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Enhancement of magnetocaloric effect in V doped intermetallic compounds $Nd(Co_{1-x}V_x)_2Si_2$ (x=0, 0.20 and 0.35)

R. Roy Chowdhury, S. Dhara[1], B. Bandyopadhyay*

Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700064, India

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ABSTRACT

We report a large enhancement of magnetocaloric entropy change in vanadium substituted intermetallic compounds $Nd(Co_{1-x}V_x)_2Si_2$ (x = 0.20 and 0.35). The antiferromagnetic parent compound $NdCo_2Si_2$ exhibits inverse magnetocaloric response. Upon vanadium doping, antiferromagnetic transition is gradually suppressed and there is a drastic modification of the ground state, with appearance of ferromagnetism in $Nd(Co_{0.65}V_{0.35})_2Si_2$. Such modifications are reflected in the magnetocaloric properties of the parent and the doped compounds. In comparison to the inverse magnetocaloric response of the parent compound, the doped compound with x = 0.35 shows a conventional magnetocaloric effect that is large in magnitude compared to the parent compound. A table-like MCE in a wide-temperature range of 5–60 K have been observed in $Nd(Co_{0.65}V_{0.35})_2Si_2$. The present study demonstrates enhancement of magnetic entropy by way of substitution at the transition metal site in these compounds.

1. Introduction

Magnetocaloric effect (MCE) is broadly defined as the isothermal entropy change or adiabatic temperature change of a material due to the application of external magnetic field. The observation of large MCE in Gd and Gd based compounds strengthened the idea of achieving magnetic refrigeration utilizing magnetocaloric effect as a substitution of conventional gas compression cooling technologies [1]. Thereafter started the research for new materials as well as new routes to enhance magnetocaloric response in a wide variety of intermetallic compounds [2–10]. Rare-earth based intermetallics, *viz*., TmZn, TmZnAl, TmAgAl, TmCoAl, Dy_2Cu_2Cd, Tm_2Cu_2Cd, Ho_2Cu_2Cd, $YbPt_2Sn_2$ have been investigated extensively for low temperature magnetic refrigeration and exciting magnetocaloric properties [11–17]. Materials exhibiting significant magnetocaloric effect near room temperature are important from technological point of view [18].

Apart from technological importance, investigations on MCE focussing on fundamental aspects provide vital information concerning the magnetic ground state as well as its modification due to perturbative effects, namely, magnetic field, external hydrostatic pressure, intrinsic chemical pressure, etc. [5,19]. The RET_2X_2 (*RE*=rare earth, T=transition metal and X = Si/Ge) compounds exhibit interesting magnetic properties and they have been extensively studied since last several years from the fundamental as well as technological perspectives [20–23]. In these so-called '122' series compounds, the atoms are arranged in monatomic layers perpendicular to *c*-axis in a sequence *RE* - X - T - X - *RE*. Many of these compounds, *e. g*., $ErCr_2Si_2$, $GdCo_2B_2$, $EuFe_2As_2$, $ErMn_2Si_2$, *etc*., have been found to exhibit giant MCE values and interesting magnetocaloric properties [24–27]. However, there are only a few reports on the effect of doping or substitution on magnetocaloric properties in RET_2X_2 compounds [28–30].

We have carried out MCE study in $Nd(Co_{1-x}V_x)_2Si_2$ (x = 0, 0.20, 0.35). In the parent compound $NdCo_2Si_2$, only Nd possesses a magnetic moment which align antiferromagnetically along *c*-axis as the compound shows three successive transitions at T_N =32 K, T_1=24 K and T_2=15 K. However, there is ferromagnetic interaction among rare-earth moments in *ab* plane. Our earlier report [31] shows that due to substitution of vanadium at the site of non-magnetic cobalt, the magnetic ground state of $NdCo_2Si_2$ is markedly modified. A ferrimagnetic transition occurs below about 60 K possibly as a result of magnetism arising in the transition metal ions, and at further low temperatures ferromagnetism is obtained. The present investigation shows that the above changes in the magnetic properties are accompanied with an enhancement of magnetocaloric entropy change.

2. Sample preparation and characterization

Polycrystalline samples of $NdCo_2Si_2$ and vanadium doped $Nd(Co_{1-x}V_x)_2Si_2$

* Corresponding author.
E-mail address: bilwadal.bandyopadhyay@saha.ac.in (B. Bandyopadhyay).
[1] Present address: Department of Physics, IIT Bombay, Powai, Mumbai 400076, India.

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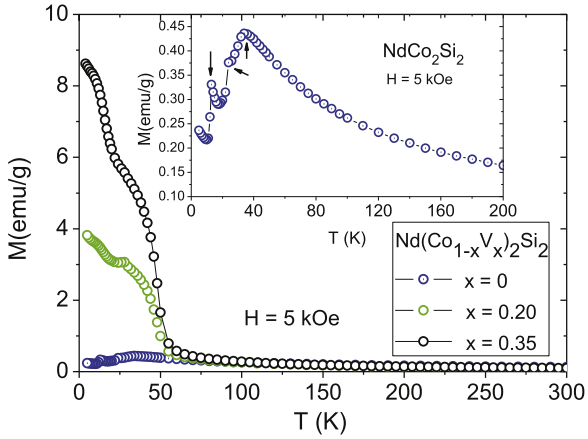

Fig. 1. Field cooled magnetization as a function of temperature of $Nd(Co_{1-x}V_x)_2Si_2$ (x=0, 0.20, 0.35) taken in warming cycle in presence of H=5 kOe. Inset shows enlarged view of magnetization of the parent compound $NdCo_2Si_2$. Arrows in the inset denote the transition temperatures.

(x=0.20 and 0.35) compounds were prepared by arc melting the constituent elements in argon atmosphere. The samples were annealed and characterized by room temperature x-ray diffraction (XRD) studies and scanning electron microscopy (SEM). The analysis of experimental data showed the occurrence of $ThCr_2Si_2$ type structure (space group I4/mmm) in all the samples. Significantly, there was systematic lattice expansion and development of lattice strain upon vanadium substitution. The details have been reported earlier [31].

3. Results and discussion

Magnetization measurements have been carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). The *dc* magnetization study have been performed in the presence of H=5 kOe external magnetic field. Magnetization as a function of temperature for all the compounds are shown in Fig. 1. For the parent compound $NdCo_2Si_2$, three distinct transitions are clearly visible in the inset of the Fig. 1, the transition temperatures matching exactly with reported results [22,31]. In vanadium doped samples the magnetization increase sharply as temperature goes below ~60 K, and its value becomes higher with decrease of temperature and increase in vanadium content.

To obtain magnetization isotherms, the samples were cooled down from room temperature in absence of any external magnetic field (ZFC condition) down to a specified temperature (T) and the magnetization (M) as a function of magnetic field (H=0–70 kOe) was recorded. This procedure was followed for all temperatures to remove any history of the previous measurement. Fig. 2 shows the behavior of the magnetic isotherms for all the compounds at some specific temperatures in the range 5–60 K.

For the parent compound (x=0, Fig. 2(a)), M *vs.* H plot at 5 K is linear and shows step-like increase in magnetization near 20 and 50 kOe as reported [22,32,31]. The magnetization increases with temperature until 30 K, *i. e.*, near T_N, which is expected in the case of a conventional antiferromagnetic compound, and decreases above T_N. With the substitution of vanadium, in contrast to the parent compound ferromagnetic-like signature starts to appear at a temperature below 30 K. In V doped compound (x=0.20, Fig. 2(b)), M is linear with H from room temperature down to 60 K. Below 60 K, M is a combination of one component that saturates at H of ~20 kOe and another component that is linear with H. With decrease in temperature, the saturation component in total M increases and the linear component decreases. Upon further V doping, *i. e.*, x=0.35; Fig. 2(c), the saturation component increases in strength and becomes dominant at low temperature. These M *vs.* H results are consistent with our

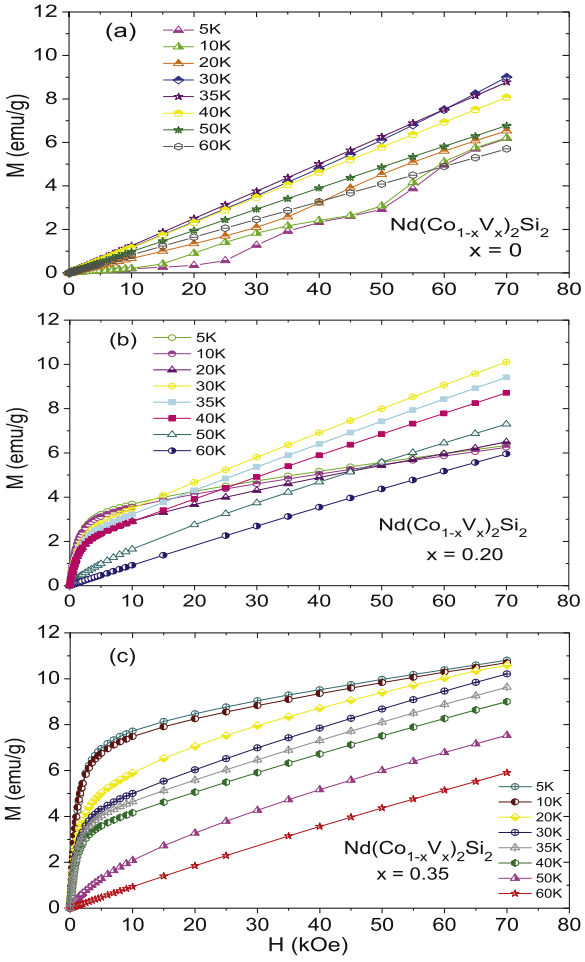

Fig. 2. Magnetization (M) as a function of external magnetic field (H) of $Nd(Co_{1-x}V_x)_2Si_2$ (x=0, 0.20, 0.35) at different temperatures.

previous observation of gradual increase of ferromagnetism as a result of V doping in these compounds [31].

Since the magnetic properties of $NdCo_2Si_2$ shows remarkable modification with V-doping it would be interesting to investigate the effect of doping on the magnetocaloric properties of this compound. We have therefore calculated the magnetic entropy changes (ΔS_M) for all the compounds using Maxwell's thermodynamic relation, given by,

$$\Delta S_M = \int_0^H (\partial M/\partial T)dH \quad (1)$$

Fig. 3 shows ΔS_M as a function of T for various doping concentrations. The nature of the temperature dependence of ΔS_M as well as its magnitude changes with the doping concentration of vanadium. MCE reflects the transformation taking place in spin configuration of magnetic materials and provide valuable information about magnetic materials, *e. g.*, the nature of magnetic ordering [33]. In antiferromagnetic/ ferrimagnetic materials, on application of external magnetic field the configurational entropy of spin structure increases, and consequently, the lattice entropy decreases ($-\Delta S_M < 0$) resulting in adiabatic cooling [34]. In case of parent compound $NdCo_2Si_2$, antiferromagnetic interaction predominates resulting in inverse magnetocaloric effect (Fig. 3(a)). At low doping of vanadium there is weakening of antiferromagnetic behavior and simultaneous appearance of ferrimagnetic-like behavior [31,35]. The larger increase of magnetocaloric entropy in $Nd(Co_{0.8}V_{0.2})_2Si_2$ (Fig. 3(b)) with respect to parent compound below 30 K possibly reflects an increase in magnetic randomness resulting from V doping. On the other hand, further increase in V doping