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Magnetic properties and magnetocaloric effect of $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ compounds

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Magnetic properties and magnetocaloric effect of NdMn_{2-x}Cu_xSi₂ compounds

Abstract

Structural and magnetic properties of NdMn_{2-x}Cu_xSi₂ compounds ($x = 0-1.0$) have been investigated by high intensity x-ray and resolution neutron diffraction (3-450 K), specific heat, dc magnetization, and differential scanning calorimetry measurements. Substitution of Cu for Mn leads to an increase in the lattice parameter a but a decrease in c at room temperature. Two magnetic phase transitions have been found for NdMn_{2-x}Cu_xSi₂ compounds with T_N for the antiferromagnetic ordering of Mn-sublattice and T_C for the Nd-sublattice ferromagnetic ordering, respectively. T_C increases significantly with increasing Cu content from 36 K at $x = 0$ to 100 K at $x = 1.0$. Moreover, it is found that the order of magnetic phase transition around T_C also changes from first order at $x < 0.6$ to second order transition for $x \geq 0.6$. The spontaneous magnetization found to decrease with the increase in Cu concentration which can be understood in the term of the dilution effect of Cu for Mn. The values of $-\Delta S_M$ around T_C decrease with increasing x from 27 J kg⁻¹ K⁻¹ for $x = 0$ to 0.5 J kg⁻¹ K⁻¹ for $x = 1.0$ under 0-5 T field. Refinement of neutron diffraction patterns for $x = 0.2$ confirms the magnetic states detected by magnetic study and also indicates that the lattice constants a and c show a distinct variation around T_C .

Keywords

xcuxsi₂, magnetic, ndmn₂, properties, effect, magnetocaloric, compounds

Disciplines

Engineering | Physical Sciences and Mathematics

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Magnetic properties and magnetocaloric effect of $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ compounds

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Structural and magnetic properties of $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ compounds ($x=0-1.0$) have been investigated by high intensity x-ray and resolution neutron diffraction (3–450 K), specific heat, dc magnetization, and differential scanning calorimetry measurements. Substitution of Cu for Mn leads to an increase in the lattice parameter a but a decrease in c at room temperature. Two magnetic phase transitions have been found for $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ compounds with T_N for the antiferromagnetic ordering of Mn-sublattice and T_C for the Nd-sublattice ferromagnetic ordering, respectively. T_C increases significantly with increasing Cu content from 36 K at $x=0$ to 100 K at $x=1.0$. Moreover, it is found that the order of magnetic phase transition around T_C also changes from first order at $x < 0.6$ to second order transition for $x \geq 0.6$. The spontaneous magnetization found to decrease with the increase in Cu concentration which can be understood in the term of the dilution effect of Cu for Mn. The values of $-\Delta S_M$ around T_C decrease with increasing x from 27 J $\text{kg}^{-1} \text{K}^{-1}$ for $x=0$ to 0.5 J $\text{kg}^{-1} \text{K}^{-1}$ for $x=1.0$ under 0–5 T field. Refinement of neutron diffraction patterns for $x=0.2$ confirms the magnetic states detected by magnetic study and also indicates that the lattice constants a and c show a distinct variation around T_C . © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4864249>]

The research efforts to find magnetic materials with a large ambient magnetic entropy change which can be used in magnetic refrigerator for cooling technology have expended in order to resolve the global warming and high energy consumption concern.¹ Magnetic materials with first order magnetic transition (FOMT) are found to exhibit large magnetocaloric effect (MCE) compared to second order magnetic transition (SOMT).^{2–5} Among them, the tetragonal intermetallic compounds RMn_2X_2 (R = rare earth; T = transition metal; and X = Si or Ge) attract special attention mainly in interesting interplay between $3d$ and $4f$ magnetism and present wide range of magnetic behaviour.^{6–8} For example, NdMn_2Si_2 compounds provide the promising prospect for enhanced magnetocaloric because of the crystal structure nature in layered allows to control of the intrinsic magnetism via inter and intra planar separations of the Mn atoms with Nd atoms performing the large magnetization due to ferromagnetic coupling between the Mn and Nd sublattices below the Nd ordering temperature.⁹ From the point on smaller atomic radius of Cu (1.28 Å) compared with Mn (1.35 Å), it is expected that the substitution of Mn with Cu in NdMn_2Si_2 leads to a significant decrease in $d_{\text{Mn-Mn}}$ and corresponding on modification of magnetic state. In this paper, we outline the influence

of the replacement Cu for Mn in $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ ($x=0-1.0$) on magnetic structure and magnetic phase transition.

The polycrystalline $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ ($x=0-1.0$) samples were prepared by arc melting in an Ar atmosphere and annealed at 900 °C for 1 week in an evacuated quartz tube. The crystal structure of the samples were checked by high intensity x-ray powder diffraction ($\lambda=0.8265$ Å; 10–300 K) carried out at the Australian Synchrotron (AS). The magnetic properties were investigated over the temperature range 6–400 K using the vibrating sample magnetometer option of a Quantum Design 14 T physical properties measurement system (PPMS). The crystallographic and magnetic structural behaviour of the sample was investigated by powder neutron diffraction using the Echidna ($\lambda=1.622$ Å) at the OPAL Reactor, Australia.

Confirmation that all of the $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ ($x=0-1.0$) samples crystallize in the expected ThCr_2Si_2 type structure with space group $I4/mmm$ was provided by analysis of the x-ray powder diffraction patterns. The x-ray diffraction patterns at variable temperatures for $x=0.2$ are shown in Fig. 1(a) as a typical example. The measured data from the diffraction patterns were analysed using the Rietveld refinement technique.¹⁰ Substitution of Cu for Mn does not change the symmetry of the crystal structure but leads to decrease of the unit cell. The lattice constants a was found to slightly

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FIG. 1. XRD pattern for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ compound at range 10–300 K ($\lambda = 0.8265(8)$ Å); (b) variation of unit cell volume V , c , and a for room temperature with Cu content; and (c) temperature dependence of magnetization, the Néel temperatures (T_N) and the Curie temperatures (T_C) of $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ compound.

increase but c decreases with increasing Cu concentration, and correspondingly the unit cell volumes, were found to decrease with the Cu content consistent with the smaller atomic radius of Cu compared to Mn. As shown in Fig. 1(b), lattice parameters a increases from 4.00(5) Å for $x = 0$ to 4.06(2) Å for $x = 1.0$, however, c is found to decrease from 10.52(4) Å for $x = 0$ to 10.26(1) Å for $x = 1.0$. The temperature dependence of the magnetization of $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ ($x = 0$ –1.0) measured in a magnetic field of $B = 0.01$ T is shown in Fig. 1(c) together with the differential scanning calorimetry (DSC). As using calculation in Ref. 11, the Néel temperature T_N is found to decrease from ~ 380 K to ~ 320 K with increase in Cu concentration from $x = 0$ to $x = 1.0$, while Curie temperature T_C increases from ~ 36 K to ~ 100 K. The reduction of unit cell volume due to Cu substitution will lead to decrease the Mn-Mn intralayer exchange interaction. Moreover, the change in electronic environment on replacing Mn ($3d^5 4s^2$) by Cu ($3d^{10} 4s^1$) is also expected to influence the magnetic structures and states of the $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ compounds.

The magnetization curves obtained for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ and $\text{NdMn}_{1.4}\text{Cu}_{0.6}\text{Si}_2$ around their ferromagnetic ordering temperatures are shown in Figs. 2(a) and 2(b). Comparison of the magnetisation curves around the ferromagnetic ordering temperatures for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ and $\text{NdMn}_{1.4}\text{Cu}_{0.6}\text{Si}_2$ reveal that pronounced hysteresis losses keep decreasing from ~ 12 J kg^{-1} to no hysteresis loss are observed for $\text{NdMn}_{1.4}\text{Cu}_{0.6}\text{Si}_2$ (indicated values for $B = 0$ –5 T as suitable to comparison). It is demonstrated clearly that magnetic hysteresis losses

FIG. 2. Isothermal magnetization curves in the vicinity of the ferromagnetic ordering temperatures for: (a) $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ ($B = 0$ –8 T) and (b) $\text{NdMn}_{1.4}\text{Cu}_{0.6}\text{Si}_2$ ($B = 0$ –5 T) compound, respectively. (c) Arrott plots of $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$; $x = 0.2$ and (d) $x = 0.6$ compounds.

decrease significantly on substitution of Cu for Mn as indicated that increasing Cu concentration contributes to a weakening of the characteristic field induced metamagnetic transition from the antiferromagnetic to the ferromagnetic state. Figures 2(c) and 2(d) show the corresponding Arrott plots (M^2 versus B/M) for the $x = 0.2$ and 0.6 samples, respectively. The Arrott plots are found to exhibit features characteristic of a first order transition for $x < 0.6$ to second order transition for $x \geq 0.6$. As been determined by 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,¹² thereby denoting a first order magnetic transition for $x < 0.6$ and been confirmed with nature of phase transitions method.¹³

The magnetic entropy change, $-\Delta S_M$, has been determined for the set of $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ compounds ($x = 0$ –1.0) from their magnetization curves for 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:¹⁴ $-\Delta S_M(T, B) = \int_0^B \left(\frac{\partial M}{\partial T} \right)_B dB$. As shown by the curves of Fig. 3(a), the $-\Delta S_M$ peak is found to consistently decrease with Cu concentration $x = 0, 0.2, 0.4, 0.6, 0.8$, and 1.0 as: $-\Delta S_M \sim 27$ J $\text{kg}^{-1} \text{K}^{-1}$ at $T_C = 36$ K; $-\Delta S_M \sim 13$ J $\text{kg}^{-1} \text{K}^{-1}$ at $T_C = 44$ K; $-\Delta S_M \sim 6.5$ J $\text{kg}^{-1} \text{K}^{-1}$ at $T_C = 60$ K; $-\Delta S_M \sim 3.5$ J $\text{kg}^{-1} \text{K}^{-1}$ at $T_C = 70$ K; $-\Delta S_M \sim 1.5$ J $\text{kg}^{-1} \text{K}^{-1}$ at $T_C = 80$ K; and $-\Delta S_M \sim 0.5$ J $\text{kg}^{-1} \text{K}^{-1}$ at $T_C = 100$ K. The decrease in magnetization on substitution of the non-magnetic Cu for Mn correspondingly reduces the value of $-\Delta S_M$. 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 expression¹⁵ $-\Delta S_M(T, B) = \int_0^T \left(\frac{C(T, B) - C(T, 0)}{T} \right) dT$, 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 heat capacity data: $\Delta T_{ad}(T, B) = \int_0^B \frac{T}{C_{B,P}} \left(\frac{\partial M}{\partial T} \right)_B dB$. Figure 3(b) shows the set of heat capacity measurements obtained for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ with

FIG. 3. (a) The magnetic entropy change, $-\Delta S_M$, determined from magnetization and the heat capacity measurements of Fig. 3(b) for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ ($\Delta B = 0-5$ T). (b) The heat capacity of $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ as measured over the temperature range 10–90 K. (c) The adiabatic temperature change, ΔT_{ad} , for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$.

$B = 0, 1, 2$, and 5 T. The corresponding $-\Delta S_M(T, B)$ values for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ are shown in Fig. 3(a) with the $\Delta T_{ad}^{max} = 3.44$ K for $\Delta B = 0-5$ T values in Fig. 3(c). The $-\Delta S_M^{max}$ for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ as determined from the heat capacity measurement $\sim 11.5 \text{ J kg}^{-1} \text{ K}^{-1}$ is comparable to the magnetic measurements using the Maxwell relation $\sim 13 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\Delta B = 0-5$ T as shown in Fig. 3(a).

The diffraction patterns ($\lambda = 1.622(1) \text{ \AA}$) and Rietveld refinements obtained for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ at 450 K, 100 K, and 40 K are shown in Fig. 4(a) typify the behaviour of the three magnetic regions (paramagnetic-antiferromagnetic-ferromagnetic) as found similar to $\text{NdMn}_{1.9}\text{Ti}_{0.1}\text{Si}_2$,¹⁶ respectively. Rietveld refinements of the neutron diffraction pattern at 450 K (paramagnetic state) confirm that $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ has the ThCr_2Si_2 structure and below $T_N \sim 375$ K, is found to exhibit the antiferromagnetic interlayer coupling structure (AFil) down to $T_C \sim 44$ K ($T = 100$ K). The AFil structure was confirmed by the magnetic scattering observed at the (111), (113), and (201) reflections (extinction rules $h+k=2n$ and $h+k+l=2n+1$) indicated a collinear antiferromagnetic structure between adjacent Mn planes in a $+ - + -$ sequence along the c -axis. When cooling to below $T_C \sim 44$ K, the magnetic scattering from the (101) and (112) reflections was found to increase ($T = 40$ K), combined with the eliminate in intensity of the (111) peak as in Fig. 4(b), confirmed that the interlayer spin components of the Mn moments align parallel, thus contribute to a canted ferromagnetic structure (Fmc) for the Mn sublattice.

The variation in the a and c lattice parameters with temperature are plotted in Fig. 4(c). Both the a and c values exhibit a monotonic decrease with temperature in the region of the antiferromagnetic transition between $T_N \sim 375$ K and $T_C \sim 44$ K, while below $T_C \sim 44$ K, the a lattice parameter expands slightly from $4.003(5) \text{ \AA}$ to $4.005(3) \text{ \AA}$, whereas the c decreases from $10.464(3) \text{ \AA}$ to $10.451(3) \text{ \AA}$ at 60 K and at 3 K. The changes in lattice parameter at $T_C \sim 44$ K according

FIG. 4. (a) Neutron diffraction patterns for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ at 450 K, 100 K, and 40 K, respectively. (b) Expanded view of the neutron diffraction pattern for $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ at selected temperatures. (c) The lattice parameters of $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ as a function of temperature.

to magnetic state changes from AFil to Fmc + F(Nd) structure indicates the presence of strong magnetostructural coupling contributing to the total entropy change around T_C .

A systematic investigation of the structural and magnetic characteristics of $\text{NdMn}_{2-x}\text{Cu}_x\text{Si}_2$ ($x = 0-1.0$) compounds has been carried out. Substitution of Cu for Mn leads to increase in the Curie temperature while decrease the Néel temperature from $T_C \sim 36$ K to 100 K and $T_N \sim 380$ K to 320 K at $x = 0$ and $x = 1.0$. The variation in the value of T_C with increasing Cu concentration can be understood in terms of changes in the Mn-Mn exchange interaction together with the effects of magnetic dilution. Analysis of the magnetisation data demonstrates that the order of magnetic phase transition around T_C changes from first order at $x < 0.6$ to second order transition for $x \geq 0.6$ and leads to significant reduction in magnetic hysteresis losses. Substitution of Mn by Cu leads to a reduction of the magnetic entropy change from $-\Delta S_M \sim 27 \text{ J kg}^{-1} \text{ K}^{-1}$ at $x = 0$ to $\sim 0.5 \text{ J kg}^{-1} \text{ K}^{-1}$ at $x = 1.0$, respectively. Neutron diffraction studies demonstrate that $\text{NdMn}_{1.8}\text{Cu}_{0.2}\text{Si}_2$ has the AFil antiferromagnetic structure in the temperature range $T_N \sim 375 \text{ K} > T > T_C \sim 44$ K and the combined Fmc + F(Nd) ferromagnetic state below $T_C \sim 44$ K.

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