



Research article

The effect of hydrogenation on the magnetocaloric properties of medium-entropy $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ alloyA.A. Kurganskaya^{*}, Zh. Liu, E.S. Kozlyakova, T.P. Kaminskaya, I.S. Tereshina, V.N. Verbetsky, S.V. Mitrokhin, A.N. Vasiliev

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ABSTRACT

We report a systematic investigation of the magnetic and magnetocaloric properties of the medium-entropy rare earth intermetallic compound $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ and its hydride $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ in applied magnetic fields up to 7 T. The parent compound crystallizes in an orthorhombic FeB-type structure (space group Pnma, #62) at room temperature and exhibits ferromagnetic ordering at $T_C \approx 60$ K. Upon hydrogenation, the crystal structure transforms to the CrB-type (space group Pnma, #62) with a reduced ferromagnetic transition temperature of $T_C \approx 6$ K. The Curie temperatures were determined through complementary methods: analysis of magnetization derivative (dM/dT) and Belov-Arrott plots. Isothermal magnetization measurements in the temperature range 2–90 K reveal a significant enhancement of the magnetocaloric effect (MCE) upon hydrogenation, with the maximum isothermal magnetic entropy change (ΔS_m) increasing from 8.3 J/(kg·K) to 13 J/(kg·K) at $\mu_0\Delta H = 5$ T near their respective T_C . Detailed analysis using multiple criteria (Banerjee criterion, Oesterreicher-Parker method, and field-dependence of ΔS_m) consistently indicates second-order magnetic phase transitions in both compounds. A comparative analysis with binary and pseudobinary analogues demonstrates unique features of the medium-entropy system, particularly in the low-field magnetocaloric response.

1. Introduction

Recent advances in materials science have established medium- and high-entropy alloys as a new paradigm for achieving enhanced functional properties through multi-component design [1–7]. These systems, characterized by their increased configurational entropy, often retain the structural motifs of their binary counterparts while exhibiting enhanced physical properties. This characteristic is particularly advantageous for applications in hydrogen storage and the development of novel functional materials for modern industrial applications [8–11].

Magnetic refrigeration technology in the cryogenic regime represents a significant advancement in cooling methods, offering both environmental sustainability and enhanced energy efficiency compared to conventional approaches [4,12–14]. One of the key challenges in this field involves developing magnetocaloric materials that effectively operate in the liquid hydrogen temperature range (13.95–20.39 K), where precise control of magnetic ordering temperatures is essential [15–18]. RNi-based compounds and their hydrides have demonstrated particularly promising characteristics for such applications. These

materials exhibit magnetic ordering temperatures that can be systematically tuned across the range of 3–75 K, with the capacity to incorporate up to 4 hydrogen atoms per formula unit. The fundamental structure of binary RNi compounds as two-sublattice magnets enables extensive compositional flexibility through substitutions in the rare-earth metal sublattice, the nickel sublattice, or both simultaneously. This versatility, combined with the ability to introduce hydrogen into their crystal lattice, serves two critical functions: it substantially expands the range of magnetic ordering temperatures in new multicomponent compounds and enables the development of materials with precisely spaced Curie temperatures needed for practical magnetic cooling applications. Our previous research has extensively documented the magnetic and magnetocaloric properties of (RR')Ni compounds and their hydrides [20–22], complemented by studies on both initial and hydrogenated (RR')(Ni,T) samples with various substitutional elements including Si, Co, and Cu in both sublattices [23–26].

The present investigation focuses on examining the structural, magnetic, and magnetothermal characteristics of the medium-entropy alloy $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ and its hydride $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$. To

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establish a comprehensive understanding of the material's properties, we have included detailed microstructural analysis using atomic force microscopy as part of the initial compound characterization.

2. Materials and methods

The $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ alloy was synthesized by arc-melting stoichiometric quantities of high-purity elements (99.9 %) under protective argon atmosphere. To compensate for rare earth volatilization during melting, these components were added with a 1 % excess. The hydride $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ was prepared using a Sievert-type apparatus with operating hydrogen pressures up to 10 MPa. Hydride composition was determined volumetrically using the van der Waals equation.

X-ray structural analysis of the samples was carried out in the Bragg-Brentano geometry using $\text{Cu-K}\alpha$ radiation in the range $2\theta = 10\text{--}120^\circ$ with a step of 0.0072° . PANalytical Empyrean diffractometer was used to record the XRD patterns, whereas Rietan 2000 refinement package was used to perform the data analysis.

The surface of the initial $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ sample was examined on a thin section by atomic force microscopy method. The studies were carried out at room temperature on a SMENA-A scanning probe microscope (SPM), Solver platform (NT-MDT, Russian Federation, Zelenograd) in the contact mode (with the use of constant force methods) in the lateral force mode using standard NSG 03 and fpc 10 cantilevers with a tip curvature radius of 10 nm, and a force constant of 0.35–6.1 N/m. The sample was scanned in areas ranging in size from $0.7 \times 0.7 \mu\text{m}$ to $70 \times 70 \mu\text{m}$. AFM images were processed using NOVA software. For processing of some AFM images, a digital method of software algorithm for processing images under a microscope – deconvolution (inverse convolution) was used, which allowed to increase the sharpness of images and visualize small details.

Magnetization isotherms of the samples were obtained in magnetic fields up to 7 T in the temperature range 2–270 K on standard PPMS-9 setup. Two methods were used to determine the Curie temperature. This combined approach allowed us to draw a conclusion about how the Curie temperatures of the studied samples change when they are placed in an external magnetic field.

One of the methods was to find the minimum in the temperature dependence of the magnetization derivative with respect to temperature. This method allows us to find the Curie temperature for a sample placed in a magnetic field.

The second method for determining the Curie temperature used in this work, the Belov-Arrot method [27], is based on the Landau phase transition theory [28]. According to the Inoue-Shimizu model [29,30], the free energy (F) of a magnetic system consisting of localized magnetic moments interacting with itinerant electrons depends on the magnetization (M) as follows:

$$F = \left(\frac{1}{2}\right)a(T)M^2 + \left(\frac{1}{4}\right)b(T)M^4 + \dots - \mu_0 H M \quad (1)$$

where $\mu_0 H$ is an external magnetic field, and a, b are temperature dependent coefficients.

From the equilibrium condition $\left(\frac{\partial F}{\partial M}\right) = 0$, we can obtain an equation describing the behavior of magnetization near the Curie temperature:

$$\frac{\mu_0 H}{M} = a(T) + b(T)M^2 + \dots \quad (2)$$

Assuming that the parameter b depends weakly on temperature, and the parameter a vanishes at $T = T_C$, we can determine the Curie temperature by neglecting the third and the following terms. To do that we make a linear $\frac{\mu_0 H}{M}(M^2)$ approximation of the strong external field part of the curves at various temperatures, so that we can extrapolate when intercept coefficient (a) becomes zero and thus yields T_C . We then

analyze the behavior of the weak external field part of the curves to determine the type of the magnetic transition.

The magnetocaloric effect was determined by an indirect method. Under isothermal conditions, the temperature of the sample remains constant, and the MCE can be characterized by the magnetic entropy change (ΔS_m). The relationship of the latter to the magnetization (M) and temperature (T) under the influence of an external magnetic field (H) is determined by Maxwell's equation:

$$\left(\frac{\partial S_m(T, H)}{\partial H}\right)_T = \left(\frac{\partial M(T, H)}{\partial T}\right)_H \quad (3)$$

Integrating, we get the following relation:

$$\Delta S_m(T, H) = \int_0^H \left(\frac{\partial M(T, H)}{\partial T}\right)_H dH, \quad (4)$$

which is used to determine MCE from magnetization isotherms.

The magnetic phase transition order was determined in three ways in this work. Firstly, the Banerjee criterion was used [31]. For this purpose, the coefficient b (see formula 2) was calculated for the linear part of the Belov-Arrot curves in low fields. This method assumes that for a second-order magnetic phase transition, the sought coefficient will be positive. Secondly, the dependence of the magnetic part of the entropy on the

value $\left(\frac{\mu_0 H}{T_C}\right)^{\frac{2}{3}}$, was studied. This method is based on the study by Oesterreicher and Parker, who assumed that the magnetic entropy at T_C as a function of field can be calculated analytically [32]. If the compound undergoes a second-order magnetic phase transition, then the dependence of the magnetic part of the entropy on the value $\left(\frac{\mu_0 H}{T_C}\right)^{\frac{2}{3}}$, will be linear.

Thirdly, another quantitative method was used to confirm the previous results [33]. Upon determining the magnetic part of the entropy ΔS_m , it can be seen that ΔS_m depends on the applied external magnetic field to the power n:

$$\Delta S_m \propto H^n \quad (5)$$

This method is based on the assertion that for samples with first order phase transition, ΔS_m depends on field with exponent $n > 2$. This method assumes that, by constructing the dependence:

$$n(T, H) = \frac{d \ln |\Delta S_m|}{d \ln H}, \quad (6)$$

and checking whether the parameter n reaches values greater than 2, we can draw a conclusion about the order of magnetic phase transition. The undoubted advantages of this method are its simplicity and reliability.

3. Results and discussion

The X-ray diffraction studies demonstrate characteristic structural transformations in the investigated system. The polycrystalline compound $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ crystallizes in an orthorhombic structure of the FeB type (space group Pnma, #63), while hydrogenation transforms it to the CrB structure type (space group Cmc21, #62) (cf. Figs. 1 and 2). This structural behavior mirrors what was previously observed in binary DyNi and pseudobinary $\text{Dy}_{0.9}\text{Gd}_{0.1}\text{Ni}$ compounds [20], where the latter was obtained through partial substitution of dysprosium with gadolinium in the rare earth sublattice. Notably, this structural transformation differs from binary GdNi and pseudobinary $\text{Gd}_{0.9}\text{Gd}_{0.1}\text{Ni}$ compounds, which maintain the CrB structure type in both their initial and hydrogenated states [20]. The structural stability appears to be characteristic of Gd-rich compositions, while Dy-containing compounds show a tendency toward structural transformation upon hydrogenation. The structural parameters for $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_x$ ($x = 0, 3$) and comparative data for DyNiH_x ($x = 0, 3.4$) and $\text{Dy}_{0.9}\text{Gd}_{0.1}\text{NiH}_x$ ($x = 0, 3$)

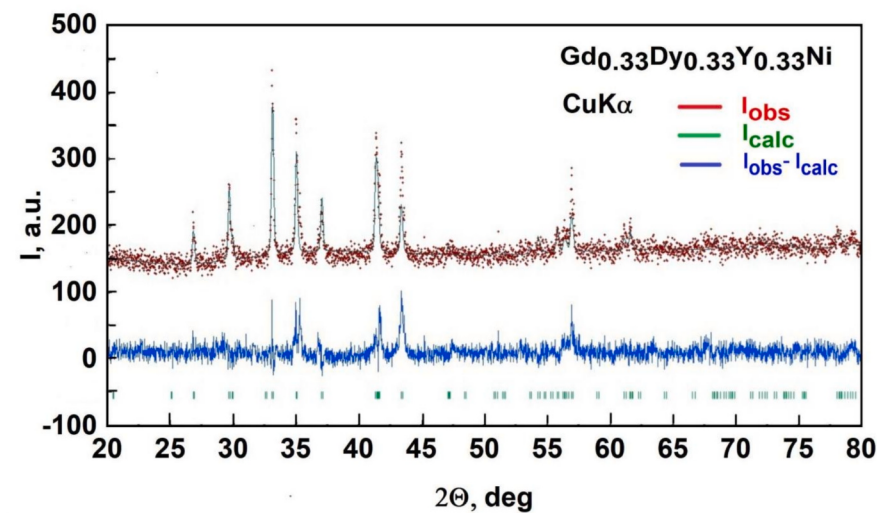


Fig. 1. Room temperature powder X-ray diffraction pattern of $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ collected with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Experimental data points (dark red), calculated profile (green), and their difference (blue) are shown. Vertical marks indicate the Bragg reflection positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

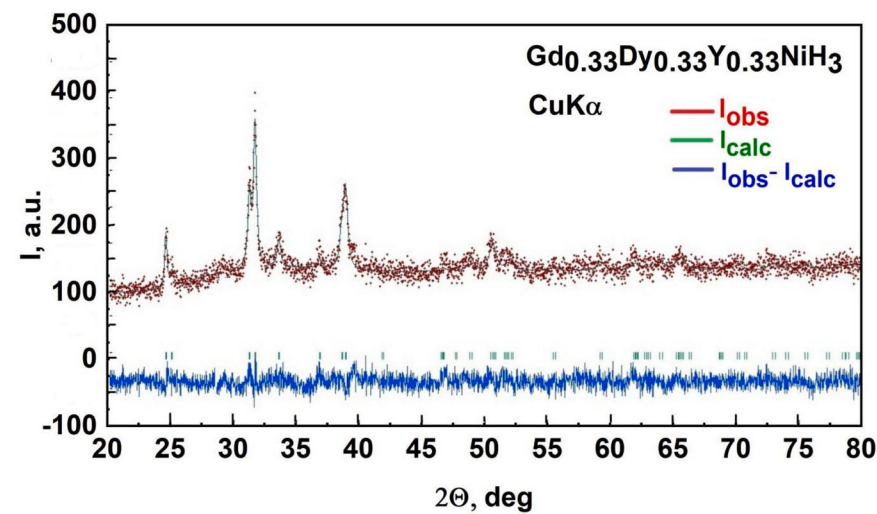


Fig. 2. Room temperature powder X-ray diffraction pattern of $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ collected with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Experimental data points (dark red), calculated profile (green), and their difference (blue) are shown. Vertical marks indicate the Bragg reflection positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

compounds are presented in Table 1. In all the compounds studied, hydrogenation leads to a significant volume expansion of approximately 22–23 %.

Atomic force microscopy investigations of the initial $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ sample reveal distinct morphological features at both microscopic and nanoscopic scales. At the microscale ($70 \times 70 \mu\text{m}$

scan area), the surface exhibits directional ordering characterized by fused filiform elements extending 35–40 μm in length, with widths of 2–7 μm and heights up to 300 nm (Fig. 3). The three-dimensional surface topography and corresponding cross-sectional profiles provide detailed insights into these structural features. Higher resolution imaging at the nanoscale ($700 \times 700 \text{ nm}$ scan area) reveals a granular morphology

Table 1
Room temperature structural parameters of the medium-entropy $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ compared to binary and pseudobinary RNi ($\text{R} = \text{Gd}, \text{Dy}$ and the mixture) compounds and their respective hydrides.

Sample	Structure type	a, nm	b, nm	c, nm	V, 10^{-3} nm^3	dV/V, %
$\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$	FeB	0.7078	0.4173	0.5467	161.5	—
$\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$	CrB	0.3725	1.1430	0.4657	198.3	22.8
GdNi [25]	CrB	0.3778	1.0334	0.4238	165.5	—
$\text{GdNiH}_{3.2}$ [25]	CrB	0.3767	1.1576	0.4733	206.4	24.7
DyNi [25]	FeB	0.7025	0.4181	0.5445	159.9	—
$\text{DyNiH}_{3.4}$ [25]	CrB	0.3719	1.1329	0.4645	195.7	22.4
$\text{Dy}_{0.9}\text{Gd}_{0.1}\text{Ni}$ [20]	FeB	0.7034	0.4177	0.5447	160.0	—
$\text{Dy}_{0.9}\text{Gd}_{0.1}\text{NiH}_3$ [20]	CrB	0.3723	1.1348	0.4672	197.1	23.3

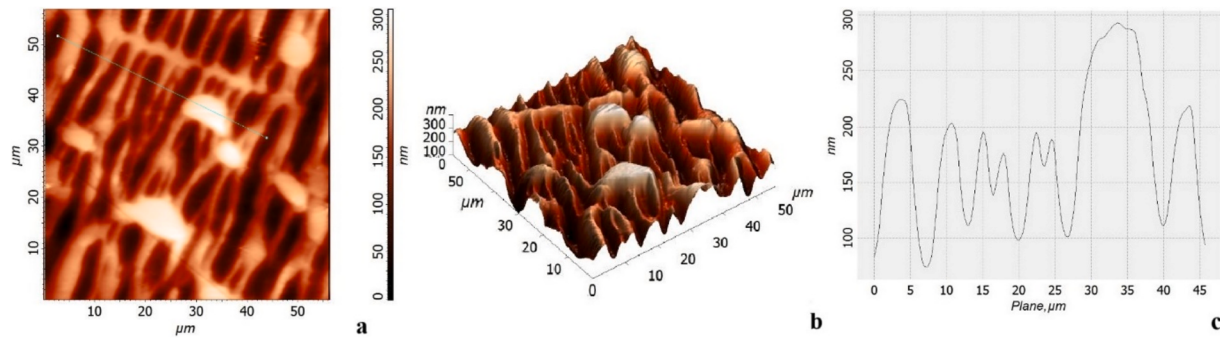


Fig. 3. Surface characterization of $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ by atomic force microscopy: (a) topographic image showing surface morphology at the microscale (scan area $70 \times 70 \mu\text{m}$), (b) three-dimensional representation of the surface topography, and (c) height profile along the selected cross-section demonstrating the vertical surface features.

comprising round and elliptical structural elements ranging from 20 to 40 nm in size. These primary structural units aggregate into larger conglomerates spanning 100–400 nm (Fig. 4).

The magnetic characteristics of the studied compounds and their binary analogues are summarized in Table 2. A systematic reduction in Curie temperature from 60–75 K to 3.5–10 K is observed upon hydrogenation across all compositions. This trend reflects a fundamental alteration in the magnetic exchange interactions induced by hydrogen incorporation.

In RNi compounds, which function as two-sublattice magnetic systems, the Curie temperature is determined by three exchange interaction components: within the rare-earth sublattice, within the nickel sublattice, and between these sublattices. Since nickel exhibits a negligible magnetic moment in these systems, we can conclude that the exchange interactions within the rare-earth sublattice provide the dominant contribution to the magnetic ordering [23]. Upon hydrogen insertion, a substantial expansion of the unit cell is observed—up to 22.8 % in volume (Table 1). According to the RKKY model, the strength of indirect exchange interactions mediated by conduction electrons decreases with increasing interatomic distance. Thus, the observed reduction in Curie temperature can be primarily attributed to the weakening of the exchange coupling within the rare-earth sublattice.

However, lattice expansion alone may not fully account for the dramatic magnetic suppression observed. Hydrogen incorporation likely alters the electronic structure by modifying hybridization between 4f orbitals and the conduction band, potentially disrupting exchange pathways or changing carrier density. Furthermore, local structural

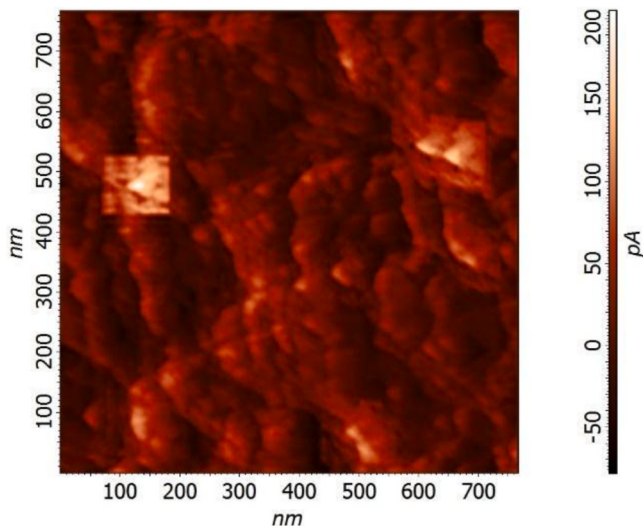


Fig. 4. Nanoscale AFM topographic image of $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ surface.

Table 2

Magnetic and magnetocaloric properties of $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$, GdNi , DyNi , $\text{Dy}_{0.9}\text{Gd}_{0.1}\text{Ni}$ compounds and their hydrides.

Sample	T_C , K, Belov- Arrotmethod	T_C , K, (dM/ dT)	T_{max} , K ($\mu_0 H =$ 5 T)	ΔS_m , J/(kg·K), ($\mu_0 H = 5$ T)
$\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$	60	66	68	8.3
$\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$	6	11	12	13
GdNi [19,34]	—	75	72	14.5
GdNiH _{3.2} [19,34]	—	10	11	14
DyNi [19,35]	—	60	63	18
DyNiH _{3.4} [19]	—	3.5	—	—
$\text{Dy}_{0.9}\text{Gd}_{0.1}\text{Ni}$ [20]	62	64	64.5	15.7
$\text{Dy}_{0.9}\text{Gd}_{0.1}\text{NiH}_3$ [20]	10	7	7	12.5

distortions introduced by hydrogen may contribute to changes in magnetic anisotropy or lead to enhanced spin disorder. These effects could be especially relevant in our mixed-lanthanide systems ($\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$), where competing exchange interactions are already delicately balanced.

Based on these anticipated significant changes in magnetic behavior, we developed a specialized magnetization measurement protocol for $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ and its hydride: initial $M(H)$ measurements were conducted at 2 K for both compounds, followed by measurements in the 40–90 K range (with 4 K steps) for the parent compound and in the ranges 9–15 K (with 2 K steps) and 15–90 K (with 5 K steps) for the hydride. This protocol enabled comprehensive characterization of magnetic behavior in both ordered and paramagnetic states.

The field-dependent magnetization measurements (Fig. 5) reveal distinct features: the parent compound $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ exhibits pronounced hysteresis at 2 K, which is significantly reduced in the hydrogenated phase. The hysteretic behavior diminishes with increasing temperature and vanishes completely at temperatures equal to or exceeding the respective Curie temperatures (see insets). These measurements suggest Curie temperatures of 62–66 K and 9–11 K for the parent and hydrogenated compounds, respectively, in applied fields. Temperature-dependent magnetization measurements in fields of 1–2 T (Fig. 6) corroborate these findings, yielding T_C values of 66 K for $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ and 11 K for $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$. Zero-field Curie temperatures, determined through Belov-Arrott analysis (Fig. 7), are 60 K and 6 K respectively, indicating a field-induced shift of 5–6 K in the ordering temperatures. These magnetic characteristics, along with corresponding data for binary GdNi, DyNi, and pseudobinary $\text{Dy}_{0.9}\text{Gd}_{0.1}\text{Ni}$ compounds and their hydrides, are compiled in Table 2.

The magnetocaloric effect, determined through indirect measurements, exhibits distinct characteristics in the parent and hydrogenated compounds. Fig. 8 shows the temperature dependencies of the magnetic part of the entropy in fields of 2, 5 and 7 T for the parent compound $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ and its hydride $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$. It is evident

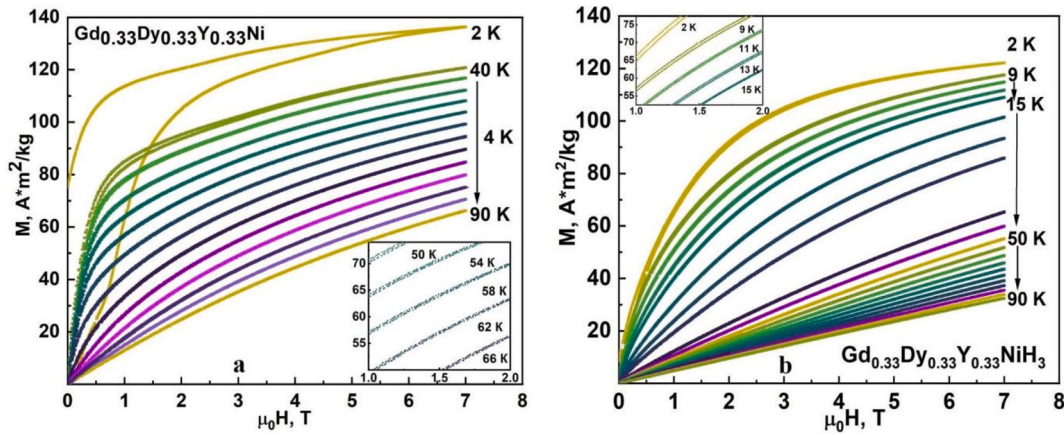


Fig. 5. Field dependence of magnetization $M(H)$ measured at $T = 2$ K for (a) $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ and (b) $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$. Insets show the $M(H)$ curves on a different scale.

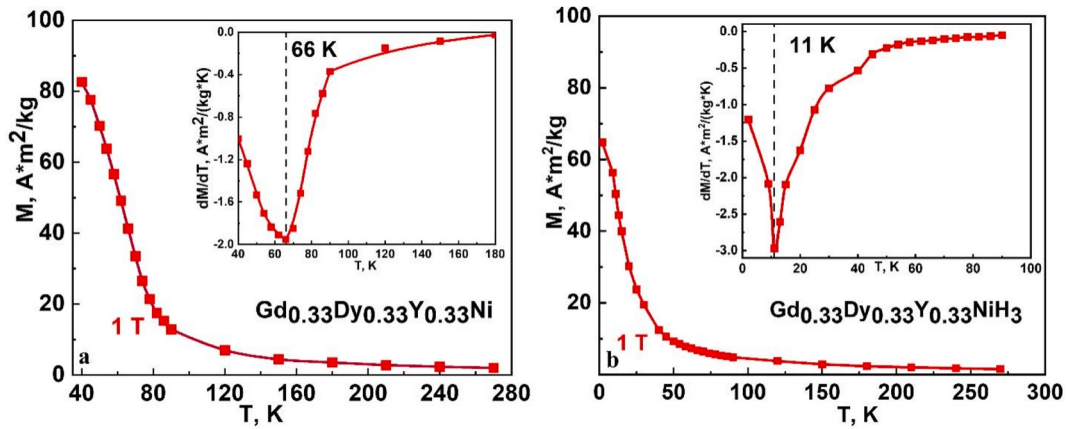


Fig. 6. Temperature dependence of the magnetization for (a) parent $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ and (b) hydrogenated $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ compounds measured in magnetic fields of 1 T. The insets present dM/dT curves revealing the magnetic ordering temperatures.

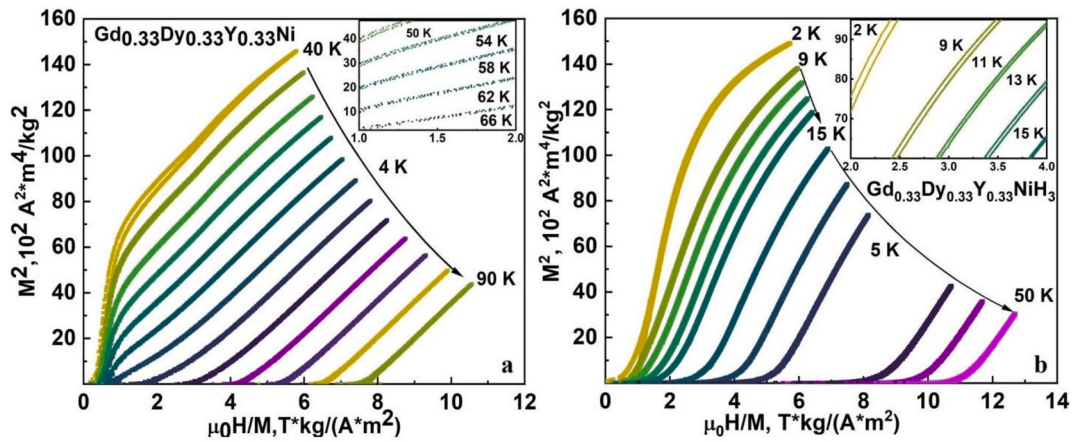


Fig. 7. Below-Arrhot curves for $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ (a) and $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ (b) compounds. The insets show the same dependencies on a different scale.

that the shape of the curves of these dependencies for the parent compound is symmetrical, whereas the curves of the hydride demonstrate a pronounced asymmetry. Table 2 shows the maximum values of the MCE in a field of 5 T and the temperatures at which these values are achieved for both studied compounds, as well as for binary GdNi, DyNi and pseudobinary $\text{Dy}_{0.9}\text{Gd}_{0.1}\text{Ni}$ compounds and their hydrides. Maximum MCE values, achieved near the respective Curie temperatures, show

interesting trends when compared to previously studied systems (Table 2). While the parent $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ compound exhibits a relatively modest MCE in a 5 T field ($\Delta S_m = 8.3$ J/(kg·K)) compared to binary and pseudobinary analogues ($\Delta S_m = 14.5$ J/(kg·K) for GdNi and $\Delta S_m = 15.7$ J/(kg·K) for $\text{Dy}_{0.9}\text{Gd}_{0.1}\text{Ni}$), hydrogenation induces a remarkable enhancement. The hydrogenated phase achieves $\Delta S_m = 13$ J/(kg·K), comparable to previously studied hydrides ($\Delta S_m = 14$ J/(kg·K))

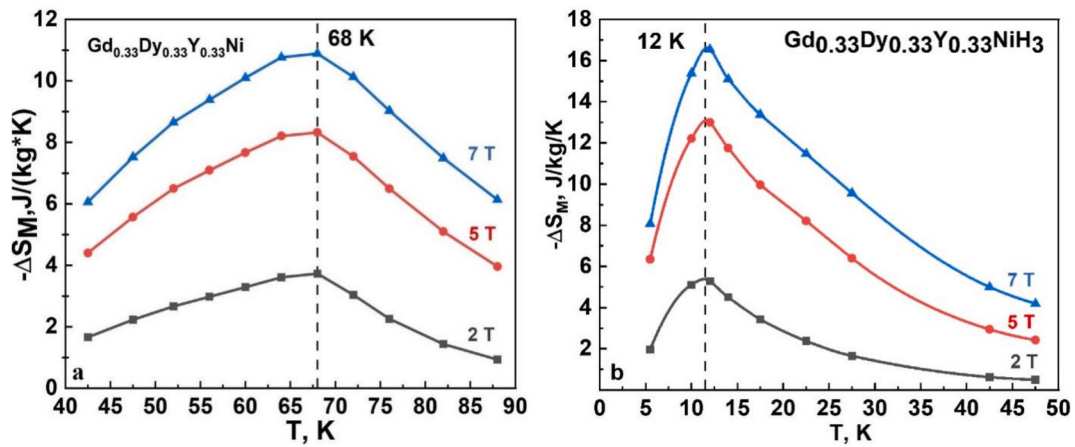


Fig. 8. Temperature dependencies of the magnetocaloric effect of $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ (a) and $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ (b) compounds.

for $\text{GdNiH}_{3.2}$ and $\Delta S_m = 12.5 \text{ J/(kg·K)}$ for $\text{Dy}_{0.9}\text{Gd}_{0.1}\text{NiH}_3$.

Notably, this behavior contrasts with that of binary and pseudobinary systems, where hydrogenation typically reduces the MCE. In the present medium-entropy system, hydrogenation increases the MCE by approximately 50 % in a 5 T field. The low-field behavior (0–1 T) reveals nearly identical MCE values for both parent and hydrogenated compounds at their respective Curie temperatures (Fig. 9a).

A comparative analysis of the field-dependent magnetic entropy change between the two hydrogenated compounds $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ and the previously studied $\text{Gd}_{0.9}\text{Dy}_{0.1}\text{NiH}_3$ [20] (Fig. 9b) reveals superior performance of the medium-entropy compound in the field range 0.25–1.50 T, with a maximum enhancement of 0.2 J/(kg·K) observed between 0.6–1.2 T. This effect may be attributed to the modification of the electronic structure through dilution of the magnetic rare earth sublattice with non-magnetic yttrium atoms.

For practical magnetic refrigeration applications, the nature of the magnetic phase transition is crucial, as first-order transitions can impede the achievement of reproducible MCE values in cyclic operation. The magnetic phase transition character in both compounds was established through three independent analytical approaches. The Belov-Arrott curves (Fig. 7) exhibit positive slopes in the low-field regime, characteristic of second-order transitions. This assessment is corroborated by

the linear relationship between ΔS_m and $\left(\frac{\mu_0 H}{T_C}\right)^{\frac{2}{3}}$ (Fig. 10a), consistent with the Oesterreicher-Parker criterion for second-order transitions. Additional confirmation comes from the field-scaling analysis, where the temperature dependence of the exponent $n(T, H) = d \ln |\Delta S_m| / d \ln H$ remains below 2 near T_C (Fig. 10b), definitively establishing the second-

order nature of the transitions in both compounds.

The convergence of these multiple analytical approaches unambiguously confirms second-order magnetic phase transitions in both the parent $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ and its hydride $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$. This characteristic, combined with the enhanced MCE values, establishes these materials as promising candidates for magnetic refrigeration applications.

4. Conclusions

To conclude, a middle-entropy rare earth intermetallic compound was synthesized, featuring equal proportions of two heavy rare earths (Gd and Dy) and a rare-earth analog (Y) at the R-site of RNi . The compound was subsequently hydrogenated to reach the $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ composition. Investigations revealed that hydrogenation induces a structural transformation from the FeB to CrB type and significantly reduces the Curie temperature from 60 K to 6 K. The magnetocaloric effect was quantified using Maxwell's equation, with the maximum isothermal magnetic entropy change value at a 5 T magnetic field increasing by approximately 50 % following hydrogenation.

Significant applied characteristics of the MCE behavior in weak magnetic fields were uncovered based on compositional variations. In magnetic fields ranging from 0–1 T, both the initial composition and its hydride exhibit identical MCE values at their respective Curie temperatures (60 K and 6 K, respectively).

Furthermore, in magnetic fields between 0.6–1.2 T, the MCE values of the middle-entropy $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ and pseudobinary $\text{Gd}_{0.9}\text{Dy}_{0.1}\text{NiH}_3$ hydrides—which have similar Curie temperatures of around 10 K—differ by only 0.2 J/(kg·K) , with the former compound

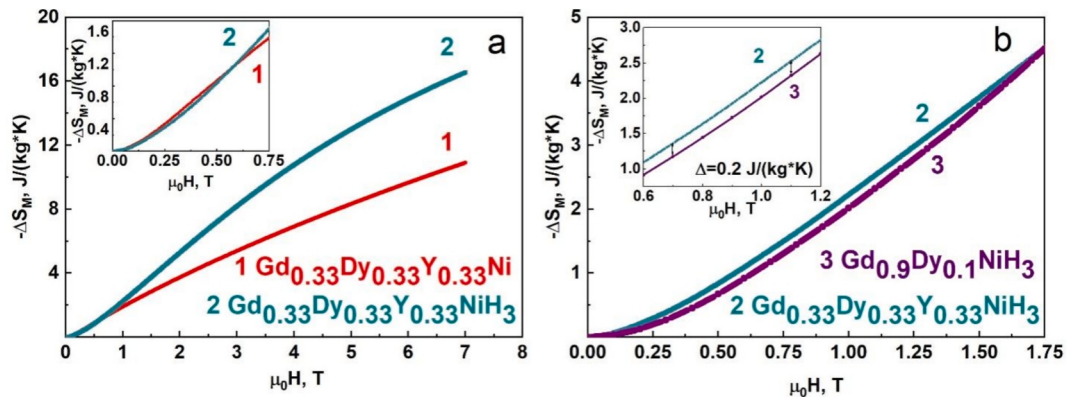


Fig. 9. Field dependencies of the magnetocaloric effect of $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{Ni}$ and $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ (a), $\text{Gd}_{0.33}\text{Dy}_{0.33}\text{Y}_{0.33}\text{NiH}_3$ and $\text{Gd}_{0.9}\text{Dy}_{0.1}\text{NiH}_3$ (b) compounds at their Curie temperatures (insets show the same dependencies on a different scale).

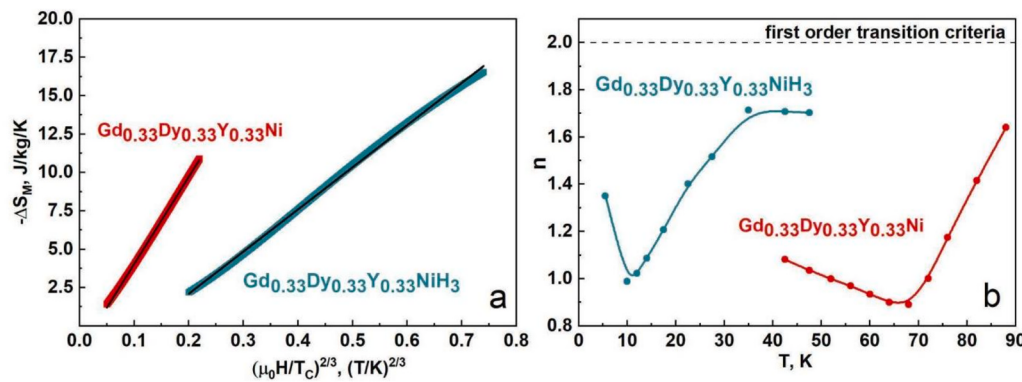


Fig. 10. Various order transition criteria. (a) Dependence of the magnetic entropy change on the parameter $\left(\frac{\mu_0 H}{T_c}\right)^{2/3}$ for $Gd_{0.33}Dy_{0.33}Y_{0.33}Ni$ and $Gd_{0.33}Dy_{0.33}Y_{0.33}NiH_3$. The solid line represents a linear fit to the data. (b) The temperature dependencies of the exponent $n(T, H) = \frac{d \ln |\Delta S_M|}{d \ln H}$ for the $Gd_{0.33}Dy_{0.33}Y_{0.33}Ni$ and $Gd_{0.33}Dy_{0.33}Y_{0.33}NiH_3$ near their Curie temperatures.

showing a slight advantage. This nuanced difference might be attributed to modifications in the electronic configuration resulting from the dilution of the magnetic rare earth sublattice with non-magnetic yttrium atoms.

Both the original $Gd_{0.33}Dy_{0.33}Y_{0.33}Ni$ compound and its hydride exhibit second-order magnetic phase transitions, a characteristic that makes these materials promising candidates for advanced magnetic refrigeration and thermal management technologies.

CRediT authorship contribution statement

A.A. Kurganskaya: Writing – original draft, Visualization, Investigation, Formal analysis. **Zh. Liu:** Visualization, Investigation. **E.S. Kozlyakova:** Investigation, Formal analysis. **T.P. Kaminskaya:** Methodology, Data curation. **I.S. Tereshina:** Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization. **V.N. Verbetsky:** Writing – review & editing, Data curation. **S.V. Mitrokhin:** Visualization, Validation. **A.N. Vasiliev:** Writing – review & editing, Resources.

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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Data availability

Data will be made available on request.

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