



HAL
open science

Angular dependence of saturation magnetization in single crystals with uniaxial magnetic anisotropy

D.S. Neznakhin, A.S. Bolyachkin, M.I. Bartashevich, L. V. B. Diop, O. Gutfleisch, K.P. Skokov

► To cite this version:

D.S. Neznakhin, A.S. Bolyachkin, M.I. Bartashevich, L. V. B. Diop, O. Gutfleisch, et al.. Angular dependence of saturation magnetization in single crystals with uniaxial magnetic anisotropy. *Journal of Magnetism and Magnetic Materials*, 2022, 547, pp.168947. 10.1016/j.jmmm.2021.168947 . hal-03821306

HAL Id: hal-03821306

<https://hal.science/hal-03821306v1>

Submitted on 19 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Angular dependence of saturation magnetization in single crystals with uniaxial magnetic anisotropy

D.S. Neznakhin^{1,2}, A.S. Bolyachkin¹, M.I. Bartashevich¹, L.V.B. Diop^{2,3}, O. Gutfleisch²,
K.P. Skokov²

¹ Ural Federal University, 620002 Yekaterinburg, Russia

² Material Science, Technical University Darmstadt, 64287, Darmstadt, Germany

³ Université de Lorraine, CNRS, IJL, F-54000 Nancy, France

ABSTRACT

A remarkable feature of some high anisotropy intermetallic compounds based on R-T systems, where R is a rare earth element and T is a 3d transition metal, is a discrepancy of saturation magnetizations obtained along easy and hard magnetization axes: M_{EA} and M_{HA} . This anisotropy of saturation magnetization should be considered when magnetization curves need to be accurately described to evaluate magnetic anisotropy constants. In this work, the angular dependence of saturation magnetization was studied aiming at experimental verification of the assumption of $M_s(\theta) = M_{EA} \cos^2 \theta + M_{HA} \sin^2 \theta$. A single crystal of Y_2Co_7 , which had a uniaxial magnetic anisotropy and saturation magnetization discrepancy of 7.9% at 300 K, was chosen for the study. Our proposed verification approach is universal and would be relevant for any intermetallic compound with a prominent anisotropy of saturation magnetization.

KEYWORDS: magnetization anisotropy; magnetic anisotropy; single crystal.

INTRODUCTION

The anisotropy of physical properties is a subject for basic research that allow to reveal fundamental properties of compounds and to develop related theoretical models. In particular, the analysis of magnetization processes along different crystallographic directions is of constant interest for magnetic compounds since it yields magnetocrystalline anisotropy constants provided the symmetry of a compound is established. Sometimes for accurate description of magnetization curves measured along the easy magnetization axis (EA) and along the hard magnetization axis (HA), it is necessary to take into account that saturation magnetizations along these axes, M_{EA} and M_{HA} respectively, are quite different. Such a phenomenon of saturation magnetization variation in respect to crystallographic axes can be called as magnetization anisotropy. It originates due to several reasons. First, thermal agitations of atomic magnetic moments could be different along EA and HA [1]. Second, different degree of quenching of the orbital angular momentum of 3d atoms in different crystallographic directions [2]. The phenomenon is especially remarkable for high anisotropy intermetallic compounds based on R-T systems where R is a rare earth element and T is a 3d transition metal [3-7]. The magnetization anisotropy can be quantitatively characterized by a dimensionless parameter [3]:

$$p = (M_{EA} - M_{HA})/M_{EA}. \quad (1)$$

To exclude the effect of high-field magnetic susceptibility χ on the parameter p , the values of M_{EA} and M_{HA} should be evaluated from corresponding magnetization curves by

extrapolation of the high-field regions (starting at $H > H_A$, where H_A is the anisotropy field) to $H = 0$. Thus, the following can be written $M_s(H) = M_s(0) + \chi H$ as a first approximation that was named as a paraprocess by Akulov [8]. However, for the processing of magnetization curves using, for example, a numeric technique [4] or the modified Sucksmith-Thompson method [5], it is not sufficient to simply obtain M_{EA} and M_{HA} ; the angular dependence of saturation magnetization should also be known. It is usually assumed that the parameter p is small, *i.e.* $p \ll 1$. In that case, the angular dependence can be proposed as an expansion into a series taking into account the symmetry of a compound [1]. For the uniaxial symmetry, it gives the following:

$$M_s(\theta) = M_{EA}(1 - p \sin^2 \theta). \quad (2)$$

where θ is a deviation angle of magnetization relative to EA. Otherwise it can be expressed as $M_s(\theta) = M_{EA} \cos^2 \theta + M_{HA} \sin^2 \theta$ substituting Eq. (1). However, there are accumulated experimental results demonstrating significant values of p for some R-T single crystals. For example, La_2Co_7 has $p = 10\%$ ($T = 300$ K) [6], $\text{Nd}_5\text{Fe}_{17}\text{H}_{16}$ has $p = 12\%$ ($T = 10$ K) [7], and for $\text{Nd}_5\text{Fe}_{17}$ the parameter p reaches even 20% ($T = 10$ K) [7]. In such cases the applicability of the expression (2) is not apparent and requires a verification.

In this work, we propose an approach for experimental verification of the expression (2) based on the analysis of high-field regions of magnetization curves measured at different angles between magnetic field and EA. This approach was applied for the study of a single crystal of Y_2Co_7 compound, which has the parameter of magnetization anisotropy of 7.9% at $T = 300$ K.

EXPERIMENTAL DETAILS

We started our study with the methodological issue related to the effect of sample shape on saturation magnetization evaluation. To estimate potential uncertainty caused by this factor, polycrystalline samples of pure Fe and Ni (purity no worse than 99.98%) and different shapes were prepared: needles, plates and cubes. Some parameters of the samples measured by a micrometer are presented in Table 1. It will be demonstrated further that for the cubic case the absolute value of shape-associated uncertainty is appropriate for the magnetization anisotropy study.

Next, the intermetallic compound Y_2Co_7 was studied. It was obtained by induction melting in an argon atmosphere followed by vacuum annealing. Chemical elements Co and Y with purity of at least 99.98% and 99.8% respectively were used for the synthesis. Annealing was performed for a week at of about 1250 °C. Then crystallites were extracted from the ingot for further selection based on their structural attestation. The single-phase composition of the finally selected sample was confirmed by X-ray powder diffraction. The compound Y_2Co_7 had a layered structure (space group $R\bar{3}m$) with the following lattice constants: $a = b = 4.995$ Å, $c = 36.145$ Å (Fig.1a). These constants are close to those obtained in Ref. 7. EDX analysis showed Y = 21.8 at. % and Co = 78.2 at. %, which is close to the stoichiometric phase Y_2Co_7 .

The sample was processed into a shape close to cubic one for measurements of magnetic properties. Its geometry is described in Table 1. The crystallographic axis [001] was perpendicular to one of the faces of the cube. Back-scattered Laue diffraction was used to confirm the single-crystalline state of the sample and to orient it (Fig.1c).

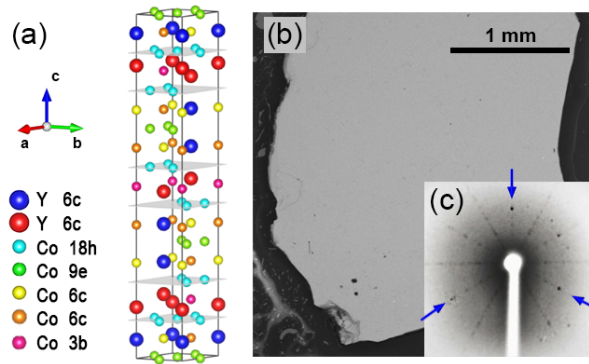


Fig.1. Crystal structure of Y_2Co_7 (a), Scanning electron microphotograph for the sample for EDX analysis (b) and back-scattered Laue diffraction pattern of the Y_2Co_7 single crystal along the [001] axis (c).

Magnetization curves were measured at 300 K in static magnetic fields up to 14 T using a Physical Property Measurement System (PPMS-14) equipped with VSM and first-order gradiometer pick-up coil assembly. To measure the high-anisotropy compound at certain angles between EA and external magnetic field the sample was firmly fixed by two quartz rods which faces were polished to desired inclination. The error of such angle positioning did not exceed 3° . During the measurements, the sample was attached to the central axis of the gradiometer in order to eliminate the error associated with sample displacement [11].

Table 1. Saturation magnetization M_s and geometry of studied samples. Parameters are presented in mm in the following order: length \times diameter for a needle; length \times width \times height for both plate and cube.

	M_s , kA/m (T = 300 K)	Needle	Plate	Cube
Ni	484	2.89×0.14	$2.05 \times 2.01 \times 0.12$	$0.88 \times 0.89 \times 0.74$
Fe	1760	3.27×0.11	$2.43 \times 2.70 \times 0.15$	$1.61 \times 1.54 \times 1.45$
Y_2Co_7	567 [10]			$1.17 \times 1.04 \times 0.93$

RESULTS AND DISCUSSION

A. The effect of sample shape on saturation magnetization

Measurements of high anisotropy compounds are usually performed on samples in the form of needle, plate, or cube. The best option is a spherical shape of a sample, but it is hard to prepare. The crystallographic axes of a single crystalline sample are oriented in a certain way in respect to the axes prescribed by a geometry. Usually, it is chosen so to get the coincidence of easy magnetization axes of magnetocrystalline and magnetic shape anisotropies. It is worthy to note that the shape of a sample can affect not only internal magnetic field but measured magnetization also.

Modern physical/magnetic properties measurement systems are equipped with first- or second-order gradiometers commonly. PPMS with VSM option has a first-order gradiometer pick-up coils assembly as a magnetic moment detector. The gradiometer consists of two identical coils wound on a cylindrical support and connected as $(- +)$. It is

non-sensitive up to the first derivative $\partial B_z/\partial z$ of the magnetic field. SQUID-based magnetometer has a second-order gradiometer consisting of four single turns of superconducting wire wound on a cylindrical support and connected as $(- + + -)$, with the two central turns at the same z coordinate. It is sensitive to the third $\partial^3 B_z/\partial z^3$ and subsequent derivatives of the magnetic field. For the latter case, it was shown that the measuring signal strongly depends on the shape of a sample due to magnetic flux reconfiguration in respect to gradiometer coils [12,13]. For example, registered magnetization of a plate sample varies of about 5% for in-plane and out-of-plane directions [12]. Measurements of spherical or cubic samples yield magnetic moment close enough to that of the equivalent dipole located in the second-order gradiometer center. Hence, it gives negligible uncertainty of the parameter of magnetization anisotropy. In our study PPMS with VSM utilizing first-order gradiometer was used. We decided to estimate the shape effect on saturation magnetization for this case experimentally.

Magnetization curves of iron and nickel polycrystalline samples of different shapes are shown in Figure 2. The most prominent magnetization discrepancy in the saturation region, *i.e.* at $\mu_0 H > 1$ T for Ni (Fig. 2a) and at $\mu_0 H > 2$ T for Fe (Fig. 2d), was observed for needle samples. Saturation magnetization along the needle axis, that is EA, was smaller than magnetization in a perpendicular direction (HA). Using Eq. (1), resulting parameters of magnetization anisotropy were estimated as -2.0% for Ni and -2.1% for Fe for chosen needle sizes. For plate-shaped samples saturation magnetization along EA (in-plane orientation) is also smaller than one for HA (out-of-plane direction). It gives $p = -0.5\%$ and $p = -0.9\%$ for Ni and Fe respectively (Fig. 2b, 2e). Cubic samples were measured along face normals that were perpendicular to each other. Such magnetizing directions are typical for the case of a sample with uniaxial magnetocrystalline anisotropy. It can be seen that p is negligible for Ni and it is of about 0.1% for Fe (Fig. 2c, 2f). Thus, the cubic shape is appropriate for reliable study of saturation magnetization features in the case of R-T compounds with high uniaxial anisotropy which parameter of magnetization anisotropy usually reaches several percent. In contrast, such a research of T-elements and compounds with small p [14,15] should be done only for spherical samples with high-quality surface.

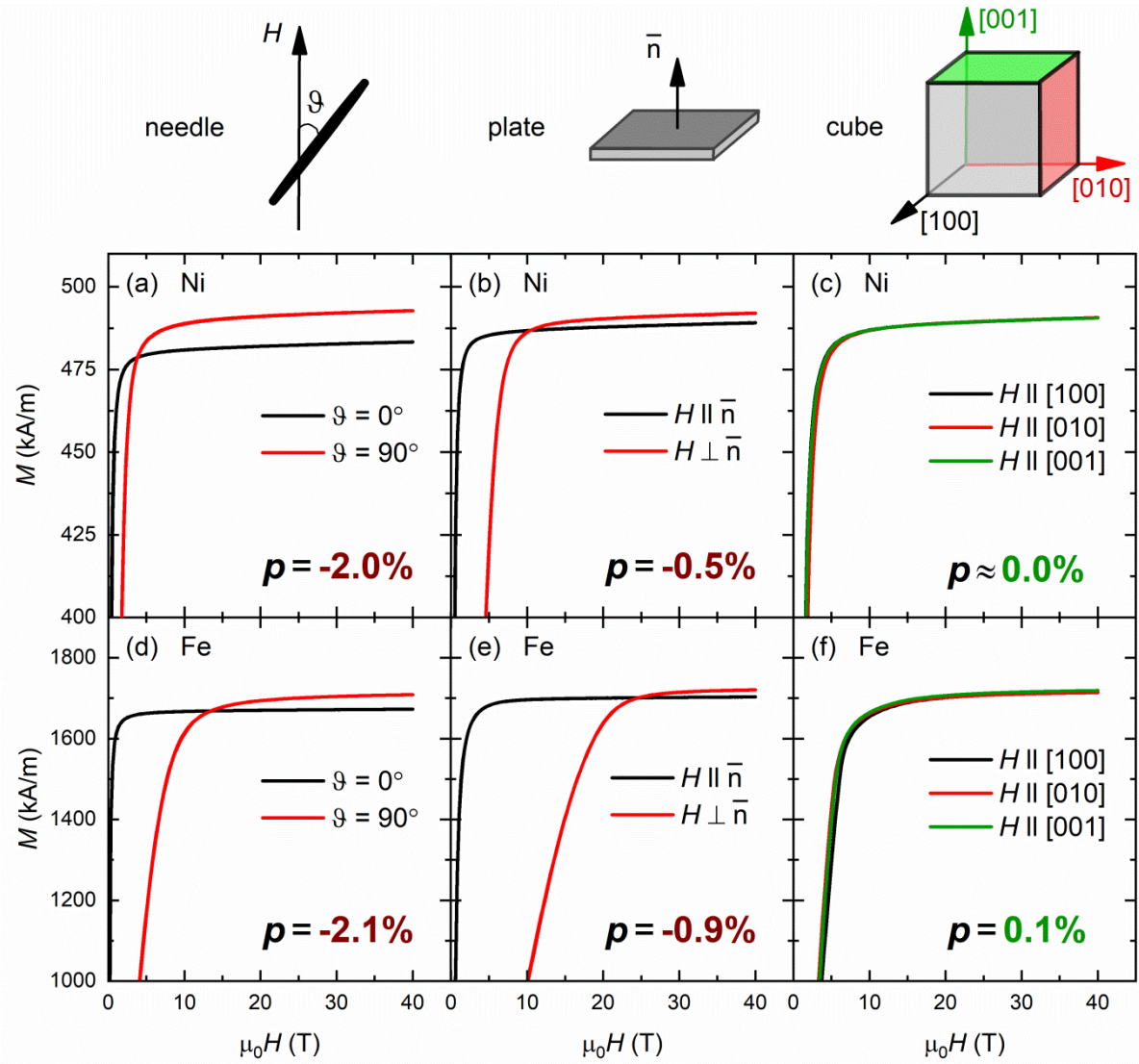


Fig.2. Magnetization curves of Ni (a-c) and Fe (d-f) polycrystalline samples of different shapes: needles (a,d), plates (b,e) and cubes (c,f) at 300 K.

B. Magnetization measurements of Y_2Co_7 single crystal

Magnetic properties of Y_2Co_7 single-crystalline sample were studied at room temperature (300 K). Y_2Co_7 is a ferromagnetic compound with high magnetic anisotropy and Curie temperature of 689 K [10]. The sample was close to the cubic shape (Table 1) with facets normal to easy magnetization axis and hard magnetization one that correspond to [001] and [210] directions respectively. Magnetization curves measured at different angles between EA and magnetic field are presented in Figure 3. Field axis was recalculated into internal magnetic field using demagnetization factors of $N_{EA} = 0.42$ and $N_{HA} = 0.29$ for EA and HA respectively. The N_{EA} was estimated from the low-field slope of $M(H_{ex})$ along EA; N_{HA} was given by $N_{HA} = (1 - N_{EA})/2$. Obtained values were in compliance with those evaluated from the equation for demagnetization factors of an ellipsoid considering the sample geometry (Table 1). High-field magnetization regions for EA and HA were linearly extrapolated to $\mu_0 H = 0$ (dash lines on Fig. 3). It gave saturation magnetizations $M_{EA} = 604$ kA/m and $M_{HA} = 556$ kA/m, as well as high-field susceptibilities $\chi_{EA} = 1.9 \cdot 10^{-5}$ and $\chi_{HA} = 2.6 \cdot 10^{-5}$. Such a difference of saturation magnetizations yielded $p = 7.9\%$ according to Eq. (1). Obtained values were used as constants for numeric approximation of the

magnetization curve along HA ($\theta = 90^\circ$). The approximation was based on energy minimization with anisotropy constants as variation parameters. Details about the procedure are described elsewhere [2]. A small misorientation angle of about 1° between magnetic field and HA was taken into account. In particular, this misorientation was responsible for smoothed kink of $M(H)$ close to anisotropy field. Result of the approximation is shown in Figure 3 in a solid black line. It allowed us to evaluate magnetocrystalline anisotropy constants $K_1 = 2.16 \text{ MJ/m}^3$ and $K_2 = -0.16 \text{ MJ/m}^3$. Then an anisotropy field can be found as $H_A = (2K_1 + 4K_2)/[M_{EA}(1 - 3p)]$ [5], yielding $\mu_0 H_A = 8 \text{ T}$.

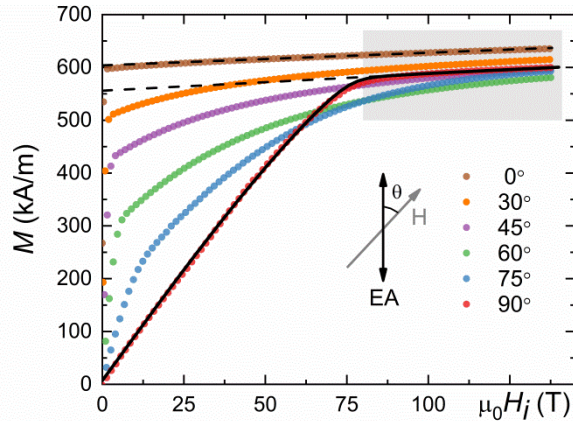


Fig.3. Magnetization curves of Y_2Co_7 single crystal measured at different angles between magnetic field $\mu_0 H$ and easy magnetization axis (EA) at 300 K. Dash lines indicate $M(H)$ extrapolations from high-field regions to $\mu_0 H = 0$ performed for EA ($\theta = 0^\circ$) and hard magnetization axis ($\theta = 90^\circ$). High-field regions are marked out by gray shading.

High field regions ($\mu_0 H > 8 \text{ T}$) of magnetization curves obtained at intermediate angles in the interval of $(0^\circ, 90^\circ)$ were chosen for further analysis (Fig. 4a). For such fields magnetization process occurred predominantly due to magnetic moment rotation. Hence, the proposed approximation could be applied also. But it was used in a different scheme: previously evaluated K_1 and K_2 were fixed as well as the remaining quantities, so saturation magnetization M_s was the only variation parameter. Results of these approximations are presented in Figure 4a in solid lines demonstrating acceptable coincidence with experimental data. Let us note that the paraprocess could become nonlinear with increasing magnetic field. It can be taken into account to improve approximation accuracy further. Saturation magnetizations M_s evaluated from approximations are shown in Figure 4b. It can be seen that experimental data correlate well with Eq. 2 plotted for previously obtained M_{EA} and M_{HA} . It validates applicability of Eq. 2 for high anisotropy compounds with a parameter of magnetization anisotropy up to 8%.

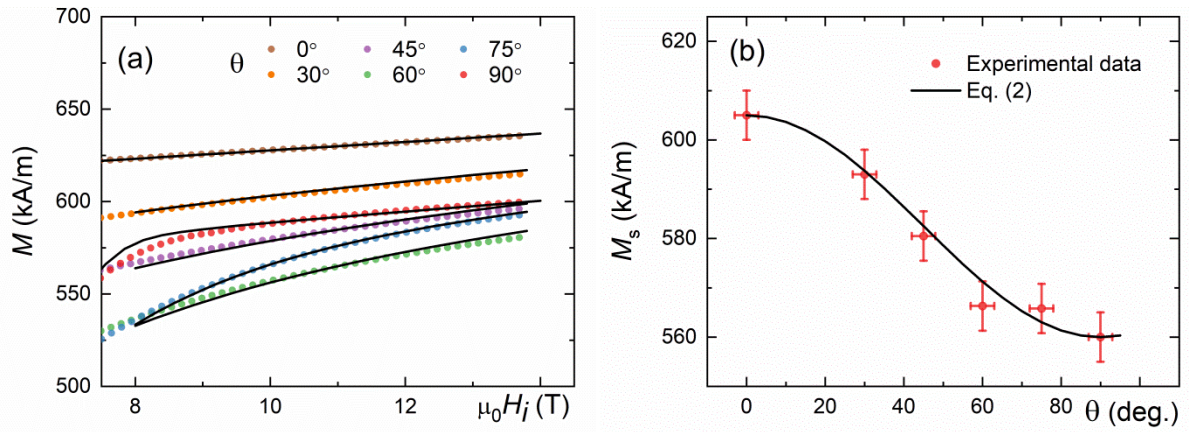


Fig.4. High-field regions ($\mu_0 H > 8$ T) of Y_2Co_7 magnetization curves at different angles θ between magnetic field $\mu_0 H$ and easy magnetization axis (EA) at 300 K (a). Numerical approximations of $M(H)$ are shown in solid lines. Angular dependence of saturation magnetization evaluated from the approximations (b).

CONCLUSION

Magnetization curves of Ni and Fe polycrystalline samples of different geometries, *i.e.* needle, plate and cube, were measured along their symmetry axes. This was done in order to estimate the effect of sample's shape on the uncertainty of saturation magnetization measuring using a commercial VSM (Quantum Design) with first-order gradiometer. The origin of the uncertainty is in the magnetic flux reconfiguration in respect to gradiometer coils. It was shown that only in prominent cases of shape anisotropy (needle, plate) the uncertainty can become an issue. It can reach the value of about 2% and has a negative sign. This effect is negligible for cubic samples. Hence, the study of magnetization anisotropy that requires precision magnetometry can be performed reliably on cubic samples for high-anisotropy compounds.

High anisotropy uniaxial Y_2Co_7 single crystal ($\mu_0 H_A = 8$ T) was studied. A series of magnetization curves of the compound were measured with magnetic field applied at intermediate angles between easy magnetization axis (EA) and hard magnetization one (HA). Saturation magnetizations were different along EA and HA: $M_{EA} = 604$ kA/m and $M_{HA} = 556$ kA/m at 300 K. The difference corresponds to the parameter of magnetization anisotropy of 7.9%. Magnetocrystalline anisotropy constants $K_1 = 2.16$ MJ/m³ and $K_2 = -0.16$ MJ/m³ were evaluated from the analysis of HA magnetization process. The angular dependence of saturation magnetization was obtained based on approximations of high-field regions of the magnetization curves ($H > H_a$). The dependence was well described by Eq. (2) that was its first experimental confirmation. In a next step, it would be meaningful to perform such a validation for compounds with extreme magnetization anisotropy like in the case of Nd_5Fe_{17} [7] with the parameter of magnetization anisotropy of about 20%. It can provide new insights about the magnetization anisotropy phenomenon.

ACKNOWLEDGES

This work was supported by Russian Science Foundation (Grant No. №19-72-00048), by the DAAD in the Michael Lomonosov Programm (Project-ID 57391664) and by the

Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) (Project-ID 405553726-TRR 270).

REFERENCES

- [1] E. R. Callen and H. B. Callen, Anisotropic magnetization, *J. Phys. Chem. Solids* **16** (1960) 310.
- [2] E.V. Rozenfel'd, A.V. Korolev, Low-temperature magnetization anisotropy in ferromagnetic materials with quenched orbital angular momentum, *J. Exp. Theor. Phys.* **108** (1995) 862–877.
- [3] J.M. Alameda, J. Deportes, D. Givord, R. Lemaire and Q. Lu, Large magnetization anisotropy in uniaxial YCo₅ intermetallic, *J. Magn. Magn. Mater.* **15-8** (1980) 1257.
- [4] A.S. Bolyachkin, D.S. Neznakhin, T.V. Garaeva, A.V. Andreev, M.I. Bartashevich, Magnetic anisotropy of YFe₃ compound, *J. Magn. Magn. Mater.* **426** (2017) 740.
- [5] A.S. Bolyachkin, D.S. Neznakhin, and M.I. Bartashevich, The effect of magnetization anisotropy and paramagnetic susceptibility on the magnetization process, *J. Appl. Phys.* **118** (2015) 213902.
- [6] M.D. Kuzmin, Y. Skourski, K.P. Skokov, K.-H. Müller, and O. Gutfleisch, Magnetic anisotropy of La₂Co₇, *Phys. Rev. B* **77** (2008) 132411.
- [7] D.Yu. Karpenkov, K.P. Skokov, M.B. Lyakhova, I.A. Radulov, T. Faske, Y. Skourski, O. Gutfleisch, Intrinsic magnetic properties of hydrided and non-hydrided Nd₅Fe₁₇ single crystals, *J. Alloys Compd.* **741** (2018)1012.
- [8] Akulov, N.S., Über den Verlauf der Magnetisierungskurve in starken Feldern, *Zeitschrift für Physik* **69** (1931) 822.
- [9] M.I. Bartashevich, N.V. Mushnikov, A.V. Andreev, and T. Goto, Instability of the Co magnetic state in Y₂Co₇-based compounds: Effect of alloying for Y-and Co-sites, *J. Alloys Compd.* **478** (2009) 34.
- [10] A.V. Andreyev, M.I. Bartashevich, A.V. Deryagin, Ye.N. Tarasov, Influence of hydrogen on crystal structure, magnetic ordering and magnetic properties of hydrides Y₂Co₇H_x, *Physics of Metals and Metallography* **62(5)** (1986) 66–71.
- [11] M.A. Garcia, E.F. Pinel, J. de la Venta, A. Quesada, V. Bouzas, J.F. Fernández, J.J. Romero, M.S.M. González and J.L. Costa-Krämer, Sources of experimental errors in the observation of nanoscale magnetism, *J. Appl. Phys.* **105** (2009) 013925.
- [12] P. Stamenov and J.M.D. Coey, Sample size, position, and structure effects on magnetization measurements using second-order gradiometer pickup coils, *Rev. Sci. Instrum.* **77** (2006) 015106.
- [13] M. Sawicki, W. Stefanowicz and A. Ney, Sensitive SQUID magnetometry for studying nanomagnetism, *Semiconductor Science and Technology* **26** (2011) 064006.
- [14] G. Aubert, P. Escudier, Anisotropic magnetization of nickel at low temperature. *J. de Physique* **32** (1971) 543-544.
- [15] R. Pauthenet, The magnetization of a single crystal of cobalt under high magnetic fields, *Comptes rendus de l'academie des sciences, Serie II* **297** (1983) 13-16. (in French)