Behavior of magnetization in high magnetic fields of (Sm,Ho)₂Fe₁₇N₂.₄ powders obtained by mechanical grinding

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Abstract. Fundamental magnetic properties of the R₂Fe₁₇ compounds are highly sensitive to the atomic substitutions and interstitial absorption of light elements (nitrogen or hydrogen). In our work, both were combined, and the influence of the substitutions in the R-sublattice and nitrogen absorption on the magnetization behavior of Sm₂Fe₁₇ compound in magnetic fields up to 58 T was studied. (Sm,Ho)₂Fe₁₇N₂.₄ nitride was prepared. Magnetisation measurements were carried out on powder samples. Nanopowders of (Sm,Ho)₂Fe₁₇N₂.₄ were obtained by mechanical grinding. The grinding time was varied from 0 to 60 minutes. The strength of the inter-sublattice coupling in all samples is estimated by analyzing high-field magnetization data. In our work is shown that nitrogenation weakens the inter-sublattice exchange interaction in the compounds up to 45 - 50 %. Grinding time and, as a consequence, particle size affects the inter-sublattice exchange interaction. To achieve a ferromagnetic state, fields are needed well in excess of 58 T.

1. Introduction

Sm₂Fe₁₇N₃ with outstanding magnetic properties was obtained for the first time by Coey and Sun in 1990 [1]. For this reason, Sm₂Fe₁₇Nₙ (0 < y ≤ 3) nitrides still remain very attractive and promising materials because they have the best combination of magnetic characteristics [2–6]. The nitrides with the maximum possible nitrogen content (y = 3 at. N/f.u.) exhibits strong uniaxial magnetocrystalline anisotropy over the entire temperature range of magnetic ordering. It has larger values of saturation magnetization and magnetic anisotropy field in comparison with the same characteristics of the Nd₂Fe₁₄B compound.

Hard magnetic materials are, as a rule, multicomponent systems properties of which depend not only on their composition, but also on their structural state. It is known, for example, that the substitution of a part of the neodymium atoms with holmium atoms and the iron atoms with cobalt atoms makes it possible to obtain thermally stable (Nd,Ho)-(Fe,Co)-B magnets [7]. The best magnetic hysteresis properties are demonstrated by materials in the nanocrystalline state [2, 8]. Currently, a large number of studies have been also carried out for the Sm₂Fe₁₇Nₙ nitrides to study the effect of the substitutions both in the Fe sublattice [9-11] and in the rare earth metal sublattice [12-14]. The properties of the iron sublattice were investigated for the compounds with nonmagnetic rare-earth metals, namely Y or Lu [5, 15-18].

Magnetization measurements in high magnetic fields are very important for compounds of the R₂Fe₁₇(N,C,H) – type containing light or/and heavy rare-earth metals [19-21]. Such studies are carried out on poly- and single-crystalline samples and make it possible to determine the parameters of
crystal-electric-field (CEF) and exchange interactions [22, 23]. However, information on the magnetization measurement of nanocrystalline powder samples and, mainly, on the effect of the particles size on their properties in high magnetic fields could not be found in scientific periodicals.

The purpose of this work is to investigate the behavior of magnetization in high magnetic fields of Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ nanopowders obtained by mechanical grinding. Preliminary [12], a comprehensive study of their structure, morphology of surface and magnetic hysteresis properties was carried out.

2. Experimental details
Details of the initial Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$ sample, its nitride Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ and nanopowders preparation and certification can be found in Ref. [12]. The milling process 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 ball-milled powders were dispersed and deagglomerated using ultrasound. 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.

The high-field magnetization measurements were performed at the Dresden High Magnetic Field Laboratory in pulsed magnetic fields up to 58 T between 4.2 and 120 K [24]. Comparative magnetic studies of the initial compound and its nitrides were performed on free powder samples. The absolute values of magnetization were calibrated using static-field data up to 14 T. Magnetization measurements were performed using a commercial PPMS-14 magnetometer (Quantum Design, USA) at different temperatures.

3. Results and discussion
The Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ nitride retained the same structural type of Th$_2$Zn$_{17}$ as the initial compound Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$. The size of the powder particles of Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ before milling is from 2 to 25 μm. Analysis of the particle size distribution for the powders that underwent mechanical treatment showed a decrease in particle size with increasing grinding time. When the grinding time was 60 min, the average particle size reached 0.5–2.5 μm [12]. It should be noted here that, after mechanical treatment, the investigated nitrides are fine powders with a tendency toward strong agglomeration, layer-by-layer coalescence of magnetic particles with each other.

Figure 1 shows field dependencies of magnetization for Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ nitrides with the grinding time 0, 15, 30, 45 and 60 min at 4.2 K. The smooth increase of magnetization is observed when the magnetic field grows from 43 to 58 T. This growth is associated with the presence of holmium magnetic moments in the compound, which are ordered antiparallel to the magnetic moments of samarium and iron. The antiparallel coupling between the magnetic moments can be broken only by the magnetic fields of sufficient strength. The resulting curve $M(\mu_0 H)$ will contain a change in slope or even jumps (an increase of magnetization at a certain field, which is called critical $\mu_0 H_{cr1}$), by analyzing which the coupling strength between the sublattices can be estimated. So, the following formulas can be used for system (Sm$_{1-x}$Ho$_x$)$_2$Fe$_{17}$ at $x = 1$ and 0.8, respectively [25]:

$$\mu_0 H_{cr1} = \lambda \cdot (M_{Fe} - 2 \cdot M_{Ho})$$  (1)
$$\mu_0 H_{cr1} = \lambda \cdot (M_{Fe} - M_{Ho} \cdot \xi)$$  (2)

where $M_{Fe}$ and $M_{Ho}$ are the magnetizations of the Fe and Ho sublattices, respectively; $\xi = 0.8/(1 + \lambda_{Sm} \chi_{Sm})$, here $\lambda_{Sm}$ and $\chi_{Sm}$ are the exchange parameter and susceptibility of the Sm sublattice, respectively. The product $\lambda_{Sm} \chi_{Sm}$ did not exceed 0.02. The contribution to the magnetization from the iron sublattice was taken into account using a compound with Lu [26]. Considering that for the Ho$_2$Fe$_{17}$ compound, the first critical field is 40 T [24], and in respect that $\lambda$ does not change when the rare-earth composition varies [27 - 30], we determined the value of the parameter of the inter-sublattice exchange interaction $\lambda = 2.8$ T/$\mu_B$ for Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$ compound. Moreover, using Eq. (2), we were able to calculate parameters $\lambda$ for nitrides Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ before
and after processing with a ball mill for 15, 30, 45 and 60 minutes. The data obtained are shown in Table 1.

![Figure 1](image)

**Figure 1.** Field dependences of magnetization for Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ nitrides with the grinding time 0, 15, 30, 45 and 60 min. at 4.2 K.

**Table 1.** Magnetic characteristics of the compound Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ at T = 4.2 K.

| Grind time, min | $\lambda$, T/µB | $\mu_0 H_{cr1}$, T (exp.) | $\mu_0 H_{cr2}$, T (cal.) |
|-----------------|-----------------|-----------------------------|-----------------------------|
| 0               | 1.47            | 43                          | 66                          |
| 15              | 1.57            | 46                          | 70.5                        |
| 30              | 1.57            | 46                          | 70.5                        |
| 45              | 1.58            | 46.2                        | 70.9                        |
| 60              | 1.52            | 44.5                        | 68                          |
Figure 2. Field dependencies of magnetization for Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ nitrides with the grinding time 0, 15, 30, 45 and 60 min. at 40 K.

It can be seen that, depending on the grinding time, not only the particle size changes, but also the magnitude of the first critical field $\mu_0H_{cr1}$, as well as the parameter of the inter-sublattice exchange interaction $\lambda$. For nitride Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ before ball milling $\mu_0H_{cr1} = 43$ T and $\lambda = 1.47$ T/$\mu_B$. Nitrides after ball milling for 15, 30 and 45 minutes show the same increased values of the critical field and exchange parameter. The increase in the grinding time to 60 minutes leads to the fact that both values are slightly reduced (see Table 1). With a further increase in the external magnetic field (above 58 T), the theoretical value ($M_{\text{ferro}} = \mu_{\text{Sm}} + \mu_{\text{Fe}} + \mu_{\text{Ho}}$ at $\mu_0H_{cr2}$) can be successfully implemented. Knowing the parameter of exchange interaction $\lambda$ and using formula (3), we can determine the value of the second critical field $\mu_0H_{cr2}$:

$$\mu_0H_{cr2} = \lambda \cdot (\text{M}_\text{Fe} + \text{M}_\text{Ho} \cdot \xi)$$  \hspace{1cm} (3)
Figure 3. Field dependencies of magnetization for Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ nitrides with the grinding time 0, 15, 30, 45 and 60 min. at 80 K.

The values of the second critical field $\mu_0 H_{c2}$ are also listed in Table 1. Our calculations show that for the transition to a ferromagnetic state induced by an external magnetic field in Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ nitrides, fields of the order of 70 Tesla and above are required.

Figures 2-4 show the transformation of the magnetization curves $M(\mu_0 H)$ with increasing temperature, namely at $T = 40$, 80 and 120 K. An analysis of the presented curves shows that at $T = 40$ K spin-reorientation transitions are also observed (as at $T = 4.2$ K) for all samples, but the value of the first critical field $\mu_0 H_{c1}$ increases. For example, $\mu_0 H_{c1} = 43$ T and 46 K at $T = 4.2$ K and 40, respectively, for Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ nitride before ball milling. As the temperature rises to $T = 80$ K, the fields we use are no longer sufficient to observe any spin-reorientation transitions for powder samples, the grinding time of which ranges from 15 to 60 min. The magnetization curves $M(\mu_0 H)$ have no singularities even at a higher temperature, namely, $T = 120$ K.
So, in binary Ho$_2$Fe$_{17}$ (or Sm$_2$Fe$_{17}$) compound at the part substitution of Sm atoms for Ho, the parameter $\lambda$ of the inter-sublattice exchange interaction does not change. For nitride Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ before and after ball milling significant ~ 45 - 50 % decrease of the parameter $\lambda$ takes place.

4. Conclusions
Nitrogenation is an efficient tool to influence the strength of the R-Fe exchange coupling in multicomponent (RR')$_2$Fe$_{17}$ (R = Sm, Ho) compounds. Calculations showed that there is a ~ 45 - 50 % decrease in the strength of R-Fe exchange in nitride with high content nitrogen. It was found that grinds (performed over different times) lead to a decrease in the particle size of the powder: the longer the grinding time, the smaller the average particle size (or their agglomerates). For the first time, high-field studies of the magnetization of nanopowders have shown that the experimentally determined value of the first critical field $\mu_0H_{c1}$ varies depending on the grinding time. However, this relationship is not linear. The highest field $\mu_0H_{c1}$ is observed for nanopowders with a grinding time of 15 to 45 minutes. The value of the second critical field $\mu_0H_{c2}$ is also determined by calculations. It has been shown that external magnetic fields of 70 T and above will be able to completely unfold the magnetic moments of Sm, Fe and Ho in one direction and force-induced ferromagnetic state will be implemented in Sm$_{1.2}$Ho$_{0.8}$Fe$_{17}$N$_{2.4}$ nitrides.

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