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Influence of interstitial and substitutional atoms on magnetocaloric effects in *R*Ni compounds

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HIGHLIGHTS

- New (GdDy)NiH_3 hydrides were obtained.
- In Dy-rich compounds, the hydrogenation leads to a change of a crystal structure.
- Hydrogenation leads to an extremely large reduction of the Curie temperature.
- ***The (GdDy)NiH3 hydrides obey high values of the plateau-like magnetocaloric effect.***

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ABSTRACT

The effects of substitutional and interstitial atoms on the magnetic and magnetocaloric properties are investigated for *R*Ni (R is rare earth) compounds attractive for magnetic solid-state cooling at cryogenic temperatures. We focused on combining weakly and highly anisotropic rare earth compounds and obtained $Gd_xDy_{1-x}Ni$ ($x = 0.1$ and 0.9) compounds and their $Gd_xDy_{1-x}NiH_3$ hydrides. We observed a considerable decrease in Curie temperatures (T_C) in the hydrides $Gd_xDy_{1-x}NiH_3$ compared to their parent alloys. The magnetocaloric effect (MCE) values of $Gd_xDy_{1-x}NiH_y$ ($y = 0$ and 3) in the vicinity of T_C were obtained and compared with literature data for the final GdNi and DyNi compounds. The maximum specific isothermal entropy changes $-\Delta s_T$ at $\mu_0\Delta H = 5$ T were 14.5, 17, and 17.5 J $kg^{-1}K^{-1}$ for GdNi, $Gd_{0.9}Dy_{0.1}Ni$, and $Gd_{0.9}Dy_{0.1}NiH_3$, respectively. For DyNi, $Gd_{0.1}Dy_{0.9}Ni$, and $Gd_{0.1}Dy_{0.9}NiH_3$, they were $-\Delta s_T = 18$, 15.5, and 12.5 J $kg^{-1}K^{-1}$ at $\mu_0\Delta H = 5$ T, respectively. $-\Delta s_T(H)$ in $Gd_{0.9}Dy_{0.1}NiH_3$ at $T = T_C$ linearly increased in fields up to 7 T, while $Gd_{0.1}Dy_{0.9}NiH_3$ at $T \geq T_C$ showed a plateau-like magnetocaloric effect at $\mu_0\Delta H = 5$ and 7 T. The observed effects were explained based on altered exchange and magnetocrystalline interactions in the modified compounds.

1. Introduction

To date, considerable research has been devoted to elucidating new magnetocaloric materials suitable for applications at cryogenic temperatures [1–4]. Magnetic resonance imaging, cryopreservation of cells in microbiology, particle accelerators, superconducting quantum interference device (SQUID) magnetometers, quantum computers, levitating vehicles, and gas liquefaction (natural gas becomes a liquid at ~111 K, while other He, N_2, O_2, and H_2 gases require even lower temperatures) for their use and transportation are examples of considerable significance. Magnetic cooling has long been used to obtain temperatures well below 1 K. The achievement of ultra-low temperatures was a breakthrough in studies of physical properties of materials and revolutionised the development of fundamental sciences. Much effort has been recently devoted to room temperature magnetic refrigeration as a clean alternative to conventional vapor-compression technology. In this paper, we assess efficient materials suitable for magnetism-based refrigeration at cryogenic temperatures (<120 K) and explore their properties under extreme conditions, for example, in high magnetic fields (up to 58 T) using highly anisotropic elements.

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The most important compounds are ferro- or ferrimagnetic materials operating near Curie temperatures, where a large magnetocaloric effect is observed [5]. The magnetism of *R*Ni (*R* is rare earth) compounds is of considerable significance as these compounds exhibit a large magnetocaloric effect (MCE) at temperatures where nitrogen becomes liquid [6–8]. *R*Ni with R = La–Gd crystallise in an orthorhombic CrB type of structure (space group *Pnma*) while the structure is an FeB type for R = Dy–Lu and YNi (space group *Cmcm*) [9,10]. The magnetic transition temperatures, magnetisation, and magnetic anisotropy of rare earth intermetallics are extremely sensitive to various treatments of starting compounds (e.g., for melt spinning [11]) and various substitutions in the rare earth and Ni sublattices. The absorption of light interstitial elements, for example, hydrogen, also significantly alters the compounds' properties [12–14].

*R*Ni compounds are known to readily interact with hydrogen to form stable intermetallic phases containing 3–4 atoms per formula unit (f.u.). The interactions with hydrogen were studied in detail [15]. Hydrogenation was shown to cause a decrease in the transition temperatures of *R*Ni from 70 to 10 K. Hydrogen absorption significantly boosts the volume and weakens the magnetic interactions. The magnitude of the change in isothermal entropy, MCE, is often maintained at the level of the parent compounds. This extends the temperature application range of the *R*Ni-type intermetallics to lower temperatures.

In this study, we investigated the changes in the structural, magnetic, and magnetocaloric properties of $Gd_xDy_{1-x}NiH_y$ ($x = 0.1$ and 0.9; $y = 0$ and 3) by combining weakly and highly anisotropic Gd^{3+} and Dy^{3+} rare earth ions with magnetic moments equal to 7 and 10 μ_B, respectively. While the magnetic anisotropy field in the GdNi compound was weak at 1 T [16], in the DyNi compound, it was an order of magnitude larger [17,18]. We compared the properties of $Gd_xDy_{1-x}NiH_y$ with those of previously studied $RNiH_y$ compounds with Gd and Dy.

1.1. *Experimental details*

Ingots of $Gd_xDy_{1-x}Ni$ ($x = 0.1$ and 0.9) weighing approximately 8 g were prepared from stoichiometric mixtures of pure elements (R 99.9% and Ni 99.999%) in an arc furnace under an Ar protective atmosphere on a copper water-cooled crucible. The samples were remelted 4 times to ensure better homogeneity. The $Gd_xDy_{1-x}NiH_3$ ($x = 0.1$ and 0.9) hydrides were synthesised by direct hydrogen absorption using a Sievert-type setup with a hydrogen pressure operating range to 100 MPa. The hydrides' composition was calculated from the volume change before and after absorption using the van der Waals equation.

X-ray diffraction (XRD) patterns were obtained in a Bragg-Brentano geometry using an Empyrean Malvern PANalytical diffractometer. Data were collected using Cu-Kα radiation in a range of $2\theta = 10$–115° at steps of 0.0072°. The diffraction patterns were analysed by a whole pattern fitting procedure using FullProf software to determine the structural properties.

The samples were measured in steady magnetic fields up to 7 T in a temperature range of 4–120 K using a SQUID magnetometer (Quantum Design, USA). High-field magnetisation measurements were conducted at the Dresden High Magnetic Field Laboratory in pulsed magnetic fields up to 58 T [19]. Comparative magnetic studies of the parent compounds and hydrides were performed on samples crushed into powder. The absolute magnetisation values in pulsed-field data were calibrated using static field data up to 7 T. To determine the magnetocaloric effect (indirect method) near the magnetic phase transition (Curie temperature), a set of magnetic isothermal *M*(H) curves was measured with steps of 2–3 K in increasing and decreasing magnetic fields up to 7 T. The isothermal entropy change was calculated from these magnetisation isotherms by integrating Maxwell's relation [20]. The estimated error in the MCE determined using this method reached 15%.

2. Results and discussion

Fig. 1 compares the XRD patterns of $Gd_{0.1}Dy_{0.9}Ni$ (a) and $Gd_{0.9}Dy_{0.1}Ni$ (b) that crystallised in an FeB type of structure (space group *Pnma*) and $Gd_{0.9}Dy_{0.1}Ni$ with a CrB structure (space group *Cmcm*). The Rietveld refinements (using FullProf) of the XRD patterns using orthorhombic phase models (space group *Pnma* #62 and *Cmcm* #63) are shown by the red lines. The samples are single phase and their lattice parameters are shown in Table 1 with the lattice parameters of $Gd_{0.1}Dy_{0.9}NiH_3$ and $Gd_{0.9}Dy_{0.1}NiH_3$ hydrides. Data for GdNi and DyNi compounds were taken from Refs. [11,21]. Note that hydrogenation of DyNi changed its crystal structure while the same effect was found for the Dy-rich $Gd_{0.1}Dy_{0.9}Ni$ compound. The unit cell expansion after hydrogenation was more than 20%.

To investigate the magnetisation curves' field behaviour and obtain information on the Ni magnetic moment in the parent $Gd_{0.1}Dy_{0.9}Ni$ and $Gd_{0.9}Dy_{0.1}Ni$ compounds and hydrides at low temperatures, the magnetisation was measured in static and pulsed magnetic fields up to 58 T. Fig. 2 shows the *M*(H) magnetisation curves of the $Gd_xDy_{1-x}NiH_y$ ($x = 0.1$ and 0.9; $y = 0$ and 3). All the compounds displayed typical ferrimagnet behaviour. The magnetisation rapidly increased in weak magnetic fields, and then its growth slowed in the compounds with a high Dy content ($Gd_{0.1}Dy_{0.9}Ni$ and $Gd_{0.1}Dy_{0.9}NiH_3$). The magnetisation saturated in fields exceeding 50 T in the $Gd_{0.1}Dy_{0.9}Ni$, while the $Gd_{0.1}Dy_{09}NiH_3$ required an even higher field of 55 T to saturate [22]. However, the compounds with high Gd content ($Gd_{0.9}Dy_{0.1}Ni$ and $Gd_{0.9}Dy_{0.1}NiH_3$) reached the magnetic saturation rather rapidly. The different *M*(H) magnetisation behaviour in the Dy-rich and Dy-lean compounds was obviously due to the highly anisotropic character of Dy^{3+} ions. This occurred because the magnetic saturation field was proportional to the magnetic anisotropy constant.

The increase in the Gd content from 0.1 to 0.9 in the $Gd_xDy_{1-x}Ni$ decreased the saturation magnetic moment from 9.65 μ_B/f. u. to 7.2 μ_B/f. u. and fully removed the hysteresis due to the isotropic nature of Gd^{3+} ions. Moreover, the magnetism of both compounds originated mainly from the rare earth sublattice and the Ni magnetic moment μ_{Ni} was ≤ 0.1 μ_B taking into account experimental magnetisation measurement errors. After hydrogenating the $Gd_{0.1}Dy_{0.9}Ni$ and $Gd_{0.9}Dy_{0.1}Ni$ compounds to the point of 3 hydrogen atoms per formula unit (at.H/f.u.), we did not observe any changes in the magnetic saturation moment. Hence, the magnetism of the $Gd_{0.1}Dy_{0.9}NiH_3$ and $Gd_{0.9}Dy_{0.1}NiH_3$ was preserved after hydrogenation. Magnetic hysteresis practically disappeared in the $Gd_{0.1}Dy_{0.9}NiH_3$. Hydrogen absorption largely increased the distances (due to the volume boost) between magnetically active highly anisotropic Dy^{3+} and weakly anisotropic Gd^{3+} ions, changing the magnetic anisotropy [23,24].

Fig. 3 demonstrates the temperature dependencies of the magnetisation of the $Gd_xDy_{1-x}NiH_y$ ($x = 0.1$ and 0.9; $y = 0$ and 3) measured in a 10 mT field (in the field cooling (FC) mode). Each compound's Curie temperature (T_C) was determined by calculating a d*M*/d*T* derivative of the temperature dependence of the magnetisation *M*(*T*) (see the inset in Fig. 3).

Analysis of previous studies and data obtained in this work (Table 1) provided valuable information on the combined influence of hydrogen doping and substitution on the Curie temperature. With a low substitution of Gd atoms by Dy atoms in the GdNi, the Curie temperature decreased only slightly from $T_C \approx 70$ K in the GdNi to 66 K in the $Gd_{0.9}Dy_{0.1}Ni$. Hydrogenation significantly decreased the T_C to 8 K in the $Gd_{0.9}Dy_{0.1}NiH_3$. In the DyNi, the substitution and interstitial atoms influenced the Curie temperature and demonstrated the following tendency. The T_C was ~60 K in the DyNi, 64 K in the $Gd_{0.1}Dy_{0.9}Ni$, and 7 K in the $Gd_{0.1}Dy_{0.9}NiH_3$. This dramatic influence of hydrogen on the T_C in *R*Ni was due to weakening of exchange interactions that directly depend on the distance between the atoms [25]. Hydrogenation increased the unit cell volume. Ni atoms in Gd-Dy-Ni compounds are known to have a low magnetic moment of 0.1 μ_B while Gd and Dy have substantial

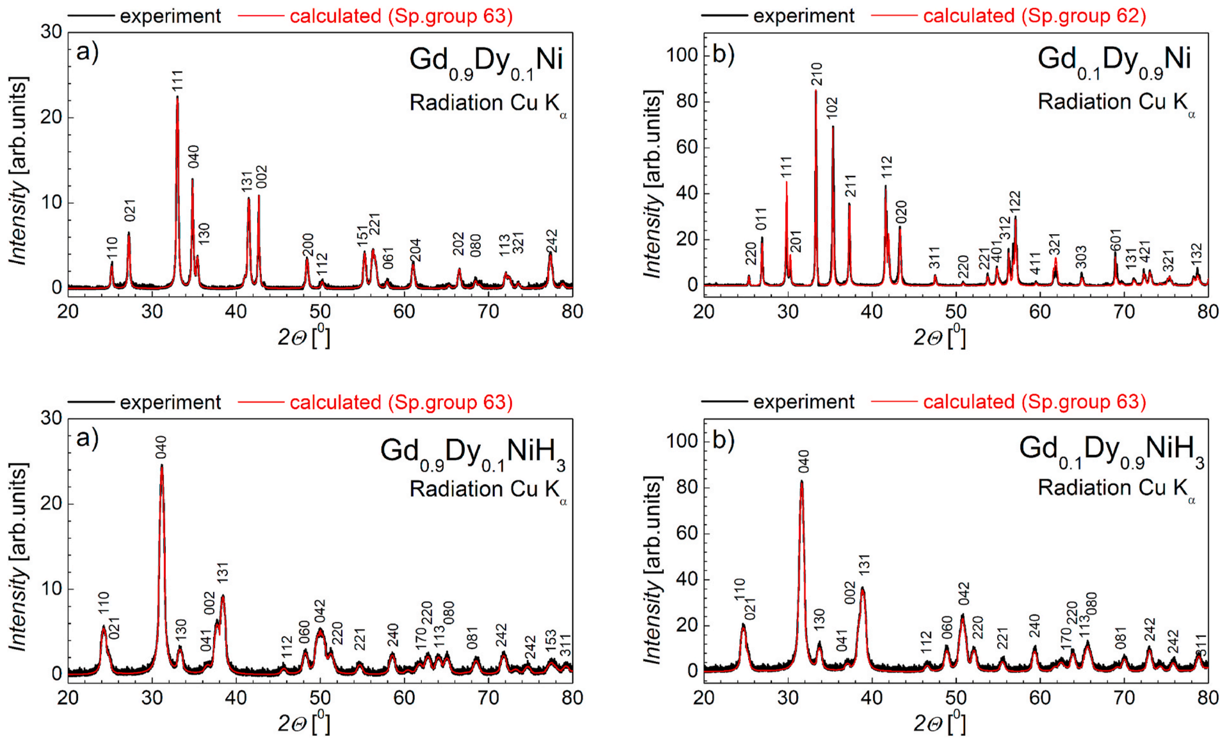

Fig. 1. The room temperature X-ray diffraction data for $Gd_{0.9}Dy_{0.1}Ni$ (a), $Gd_{0.9}Dy_{0.1}NiH_3$ (b), $Gd_{0.1}Dy_{0.9}Ni$ (a), and $Gd_{0.1}Dy_{0.9}NiH_3$ (b).

Table 1
The room temperature structural parameters, Curie temperature T_C, and specific isothermal entropy changes under a field change of 5 T.

Sample	Structure type	a, nm	b, nm	c, nm	T_C, K	$(-\Delta s_T)_{max}$, J [a]$kg^{-1}K^{-1}$ (at $\mu_0\Delta H = 5$ T)
GdNi [8]	CrB	0.3778	1.0334	0.4238	69–71	14.5
$GdNiH_{3.2}$ [8]	CrB	03767	1.1576	0.4733	10	14
$Gd_{0.9}Dy_{0.1}Ni$	CrB	0.3766	1.0322	0.4241	66	17
$Gd_{0.9}Dy_{0.1}NiH_3$	CrB	0.3769	1.1454	0.4765	8	17.5
DyNi [9,10]	FeB	0.7025	0.4181	0.5445	59–61	18
$DyNiH_{3.4}$ [8–11]	CrB	0.3719	1.1329	0.4645	3.5	–
$Gd_{0.1}Dy_{0.9}Ni$	FeB	0.7034	0.4177	0.5447	64	15.5
$Gd_{0.1}Dy_{0.9}NiH_3$	CrB	0.3723	1.1348	0.4672	7	12.5

[a] In the Proof there is a line break which is incorrect - between **J and kg^{-1}K^{-1}**

moments of 7 μ_B and 10 μ_B, respectively. The exchange interactions in the *R*Ni was provided by hybridised 3d-5d states. Hydrogenation increased the concentration of electrons in the 3d band by completing it. The resulting magnetic moment of the 3d subsystem in the $Gd_xDy_{1-x}NiH_3$ became extremely low, exchange interactions strongly decreased, and the Curie temperature decreased.

We considered the magnetocaloric effect in the studied compounds. Generally, there are several ways to determine the MCE in magnetic materials in the vicinity of the magnetic phase transitions [26], indirect (by recalculating the magnetisation and heat capacity data) and direct measurements of the adiabatic temperature change in samples after the magnetic field changes. An indirect method of evaluating the MCE features was used in this study. Measuring the magnetisation's field dependencies at various temperatures near the Curie temperature allowed us to evaluate the magnetocaloric effects on the samples. Magnetisation isotherms of the $Gd_xDy_{1-x}NiH_y$ ($x = 0.1$ and 0.9; $y = 0$ and 3) were measured at selected temperatures in the vicinity of their ordering temperatures up to the maximum applied magnetic field of 7 T (see Fig. 4). The specific isothermal entropy change Δs_T in the samples under the influence of the varied field was estimated using the following equation [5]:

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

Fig. 5 shows the temperature dependencies of Δs_T of the $Gd_xDy_{1-x}NiH_y$ ($x = 0.1$ and 0.9; $y = 0$ and 3) at $\mu_0\Delta H = 2$, 5, and 7 T. We first compared the values of the maximum entropy $-\Delta s_T$ change with the literature's data on GdNi and DyNi (see Table 1). In the GdNi, $-\Delta s_T = 14.5$ J/kg·K at $\mu_0\Delta H = 5$ T and $-\Delta s_T = 17$ J/kg·K in the $Gd_{0.9}Dy_{0.1}Ni$. Therefore, partial replacement of Dy for Gd increased the MCE. Hydrogenation also slightly increased the MCE, $-\Delta s_T = 17.5$ J/kg·K in the $Gd_{0.9}Dy_{0.1}NiH_3$ at $\mu_0\Delta H = 5$ T. Conversely, $-\Delta s_T = 18$ J/kg·K in the DyNi [7] and $-\Delta s_T = 15.5$ J/kg·K in the $Gd_{0.1}Dy_{0.9}Ni$ at $\mu_0\Delta H = 5$ T. Hydrogenation of the $Gd_{0.1}Dy_{0.9}Ni$ further decreased the MCE to $-\Delta s_T = 12.5$ J/kg·K in the $Gd_{0.1}Dy_{0.9}NiH_3$ at $\mu_0\Delta H = 5$ T. The different tendencies in the two series of compounds might have related to the different crystal structures. The MCE values in the GdxDy1-xNiHy compounds also exceeded values demonstrated by rare earth metals, for example, Er, which had the magnetic phase transition temperatures in the considered temperature range [5].

We considered the field and temperature features of the magnetocaloric effects' behaviour in the compounds. Comparing the $-\Delta s_T$ (T)

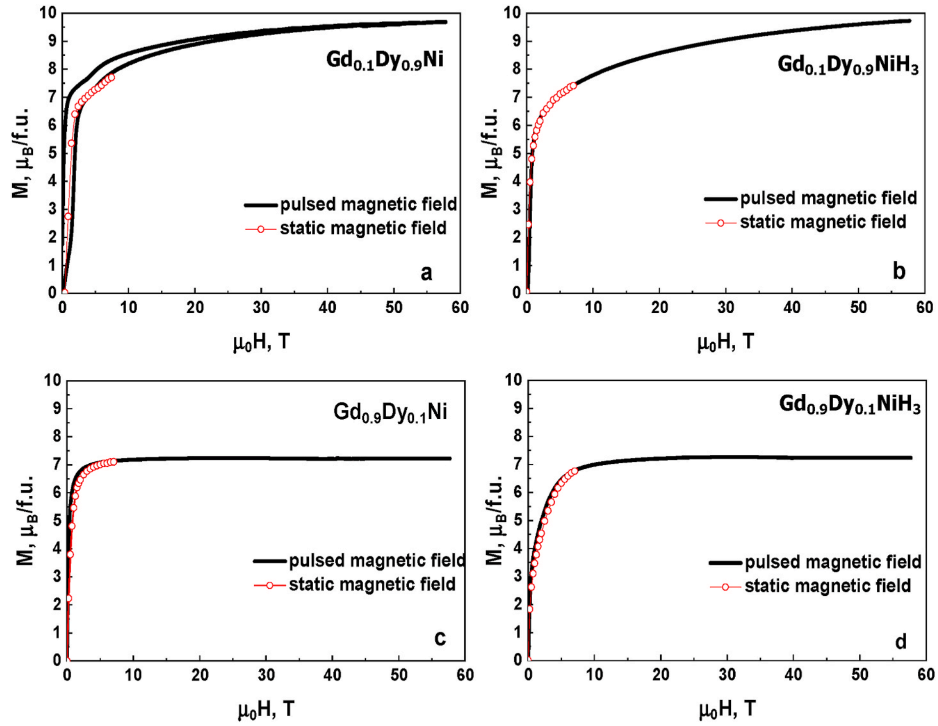

Fig. 2. Magnetisation curves of the $Gd_{0.1}Dy_{0.9}Ni$ (a), $Gd_{0.1}Dy_{09}NiH_3$ (b), $Gd_{0.9}Dy_{0.1}Ni$ (c), and $Gd_{0.9}Dy_{0.1}NiH_3$ (d) at 1.8 K in static magnetic fields (open circles) and pulsed magnetic fields (solid line).

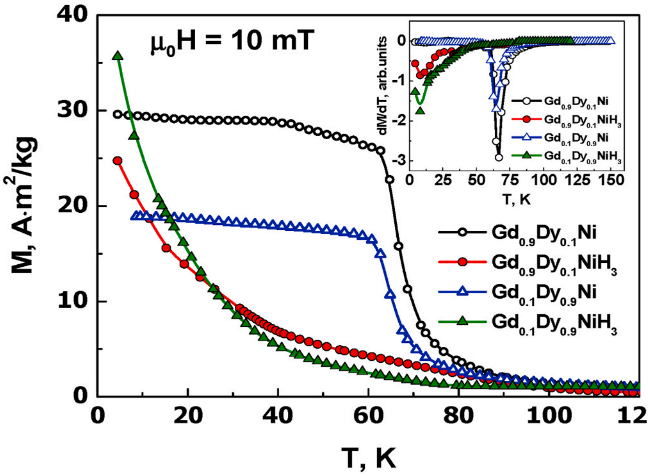

Fig. 3. Temperature dependencies of the magnetisation $M(T)$ of the $Gd_xDy_{1-x}NiH_y$ ($x = 0.1$ and 0.9; $y = 0$ and 3) measured in a 10 mT field. Inset: The temperature dependence of the dM/dT derivative of the same compounds.

curves of the $Gd_{0.9}Dy_{0.1}Ni$ and its $Gd_{0.9}Dy_{0.1}NiH_3$ hydride, the maximum MCE value depended on the applied magnetic field's value (see Fig. 5a and b, respectively). The magnitude of the MCE in the $Gd_{0.9}Dy_{0.1}NiH_3$ hydride was $-\Delta s_T = 25$ J kg^{-1}K^{-1} at $\mu_0\Delta H = 7$ T, which largely exceeded the corresponding value of the parent $Gd_{0.9}Dy_{0.1}Ni$ alloy in the same field, 21 J kg^{-1}K^{-1}. Conversely, the parent compounds demonstrated a larger MCE in fields up to 2 T, $-\Delta s_T = 9$ J kg^{-1}K^{-1} compared to 5.5 J kg^{-1}K^{-1} in the hydrogenated compound. This behaviour was likely associated with the magnetocrystalline anisotropy's effects on the MCE due to the highly anisotropic Dy^{3+} ions.

We also compared the $-\Delta s_T$(T) dependences of the Dy-rich $Gd_{0.1}Dy_{0.9}Ni$ compound and its hydride. The $-\Delta s_T$(T) curves were symmetric with respect to the maximum T_C in the parent $Gd_{0.1}Dy_{0.9}Ni$ compound (see Fig. 5c). Δs_T(T) of the hydride compound $Gd_{0.1}Dy_{0.9}NiH_3$ was no longer symmetric. At temperatures above the T_C, we observed a plateau-like MCE (see Fig. 5d), which was most pronounced in the fields 5 and 7 T. The MCE's magnitude decreased very slowly as the temperature increased and had rather high values in the large temperature span. This may also be attractive. Note that the plateau-like effect was characteristic of inhomogeneous magnets and a direct consequence of the inhomogeneity's influence on the MCE [27–29]. For example, in Ref. [27] rare earth-doped (R1-xRx)Ni2 compounds were studied in detail. To theoretically discuss the magnetocaloric effects on this type of doped compound, a Hamiltonian model including the rare earth ions' localised moments and the transition elements' itinerant electrons was used. This proved the broadening of the MCE peaks and the plateau-like behaviour of the ΔsT(T) curves.

Fig. 6 shows the field dependencies of the materials' MCE at their Curie temperatures. The inset in Fig. 6 shows the MCE rate change with respect to the applied field $|\Delta s_T|/\Delta H$ (in other words, the Δs_T values were normalised to field changes at which they were measured). This simple representation indicated that some of the compounds demonstrated a relatively large entropy change $|\Delta s_T|/\Delta H \geq 3$ J kg^{-1}K^{-1}T (in the $Gd_{0.9}Dy_{0.1}Ni$, $Gd_{0.9}Dy_{0.1}NiH_3$, and $Gd_{0.1}Dy_{0.9}Ni$) while the other was $|\Delta s_T|/\Delta H < 3$ J kg^{-1}K^{-1}T (in the $Gd_{0.1}Dy_{09}NiH_3$). Fig. 6 shows that the $-\Delta s_T$(H) curve changed considerably in the $Gd_{0.9}Dy_{0.1}NiH_3$ compared to the curve of the parent alloy $Gd_{0.9}Dy_{0.1}Ni$. We observed a practically linear dependence of $-\Delta s_T$ on the applied field up to 7 T.

We concluded that both substitutions and hydrogen doping were quite effective in modifying the exchange and magnetocrystalline interactions in the *R*Ni compounds [30,31]. Hydrogenation shifted the Curie temperatures toward lower temperatures. Combining the highly anisotropic Dy^{3+} ($\mu_{Dy} = 10$ μ_B) with the weakly anisotropic Gd^{3+} ($\mu_{Gd} = 7$ μ_B) and the simultaneous introduction of hydrogen into the crystal lattice of the parent compounds allowed us to obtain materials with enhanced MCE values. We also observed additional effects such as a plateau-like MCE in the $Gd_{0.1}Dy_{0.9}NiH_3$ at $T > T_C$ that can be used to construct cryogenic refrigerators [32].

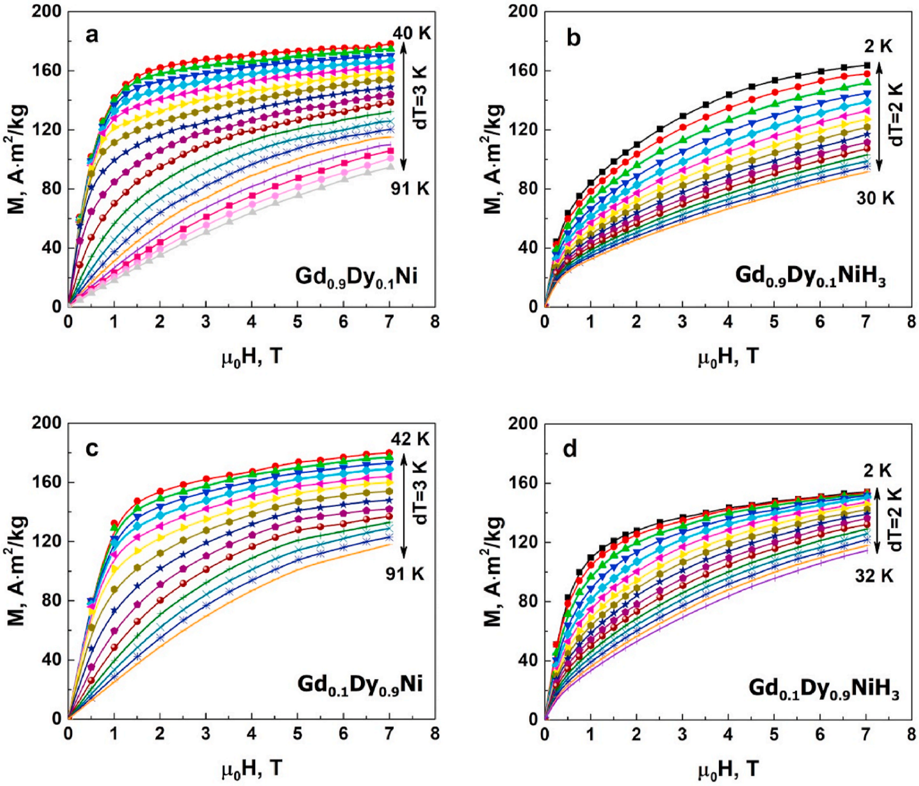

Fig. 4. Magnetisation isotherms of the $Gd_{0.9}Dy_{0.1}Ni$ (a), $Gd_{0.9}Dy_{0.1}NiH_3$ (b), $Gd_{0.1}Dy_{0.9}Ni$ (c), and $Gd_{0.1}Dy_{0.9}NiH_3$ (d) near their Curie temperatures.

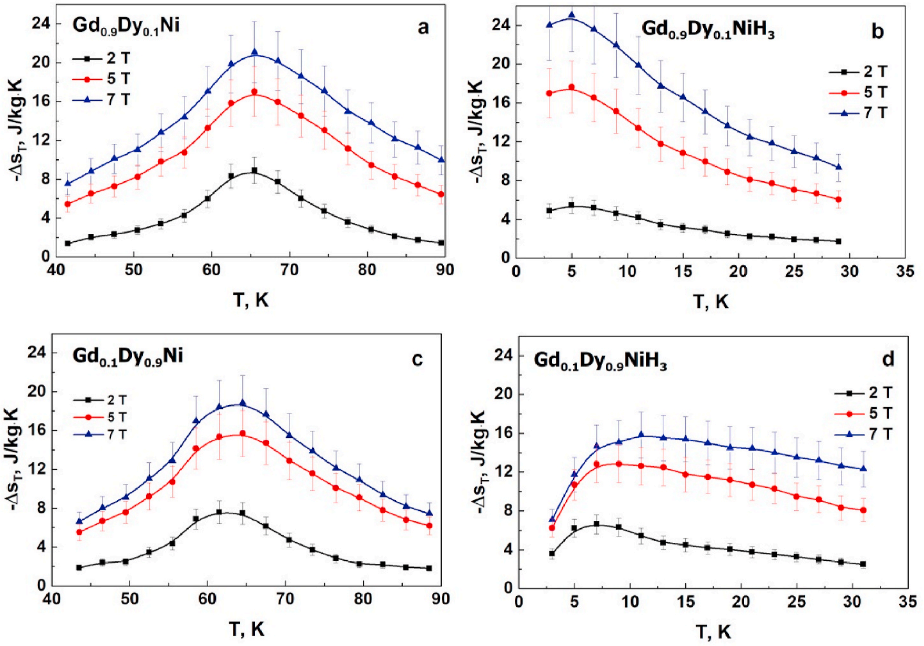

Fig. 5. The temperature dependencies of the specific isothermal entropy change -Δs_T in the $Gd_{0.9}Dy_{0.1}Ni$ (a), $Gd_{0.9}Dy_{0.1}NiH_3$ (b), $Gd_{0.1}Dy_{0.9}Ni$ (c), and $Gd_{0.1}Dy_{09}NiH_3$ (d) at $\mu_0\Delta H = 2$, 5, and 7 T.

3. Conclusions

We studied the combined effects of substituting atoms and hydrogen doping on the magnetic and magnetocaloric properties of $Gd_xDy_{1\text{-}x}NiH_y$ ($x = 0.1$ and 0.9; $y = 0$ and 3) compounds. Among the studied compounds, the highest MCE was demonstrated by the $Gd_{0.9}Dy_{0.1}NiH_3$, in which the Δs_T increased practically linearly as the field increased. The temperature at which we observed the maximum MCE in the $Gd_{0.9}Dy_{0.1}NiH_3$ decreased considerably with respect to the parent $Gd_{0.9}Dy_{0.1}Ni$ compound ($T_C = 66$ K) and was 8 K. The advantage of the $Gd_{0.1}Dy_{0.9}NiH_3$ hydride compared to the $Gd_{0.1}Dy_{0.9}Ni$ was that the high MCE values were preserved at temperatures higher than its T_C of 7 K. By

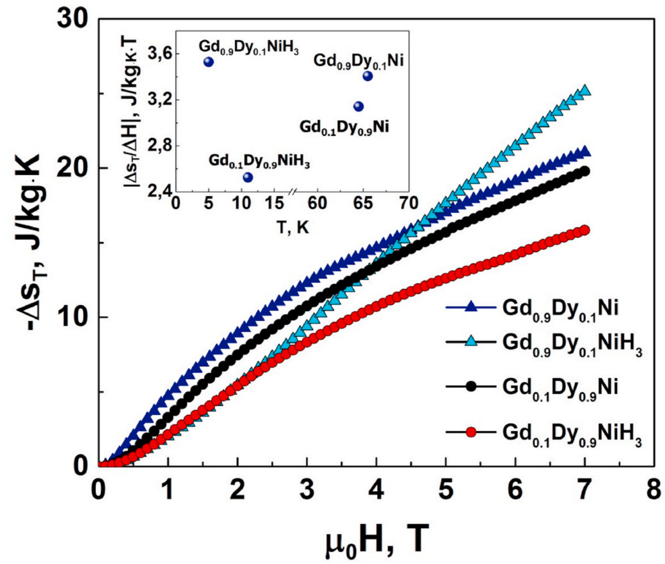

Fig. 6. The field dependencies of specific isothermal entropy change -Δs_T of the $Gd_xDy_{1-x}NiH_y$ ($x = 0.1$ and 0.9; $y = 0$ and 3) at their Curie temperatures. Inset: Entropy change $|\Delta s_T|/\Delta H$ of the compounds.

modifying the exchange and anisotropy interactions through atomic substitution and hydrogen doping and forming inhomogeneous magnets, we obtained new materials with improved MCE properties suitable for use at cryogenic temperatures. By varying the samples' hydrogen content and Gd/Dy ratios, we designed materials with desired properties.

CRediT authorship contribution statement

V.B. Chzhan: Investigation. **A.A. Kurganskaya:** Investigation, Writing – review & editing, Writing. **I.S. Tereshina:** Investigation, Writing – review & editing, Writing, Supervision, Project administration, Funding acquisition. **A. Yu Karpenkov:** Software, Formal analysis. **I.A. Ovchenkova:** Investigation, Writing – review & editing, Writing. **E. A. Tereshina-Chitrova:** Investigation, Writing – review & editing, Writing. **A.V. Andreev:** Resources, Supervision. **D.I. Gorbunov:** Investigation. **S.A. Lushnikov:** Resources, Investigation. **V.N. Verbetsky:** Resources, Investigation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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