Study of the effect of nitrogen and hydrogen on the structure and magnetic properties of (Sm,Er)$_2$Fe$_{17}$ alloys

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Abstract. Materials based on the Sm$_2$Fe$_{17}$ compound with nitrogen have great potential for the manufacture of highly efficient permanent magnets. The initial, nitrided, and hydrogenated alloys based on the Sm$_2$Fe$_{17}$ intermetallic compound with partial substitution of erbium atoms for samarium atoms Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$(H,N)$_x$ have been studied by X-ray phase analysis and scanning electron microscopy. Nanopowders of Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$N$_2$ were obtained by mechanical grinding. The grinding time was varied from 0 to 60 minutes. The magnetic hysteresis properties of all powder samples were studied in static magnetic fields up to 7 T, as well as in pulsed magnetic fields up to 60 T. The strength of the intersublattice exchange interaction was estimated. The obtained values $\lambda$ are valid only for the explored concentration of Sm/Er ions.

1. Introduction
The intermetallic compounds Nd$_2$Fe$_{14}$B and Sm$_2$Fe$_{17}$N$_3$ are of interest to both scientists and technologists since it is on their basis that high-energy hard-magnetic materials are currently being developed [1–3]. Partial replacement of Nd or Sm (light rare earth metal (REM)) with heavy ones (Dy, Ho, Er), as well as Co for Fe, as a rule, leads to an increase in the coercive force of magnets (due to an increase in magnetic anisotropy), an improvement in thermal stability [4–7]. In this work, it is planned, first of all, to study the structure and magnetic properties of the substituted composition Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$. The influence of such processes as hydrogenation, nitrogenation, grinding of powder nitrides in a high-energy mill (for different times) on the structural state and magnetic characteristics of obtained samples will also be investigated.

The use of a high external magnetic field can be considered an external factor affecting magnetization of alloys containing heavy rare-earth metals in their composition. It is known that the latter have a significant magnetic moment and are ordered antiparallel to the Fe sublattice. A strong magnetic field can disrupt the collinear magnetic structure, cause a sharp increase in magnetization,
and even observe the phenomenon of an external magnetic field-induced ferrimagnetic state [8–10]. An analysis of the field dependences of the magnetization at T = 4.2 K makes it possible to estimate the intersublattice exchange interaction parameter and the effect on it of hydrogen and nitrogen atoms incorporated into the crystal lattice of the R-Fe compound (R is REM) [11].

2. Experimental details
For Sm$_{1.8}$Er$_{0.2}$Fe$_{17}$ sample, its hydride Sm$_{1.8}$Er$_{0.2}$Fe$_{17}$H$_{4.6}$ and nitride Sm$_{1.8}$Er$_{0.2}$Fe$_{17}$N$_2$ all details of preparation and certification can be found in Refs. [12, 13]. The milling process of Sm$_{1.8}$Er$_{0.2}$Fe$_{17}$N$_2$ was conducted at room temperature using a high-energy ball mill by Planetary Mono Mill PULVERISETTE 6 (Fritsch, Germany) with the diameter of the stainless-steel balls of 6.5 mm. Samples were milled for 15, 30, 45, and 60 min at a rotating rate of 300 rpm. The particles sizes of the milled powders were determined by a 20 kV-field emission SEM, supplied by TESCAN VEGA3 (Czech Republic) and the free software ImageJ. Magnetic measurements were performed on a fixed powder samples using a PPMS-9 at room temperature in magnetic field up to 9 T. The high-field magnetization measurements were performed at the Dresden High Magnetic Field Laboratory in pulsed magnetic fields up to 58 T at 4.2 K [14].

3. Results and discussion
The X-ray phase and microstructural analyses of the cast alloy Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$ showed that the sample consisted of the main phase of type 2:17 and several secondary phases α-Fe and (Sm, Er)Fe$_3$. As a result of high-temperature homogenization, the sample consists of 95 wt% of the main phase of type 2:17 and contains 5% of the soft magnetic phase α-Fe (see Fig. 1(1) and 1(2)). Partial substitution of Er for Sm does not lead to a change in the structure of the base compound Sm$_{2}$Fe$_{17}$. analysis of X-ray diffraction patterns shows that the sample retains the rhombohedral type of structure Th$_2$Zn$_17$ (space group R m, No.166).

Stable compositions Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$H$_{4.6}$ and Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$N$_2$ were also obtained in this work. The introduction of hydrogen and nitrogen into the starting compound’s crystal lattice causes a noticeable shift of diffraction lines of phase 2:17 in the range of small angles, as shown in Fig. 1 (3) and (4). The results of X-ray diffraction studies for all samples synthesized in this work are shown in Table 1, where, for comparison, the unit cell parameters for Sm$_{2}$Fe$_{17}$, its hydrides Sm$_{2}$Fe$_{17}$H$_x$ (2 ≤ x ≤ 4.7), and nitride Sm$_{2}$Fe$_{17}$N$_x$ are also shown [2,15–17]. The type of crystal structure of hydride and nitride is retained. The absorption of hydrogen and, especially, nitrogen is accompanied by the expansion of the unit cell and anisotropic change in the lattice parameters, predominantly in the basal plane [18]. The average volume expansion ΔV/V during hydrogenation was about 3.6%. In contrast, the introduction of 2 atoms of nitrogen per formula unit leads to an increase in the unit cell volume by 5.9%. Table 1 shows that the results obtained generally agree well with the hydride and nitride data received based on the Sm$_{2}$Fe$_{17}$ compound. Based on comparing the characteristics of the Sm$_{2}$Fe$_{17}$(N,H)$_x$ and Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$(N,H)$_x$ systems, a lower absorption capacity for hydrogen and nitrogen is noted for the substituted compositions. According to the literature data [16], the maximum hydrogen content is up to 5 at.H/f.u. for hydrides based on Sm$_{2}$Fe$_{17}$; for nitride, the absorption capacity of Sm$_{2}$Fe$_{17}$N$_x$ reaches its maximum value x = 3 at.N/f.u. The reason for obtaining lower x values for the substituted compound (Sm,Er)$_2$Fe$_{17}$ is since the crystal structure becomes more compact (due to the lanthanide compression effect), and the volume of voids occupied by atoms of light interstitial elements decreases.

We also investigated the effect of the grinding regimes of Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$N$_2$ nitride powders on their structure and magnetic properties. It was found that Sm-Er-Fe-N powders after mechanical activation for 15, 30, 45, and 60 minutes, like Sm-Fe-N powders, do not change the structural type (Th$_2$Zn$_{17}$). As seen from the X-ray diffraction spectra (Fig. 1 (5) - (8)), as a result of an increase in grinding duration, the intensity of the Sm-Er-Fe-N lines gradually decreases, and the diffraction lines become wider. The degree of amorphization of finely dispersed powders increases. A similar phenomenon was observed for Sm-Fe-N powders in Ref. [19]. It should also note that the studied Sm-Er-Fe-N powders are...
Figure 1. X-ray diffraction patterns. (1) A sample of Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$ in as-cast state; (2) A parent sample after annealing at 1273 K; (3) A hydride Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$H$_{4.6}$; (4) A nitride Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$N$_{2}$; (5)-(8) Sm-Er-Fe-N ball-milled powders at RT for 15, 30, 45 and 60 min, respectively.

resistant to oxidation. According to the data in Table 1, the unit cell parameters $a$, $c$, and $V$ - the unit cell volume, depending on the duration of grinding, slightly decrease, but the same ratio $c/a$ remains.

Table 2 shows the values of the main magnetic characteristics obtained in this work (saturation magnetization $\sigma_S$ and coercive force $H_C$). The values of the saturation magnetization $\sigma_S$ of the hard magnetic phase 2:17 in the sample before and after hydrogenation were calculated by the formula:

$$\sigma_S(2:17) = \frac{\sigma_S(\text{sample}) - \sigma_S(\alpha\text{-Fe}) \cdot \omega(\alpha\text{-Fe})}{\omega(2:17)} \times 100,$$

where $\sigma_S(\alpha\text{-Fe}) = 210$ A m$^2$/kg; $\omega$ - the presence of the phase ($\alpha$-Fe or 2:17) in the sample, wt. %.

Since the $\alpha$-Fe phase’s content after nitriding in the sample was present as a trace level, the obtained experimental values of the magnetization $\sigma_S$ (sample) were not recalculated.

As can be seen from Table 2, the saturation magnetization values for hydride powder and especially nitride powder exceed the same value for the initial Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$ intermetallic compound at room temperature, which is in good agreement with the known literature data for Sm$_2$Fe$_{17}$, its hydride Sm$_2$Fe$_{17}$H$_x$, and nitride Sm$_2$Fe$_{17}$N$_y$ [2]. Considering the recalculcation of the value of $\sigma_S(2:17)$ for Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$ and Sm$_{1.8}$Er$_{0.2}$Fe$_{17}$H$_{4.6}$, they amount to 82.5 and 113.8 A m$^2$/kg, respectively.

Nitrogenation changes the main magnetic characteristics of Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$ and leads to an increase in saturation magnetization to a greater extent (by 37.5%) than hydrogenation (by 27.5%). A similar trend is observed for the coercive force: its values are significantly higher (~ 30 times) compared to the initial sample and its hydride. The reason for the low values of the coercive force for Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$ and Sm$_{1.8}$Er$_{0.2}$Fe$_{17}$H$_{4.6}$ is associated with magnetic anisotropy of the easy plane type, in which the magnetic moments of atoms (Sm, Er) and Fe are oriented in the basal plane and rotate quite easily under the action of an external magnetic field. On the contrary, as in the case of Sm$_2$Fe$_{17}$N$_y$ [2], the incorporation of nitrogen atoms into Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$ leads to a highly coercive state of the obtained nitride, especially after high-energy ball-grinding. It is known [19, 20] that the coercive force, as a rule, increases with decreasing particle size.
1. X-ray diffraction characteristics of (Sm_{1.2}Er_{0.8})_{17}, the hydrides, the nitrides and ball-milled derivatives in comparison with published data [2, 15–17].

| Compound                  | Milling time t_{mil}, min | a-Fe, wt.% | a, Å  | c, Å  | c/a  | V, Å^3 | ΔV/V, % |
|---------------------------|----------------------------|------------|-------|-------|------|--------|--------|
| Sm_{2}Fe_{17} [15]        | -                          | -          | 8.553 | 12.442| 1.455| -      | -      |
| Sm_{2}Fe_{17}H_{2} [15]   | -                          | -          | 8.653 | 12.506| 1.445| -      | 2.9    |
| Sm_{2}Fe_{17} [16]        | -                          | -          | 8.554 | 12.443| 1.455| 788.4 | -      |
| Sm_{2}Fe_{17}H_{4.7} [16] | -                          | -          | 8.682 | 12.550| 1.446| 819.2 | 3.9    |
| Sm_{2}Fe_{17} [2, 17]     | -                          | traces     | 8.55  | 12.43 | 1.454| 786.9 | -      |
| Sm_{2}Fe_{17}N_{2.3} [2, 17] | -                          | -          | 8.73  | 12.64 | 1.448| 833.7 | 6.3    |
| Sm_{2}Er_{0.8}Fe_{17} [17]| -                          | 8.504      | 12.380| 1.456 | -    | -      | -      |
| Sm_{2}Er_{0.8}Fe_{17}H_{4.6} [17] | -                          | 8.650      | 12.656| 1.463 | -    | -      | -      |
| Sm_{1.2}Er_{0.8}Fe_{17}    | 4                          | 8.641      | 12.505| 1.447 | 808.7| 3.6    |        |
|                           |                            | 0          | traces| 8.668 | 12.627| 1.457| 827.2 |
|                           |                            | 15         | traces| 8.665 | 12.598| 1.454| 826.9 |
|                           |                            | 30         | traces| 8.659 | 12.590| 1.454| 824.3 |
|                           |                            | 45         | traces| 8.656 | 12.585| 1.454| 823.2 |
|                           |                            | 60         | traces| 8.625 | 12.580| 1.454| 822.8 |

| Compound                  | Milling time t_{mil}, min | Particle size, μm | σ, emu/g^a | Hc, Oe |
|---------------------------|----------------------------|-------------------|------------|--------|
| Sm_{2}Er_{0.8}Fe_{17}      | -                          | ≤ 50              | 89 (82.5)  | 48.5   |
| Sm_{2}Er_{0.8}Fe_{17}H_{4.6}| -                          | -                 | 121.8 (114)| 50     |
|                           | 0                          | 0.2-25            | 132.3      | 1350   |
|                           | 15                         | 0.2-5             | 113.0      | 2350   |
|                           | 30                         | 0.2-4             | 111.6      | 2060   |
|                           | 45                         | 0.2-3.5           | 121.5      | 3140   |
|                           | 60                         | 0.2-2.7           | 131.5      | 3915   |

^a The values of the saturation magnetization are given in parentheses, calculated by the formula (1).

In our experiments, a monotonic increase in the value of the coercive force of Sm_{1.2}Er_{0.8}Fe_{17}N_{2} nitride powders from 1350 Oe before grinding to 3915 Oe after grinding for 60 minutes was observed. As shown in Table 2, the particle size of Sm-Er-Fe-N powders also decreases depending on the duration of the grinding procedure. It should note that agglomerates appear with an increase in the time of grinding. In this case, the growth of coercive force is due to the rise in single-domain particles in powders.

Figure 2 shows field dependences of magnetization for Sm_{1.2}Er_{0.8}Fe_{17} and Sm_{1.2}Er_{0.8}Fe_{17}H_{4.6} at 4.2 K. It is seen that both samples demonstrate a sharp increase in the magnetization in a certain magnetic field, μ_{Hcrt}. This growth is associated with the Er magnetic moments, which are ordered antiparallel to the Fe and Sm magnetic moments. The antiparallel coupling between the Er (Fe, Sm) magnetic moments can be broken by magnetic fields of sufficient strength. By analyzing μ_{Hcrt} values, the coupling strength between the sublattices (λ) can be estimated. The following formula can be used for calculation for all samples [21]:

\[ μ_{Hcrt} = λ · (M_{Fe} - M_{Er} · ξ) \]  

(2)

where ξ = 1/(1+λ_{Sm}·χ_{Sm}), here λ_{Sm} and χ_{Sm} are the exchange parameter and susceptibility of the Sm sublattice, respectively [22]. The product λ_{Sm}·χ_{Sm} did not exceed 0.02. The contribution to the magnetization from the Fe sublattice was taken into account using isostructural compounds with Y and
**Figure 2.** Field dependences of magnetization for Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$N$_2$ and Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$H$_{4.6}$ at 4.2 K.

**Figure 3.** Field dependences of magnetization for Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$N$_2$ (t = 0 and 30 min) at 4.2 K.

Lu [2, 23-26]. The $\mu_0H_{cr1}$ values 37 and 40 T for Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$ and Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$H$_{4.6}$, respectively. As a result, we obtained $\lambda = 1.35$ for initial compound and 1.45 T/$\mu$B for its hydride. Figure 3 shows field dependences of magnetization for Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$N$_2$ after grinding times 0 and 30 min at 4.2 K. Both samples also demonstrate an increase in the magnetization. In contrast to Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$ and Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$H$_{4.6}$, the transition induced by an external magnetic field in nitrides is less pronounced. It was found that the $\mu_0H_{cr1}$ values practically do not change with an increase in the grinding time from 0 to 60 min and is 40 T. This means that the value of the intersublattice exchange interaction ($\lambda = 1.3$ T/$\mu$B) does not depend on the particle size of the studied powders (on the size factor [27, 28]).

Thus, high-field magnetization studies are important for estimation of exchange interactions for both binary compounds R$_2$Fe$_{17}$(N,H)$_x$ [29-30] and for substituted compositions (Sm,Er)$_2$Fe$_{17}$(N,H)$_x$.

### 4. Conclusion

In this paper, we report on the structure and magnetic properties of the (Sm,Er)-Fe-(N,H) samples and nitrided powders prepared by high-energy ball milling. Sm$_{1.8}$Er$_{0.2}$Fe$_{17}$N$_2$ and Sm$_{1.8}$Er$_{0.2}$Fe$_{17}$H$_{4.6}$ have a Th$_2$Zn$_{17}$-type of structure as the parent compound. Analysis of milled powders’ particle size indicated that the increasing milling time promotes agglomerates’ appearance. The magnetic study showed that ball-milling processing increases the coercivity of the materials: highest value was found for the Sm$_{1.2}$Er$_{0.8}$Fe$_{17}$N$_2$ powder subjected to grinding for 60 minutes. The observed regularities in the magnetic properties formation of (Sm,Er)-Fe-N are essential for preparation hard magnetic materials.

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