Magnetic Properties and Magnetocaloric Effect in Layered $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$

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Abstract. The structural and magnetic properties of the compounds $\text{NdMn}_{2-x}\text{V}_x\text{Si}_2$ have been studied by x-ray and high resolution neutron powder diffraction, specific heat, dc magnetization, and differential scanning calorimetry measurements over the temperature range 3-450 K. The Curie temperature and Néel temperature of layered $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ are indicated at $T_C \sim 24$ K and $T_N \sim 376$ K respectively. The giant magnetocaloric effect (GMCE) around T_C is found in layered $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ associated with first order magnetic transition from antiferromagnetic [AFil-type] to ferromagnetic [F(Nd)+Fmc]. This behavior has been confirmed as contribution of the magnetostructural coupling by using neutron powder diffraction. The magnetic entropy change $-\Delta S_M \sim 25.4 \text{ J kg}^{-1} \text{ K}^{-1}$ and adiabatic temperature change $\Delta T_{ad} \sim 6.7$ K have been determined using magnetization and specific heat measurement under 0-8 T field applied. This compound belongs with the small thermal ~ 0.8 K and magnetic ~ 0.1 T hysteresis characteristic providing high potential material for magnetic refrigerator.

1 Introduction

The study of the magnetocaloric effect (MCE) has become an interesting area of research in the field of magnetic materials, with increasing prospects as the basis of magnetic cooling to replace conventional refrigeration [1-4]. Magnetic materials with large MCE have been extensively studied experimentally and theoretically; the first order magnetic phase transition is accompanied by large thermal and field hysteresis in the temperature and magnetic field dependent magnetization. This behavior limits their usage in practical applications. The research objective in probing suitable new materials is to find a large MCE that is free from any hysteresis. Such compounds need further investigation, and it is really important to understand their basic properties which contribute to the large MCE.

The ternary intermetallic compounds of the RT_2X_2 (R = rare earth, T = transition metal, X = Si or Ge) family have attracted considerable attention due to their rich variety of interesting phenomena, including superconductivity, magnetism, mixed valence, heavy fermions, and Kondo behavior [5]. The RT_2X_2 compound form in the ThCr_2Si_2 structure (space group $I4/mmm$), and the naturally layered nature of this crystal structure leads to an extreme sensitivity of the magnetic order to the interatomic distances.

Here, we present a detailed investigation of the influence of replacing Mn atoms by V atoms on the magnetic structure and magnetic phase transition in $\text{NdMn}_{2-x}\text{V}_x\text{Si}_2$ compounds ($\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$). The main interest is to explore the effects of replacing Mn atoms of atomic radius $r(\text{Mn}) = 1.27 \text{ \AA}$ and electronic configuration Mn ($3d^5 4s^2$) with larger V atoms of atomic radius $r(\text{V}) = 1.34 \text{ \AA}$ and electron configuration V ($3d^3 4s^2$). In the case of $\text{NdMn}_{2-x}\text{Co}_x\text{Si}_2$ [6] for example, replacement of Mn by the smaller Co atoms, $r(\text{Co}) = 1.25 \text{ \AA}$ of electronic configuration Co ($3d^7 4s^2$), leads to a decrease in magnetic entropy change from $\sim 14.4 \text{ J kg}^{-1} \text{ K}^{-1}$ with $x=0.2$ to $12.4 \text{ J kg}^{-1} \text{ K}^{-1}$ with $x=0.4$ ($\Delta B = 0-5 \text{ T}$) but the Curie temperature $T_C \sim 45 \text{ K}$ does not change with ($x=0.2, 0.4, 0.8$ and 1). In this study, we will investigate the effects of V substitution for Mn in NdMn_2Si_2 compound on the structural and magnetic properties which are expected to increase the distance between magnetic atoms, thus modifying the magnetic states of both the Nd and the Mn sublattices.

2 Experimental

The layered $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ were prepared by arc melting and then annealed at 900°C for one week in an evacuated quartz tube to improve crystallization of the sample [7], and then quenched into water. The crystal structure of the

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samples were checked by room temperature powder x-ray diffraction (XRD) measurements using $\text{CuK}\alpha_1$ radiation with the diffraction patterns refined using the Fullprof software package [8]. The magnetic behavior and transitions were investigated by superconducting quantum interference device (10–300 K) and differential scanning calorimetry (DSC) (300–450 K) measurements.

3 Result and discussion

Fig. 1. X-ray diffraction of $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ compound at room temperature respectively.

The room temperature x-ray diffraction (XRD) data in figure 1 shown that layered $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ crystallize in the ThCr_2Si_2 type structure with space group $I4/mmm$ [9]. The measured data from the diffraction patterns were analysed using the Rietveld refinement technique [8], indicating substitution of V for Mn does not change the crystal structure but leads to an expansion of the unit cell compared with pure NdMn_2Si_2 [22, 28]. The lattice constants $a = 4.0056 \text{ \AA}$ and $c = 10.542 \text{ \AA}$, and correspondingly the unit cell volumes $V = 169.1446 \text{ \AA}^3$, were found to increase with the V content consistent with the larger atomic radius of V compared to Mn.

3.1. Magnetic studies

The temperature dependence of the magnetization of $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ measured in a magnetic field of $B = 0.01 \text{ T}$ over the temperature range $\sim 10\text{--}300 \text{ K}$ is shown in figure 2 together with the differential scanning calorimetry (DSC) curves over the temperature range $\sim 300\text{--}450 \text{ K}$. The values of the Néel temperature $T_N \sim 376 \text{ K}$ and the Curie temperature $T_C \sim 24 \text{ K}$ for the compound as defined by $1/M$ versus temperature and the maxima of the dM/dT versus temperature graphs respectively. For the DSC measurements, the phase transition temperatures were determined by the maxima of the DSC signals (see figure 1). Comparison of results obtained under otherwise identical conditions for cooling and warming revealed the thermal hysteresis $\Delta T \sim 0.8 \text{ K}$. On the other hand, substitution V concentration is also expected to weaken the exchange interactions of Mn-Mn between layers and the Mn-Nd due to the magnetic dilution effect. Moreover, the change in electronic environment on replacing Mn

Fig. 2. Temperature dependence of magnetization of $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ as measured in a field of 0.01 T (left axis; red open symbols for zero field cooling, FC, and blue symbol for field cooling, ZFC); and differential scanning calorimetry measurements for the temperature range $300\text{--}450 \text{ K}$ with value of T_C and T_N (inset).

($3d^5 4s^2$) by V ($3d^3 4s^2$) is also expected to influence the magnetic structures and states of the $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ compounds. This is supported by Density Functional Theory calculations for RMn_2Ge_2 ($R = \text{Y}$ or Ca) compounds [10] which indicate that to a large extent, the magnetic moment is determined mainly by the interatomic Mn-Mn distances, while the interstitial electron density contributes to the change in magnetic structures as been confirmed by neutron diffraction analysis.

Fig. 3. (a) Isothermal magnetization curves in the vicinity of the ferromagnetic ordering temperatures for $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ ($T_C = 24 \text{ K}$ with $B = 0\text{--}8 \text{ T}$) as closed symbol for increase and open symbols for decrease field applied; and (b) Arrott plots of M^2 versus B/M for the set of $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ compound.

The magnetization curves obtained for $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ for fields in the range $B = 0\text{--}8 \text{ T}$ around their ferromagnetic ordering temperatures are shown in figures 3, respectively. These data were obtained for increasing and decreasing fields at 2 K intervals spanning

a range of about 24 K around T_C , thus providing information about magnetic hysteresis $\Delta B \sim 0.1$ T. These phenomena demonstrated clearly that magnetic hysteresis decrease significantly on substitution of V for Mn as V concentration contributes to a weakening of the characteristic field induced metamagnetic transition from the antiferromagnetic to the ferromagnetic state. Basically, giant MCE values and magnetic entropy changes are usually obtained with a first order magnetic transition due to a large rate of change of magnetisation compared with materials that exhibit a second order transition. Figures 3(b) show the corresponding Arrott plots (M^2 versus B/M) for the $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ sample respectively. The Arrott plots are found to exhibit features characteristic of a first order transition for all of the samples. In particular the S-shaped nature of the Arrott plot near T_C denotes a negative order of the sign of the coefficient $c_2(T)$ in the Landau expansion of the magnetic free energy [11], thereby denoting a first order magnetic transition.

3.2. Magnetic entropy; magnetocaloric effect

The magnetic entropy change, $-\Delta S_M$, has been determined for the $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ compound from the magnetization curves for both increasing and decreasing field values as functions of temperature and magnetic field ($\Delta B = 0-5$ T). The magnetic entropy change has been derived by applying the standard Maxwell relation [12]:

$$-\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH. \quad (1)$$

As shown by the curves of figure 4, the $-\Delta S_M$ peak (closed symbols for increasing field values and open symbols for decreasing field values) gradually broadens towards higher temperatures with increasing magnetic field (from $\Delta B = 0-8$ T), behaviour characteristic of a field induced transition from an antiferromagnetic to a ferromagnetic state. The changes in magnetic entropy for the $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ compound ferromagnetic ordering temperatures are indicated in this paper as calculated from decreasing applied fields in order to satisfy the suitability of different experimental and related analytical approaches to establish the isothermal entropy change [13].

The entropy values at the respective Curie temperatures are: $-\Delta S_M \sim 25.4 \text{ J kg}^{-1} \text{ K}^{-1}$ ($\Delta B = 0-8$ T); $-\Delta S_M \sim 21.4 \text{ J kg}^{-1} \text{ K}^{-1}$ ($\Delta B = 0-5$ T); $-\Delta S_M \sim 13.8 \text{ J kg}^{-1} \text{ K}^{-1}$ ($\Delta B = 0-2$ T) at $T_C = 24$ K respectively. Never the less it is noted that the MCE values of $-\Delta S_M \sim 21.4 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ at 0-5 T applied field is higher than with MCE values for other materials with small hysteresis that exhibit transitions in the temperature region below 100 K. These materials include: TbCoC_2 [14] ($-\Delta S_M = 15 \text{ J kg}^{-1} \text{ K}^{-1}$ at 28K), GdCoAl [15] ($-\Delta S_M = 10.4 \text{ J kg}^{-1} \text{ K}^{-1}$ at 100K) and TbCoAl [15] ($-\Delta S_M = 10.5 \text{ J kg}^{-1} \text{ K}^{-1}$ at 70K), all of which - in common with $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ - importantly very small field hysteresis losses.

Fig. 4. The temperature dependence of the isothermal magnetic entropy change, $-\Delta S_M$, for $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ as determined from the magnetization isotherms for $\Delta B = 0-1$ T, $\Delta B = 0-2$ T, $\Delta B = 0-3$ T, $\Delta B = 0-4$ T, $\Delta B = 0-5$ T, $\Delta B = 0-6$ T, $\Delta B = 0-7$ T and $\Delta B = 0-8$ T.

The magnetic entropy change, $-\Delta S_M(T, B)$ has also been derived from heat calorimetric measurements of the field dependence of the heat capacity using the expression [2, 16, 17]:

$$-\Delta S_M(T, B) = \int_0^T \left(\frac{C(T, B) - C(T, 0)}{T} \right) dT \quad (2)$$

where $C(T, B)$ and $C(T, 0)$ are the values of the heat capacity measured in field B and zero field, respectively. The corresponding adiabatic temperature change, ΔT_{ad} can be evaluated from $-\Delta S_M(T, B)$ and the zero field heat capacity data as:

$$\Delta T_{ad}(T, B) = \int_0^B \frac{T}{C_{B,P}} \left(\frac{\partial M}{\partial T} \right)_B dB \quad (3)$$

Figure 5(a) shows the set of heat capacity measurement obtained for $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ with $B = 0, 2, 5$ and 8 T. The corresponding $-\Delta S_M(T, B)$ values for $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ are shown in figure 5(b) with the ΔT_{ad} values shown in figure 5(c). The peak value of the adiabatic temperature change is $\Delta T_{ad}^{max} \sim 6.7$ K for $\Delta B = 0-8$ T. As shown in figure 5(b), the maximum magnetic entropy change for $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ as determined from the heat capacity measurements of $-\Delta S_M^{max} \sim 24.7 \text{ J kg}^{-1} \text{ K}^{-1}$ and $19.4 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\Delta B = 0-8$ T and $0-5$ T are comparable to the maximum entropy change $-\Delta S_M^{max} \sim 25.4 \text{ J kg}^{-1} \text{ K}^{-1}$ and $21.4 \text{ J kg}^{-1} \text{ K}^{-1}$ as determined from the magnetization measurements using the Maxwell relation. The good agreement between the two sets of measurements confirms that the $-\Delta S_M$ values derived for $\text{NdMn}_{1.9}\text{V}_{0.1}\text{Si}_2$ from the magnetization measurements represent the MCE behaviour within experimental errors [18-20].

The relative cooling power (RCP) is an important parameter of the magnetocaloric material, providing an accepted criterion to evaluate the refrigeration efficiency in practical application. The RCP is used to evaluate the cooling power of magnetic refrigerants by measuring how much heat can be transferred between two

Fig. 5.(a) The heat capacity of NdMn_{1.9}V_{0.1}Si₂ as measured over the temperature range 10-80 K in magnetic fields B = 0 T, 2 T, 5 T and 8 T; (b) The magnetic entropy change, $-\Delta S_M$, determined from the heat capacity measurements of figure 5(a) for NdMn_{1.9}V_{0.1}Si₂ ($\Delta B = 0-2$ T, $\Delta B = 0-5$ T and $\Delta B = 0-8$ T). (c) The adiabatic temperature change, ΔT_{ad} , for NdMn_{1.9}V_{0.1}Si₂ as determined from the heat capacity.

temperatures (low and high in temperature span range) in one ideal refrigeration cycle. The RCP is defined similar to previous study[21]:

$$RCP = -\Delta S_M^{max} \delta T^{FWHM}. \quad (4)$$

$-\Delta S_M^{max}$ denotes the maximum entropy change and δT represents the full width at half maximum (FWHM) of the temperature dependence of the magnetic entropy change $-\Delta S_M$. It was found that the RCP for NdMn_{1.9}V_{0.1}Si₂ are ~ 204 J kg⁻¹ for $\Delta B = 0-8$ T; ~ 130 J kg⁻¹ for $\Delta B = 0-5$ T and ~ 50 J kg⁻¹ for $\Delta B = 0-2$ T respectively.

4 Conclusions

A systematic investigation of the structural and magnetic characteristics of NdMn_{1.9}V_{0.1}Si₂ compound has been carried out. Substitution of V for Mn leads to decreases in the Curie temperature and the Néel temperature from $T_C \sim 36$ K and $T_N \sim 380$ K for NdMn₂Si₂ to $T_C \sim 24$ K and $T_N \sim 376$ K. A metamagnetic transition from the antiferromagnetic (AFil-type) to the ferromagnetic state due to the application of magnetic field was observed above T_C for NdMn_{1.9}V_{0.1}Si₂. Substitution of Mn by V slightly leads to a reduction of the magnetic entropy change. However, analysis of the magnetisation data demonstrates that the first order magnetic transition of NdMn₂Si₂ around T_C remains unchanged on replacement of Mn by V, and this substitution leads to significant reduction in thermal and magnetic hysteresis providing promising material for magnetic refrigerator.

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