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Successive magnetic transitions and low temperature magnetocaloric effect in RE_2Ni_7 (RE=Dy, Ho)

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ABSTRACT

Magnetic properties of rare-earth intermetallics RE_2Ni_7 (RE=Dy, Ho) are reported. Both the samples undergo two successive magnetic transitions at T_h (paramagnetic to ferromagnetic) and T_l (spin reorientation) below 100 K. The transitions are found to be second order in nature as evident from the Arrot plot analysis. Large reversible magnetocaloric effect (MCE) was observed at low temperature in the studied samples. The maximum value of the magnetic entropy change in Ho_2Ni_7 is found to be -12.5 J/kg K (for 0 to 50 kOe of field change) around 25 K with a high relative cooling power (RCP) of 534 J/kg. The Dy counterpart also shows moderately large values of MCE (-7.3 J/kg K) and RCP (475 J/kg) around the magnetic transition region for similar change in the magnetic field. RE_2Ni_7 compounds can be promising materials for magnetic refrigeration in the temperature range of helium and hydrogen liquefaction.

1. Introduction

The magnetocaloric effect (MCE) of a material is generally defined by the isothermal entropy change ΔS_M and the adiabatic temperature change ΔT_M upon the variation of the applied magnetic field (H) and it is key to the magnetic cooling technique. In a spin system, isothermal application of H causes a decrease in entropy and subsequent adiabatic demagnetization allows the spins to become disordered again by means of thermal energy provided by the sample, which causes cooling. In certain materials, H can induce first order structural transition, where both magnetic and lattice entropy may be involved in the whole process. Consequently, ΔS_M (and hence ΔT_M) is considerably large around such magneto-structural transition. A variety of rare earth (RE) based compounds with giant magnetic entropy changes have been observed near the first order phase transition (FOPT), such as, RCo_2 (R=Er, Ho, and Dy) [1,2], $Gd_5Si_2Ge_2$ [3], $La(Fe_{1-x}Si_x)_{13}$ and their hydrates [4].

The MCE obtained from FOPT has some inherent problems related to the irreversibility and cycling effect. The window of the operating temperature is also considerably narrow in case of FOPT. In contrast, the entropy change near the second order phase transition (SOPT) is free from all these drawbacks. However, an SOPT is generally involved only with the magnetic entropy, and hence ΔS_M can be lower than that of an FOPT. Continuing efforts are going on to identify materials which can be useful with high value of MCE near an SOPT. Room-temperature magnetic refrigerators have been found to be a good alternative to conventional vapour-cycled refrigeration because they are efficient and environmental friendly. In addition, there are efforts to achieve magnetic cooling procedure to obtain very low temperature (T) [5–9], which has immense practical applications in the field of hydrogen and helium liquefaction [10,11].

In the present work, we focus on RE-transition metal (TM) intermetallic compounds, Dy_2Ni_7 and Ho_2Ni_7, which exhibit large ΔS_M at low-T. RE_2Ni_7 (RE=rare-earth) crystallize in the rhombohedral structure [12] with space group $R\bar{3}m$. In this series, Y_2Ni_7 is the most well studied sample showing weak ferromagnetic ground state. The other magnetic RE compounds (RE=Nd, Gd, Tb, Dy, Ho, Er) show ferromagnetic (FM) ground state with Curie temperature (T_C) around 100 K [13,14]. The magnetic properties of RE intermetallics are primarily governed by the Ruderman–Kittel–Kasuya–Yosida (RKKY) [15] type exchange interaction and magnetocrystalline effects [16], which can together give rise to fascinating magnetic ground states. The magnetism in RE_2Ni_7 is interesting due to the presence of Ni atoms with partially filled 3d orbital in addition to the 4f moment.

2. Experimental details

The polycrystalline compounds RE_2Ni_7 (for RE=Dy and Ho) were prepared by argon arc melting the constituent elements (purity better than 99.9 wt%) followed by annealing at 1000 °C for 500 h in evacuated quartz tube. The powder X-ray diffraction

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(XRD) patterns were collected on a Bruker AXS diffrcatometer using Cu K_α radiation. The collected patterns were used for phase identification using the GSAS software package [17]. Rietveld refinement data along with the XRD patterns of these compounds are shown in Figs. 1(a) and (b) and the crystallographic data (a, b, c, V) obtained from the refinement of RE_2Ni_7 compounds are depicted in Table 1. The refinements show good convergence for both the samples with acceptable reliability parameters (R_{WP}, R_P) and goodness of fit (χ^2_{FIT}). It confirms that the samples were formed in single phase with rhombohedral Gd_2Co_7 type crystal structure. The calculated lattice parameters match well with the previously reported data [12].

Magnetization (M) for the present investigation was measured using quantum design SQUID magnetometer (MPMS XL, Evercool model) on bulk polycrystalline sample. The T dependence of M for both the samples was measured in 2 kOe of field during heating (between 4 and 300 K) after the samples had been zero field cooled (ZFC) to the lowest temperature (4 K). The isothermal M–H curves were recorded at constant temperatures with the samples in the ZFC condition.

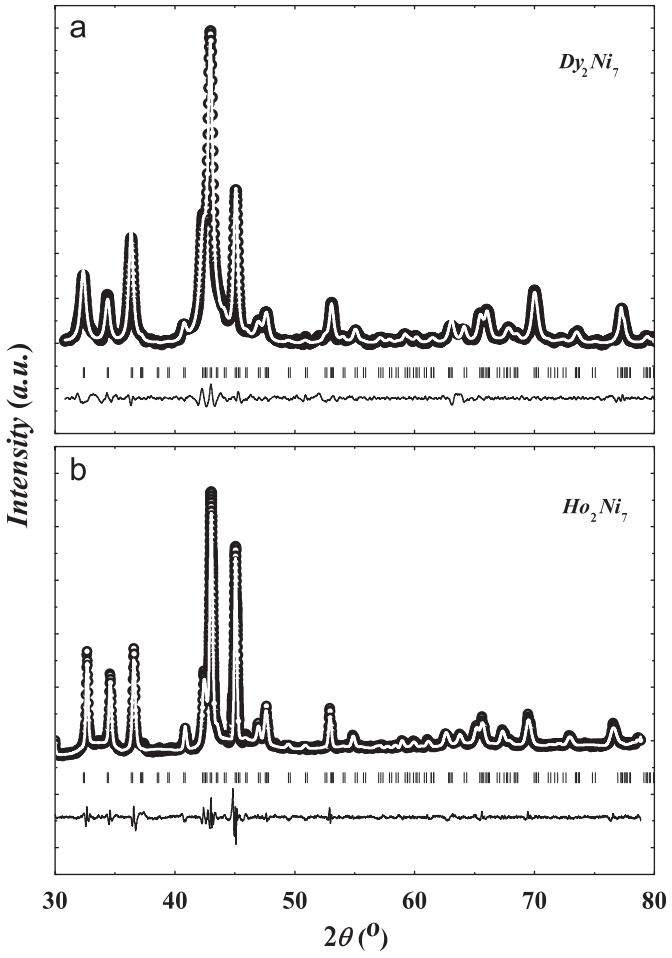

Fig. 1. (a) and (b) show X-ray powder diffraction patterns of RE_2Ni_7 (RE=Dy, Ho) compounds. Open circles (black) represent observed data and the lines (white) drawn through the data points correspond to the fitted Rietveld patterns. The difference between experimental and the fitted patterns is shown at the bottom of each plot by continuous lines. The upper set of vertical bars represents calculated positions of Bragg peaks of the rhombohedral Gd_2Co_7 type structure.

Table 1
Rietveld refinement data and fitting parameters of RE_2Ni_7 (for RE=Dy and Ho) compounds (rhombohedral Gd_2Co_7 type structure with space group: $R\bar{3}m$). R_{WP} and R_P are the reliability factors and χ^2_{FIT} is the goodness of fit.

	a (Å)	c (Å)	V (Å)	R_{WP}	R_P	χ^2_{FIT}
Dy_2Ni_7	4.935	36.223	764.054	0.1022	0.0647	2.06
Ho_2Ni_7	4.998	36.658	793.361	0.0506	0.0324	1.41

3. Results

3.1. Magnetic susceptibility

The T variation of the dc magnetic susceptibility ($\chi = M/H$) for Dy and Ho compounds are shown respectively in Figs. 2(a) and (b). Both the samples show upturn below about 100 K signifying the development of magnetic order in the system. The insets of Figs. 2(a) and (b) show the T derivative of χ where two distinct transitions are visible (at T_h and T_l respectively) for both the samples. In Dy_2Ni_7, the high temperature transition T_h is found to be at 80 K, while in Ho_2Ni_7, T_h=68 K. On the other hand, the lower transition T_l is found to be 35 K and 25 K for the Dy and Ho compounds respectively. Such multiple magnetic transitions in RE-intermetallics is not uncommon, particularly for systems containing heavy RE elements, where magneto-crystalline anisotropy can play a major role in stabilizing the magnetic structure. We measured T variation of χ in the heating and cooling protocols, however no thermal hysteresis is observed. The resistivity data (not shown here) also do not show any hysteresis. The result indicates that the transitions at T_l and T_h are presumably second order in nature.

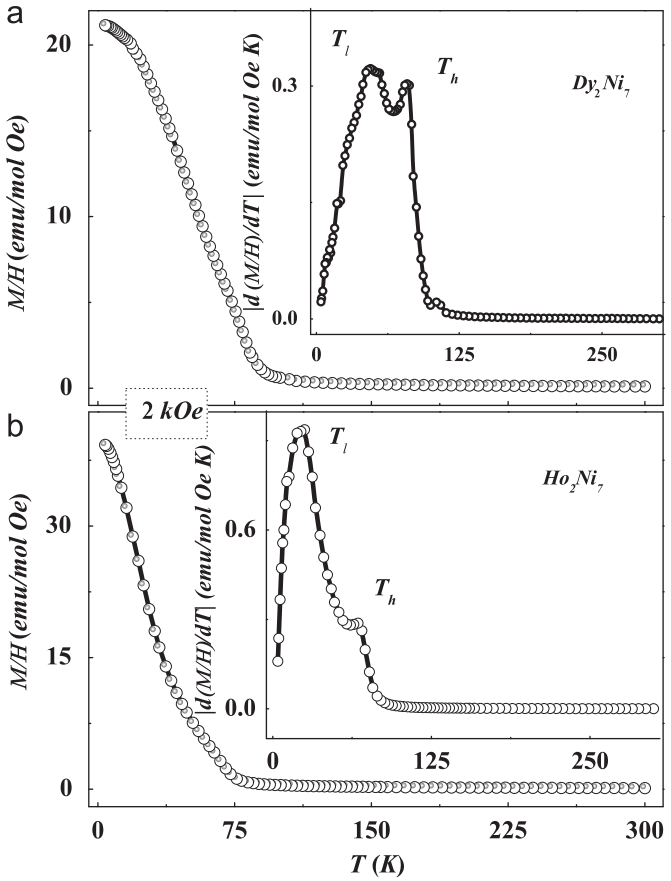

Fig. 2. (a) and (b) represent temperature dependence of dc-susceptibility $\chi(T)$ for an applied field of 2 kOe in the zero field cooled condition for Dy_2Ni_7 and Ho_2Ni_7 respectively. Insets show first derivative of $\chi(T)$ with respect to temperature.