

Magnetic Properties of Hydrides of $\text{RNi}_{1-x}\text{Si}_x$ Compounds ($\text{R} = \text{Dy, Gd}, x = 0.05, 0.02$)

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Received July 3, 2018

Abstract—The magnetic properties of intermetallic compounds $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ and hydrides based on them have been studied. It is found that a partial substitution of Si atoms for Ni atoms does not cause significant changes in the magnetic characteristics such as the Curie temperature. At the same time, incorporation of hydrogen into the crystal lattice of the $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ compounds leads to significant decrease in the Curie temperature, attenuation of exchange interactions due to significant increase in the unit cell volume (more than 20%), and an increase in the distances between magnetoactive ions. The magnetism of the initial and also hydrogenated compositions are mainly determined by the contribution from the subsystem of the rare-earth ions.

DOI: 10.1134/S1063783419010153

1. INTRODUCTION

Recently the magnetic properties of compounds of rare-earth metals (REM) with silicon [1, 2] and also more complex compounds, namely, REM (R)—3*d* metal (Fe, Co, Ni)—silicon have been extensively studied using the most advanced methods including the measurements in high (to 60–100 T) magnetic fields at low temperatures [3–12].

REM—Si compounds crystallize in the structural types FeB and CrB [13, 14]. It is important that the same structural type also takes place in compounds of REMs with nickel (RNi) that actively interact with hydrogen with the formation of hydride phases containing 3–4 atoms per formula unit of an intermetallic compound. It is known [15–17] that the hydrogenation can lead to significant changes in the magnetic properties of the initial intermetallic compounds. In RNi compounds simultaneous doping with silicon and subsequent incorporation of hydrogen in their crystal lattices can change the Curie temperature, the saturation magnetization, and the magnetic anisotropy.

In this work, we studied the magnetic properties of two intermetallic compounds, namely, $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ and also hydrides based on them. The properties of the initial GdNi and DyNi compounds and their hydrides were studied before [18–20]. The processes of interaction of RNi with hydrogen were already studied in detail [21].

2. EXPERIMENTAL

The samples of the intermetallic $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ compounds were prepared by melting of the charge from pure components in an electric-arc furnace in an inert atmosphere and, then, they were annealed for 240 h at a temperature of 600°C in vacuum. The hydrides were synthesized by the volumetric technique at a Sievers-type setup with the operation range of hydrogen pressure to 100 bars. The X-ray phase analysis was carried out on a diffractometer with a Guinier chamber (Cu_α -radiation). The magnetization curves were measured using the standard equipment (PPMS-9) in magnetic field to 5 T. The samples were taken as a finely dispersed powder.

3. RESULTS AND DISCUSSION

The analysis of the X-ray diffraction data (Table 1) showed that the melted samples of the intermetallic compounds and the synthesized $\text{GdNi}_{0.98}\text{Si}_{0.02}\text{H}_{3.0}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}\text{H}_{4.0}$ hydrides were single-phase. The lattice parameters of the samples of the $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ intermetallic compounds were close to the available data [14].

It can be noted that the incorporation of even small amount of silicon to the compositions of the GdNi and DyNi intermetallic interactions changes their structural properties and the properties of the hydride based on them. For example, in the case of formation of the hydride with $\text{DyNi}_{0.95}\text{Si}_{0.05}$, the structural FeB

Table 1. X-ray diffraction data for the $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ intermetallic compounds and hydrides based on them

| Compound | Type of structure | a , Å | b , Å | c , Å | $\Delta V/V\%$ |
|--|-------------------|----------|----------|----------|----------------|
| $\text{GdNi}_{0.98}\text{Si}_{0.02}$ | CrB | 3.784(3) | 10.33(2) | 4.284(3) | – |
| $\text{GdNi}_{0.98}\text{Si}_{0.02}\text{H}_{3.0}$ | CrB | 3.793(2) | 10.87(2) | 4.980(2) | 21.0 |
| $\text{DyNi}_{0.95}\text{Si}_{0.05}$ | FeB | 7.065(3) | 4.187(2) | 5.454(3) | – |
| $\text{DyNi}_{0.95}\text{Si}_{0.05}\text{H}_{4.0}$ | FeB | 7.670(2) | 4.360(2) | 5.990(2) | 23.0 |

type is retained and is not changed to CrB type, as is the case with the DyNi intermetallide that does not contain silicon.

The magnetic characteristics of the prepared samples were measured by the following scheme: the temperature dependences of the magnetization were measured in a weak magnetic field of 0.05 T and in high magnetic fields of 2 and 4 T over wide temperature range including the magnetic ordering region and also the temperature range in which the samples were in

the paramagnetic (disordered) state. Then, we built the temperature dependences of the reciprocal susceptibility (from the measurements of $M(T)$ in fields of 2 and 4 T) to have a possibility (in the case as the Curie–Weiss law is fulfilled) to calculate the effective magnetic moments and the paramagnetic Curie temperature. Figures 1–4 show the experimental curves $M(T)$ and $1/\chi(T)$ for compositions $\text{GdNi}_{0.98}\text{Si}_{0.02}$, $\text{GdNi}_{0.98}\text{Si}_{0.02}\text{H}_{3.0}$, $\text{DyNi}_{0.95}\text{Si}_{0.05}$, and $\text{DyNi}_{0.95}\text{Si}_{0.05}\text{H}_{4.0}$, respectively. Table 2 lists the data on the main magnetic character-

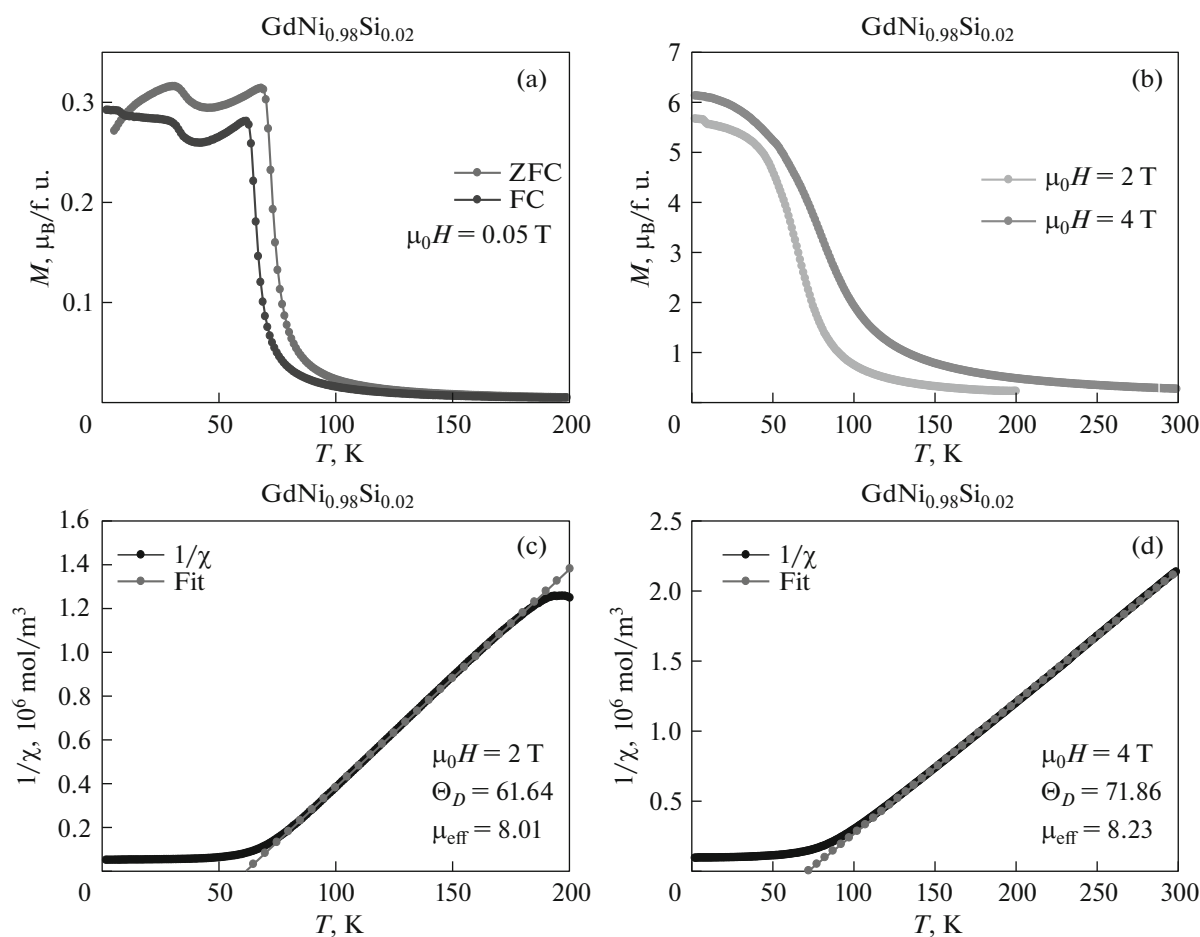


Fig. 1. Temperature dependences of the magnetization of intermetallic $\text{GdNi}_{0.98}\text{Si}_{0.02}$ compound measured in magnetic fields (a) $\mu_0H = 0.05$ and (b) 2 and 4 T. Temperature dependences of the reciprocal susceptibility measured in magnetic fields $\mu_0H =$ (c) 2 and (d) 4 T.

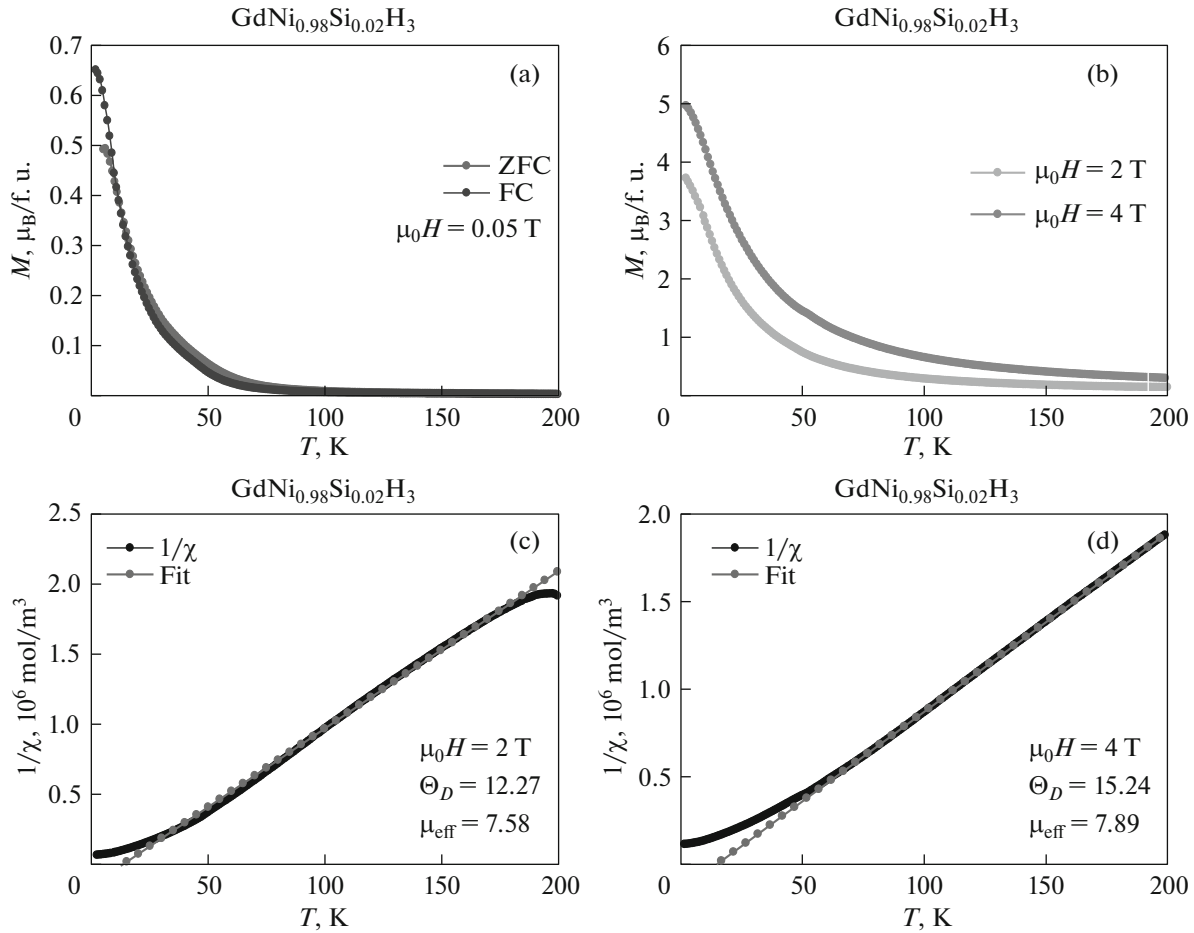


Fig. 2. Temperature dependences of the magnetization of intermetallic $\text{GdNi}_{0.98}\text{Si}_{0.02}\text{H}_3$ compound measured in magnetic fields $\mu_0H =$ (a) 0.05 and (b) 2 and 4 T. Temperature dependences of the reciprocal susceptibility measured in magnetic fields $\mu_0H =$ (c) 2 and (d) 4 T.

istics of the compounds under study. For comparison, Table 2 also gives the results of the studies of intermetallic compounds GdNi and DyNi.

An analysis of the tabulated data gives important information on the combined influence of the substitational atoms and the interstitial atoms. First, we dis-

Table 2. Magnetic characteristics of the intermetallic compounds and their hydrides

| Compound | T_C , K ($\mu_0H = 0.05$ T) | Θ_p , K ($\mu_0H = 4$ T) | μ_S, μ_B ($\mu_0H = 4$ T) $T = 4.2$ K | μ_{eff}, μ_B ($\mu_0H = 4$ T) | μ_{eff}, μ_B R^{3+} |
|--|-----------------------------------|-------------------------------------|--|--|--|
| GdNi | 75 | 75 | 6.9 | 8.3 | 7.94 |
| $\text{GdNi}_{0.98}\text{Si}_{0.02}$ | 75 | 72 | 6.2 | 8.23 | 7.94 |
| $\text{GdNi}_{0.98}\text{Si}_{0.02}\text{H}_{3.0}$ | 12 | 15 | 5.1 | 7.9 | 7.94 |
| DyNi | 59 | 49 | 5.4 | 10.4 | 10.63 |
| $\text{DyNi}_{0.95}\text{Si}_{0.05}$ | 62 | 60 | 7.3 | 10.43 | 10.63 |
| $\text{DyNi}_{0.95}\text{Si}_{0.05}\text{H}_{4.0}$ | 10 | 2.3 | 5.65 | 10.43 | 10.63 |

* T_C is the Curie temperature, Θ_p is the paramagnetic Curie temperature, μ_S are saturation magnetic moments of the compounds per REM atom, μ_{eff} are the effective magnetic moments of the compounds per REM atom, $\mu_{\text{eff}}(\text{R}^{3+})$ is the theoretical value $[g_J^2 J(J+1)]^{1/2}$ of the effective magnetic moments of REM ions R^{3+} .

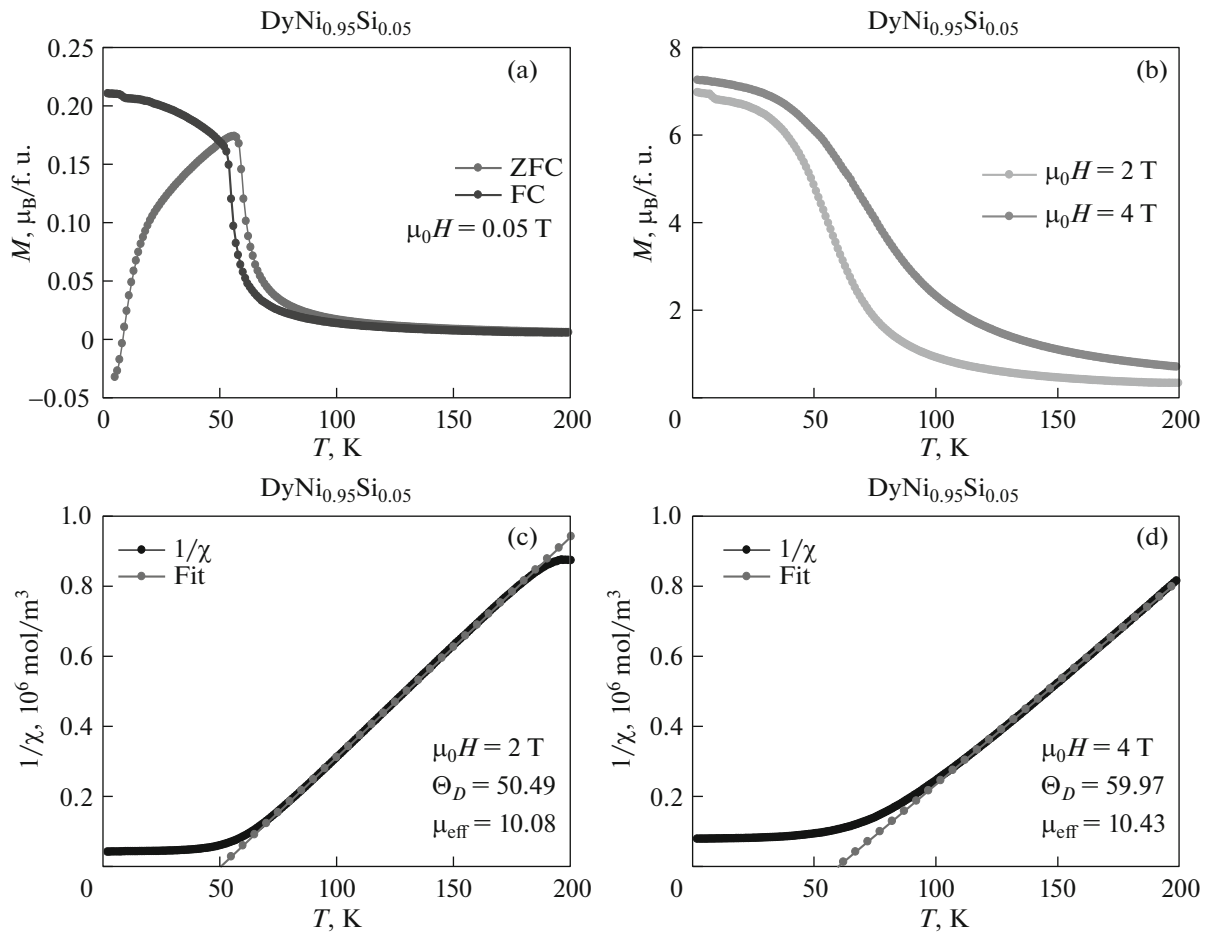


Fig. 3. Temperature dependences of the magnetization of intermetallic $\text{DyNi}_{0.95}\text{Si}_{0.05}$ compound measured in magnetic fields (a) $\mu_0 H = 0.05$ and (b) 2 and 4 T. Temperature dependences of the reciprocal susceptibility measured in magnetic fields $\mu_0 H =$ (c) 2 and (d) 4 T.

discuss the data for the initial intermetallic compounds, namely, $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ and their basis GdNi and DyNi compositions. To determine the Curie temperatures, we used the thermomagnetic analysis. Temperature T_C was determined as the temperature of the sharpest decrease in the magnetization ($\mu_0 H = 0.05$ T, Figs. 1a–4a) during the transition from the ferromagnetic to paramagnetic state, i.e., the temperature, where dM/dT is maximum. We failed to observe any change in the Curie temperature in the compounds with gadolinium $\text{GdNi}_{0.98}\text{Si}_{0.02}$ as compared to that of the GdNi compound; a possible cause is low silicon content in the compound. At the same time, it is found that T_C increased by three degrees in the compound with dysprosium $\text{DyNi}_{0.95}\text{Si}_{0.05}$ as compared to that of DyNi. Dependence $M(T)$ was measured both in the ZFC regime (cooling in a zero magnetic field) and in the FC regime (cooling in a magnetic field). Both samples $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ demonstrate a noticeable temperature hysteresis. Moreover, the low-temperature behaviors

of the $M(H)$ curves for the compound with dysprosium are strongly different at ZFC and FC due to the motion of domain boundaries [22] and as a result of the presence of the high-anisotropic Dy^{3+} ion in the composition.

Another important characteristic of intermetallic compounds are the saturation magnetic moments of the compounds per REM atom (μ_S) at temperatures near the absolute zero. In our case, we indicate (Table 2) these values for the $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ compositions at $T = 4.2$ K in the external magnetic field $\mu_0 H = 4$ T. Here, it should be noted that these values do not coincide to the values obtained in field $\mu_0 H = 2$ T (Figs. 1b and 3b), which demonstrates a paraprocess at low temperatures. From Table 2, it is seen that the partial substitution of Si atoms for Ni atoms in the GdNi intermetallic compound leads to insignificant decrease in the saturation magnetic moment ($6.9\mu_B$ in GdNi and $6.2\mu_B$ in $\text{GdNi}_{0.98}\text{Si}_{0.02}$), as a result of changing the electronic structure of GdNi. In the compounds with gadolin-

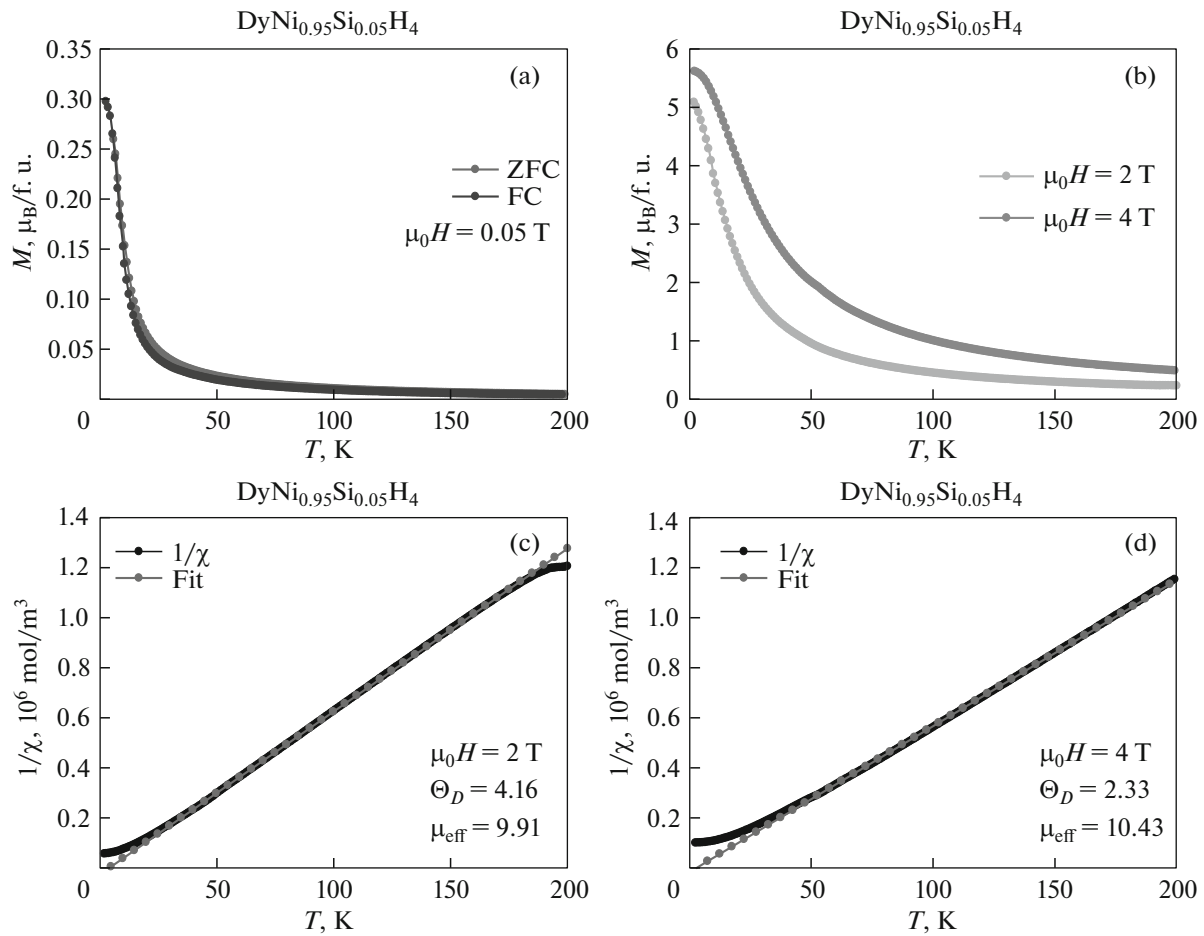


Fig. 4. Temperature dependences of the magnetization of intermetallic $\text{DyNi}_{0.95}\text{Si}_{0.05}\text{H}_4$ compound measured in magnetic fields (a) $\mu_0 H = 0.05$ and (b) 2 and 4 T. Temperature dependences of the reciprocal susceptibility measured in magnetic fields $\mu_0 H =$ (c) 0.05 and (d) 4 T.

ium, the situation is not so unambiguous as in those with dysprosium, and the saturation magnetic moments of the compounds per the REM atom are $5.4\mu_B$ in DyNi and $7.3\mu_B$ in $\text{DyNi}_{0.95}\text{Si}_{0.05}$. This seems likely to be due to the fact that the compared data were obtained in different conditions, while the determined value is very sensitive to the value of the applied magnetic field and temperature. In any case, it should be noted that the saturation magnetic moments μ_{extS} of the DyNi and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ compounds (Table 2) are markedly lower than the theoretical value $\mu_0(R^{3+}) = gJ$ of the magnetic moment of Dy ($10.0\mu_B$). This phenomenon is related to partial “freezing” of the dysprosium orbital moment by the crystal field of the surrounding atoms.

The behavior of the paramagnetic Curie temperature conserves the tendencies noted above, namely, it slightly decreases for the GdNi and $\text{GdNi}_{0.98}\text{Si}_{0.02}$ compounds (75 K and 72 K, respectively). A large difference (due to the causes indicated above), namely,

49 K and 60 K, was observed for DyNi and $\text{DyNi}_{0.95}\text{Si}_{0.05}$, respectively. However, it is important to note that the effective magnetic moments (μ_{eff}) of the compounds per an REM atom for all the compounds considered above ($\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ and their basis GdNi and DyNi compositions) almost coincide each other (Table 2) and are close to the available data. This result shows that nickel atoms do not have a marked magnetic moment, and, thus, the magnetic properties of GdNi and DyNi and their substituted $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ compositions are mainly due to the contribution of the magnetic moments of trivalent rare-earth ions. The calculated values of μ_{eff} , the effective magnetic moments of the compounds with gadolinium (GdNi and $\text{GdNi}_{0.98}\text{Si}_{0.02}$) per the REM atom (Table 2) is higher than the theoretical value $\mu_{\text{eff}} = 7.94\mu_B$ and are $8.3\mu_B$ and $8.23\mu_B$, respectively. This phenomenon is characteristic not only for the gadolinium compounds, but also for pure gadolinium and also its solid solutions with hydrogen

[22], and related to the conduction electron polarization. As is seen, the introduction of silicon (semiconductor) slightly decreases the value of this additional contribution to magnetic moment μ_{eff} , which confirms the nature of the observed phenomenon.

The incorporation of quite large amount of hydrogen into the crystal lattices of the $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ compounds (3 and 4 at H/f.u., respectively) leads to a sharp (seven-fold) decrease in the Curie temperatures (Table 2). It is known that the Curie temperatures of compounds of REM with $3d$ transition metals contain three contributions from $3d-3d$, $4f-3d$, and $4f-4f$ exchange interactions. These contributions are extremely sensitive to substantial and interstitial atoms, and also to action of a hydrostatic pressure [23–25].

We can state, as the main result, that the crystal lattice expansion by more than 20% and the increase in the distances between magnetically active ions led to an attenuation of exchange interactions as inside the REM and nickel sublattices so, it is likely, between the sublattices.

Based on the Curie–Weiss law, we determined the paramagnetic Curie temperatures and the effective magnetic moments per one molecule for the $\text{GdNi}_{0.98}\text{Si}_{0.02}\text{H}_{3.0}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}\text{H}_{4.0}$ hydrides. For $\text{GdNi}_{0.98}\text{Si}_{0.02}\text{H}_{3.0}$, $\mu_{\text{eff}} = 7.9\mu_{\text{B}}$ per REM atom and $\Theta_p = 15$ K. At the same time, for $\text{DyNi}_{0.95}\text{Si}_{0.05}\text{H}_{4.0}$, $\mu_{\text{eff}} = 10.43\mu_{\text{B}}$ per REM atom and $\Theta_p = 2.3$ K. It is seen that the paramagnetic temperature decreases sharply that also demonstrates the attenuation of the exchange interactions. Similar behavior was also observed for the $\text{GdNiH}_{3.2}$ and $\text{DyNiH}_{3.4}$ hydrides synthesized and studied before [18].

4. CONCLUSIONS

The influence of hydrogen on the magnetic properties of the $\text{GdNi}_{0.98}\text{Si}_{0.02}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}$ intermetallic compounds is mainly in an attenuation of the exchange interactions due to an increase in the interatomic distances and, as a result, significant decrease in the transition temperature from the magnetically ordered to magnetically disordered state. In the $\text{GdNi}_{0.98}\text{Si}_{0.02}\text{H}_{3.0}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}\text{H}_{4.0}$ hydrides, these transition temperatures have close values (12 K and 10 K, respectively), i.e., they demonstrate a weak dependence on the composition and the hydrogen content. The paramagnetic Curie temperatures that immediately characterize the value of the exchange interactions also show the decrease; however, their values are different and equal to 15 K and 2.3 K for $\text{GdNi}_{0.98}\text{Si}_{0.02}\text{H}_{3.0}$ and $\text{DyNi}_{0.95}\text{Si}_{0.05}\text{H}_{4.0}$, respectively.

The calculated values of the magnetic moments for the initial compounds are not changed after the hydrogenation and are close to the magnetic moments of the free REM ions. The nickel atoms have only insignifi-

cant magnetic moment in all the compounds. Actually, the electron shell of nickel atoms ($3d^8$) is nearly occupied. The appearance of additional electrons given by hydrogen atoms leads to its complete occupation. As a result, the magnetic moment of the nickel subsystem is close to zero, the exchange interactions are weakened significantly, and the gadolinium and dysprosium subsystems make the main contributions to the magnetism.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 16-03-00639.

REFERENCES

1. P. Schobinger-Papamantellos, K. H. J. Buschow, and J. Rodriguez-Carvajal, *J. Magn. Magn. Mater.* **323**, 2592 (2011).
2. S. A. Shaheen, *J. Appl. Phys.* **63**, 3411 (1988).
3. F. Yuan, Y. Mozharivskiy, A. V. Morozkin, A. V. Knotko, V. O. Yapaskurt, M. Pani, A. Provino, and P. Manfrinetti, *J. Solid State Chem.* **219**, 247 (2014).
4. A. V. Morozkin, A. V. Knotko, V. O. Yapaskurt, P. Manfrinetti, M. Pani, A. Provino, R. Nirmala, S. Quezado, and S. K. Malik, *J. Solid State Chem.* **235**, 58 (2016).
5. A. V. Andreev, D. I. Gorbunov, and Y. Skourski, *J. Alloys Compd.* **694**, 761 (2017).
6. E. A. Tereshina and A. V. Andreev, *Intermetallics* **18**, 641 (2010).
7. E. Gaudin and B. Chevalier, *J. Solid State Chem.* **180**, 1397 (2007).
8. I. S. Tereshina and S. A. Nikitin, *J. Magn. Magn. Mater.* **300**, E497 (2006).
9. B. Chevalier and E. Gaudin, *J. Alloys Compd.* **442**, 149 (2007).
10. E. Gaudin, S. Tence, F. Weill, J. Fernandez, and B. Chevalier, *Chem. Mater.* **20**, 2972 (2008).
11. A. V. Andreev, I. S. Tereshina, and D. I. Gorbunov, *J. Alloys Compd.* **621**, 415 (2015).
12. A. V. Andreev, M. D. Kuz'min, and S. Yoshii, *J. Alloys Compd.* **509**, 5042 (2011).
13. S. B. Hendricks and P. R. Kostling, *Z. Kristallogr.* **74**, 511 (1930).
14. R. P. Elliot, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1965).
15. E. A. Tereshina, H. Drulis, Y. Skourski, and I. S. Tereshina, *Phys. Rev. B* **87**, 214425 (2013).
16. S. Nikitin, I. Tereshina, E. Tereshina, and W. Suski, *J. Alloys Compd.* **451**, 477 (2008).
17. I. S. Tereshina, M. Doerr M, Y. Skourski, E. A. Tereshina, K. Watanabe, I. V. Telegina, and H. Drulis, *IEEE Trans. Magn.* **47**, 3617 (2011).

18. Yu. L. Yaropolov, V. N. Verbetsky, A. S. Andreenko, K. O. Berdyshev, and S. A. Nikitin, *Inorg. Mater.* **46**, 364 (2010).
19. W. Iwasieczko, H. Drulis, Yu. L. Yaropolov, S. A. Nikitin, and V. N. Verbetsky, *J. Alloys Compd.* **509**, 827 (2011).
20. Yu. L. Yaropolov, V. N. Verbetskii, S. A. Nikitin, and A. S. Andreenko, *Nanosist. Nanomater. Nanotekhnol.* **8**, 271 (2010).
21. Yu. L. Yaropolov, V. N. Verbetsky, V. A. Somenkov, and V. P. Glazkov, *Int. J. Hydrogen Energy* **36**, 1222 (2011).
22. E. A. Tereshina, S. Khmelevskiy, G. Politova, T. Kaminskaya, H. Drulis, and I. S. Tereshina, *Sci. Rep.* **6**, 22553 (2016).
23. E. A. Tereshina, A. V. Andreev, J. Kamarad, and H. Drulis, *J. Alloys Compd.* **492**, 1 (2010).
24. E. A. Tereshina, H. Yoshida, A. V. Andreev, I. S. Tereshina, K. Koyama, and T. Kanomata, *J. Phys. Soc. Jpn.* **76**, 82 (2007).
25. A. V. Andreev and E. A. Tereshina, *J. Alloys Compd.* **450**, 51 (2008).

Translated by Yu. Ryzhkov