sweeps to various applied fields. The results are compared with those reported earlier for TbNiAl$_4$. DyNiAl$_4$ is found to exhibit the largest magnitude of entropy change in polycrystalline form.

2. Experimental details

The polycrystalline GdNiAl$_4$ and DyNiAl$_4$ specimens investigated in this work were synthesised by repeated argon arc melting of stoichiometric amounts of 99.9% pure rare earth plus 99.99% pure Ni and Al. The resulting ingots were wrapped in tantalum foil and annealed under vacuum at 1100 ºC for several days. All specimens were then checked for impurity phases using powder x-ray diffraction (XRD) and this was followed by further annealing as

required. A reference polycrystalline $TbNiAl_4$ sample was created by grinding single crystal (see [1]) off cuts. The powdered materials were then pressed into pellets for the magnetisation and heat capacity measurements. The magnetisation measurements were carried out using either a Quantum Design MPMS (Toyama) or a PPMS (Canberra) magnetometer. The instruments are capable of measurements down to 2 K and in applied magnetic fields up to 7 T (Toyama) or 9 T (Canberra). The specific heat of $DyNiAl_4$ was measured in zero applied magnetic field using the relaxation method on a PPMS (Toyama).

3. Results

3.1 Magnetic phase transitions for $DyNiAl_4$

The basic properties of $GdNiAl_4$ were investigated elsewhere using a suite of techniques [6] and the Néel temperatures in zero applied field were reported to be $T_N \approx 24.7$ K and $T_{N'} \approx 20.8$ K. In the case of $DyNiAl_4$ such information was not available and new measurements were carried out. Based on specific heat data recorded in zero applied field, $DyNiAl_4$ undergoes magnetic transitions at $T_N \approx 18$ K and $T_{N'} \approx 15$ K, as shown in Fig. 1(a). Because of strong anisotropy effects, it is not ideal to use a polycrystalline sample for investigations of the field dependence of the low temperature magnetisation. Nevertheless, the results shown in Fig. 1(b) fall into ranges of applied field with three distinct slopes. This is indicative of two metamagnetic transitions in the experimentally accessible range of applied field.
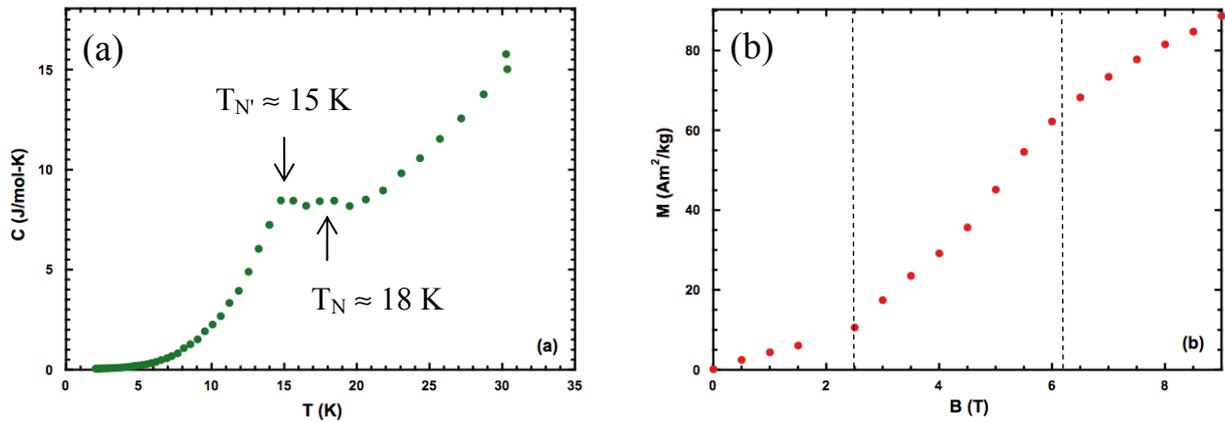

Fig. 1. Bulk measurements for polycrystalline $DyNiAl_4$ (a) Specific heat in zero applied field
(b) Mass magnetisation as a function of applied field at 2 K (the vertical dashed lines provide an indication of the boundaries between the ranges of field where the results have distinct slopes).

3.2. Magnitude of the magneto-caloric (MCE) effect

For each of the specimens, the experimental magnetisation (M) was recorded as a function of increasing applied field (H) for a set of constant temperatures close to the phase transitions. The changes in magnetic entropy ΔS_m, with the field increased from $H_1 = 0$ to $H_2 = \Delta H$, were then determined via calculation using the Maxwell relation

$$\Delta S_m(T, \Delta H) = \int_{H_1}^{H_2} \left(\frac{\partial M(H,T)}{\partial T} \right)_H dH$$
$$\approx \frac{1}{\delta T} \left[\int_{H_1}^{H_2} M(T + \delta T, H) dH - \int_{H_1}^{H_2} M(T, H) dH \right]$$

(1)

and plotted as a function of temperature for each of the H values.

TbNiAl₄ (polycrystalline compared with single-crystal)

In order to provide a useful reference for the current polycrystalline specimen measurements, results were first recorded for polycrystalline TbNiAl₄ (Fig. 2(a)) and compared with the results published previously for single-crystal TbNiAl₄ [2] (Fig. 2(b)). Note that, in the single crystal case, only *H* parallel to the *a*-axis is important. Because of the TbNiAl₄'s strong magnetic anisotropy it is only for this particular magnetic field alignment that significant magnetic entropy change is associated with magnetic phase transitions. The changes in magnetic entropy ΔS_m for polycrystalline TbNiAl₄ (Fig. 2(a)) have a similar overall temperature dependence but the magnitudes are much smaller (typically 20 – 30 times smaller) than those observed for the single crystal (Fig. 2(b)). The regions of positive entropy change (associated with the change of phase) below and near the zero field phase transition temperatures are also less prominent in the polycrystalline case. These differences are expected since the majority of the randomly-orientated grains will experience an applied field directed away from the key *a*-axis.
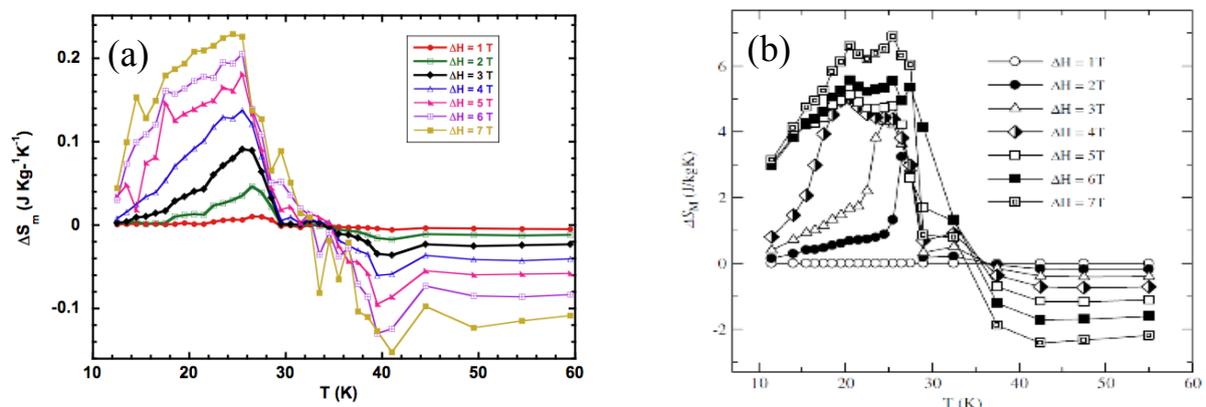

Fig. 2. Magnetic entropy changes ΔS_M for TbNiAl₄ as a function of temperature
(a) for a polycrystalline sample with cumulative applied fields up to 9 T, and
(b) for a single-crystal sample with cumulative applied fields up to 7 T aligned with the *a*-axis [2].

GdNiAl₄ and DyNiAl₄ (polycrystalline)

Again, the entropy change curves for polycrystalline GdNiAl₄ (Fig. 3(a)) and DyNiAl₄ (Fig. 3(b)) have similarly-shaped temperature distributions. The entropy change magnitude for GdNiAl₄ is typically only slightly larger than for the polycrystalline TbNiAl₄ and, as expected for the lower Neél temperatures, it peaks over a narrower temperature range. In contrast, the peak entropy changes for polycrystalline DyNiAl₄ are comparable with those observed for
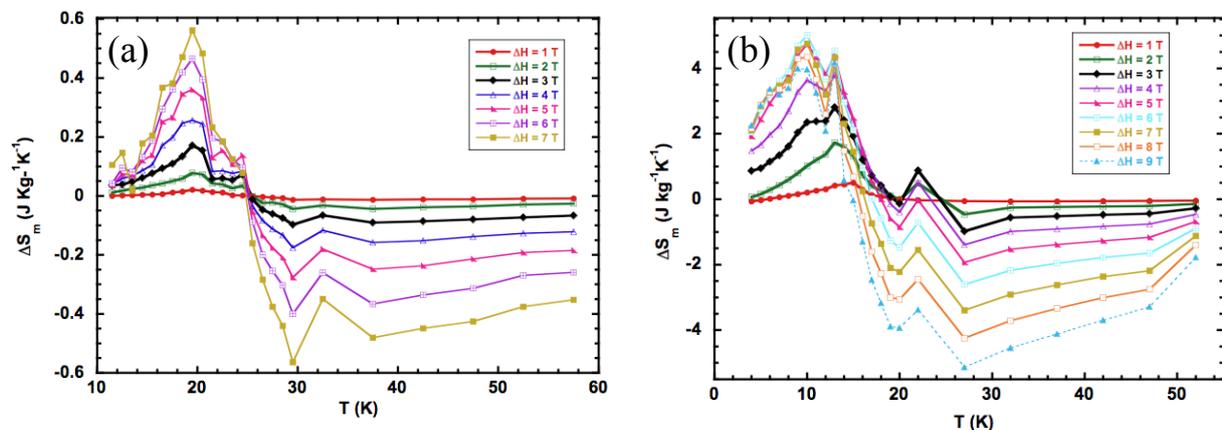

Fig. 3. Magnetic entropy changes ΔS_M as a function of temperature for polycrystalline samples of
(a) GdNiAl₄ with cumulative applied fields up to 7 T, and (b) DyNiAl₄ with cumulative applied fields up to 9 T.

single-crystal TbNiAl$_4$, even though they occur in the even lower temperature range of 12 to 15 K. This much larger entropy change for the polycrystalline Dy compound is unexpected and is suggestive of comparatively weaker magnetic anisotropy.

4.   Discussion

An initial result of this paper is the observation, via specific heat data, of evidence for the presence of an intermediate magnetic phase for DyNiAl$_4$, where the trivalent Dy^{3+} ion is a Kramers ion. Although this is a characteristic common across some other RNiAl$_4$ such as the Pr-, Tb- and Gd-based compounds, intermediate phases are not observed for several Kramers ion based alloys, including NdNiAl$_4$ [5] and ErNiAl$_4$ [7].

In the main body of the work, the inverse MCE associated with a field driven phase transition for several RNiAl$_4$ compounds was explored. Previous work had shown that single crystal TbNiAl$_4$ has a significant inverse MCE with magnetic fields applied along the *a* axis. Here these single crystal results were compared, firstly, with those for chemically identical polycrystalline material to validate the use of the latter type of sample for additional observations. Following on from this, the comparison is extended to magnetic entropy results, based on experimental magnetisation data, for polycrystalline GdNiAl$_4$ and DyNiAl$_4$. In particular, the Dy case shows large entropy changes, with a polycrystalline sample almost matching ΔS_m magnitudes of the single crystal TbNiAl$_4$. Interpretation of such results for polycrystalline materials requires due consideration of both the intrinsic (dominant easy axis) magnetic properties of a material as well as the magnetic anisotropy. Nevertheless, our results are somewhat surprising, given that the lower ordering temperature for DyNiAl$_4$ is indicative of a weaker R-R exchange interaction and conventional wisdom would suggest that the Gd based compound should be subject to much less crystal field driven magnetic anisotropy. Development of a working set of crystal field parameters for the RNiAl$_4$ is under way and should assist in the search for an explanation of these puzzling observations.

References

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