

New Magnetic Materials Based on RNi Compounds for Cryogenic Technology

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Abstract—Magnetocaloric properties of $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})$ and $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})$ compounds and their hydrides $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_3$ and $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_4$ have been studied in a temperature interval of 2–100 K. It is established that the partial substitution of Si atoms for Ni atoms and subsequent hydrogenation can lead to significant changes in the Curie temperature, magnitude of the magnetocaloric effect, and temperature at which this effect is at maximum. In the hydrides, the characteristic temperatures shift to lower values by several dozen degrees while the magnetocaloric effect increases or remains the same, which can significantly expand the application of these materials in cryogenic technology.

Keywords: rare-earth intermetallics, Curie temperature, magnetocaloric effect.

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At present, the search for new magnetocaloric materials and applications of the magnetocaloric effect (MCE) in storage and transport of liquified gases (nitrogen, hydrogen, helium, etc.) is a topical direction of investigations. The magnetic properties of RNi compounds, where R is a rare-earth metal (REM), and their hydrides is of considerable interest since these materials exhibit high MCE at low temperatures [1–4]. The structure and thermomagnetic properties of R–Ni–H systems have been studied in detail [5–10]. The RNi compounds are known to crystallize in structures of FeB or CrB type, depending on the particular REM. It is important to note that same structural types are also typical of REM compounds with silicon (RSi), so that partial substitution of silicon atoms for nickel can provide an additional mechanism for the control over magnetic properties of these compounds.

The present work was aimed at studying the magnetocaloric properties of $\text{Gd}(\text{Ni}_x\text{Si}_{1-x})\text{H}_y$ ($x = 1, 0.98$; $y = 0, 3$) and $\text{Dy}(\text{Ni}_x\text{Si}_{1-x})\text{H}_y$ ($x = 1, 0.95$; $y = 0, 4$) compounds. We have also analyzed the magnetic properties of RNi compositions with partial substitution of silicon for nickel in comparison to the previously studied base compositions of DyNi, GdNi, and their hydrides [8–10].

The synthesis and characterization of the initial samples of $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})$ and $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})$ and their hydrogenation to $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_3$ and

$\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_4$ hydrides have been described in detail previously [11]. Magnetization of these compounds was measured in broad temperature range from 2 to 100 K on commercial equipment (PPMS-9, Quantum Design Co., United States). The MCE characteristics were calculated using methods described in [12].

Analysis of the obtained X-ray diffraction (XRD) data showed that the as-cast intermetallic compounds and related hydrides are single-phase materials and the crystalline lattice parameters of intermetallics were close to published values [13]. XRD data for the studied and reference RNi (R = Gd, Dy) samples and their hydrides are presented in Table 1. It can be seen that the initial compounds $\text{Gd}(\text{Ni}_x\text{Si}_{1-x})$ ($x = 1, 0.98$) crystallize in orthorhombic structure of the CrB type (space group C_{mcm}), while $\text{Dy}(\text{Ni}_x\text{Si}_{1-x})$ ($x = 1, 0.95$) compounds form orthorhombic structure of the FeB type (space group P_{nma}). It is noteworthy that, while the hydrogenation of DyNi leads to a change in the structure type (from FeB to CrB), the introduction of a small amount of silicon allows the FeB structure type to be retained during subsequent hydrogenation. The hydrogenation of gadolinium compounds $\text{Gd}(\text{Ni}_x\text{Si}_{1-x})$ ($x = 1, 0.98$) retains the initial structure type. In addition, the introduction of hydrogen into the crystalline lattice of these compounds leads to an increase in the unit cell volume on the average by 20–25% [8, 11].

Table 1. XRD data, Curie temperatures, and magnetic entropy of $\text{Gd}(\text{Ni}_x\text{Si}_{1-x})\text{H}_y$ and $\text{Dy}(\text{Ni}_x\text{Si}_{1-x})\text{H}_y$

Compound	Structure type	a , nm	b , nm	c , nm	T_C , K	$(-\Delta S_M)_{\max}$, J/(kg K) at $\mu_0 H = 5\text{ T}$
GdNi [7]	CrB	0.3778	1.0334	0.4238	69–71	14.5 ($T_{\max} = 72\text{ K}$)
GdNiH _{3.2} [7]	CrB	0.3767	1.1576	0.4733	10	14 ($T_{\max} = 11\text{ K}$)
Cd(Ni _{0.98} Si _{0.02})	CrB	0.3784	1.033	0.4284	75	14.7 ($T_{\max} = 67\text{ K}$)
Cd(Ni _{0.98} Si _{0.02})H ₃	CrB	0.3793	1.087	0.498	12	18 ($T_{\max} = 5\text{ K}$)
DyNi [8, 9]	FeB	0.7025	0.4181	0.5445	59–61	18 ($T_{\max} = 62\text{ K}$)
DyNiH _{3.4} [8–10]	CrB	0.3719	1.1329	0.4645	3.5	—
Dy(Ni _{0.95} Si _{0.05})	FeB	0.7065	0.4187	0.5454	62	15.2 ($T_{\max} = 55\text{ K}$)
Dy(Ni _{0.95} Si _{0.05})H ₄	FeB	0.767	0.436	0.599	10	14.2 ($T_{\max} = 9\text{ K}$)

Table 1 also shows values of Curie temperature T_C obtained in this work and reported in the literature based on the measurements of thermomagnetic properties and temperature dependences of the heat capacity [7, 8, 11]. Analysis of these data provides important information on the mutual influence of substituted and incorporated atoms on the T_C value. As can be seen, even a small fraction of silicon atoms substituted for nickel in RNi compounds allows the temperature of magnetic ordering to be increased by 3–5 K. The influence of dissolved hydrogen on the Curie temperature of $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})$ and $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})$ compounds reduces to a significant decrease in T_C that is explained by the weakening of the exchange interaction in intermetallics caused by increasing interatomic distances [14].

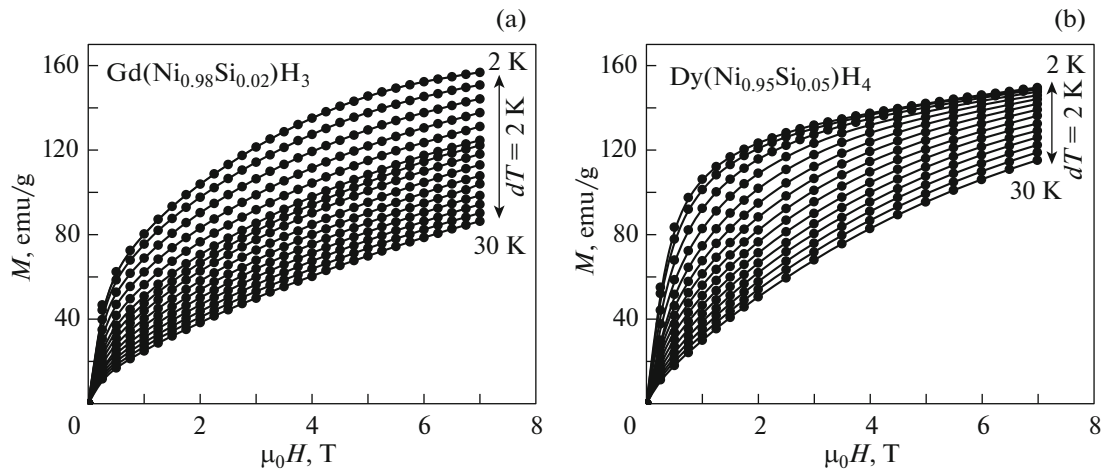
Measurements of the field dependences of magnetization at various temperatures in the vicinity of Curie temperature T_C allow the MCE magnitude of a material under the action of applied magnetic field to be esti-

mated (Figs. 1, 2). Figure 1 presents an example of magnetization curves measured for (a) $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_3$ and (b) $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_4$ hydrides. Indirect estimation of the MCE can be obtained by calculating a change in the magnetic entropy (ΔS_M) via the following Maxwell's relation [15]:

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

This equation relates the entropy to derivative of magnetization M with respect to temperature T at constant applied magnetic field varied from 0 to H .

Results of calculations of the (ΔS_M) value for $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_y$ ($y = 0, 3$) and $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_y$ ($y = 0, 4$) systems are presented in Fig. 2. A comparison of the data reported for RNi ($R = \text{Gd}, \text{Dy}$) compounds to our results obtained for R–Ni–Si systems showed that partial substitution of Si for Ni atoms did not significantly influence the MCE magnitude ($-\Delta S_M = 14.5\text{ J/(kg K)}$ for GdNi and $-\Delta S_M = 14.7\text{ J/(kg K)}$ for

**Fig. 1.** Field dependences of magnetization measured for (a) $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_3$ and (b) $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_4$ hydrides at various temperatures.

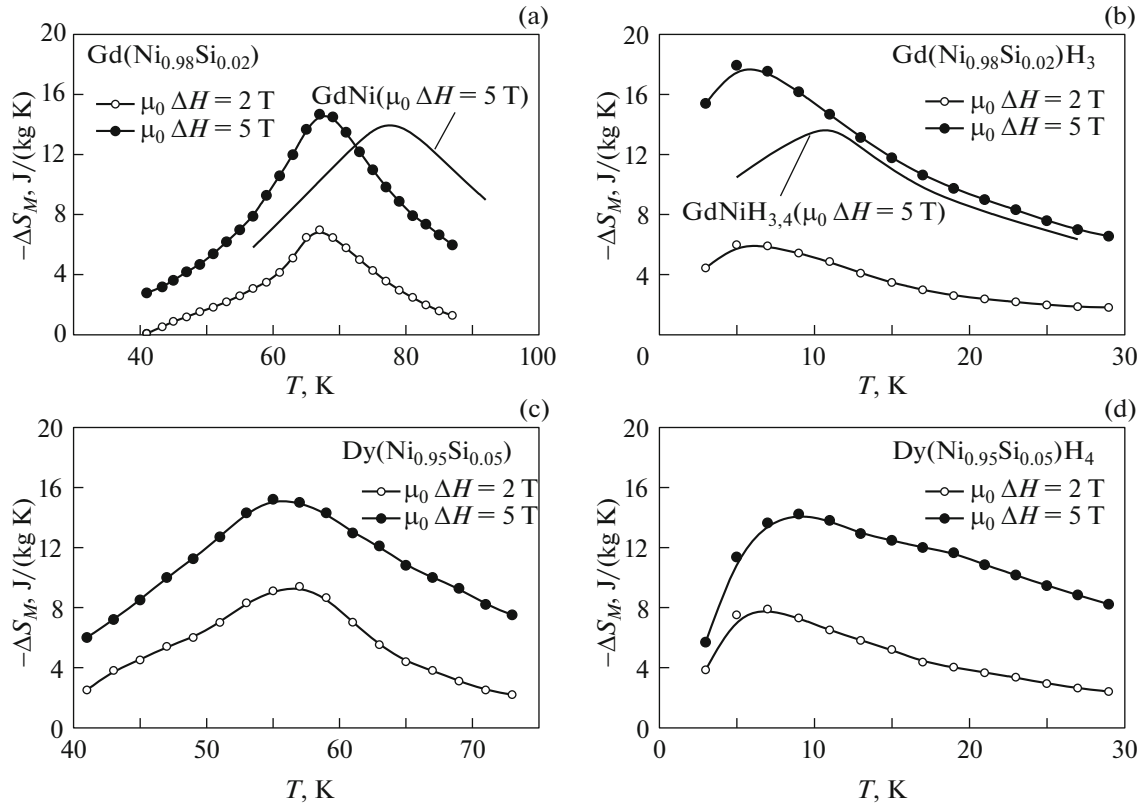


Fig. 2. Temperature dependences of MCE magnitude $-\Delta S_M$ calculated for (a) $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})$ and GdNi , (b) $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_3$ and $\text{GdNiH}_{3.4}$, (c) $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})$, and (d) $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_4$ in various magnetic fields.

$\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})$ in magnetic field of $\mu_0 \Delta H = 5$ T) and decreases MCE in the case of $R = \text{Dy}$ ($-\Delta S_M = 18$ J/(kg K) for DyNi and $-\Delta S_M = 15.2$ J/(kg K) for $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})$ at $\mu_0 \Delta H = 5$ T).

In the R–Ni–Si system, hydrogenation differently influences the MCE magnitude depending on the REM type. In the case of $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_3$, the MCE increases by 3.3 J/(kg K) and amounts to $-\Delta S_M = 18$ J/(kg K) at $\mu_0 \Delta H = 5$ T. For $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_4$, the MCE decreases by 1 J/(kg K) and amounts to $-\Delta S_M = 14.2$ J/(kg K) at $\mu_0 \Delta H = 5$ T. This difference in the influence of hydrogen on the MCE magnitude can be explained by the variable content of hydrogen and silicon in the material, different crystalline structures of $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_y$ ($y = 0, 3$) and $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_y$ ($y = 0, 4$) compounds, and character of hydrogen impurity ordering in crystalline lattices of the CrB and FeB types [9]. Same factors probably influence a shift of the temperature of MCE maximum (T_{\max}) relative to the Curie temperature. Indeed, RNi compounds and their hydrides exhibit a shift of T_{\max} relative to T_C toward higher temperatures (by 1–3 K), while the T_{\max} values in R–Ni–Si compounds and their hydrides shift to lower values (by 7–8 K). The only exclusion has been observed for $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_4$, in which the MCE remains constant in a temperature interval of 7–

11 K ($T_C = 10$ K), which is referred to in literature as the “table-like effect.”

Analysis of the data presented in Table 1 also shows that the MCE magnitude in all compounds studied varies within 14–18 J/(kg K). Note that the maximum effect in these compounds has been observed for the intermetallic compound DyNi and the sample modified with both substituted atoms and interstitial impurity, $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_3$, which is evidence of efficiency of the combined approach to variation of the material composition [16]. Therefore, by changing the contents of silicon and hydrogen, it is possible to create a set of materials with the same MCE but variable T_C and T_{\max} values. These multicomponent systems can be used for obtaining functional materials for cascade refrigerators [17].

In conclusion, it should be emphasized that partial substitution of Si atoms for Ni in RNi compounds and their subsequent hydrogenation can significantly change not only the Curie temperature and MCE magnitude, but also the temperature at which the MCE maximum takes place. The values of $-\Delta S_M$ discovered in $\text{Gd}(\text{Ni}_{0.98}\text{Si}_{0.02})\text{H}_y$ ($y = 0, 3$) and $\text{Dy}(\text{Ni}_{0.95}\text{Si}_{0.05})\text{H}_y$ ($y = 0, 4$) are comparable with and even exceed those observed in other magnetocaloric materials [18]. It is important that the maximum

of $-\Delta S_{M(T)}$ is achieved in the interval of $T_{\max} = 3\text{--}75$ K, so that these compounds are promising materials for low-temperature magnetic refrigerators used for cooling liquified natural gases.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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