Solid State Communications 151 (2011) 1240–1243

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

The magnetocaloric effect and low temperature specific heat of SmNi

H. Drulis [a,*], A. Hackemer [a], A. Zaleski [a], Yu.L. Yaropolov [b], S.A. Nikitin [b,c], V.N. Verbetsky [b]

[a] Polish Academy of Sciences, Trzebiatowski Institute of Low Temperature and Structure Research, P.O. Box 1410, 50-950 Wroclaw 2, Poland

[b] Lomonosov Moscow State University, GSP-3, Leninskie Gory, Moscow, 119992, Russia

[c] International laboratory of High Magnetic Fields and Low Temperatures, Wroclaw, Poland

ARTICLE INFO

Article history:
Received 26 April 2011
Received in revised form
23 May 2011
Accepted 30 May 2011
by C. Lacroix
Available online 12 June 2011

Keywords:
A. Magnetically ordered materials
B. Magnetocaloric effect
C. Thermodynamic properties
E. Heat capacity measurements

ABSTRACT

The magnetocaloric effect (MCE) in a magnetic SmNi sample was evaluated from magnetization and heat capacity measurements. The MCE phenomena in the vicinity of magnetic phase transitions in terms of magnetic entropy change, ΔS_M, and adiabatic temperature change, ΔT_{ad}, are reported. Isothermal magnetization $\sigma(H)_{T=\text{const}}$ measurements at several temperatures around the transition $T_c = 43$ K were carried out and used for ΔS_M *versus* T calculations. A similar dependence of the magnetic entropy change $-\Delta S_M = (S_H - S_0)$ was evaluated from heat capacity $C_p(T)$ measurements under zero field and 5 T. The SmNi system provides magnetic refrigerants that induce an adiabatic cooling of about $\Delta T_{ad} \approx 1.2$ K during the magnetization process with a field of 5 T in the temperature range of 35–45 K. The temperature dependence of $C_p(T)$ is analyzed in terms of the magnetic and the lattice contributions.

1. Introduction

Recently, there has been enhanced scientific activity in the development of magnetocaloric materials [1–4]. The magnetocaloric effect (MCE) is manifested as an isothermal magnetic entropy change or as an adiabatic temperature change of a magnetic material when exposed to an external magnetic field. This effect occurs due to the change in the degree of alignment of the magnetic moments under the influence of an applied magnetic field. The MCE is evaluated from the magnetic entropy change ΔS_M induced by an iterative magnetize–demagnetize operation. The value of ΔS_M is usually maximized around a magnetic transition temperature, such as the Curie point of the ferromagnet [5]. It has already been reported that some RNi (R = Dy, Er, Gd), compounds undergo field-induced spin flop processes [6]. Due to their large magnetic moments and interesting magnetic phase transitions, the rare earth elements and their compounds are considered to be the materials best suited for achieving a large MCE [1,2]. In this paper we present the magnetic and thermodynamic properties of the SmNi compound from the magnetocaloric effect point of view. Earlier magnetic susceptibility measurements [7,8] have shown that SmNi undergoes ferromagnetic type transitions at low temperatures. It was shown that the ordered magnetic state is complex. It is a canted spin structure, that is, a non-collinear spin structure with an antiferromagnetic component along the c axis and a ferromagnetic one along the b axis [8]. Generally, such structures give rise to a metamagnetic transition under the influence of an external magnetic field causing large changes in the magnetic entropy [9].

2. Experimental details

SmNi samples were synthesized by the arc melting in an argon gas atmosphere of nickel (purity of 99.99%) and samarium (99.9%) metals. The starting amount of Sm metal was corrected for 0.5 wt% due to possible waste of metal during the melting process. To ensure homogeneity, the samples were turned and remelted several times. X-ray powder diffraction studies were performed with a Huber G670 Image Plate Guinier camera, Cu $K_{\alpha 1}$ radiation and shows that the material is single phase of CrB type structure with the lattice constants $a = 3.782(3)$ Å, $b = 10.375(4)$ Å and $c = 4.301(2)$ Å, respectively. Magnetic measurements were carried out in the temperature range of 1.7–300 K in an applied magnetic field up to 5 T using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Specific heat measurements were performed with a PPMS platform in the 2–400 K temperature range.

3. Results and discussion

3.1. Magnetocaloric effect measurements

Magnetization measurements were carried out for the polycrystalline SmNi sample. In Fig. 1 the temperature dependence

* Corresponding author. Tel.: +48 71 343 50 21; fax: +48 71 344 10 29.
E-mail address: h.drulis@int.pan.wroc.pl (H. Drulis).

0038-1098/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2011.05.047

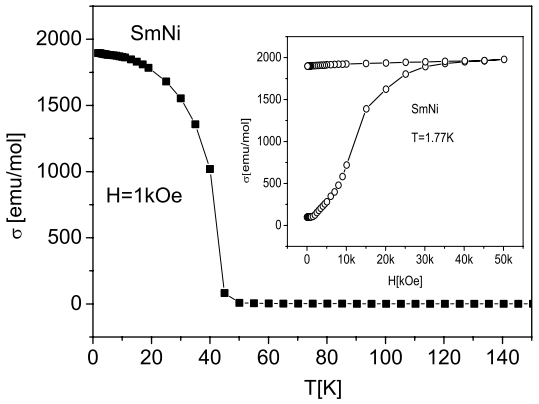

Fig. 1. Temperature dependence of the magnetization (σ–T) of a polycrystalline SmNi sample measured in the 2–150 K temperature range in the field cooling procedure (FC). The inset shows the (σ–H) curves at 1.77 K up to 5 T.

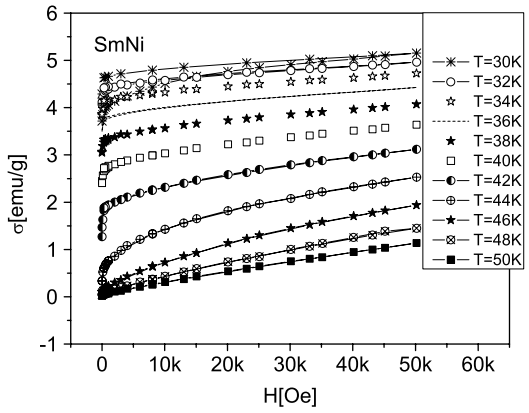

Fig. 2. Magnetization curves *versus* magnetic field for several temperatures around $T = 42$ K.

of the magnetization (σ–T) curve measured in the 2–150 K temperature range in the field cooling procedure (FC) is presented. The magnitude of the magnetization is very close to that reported in [7] for an SmNi single-crystalline sample. The magnetization curve indicates the ferromagnetic nature at temperatures lower than about 43 K. The conclusion concerning a ferromagnetic nature of the sample must be treated as a first approximation. The inset of Fig. 1 shows the magnetization *versus* magnetic field (σ–H) curve at $T = 1.77$ K and reveals a state rather more complex than a ferromagnetic one formed by Sm magnetic moments. One can note that the magnetization curve in the inset shows a metamagnetic transition at about 12 kOe.

The magnetocaloric effect can be measured directly as an adiabatic change of temperature or can be calculated via a combination of magnetization data and field dependent thermal measurements. Under adiabatic conditions, the magnetic entropy change ΔS_M must be compensated by an equal but opposite change of the lattice entropy, ΔS_L, and the thermodynamic rules of $\Delta S_M + \Delta S_L = 0$ have to be fulfilled. This will result in a temperature change, ΔT_{ad}, of the material. The adiabatic temperature change ΔT_{ad} can be measured or recalculated from the relation

$$\Delta T = [T/C_{p,H}]\Delta S_M(H) \tag{1}$$

where $C_{p,H}$ is the specific heat measured with the field H applied.

For $\Delta S_M(H)$ one can introduce the values calculated from thermal or magnetic measurements. The entropy change $\Delta S_M(H)$ associated with the change of the magnetization is given as

$$\Delta S_M = \int_0^H \{\partial\sigma/\partial T\}_H \mathrm{d}H \tag{2}$$

and can be obtained from magnetic measurements by integration of $(\partial\sigma/\partial T)$ from $H = 0$ to $H_{max.}$. Magnetic measurements deliver reliable magnetic entropy change only in the vicinity of the magnetic transition temperature. Therefore, for $(\partial\sigma/\partial T)$ peaks at the ordering temperature, the largest MCE is expected close to a magnetic phase transition. In Fig. 2, the field dependence of the magnetization isotherms, $\sigma(H)$, at several temperatures in the vicinity of the suggested magnetic phase transitions are shown. The results of $\Delta S_M(H)$ calculations for the field of 1–2–3–4–5 T as a function of temperature are presented in Fig. 3. The maximum value of the magnetic entropy change is about 2 J/kg K for the field change 0–5 T at a temperature of about $T = 42$ K.

Fig. 4 shows the temperature variation of the molar heat capacity for SmNi under zero field and 5 T in the temperature range of 2–120 K. It is seen that the heat capacity in zero field (ZF) displays a large discontinuity at about $T = 42$ K due to a paramagnetic–ferromagnetic phase transition. When the external

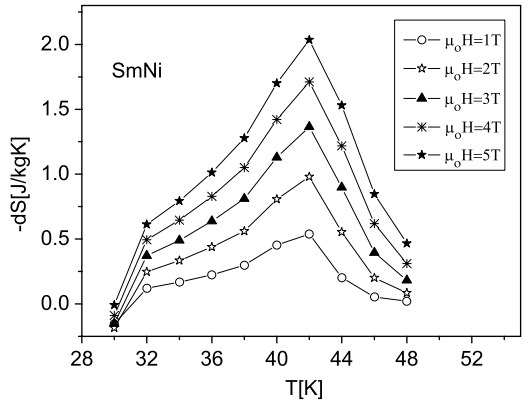

Fig. 3. Temperature dependence of magnetic entropy changes in SmNi for field changes of 1, 2, 3, 4 and 5 T.

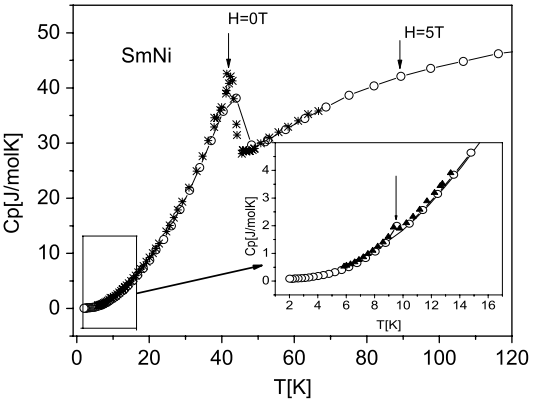

Fig. 4. Heat capacity of SmNi *versus* temperature in zero and 5 T magnetic fields in the 2–150 K temperature range. In the inset, the details for $C_p(T)$ measured around $T = 10$ K are presented. Open circles (**O**) and the full line display the $C_p(T)$ data in zero and 5 T, respectively, registered with the PPMS. The full triangles (▲) show $C_p(T)$ data taken in zero magnetic field using the homemade apparatus.

magnetic field of 5 T is switched on, the value of the C_p^{max} heat capacity diminishes and the peak is shifted to slightly higher temperatures. More detailed analysis of $C_p(T)$ at the lowest temperature range (see the inset of Fig. 4) revealed another small anomaly at about $T = 9.75$ K. To be sure that this anomaly was not an artifact, the heat capacity measurements were repeated twice using two different calorimetric instruments (PPMS and a homemade apparatus) for two different SmNi samples. Within the frame of accuracy, both experiments showed the same results. This anomaly disappears when $C_p(T)$ measurements are carried out in

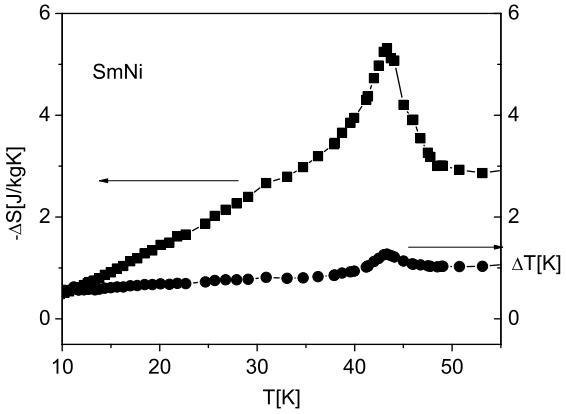

Fig. 5. Left side: (◯) magnetic entropy change, ΔS_M, estimated from heat capacity measurements as a function of temperature in the range of 2–55 K for $\Delta H = 5$ T. Right side: (•) adiabatic temperature change, ΔT_{ad}, as a function of temperature calculated from heat capacity measurements.

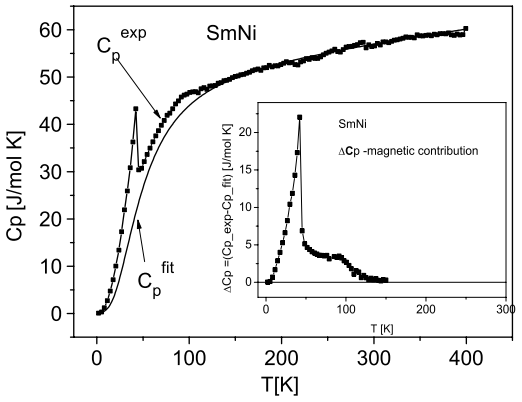

Fig. 6. The results of heat capacity measurements on SmNi in the 2–400 K temperature range. The full line represents the lattice specific heat contribution calculated for a number $N_D = 6$ of Debye-like modes with an average Debye temperature $\theta_D = 199K$. In the inset, the magnetic contribution of Sm^{3+} ion magnetic moments to $C_p(T)$ for SmNi is displayed.

a field of 5 T. The experiments performed clearly indicate that the low temperature anomaly in SmNi at $T = 9.75$ K is likely connected with a spin-reorientation transition (SRT) due to a large crystalline anisotropy of Sm ions and due to the non-collinear spin structure of an antiferromagnetic component along the c axis as suggested in Ref. [8].

When a magnetic material is magnetized by the application of a magnetic field, the magnetic energy associated with the magnetic degrees of freedom is changed and the so-called magnetic entropy change, $\Delta S_M(T) = S(T)_H - S(T)_0$, can be estimated from calorimetric measurements by integration:

$$\Delta S_M(T,H) = S(T)_H - S(T)_0 = \int \{C_p(T)_H/T - C_p(T)_0/T\}\mathrm{d}T \quad (3)$$

where $S(T)_H$ and $S(T)_0$ are the entropy values, whereas $C_p(T)_H$ and $C_p(T)_O$ are the heat capacity values measured in field H and in zero field, respectively. Usually, applying a magnetic field to a ferromagnetic (FC) material will lower its magnetic entropy. The entropy change, $-\Delta S_M(T,H)$, as a function of temperature in the range of 2–55 K with a field change of 0–5 T is shown in Fig. 5. The $-\Delta S_M$ runs over the positive $-\Delta S_M$ values expected for the conventional magnetocaloric effect, going through the maximum value of 5.3 J/kg K at a temperature of 42 K. Results for MCE in terms of an adiabatic temperature change ΔT_{ad} calculated from Eq. (1) for a 0–5 T magnetic field change is displayed in Fig. 5. Both the magnetic entropy change ΔS_M and the specific heat C_p values have to be introduced in Eq. (1), at the same field and temperature. For $-\Delta S_M$ we introduce the values calculated from the magnetic measurements as presented in Fig. 3. The calculations indicate that the SmNi compound provides a magnetic refrigerant that induces an adiabatic cooling of about $\Delta T_{ad} \approx 1.2$ K during the magnetization process with $\mu_0 H = 5$ T at temperatures around $T = 42$ K.

3.2. Low temperature specific heat data

As far as we are aware, $C_p(T)$ measurements for SmNi, if they exist, have not been reported to date. Accurate knowledge of C_p material over its entire stability regime is of vital scientific and technical importance. This was why we decided to report in addition, in Fig. 6, the temperature dependence of the heat capacity $C_p(T)$ data measured for an SmNi sample in the wide 2–400 K temperature range.

For metallic-like, three-dimensional materials at the lowest (up to $\approx$ 10 K) temperatures, C_p can be approximated by the well-known relationship

$$C_p \approx C_v = \gamma T + \beta T^3 \quad (4)$$

where γ and β are the coefficients of the electronic and lattice heat capacities, respectively. When the material is magnetically ordered at low temperatures Eq. (4) does not allow us to establish electronic and lattice contributions using its modification $C_v/T = \gamma + \beta T^2$, as is usually done. Nevertheless, $C_p(T)$ in the 2–400 K temperature range can be approximated by a sum of three components:

$$C_v = \gamma T + C_m + N_D C_v(\Theta). \quad (5)$$

The second term on the right hand side describes all the magnetic contributions, whereas the third term reflects the Debye-like vibration modes contributing to C_v and is given by the well-known Debye function

$$N_D C_V = N_1 R/4(\theta_D/T)^2 \mathrm{csch}^2(1/2(\theta_D/T)) \quad (6)$$

where θ_D is the Debye temperature. To extract the magnetic C_m contribution from C_p, one should know both of the other terms. Ordinarily, the lattice contribution is exemplified by that of a lattice of an isomorphic non-magnetic compound. In our case, it could be LaNi or YNi. Unfortunately, we cannot use either. The C_p data for LaNi are, as far as we know, not available. YNi has the orthorhombic FeB type (*Pnma*) crystallographic structure [10], whereas SmNi crystallizes in a monoclinic CrB type structure. In spite of these obstacles, it is possible to separate the C_m magnetic contributions for SmNi by analysing the magnetic entropy change as a function of temperature.

It is reasonable to assume that the $C_p(T)$ of SmNi at temperatures much higher than a transition temperature $T \gg 42$ K is described only by the lattice Debye-like energy phonons and by linear electronic contributions. Having this in mind, we performed a theoretical least squares fit to the experimental $C_p(T)$ curve in the 200–400 K temperature range. Quite good agreement between the calculated and experimental results was obtained by taking the number of Debye-like modes $N_D = 6$ with an average $\theta_D = 199$ K and $\gamma = 26.7$ mJ/mol K^2. We have found that these parameters fit quite well also to the experimental points in the temperature range from 400 K down to 130 K. In Fig. 6, this curve is shown as a full line in the whole 2–400 K experimental temperature range. Subtracting this theoretical curve from the experimental one, the magnetic specific heat contribution $C_m(T)$ for the SmNi compound has been separated and is shown in the

inset of Fig. 6. As one can see, the magnetic heat contribution extends far above the transition temperature $T = 42$ K up to 130 K, where its value reaches zero. The whole magnetic entropy change calculated from 2–130 K using the $\Delta C_p(T)$ curve is equal to $\Delta S_m = 14.92$ J/mol K whereas the entropy change calculated up to the transition temperature $T_c = 42$ K is equal to $\Delta S_m = 7.5$ J/mol K. This value is about 30% larger than the value which one can expect for the doublet ($\Delta S_m = R \ln 2 = 5.76$ J/mol K) magnetic ground state $^6H_{5/2}$ of Sm^{3+} ions. The results obtained suggest that apart from the magnetic ordering phenomena, the thermal excitations within the crystal electric field levels of Sm^{3+} ions (Schottky effect) must also participate in the magnetic entropy change. The entropy determined by the Schottky thermal excitations within the CF energy levels with degeneracy: $g_0, g_1, g_2, \ldots$, is given by the relation $\Delta S_{sch} = R \ln(g_0/g_0 + g_1/g_0 + g_2/g_0 \cdots)$. It is easy to show that an excellent agreement between the experimentally determined entropy and the calculated one for the SmNi compound is obtained if $\Delta S_{sch} = R \ln 3 = 9.13$ J/mol K. This is exactly what is expected when three crystal field energy doublets Γ_1, Γ_2 and Γ_3 of Sm^{3+} are engaged in thermal excitations.

4. Conclusion

The magnetization and specific heat measurements indicate that the SmNi compound provides magnetic refrigerant that induces adiabatic cooling of about $\Delta \boldsymbol{T_{ad}} \approx 1.2$ K during the magnetization process with $\mu_0 H = 5$ T at temperatures around $T \approx 42$ K.

The $C_p(T)$ investigations of SmNi clearly indicate that besides the paramagnetic/ferromagnetic phase transition anomaly at $T = 42$ K, another low temperature anomaly at $T = 9.75$ K appears, which is likely connected with a spin-reorientation transition (SRT) due to a large crystalline anisotropy of Sm ions and due to the non-collinear spin structure of an antiferromagnetic component along the c axis. The magnetic heat contribution in SmNi does not extend far above the transition temperature, $T = 42$ K. This contribution already reaches a zero value at 130 K. It has been shown that an excellent agreement between the experimentally determined entropy and the calculated entropy is obtained for $\Delta S_{sch} = R \ln 3$, which is expected for the three crystal field energy doublets Γ_1, Γ_2 and Γ_3 of Sm^{3+} ions.

Acknowledgments

We are grateful to Dr. M. Drulis for fruitful discussion and Dr. W. Iwasieczko for some magnetic measurements.

References

[1] A.S. Andreenko, K.P. Belov, S.A Nikitin, A.M. Tishin, Sov. Phys. Usp. 32 (1989) 649.
[2] K.A. Gschneidner, V.K. Pecharsky, A.V Tskol, Rep. Progr. Phys. 68 (2005) 1479.
[3] K.A. Gschneidner, V.K. Pecharsky, Int. J. Refrig. 31 (2008) 945.
[4] A.M. Tishin, J. Appl. Phys. 68 (1990) 6480.
[5] M. Foldeaki, W. Schnelle, E. Gmelin, P. Benard, B. Koszegi, A. Giguere, R. Chahine, T.K. Bose, J. Appl. Phys. 82 (1997) 309.
[6] K. Sato, Y. Yosida, Y. Isikawa, K. Mori, J. Magnt. Magnt. Mater. 54–57 (1986) 467.
[7] S.C. Abrahams, J.L. Bernstein, R.C. Sherwood, J.H. Wernick, H.J. Williams, J. Phys. Chem. Solids 25 (1964) 1069.
[8] Y. Isikawa, K. Mori, K. Ueno, K. Sato, K. Maezawa, J. Magnt. Magnt. Materials 52 (1985) 434.
[9] P. Kumar, K.G. Suresh, A.K. Nigam, O. Gutfleisch, J. Phys. D; Appl. Phys., 41 (208) 245006.
[10] D. Gignoux, J.S. Shah, Solid State Commun. 11 (1972) 1709.