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New magnetocaloric material based on $GdNiH_{3.2}$ hydride for application in cryogenic devices

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The paper presents the investigation of $GdNiH_{3.2}$ hydride magnetocaloric properties. The isothermal magnetization in the fields up to 5 T and heat capacity data are obtained for $GdNiH_{3.2}$ and GdNi compounds. The maximum value of magnetic entropy change ΔS_M in $GdNiH_{3.2}$ is extremely large and obtained in much lower temperature range compared to GdNi. It is shown that the hydrogenation does not noticeably affect the value of ΔS_M but shifts $\Delta S_M(T)$ maximum to lower temperatures ($\sim$ 11 K). The possibility of $GdNiH_{3.2}$ application in cryogenic devices is discussed.

1 Introduction The production of efficient magnetic refrigerators operating in the range of low temperatures ($<$ 10 K) requires the application of magnetocaloric materials possessing the low transition temperatures along with large values of magnetic entropy change ΔS_M in applied magnetic fields. Such a combination of characteristics is non-trivial and is not satisfied often for magnetic materials. Moreover, the material with low transition temperature yet showing a weak respond of magnetization to applied magnetic field would not be an effective magnetocaloric material. The promising materials with large values of magnetocaloric effect (MCE) for application in low-temperature operating refrigerators are rare-earth and 3d-transition metal [1–5] compounds. Regardless of some progress in this area the further development of efficient magnetocaloric materials with large values of magnetic entropy change and low transition temperatures is needed.

It was reported previously [6,7] that GdNi is a ferromagnet with Curie temperature (T_C) $\sim$70 K. The Gd ions are known to possess the largest magnetic moment in lanthanides group, thus the compounds based on Gd should have the large values of magnetization in low temperature region. However, in GdNi T_C is relatively high, thus the requirement for material's application in low-temperature range (below 10 K) is not satisfied. The more promising material could be the hydride $GdNiH_{3.2}$, which shows [8] the values of transition temperature near 10 K. The data on magnetic entropy change dependencies in $GdNiH_{3.2}$ were not reported previously.

The aim of this work was to investigate the magnetocaloric properties, magnetic entropy change ΔS_M and temperature dependencies of heat capacity C_P in $GdNiH_{3.2}$ and GdNi, and to determine the temperature range with high values of ΔS_M.

2 Experimental details The initial GdNi compounds were prepared by arc melting. The $GdNiH_{3.2}$ sample was obtained by hydrogenation of initial GdNi compound using a Sievert type apparatus. The $GdNiH_{3.2}$ hydride was obtained at room temperature under hydrogen pressure about 0.1 MPa. The composition of the hydride was calculated from volumetric measurements by Van der Vaals equation. X-ray powder diffraction (with Cu-K_α radiation) measurements for starting alloy and hydride were performed to es-

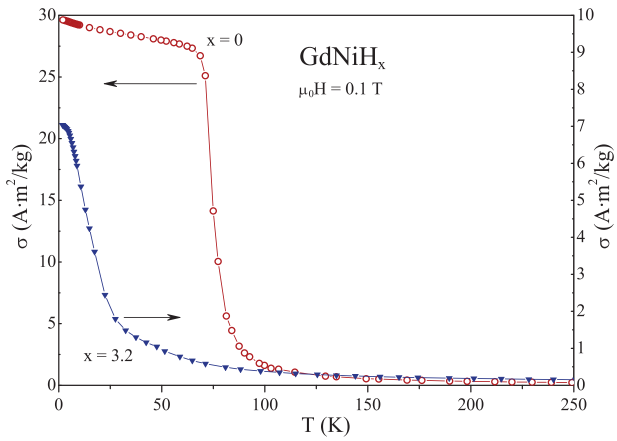

Figure 1 Temperature dependencies of magnetization σ in GdNi and $GdNiH_{3.2}$ in a field 0.1 T

tablish the phase composition of the samples and calculate their lattice parameters. The magnetization data for GdNi and $GdNiH_{3.2}$ was obtained by SQUID-magnetometer in the $2-250$ K temperature range. The σ-H isotherms were measured in fields up to 5 T at temperatures near transition temperature. The heat capacity measurements were performed with a PPMS platform in the $2-100$ K temperature range.

3 Structural properties According to the data of X-ray studies, the introduction of hydrogen atoms to GdNi leads to expansion of the unit cells without structural transformation. Ternary hydride $GdNiH_{3.2}$ possesses orthorhombic CrB-type structure, the same as initial GdNi compound. The obtained lattice parameters for GdNi are: $a = 3.778$ Å, $b = 10.337$ Å, $c = 4.238$ Å, and for $GdNiH_{3.2}$: $a = 3.767$ Å, $b = 11.576$ Å, $c = 4.733$ Å respectively. The unit cell volume increase after the hydrogen insertion equals ~24 %.

4 Magnetic properties Table 1 presents data on magnetic properties of GdNi and $GdNiH_{3.2}$ according to the recent papers [8–10]. The temperature dependencies of magnetization σ in a field of 0.1 T obtained in a present work is shown in Fig. 1. It is seen that in GdNi the sharp decrease of magnetization occurs at temperatures below 90 K, with the maximum of $\partial\sigma/\partial T$ at 75 K, then followed by minor decrease at temperatures below 70 K. Such behavior of magnetization curve is typical for classic ferromagnets possessing spontaneous magnetic moment at $T < T_C$. Unlike GdNi, the continuous increase of magnetization is observed in $GdNiH_{3.2}$ at temperature range below 70 K and down to the lowest temperatures achieved (~ 2 K). The maximum of $\partial\sigma/\partial T$ in this case occurs at $T \sim 10$ K, which can be referred as the transition temperature T_{tr} in $GdNiH_{3.2}$.

Table 1 Magnetic properties of GdNi and $GdNiH_{3.2}$.

Compound	θ_P , K	μ_{eff} , μ_B	Ordering temperature, K
GdNi	80	8.3	69-71
$GdNiH_{3.2}$	21	7.5	10

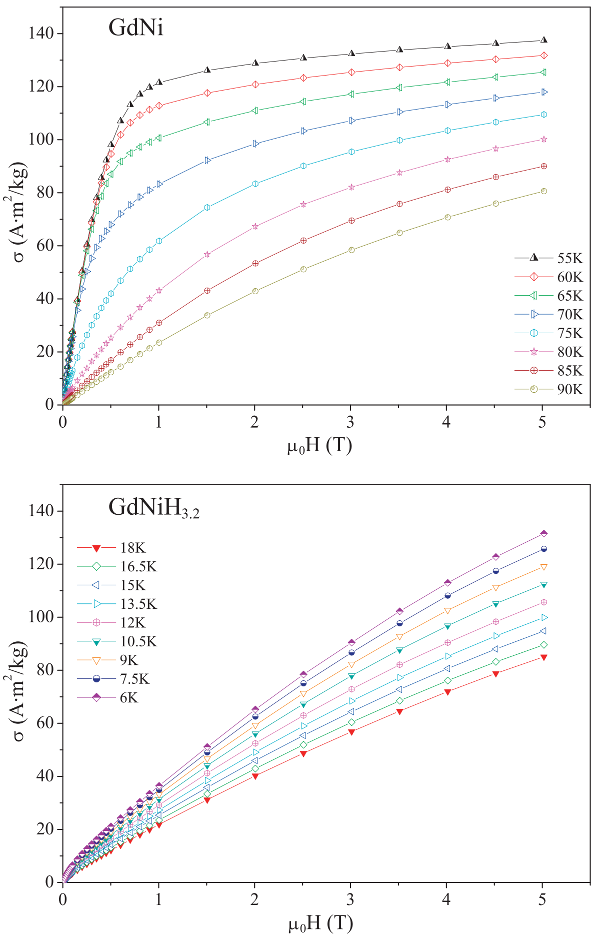

Figure 2 Isothermal magnetization σ curves for GdNi and $GdNiH_{3.2}$ in fields 0-5 T

The value of magnetization in a field of 0.1 T at 4.2 K is four times lower for $GdNiH_{3.2}$ compared to the value for GdNi. That character presumably applies to the appearance of spin-glass state in $GdNiH_{3.2}$. This state is suppressed by high magnetic fields, as could be seen from considerably small difference (~10 %) in values of σ in 5 T field on isothermal magnetization curves for GdNi and $GdNiH_{3.2}$ (data in Fig. 2). These curves demonstrate the smooth magnetization growth with applied magnetic field in $GdNiH_{3.2}$ in the range of $T_{tr} \sim 10$ K as well as below T_{tr} down to lower temperatures.

5 Discussion A high magnetic field, as mentioned above, suppresses the magnetic moments disorder in

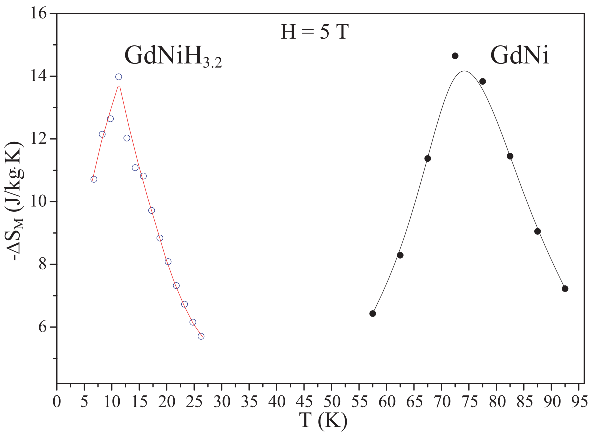

Figure 3 Magnetic entropy change ΔS_M as a function of temperature for GdNi and $GdNiH_{3.2}$

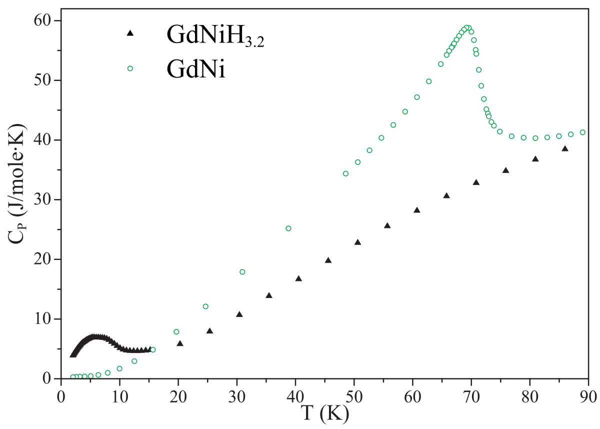

Figure 4 Temperature dependencies of GdNi and $GdNiH_{3.2}$ heat capacity C_P

$GdNiH_{3.2}$ hydride. This feature in magnetic properties of $GdNiH_{3.2}$ provides the existence of high values of magnetic entropy changes around T_{tr}. This fact can be demonstrated as following. It is known that the magnetic entropy change ΔS_M related to the variation of magnetization in applied field can be defined as

$$\Delta S_M = \int_0^H \left(\frac{d\sigma}{dT}\right)_H dH. \quad (1)$$

The ΔS_M value can be obtained from magnetization data by integrating the curves $\partial\sigma/\partial T = f$(H) in the field limits from 0 to H_{max}. The mentioned relation considers the change in magnetization with temperature and magnetic field in the forced magnetization region. The mentioned change is mostly intense at the range of magnetic transition temperature when the moments orient along the direction of applied magnetic field. The value of $\partial\sigma/\partial T$ has a peak at T_C (T_{tr}), and therefore the maximum of MCE is expected to be at transition temperature.

The integration carried out with experimental data on isothermal magnetization $\sigma(H)$ by Eq. (1) around T_C and T_{tr} provided the ΔS_M values for GdNi and $GdNiH_{3.2}$. The ΔS_M curves obtained for the field variation 0-5 T are shown in Fig. 3. The first thing to notice at these results is rather large value of ΔS_M maximum in $GdNiH_{3.2}$: ~14 J/kg·K in a field of 5 T, while ΔS_M maximum in GdNi equals ~14.5 J/kg·K.

The present values of ΔS_M are comparable with those of commonly used magnetocaloric materials. According to recent works, the values for Gd ΔS_M=10 J/kg·K, $Gd_5(SiGe)_4$ ΔS_M ~ 33.3 J/kg·K, $TbAl_2$ ΔS_M~15.5 J/kg·K in the field of 5 T are reported [5]. As distinct from the above-mentioned compounds the maximum of ΔS_M in $GdNiH_{3.2}$ is reached at temperatures ~11 K, allowing to suggest that the investigated material is promising for low-temperature magnetic refrigerators.

The temperature dependence of $GdNiH_{3.2}$ heat capacity C_P differs significantly from the one of GdNi (Fig. 4). The GdNi shows a sharp maximum of C_P in the range of magnetic transition (~70 K) which is related with a ferromagnetic ordering below this temperature, and the value of C_P peak (the difference between observed peak value and corresponding value if the curve showed linear behaviour) is ~18 J/mol·K. Conversely, in $GdNiH_{3.2}$ the slight increase of C_P is observed around 10 K and then followed by decrease below ~5 K. The value of C_P peak in $GdNiH_{3.2}$ near T_{tr} equals ~3 J/mol·K.

Consequently, the character of C_P maximum in $GdNiH_{3.2}$ and GdNi differs radically. That is explained with the transition from paramagnetic state to the state of spin-glass in $GdNiH_{3.2}$. The existence of spin-glass state is associated with the lowering of exchange interaction in $GdNiH_{3.2}$ due to hydrogen atoms insertion, thus that exchange interaction energy becomes comparable with the crystal field energy. This leads to the magnetic moments disorder in crystal lattice.

It is known, that Ni atoms in the mentioned GdNi compound carry a small magnetic moment $(0,1\mu_B)$ at the same time Gd atoms carry a substantial moment of $7\mu_B$. The exchange interactions in GdNi is provided by hybridized *3d-5d* states (the top of *3d*-band and the bottom of *5d*-band). Hydrogen atoms insertion increases the concentration of electrons in *3d*-band, leading to its completion. As a result the magnetic moment of *3d*-subsystem in $GdNiH_{3.2}$ becomes extremely small and the exchange interaction strongly decreases. The exchange field thus become comparable with the crystal field (the spin-glass state).

6 Conclusions Therefore, the investigation have shown that the hydrogen insertion in the lattice of GdNi ferromagnet significantly transforms the magnetic features.

spin-glass state in $GdNiH_{3.2}$ transforms to the state with magnetic moments oriented along applied magnetic field as in GdNi, thus resulting in a high values of ΔS_M in applied magnetic field.

It is significant that the maximum of ΔS_M in $GdNiH_{3.2}$ is reached at low temperatures $\sim$11 K, thus $GdNiH_{3.2}$ is suggested to be promising for application in low-temperature magnetic refrigerators.

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