Origin of field-induced discontinuous phase transitions in Nd_2Fe_{17}

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Magnetic properties of a trigonal ferromagnet Nd_2Fe_{17} have been studied on single crystals in steady (14 T) and pulsed (32 T) magnetic fields. The easy-magnetization direction lies close to the [120] axis, deviating from the basal plane by 2.9° (at $T = 5$ K). Of particular interest is the low-temperature magnetization process along the high-symmetry axis [001], which is the hard direction. This process is discontinuous and involves two first-order phase transitions (FOMPs). One of them (at 20 T) is a symmetry FOMP similar to that observed in Sm_2Fe_{17}. The second transition (at 10.4 T) is unusual: as the magnetization turns abruptly toward the applied field, it also changes its azimuthal orientation (the angle φ) by 60°. Both transitions can be reasonably accounted for by the presence of a significant sixth-order trigonal anisotropy term.

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I. INTRODUCTION

The R_2Fe_{17} compounds (where R stands for a rare-earth element or yttrium) are interesting because of their unusual anisotropic magnetic properties, and it is for that reason that single crystals of R_2Fe_{17} have been the subject of intensive study during the last decades. A notable exception are the compounds with the lightest rare-earths, in particular Nd_2Fe_{17}, which are little studied. The reason for the deficiency lies in the difficulty of obtaining these R_2Fe_{17} in single-crystalline form—the lighter the R the greater the difficulty—and the end compound, La_2Fe_{17}, does not form at all. As regards Nd_2Fe_{17}, its magnetic behavior remains largely a mystery, despite an earlier publication of the single-crystal magnetization curves [1]. Namely, the magnetization process in the hard direction [001] is not a continuous one—as many as two discontinuities are observed. One of them, at about 10 T, is rather clear, whereas the other one, at ∼18 T, is more a conjecture than an observation. While the former is undoubtedly associated with a first-order phase transition (FOMP), the latter lacks any explanation and one reasonably asks if it might be an artifact. Having two different FOMPs would be unprecedented for a ferromagnet. No parallel can be drawn in this matter to the multiple transitions observed in the ferrimagnetic R_2Fe_{17} with heavy rare-earths (R = Ho [2], Er [3], Tm [4]); such transitions would be impossible in Nd_2Fe_{17}, a ferromagnet. Further doubts about the higher-field anomaly in Nd_2Fe_{17} are brought about by the fact that it is not reproduced by Koyama's own calculations (Fig. 18a of Ref. [1]), whereas they do confirm the presence of the lower-field FOMP. Yet, this anomaly was observed, at about the same field, in an Al-doped single crystal, $Nd_2(Fe_{0.96}Al_{0.04})_{17}$ [5], and there it was a rather more prominent jump. Leaving aside the open question of whether the doped compound is truly representative of pure Nd_2Fe_{17}, the presence of two jumps in the same positions, whose heights vary from one sample to the next, speaks rather in favor of coexistence of two different phases, like in Tb_2Fe_{17} single crystals [6]. It should be noted that Koide *et al.* [5] also showed a calculated magnetization curve where both FOMPs were present.

Resuming the situation about Nd_2Fe_{17} in the literature, neither the reality nor the possible mechanism of the double FOMP can be regarded as established. We therefore deemed it necessary to produce a quality single crystal of Nd_2Fe_{17} and to perform a thorough study of its magnetization. This study is reported in the subsequent sections, organized as follows. Upon a presentation of the experimental techniques (Sec. II) and results (Sec. III), the theoretical model is exposed in Sec. IV. This is followed by a discussion (Sec. V) and a summary (Sec. VI).

II. EXPERIMENTAL DETAILS

Nd_2Fe_{17} single crystals were grown by the reactive flux method using excess Nd as a flux. The starting alloy of composition $NdFe_7$ was prepared by melting high-purity elements (Nd: 99.9%, Fe: 99.99%) in an induction furnace under a purified argon gas atmosphere. The obtained ingot was placed in an alumina crucible, sealed in an evacuated quartz tube, and annealed in a resistive furnace as follows. It was heated up to 1100 °C at a rate of 5 °C/h and kept at this temperature for 10 min. Then the temperature was reduced slowly at a rate of 0.2 °C/h down to 1000 °C, kept there for 4 weeks, and subsequently quenched in water. This mode is favorable for growth of large crystalline grains. The ingot was then broken into single-crystal particles, and several 2-mm large grains were picked out. Energy-dispersive x-ray microanalysis revealed for the grains a final composition of $Nd_2Fe_{16.98}$, while excess neodymium was found in the intergranular space. The single crystallinity and orientation of the grains were checked by back-scattering Laue x-ray diffraction. A few

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grains were ground and the crystallographic phase purity of the powder was checked by x-ray diffraction using a Stoe Stadti P diffractometer in transmission mode with Mo-Kα_1 radiation at room temperature. The unit-cell parameters were determined by least-squares refinement of the diffraction pattern, including all the observed Bragg reflections. The values found are $a = 8.586$ Å and $c = 12.464$ Å, in good agreement with previous reports on polycrystalline samples. The analysis of the diffraction diagram confirmed for Nd_2Fe_{17} the rhombohedral space group $R\bar{3}m$.

Magnetization isotherms were measured on oriented crystals in steady magnetic fields up to 14 T at temperatures ranging from 5 to 350 K using a commercial vibrating-sample magnetometer (Quantum Design PPMS-14). The magnetization measurements were extended up to 32 T using a nondestructive pulsed-field coil at the High Magnetic Field Laboratory in Dresden-Rossendorf, Germany. A single 1.44-MJ capacitor module was used. When fully charged, this could produce a maximum magnetic field of 60 T with a rise time of about 7 ms and a total pulse duration of 25 ms. In our experiments the capacitor bank was charged to about one-half. The magnetization was detected by the induction method using a coaxial pick-up coil system. A detailed description of the pulsed-field magnetometer can be found in Ref. [2]. All pulsed-field data were calibrated against the magnetization measured in steady magnetic fields.

III. RESULTS

Figure 1 presents the magnetization curves of a Nd_2Fe_{17} single crystal at $T = 250$ K in steady magnetic fields applied along the crystallographic directions [100], [120], and [001]. One can appreciate that the threefold symmetry axis [001] is the hard magnetization direction. The curves along the two principal directions in the basal plane, the [100] and [120] axes, coincide. No anisotropy within the basal plane is detected at this temperature. Along the easy magnetization direction, after a rapid initial growth to just over 130 A m^2/kg, the magnetization changes slowly, reaching 148 A m^2/kg in a magnetic field of 14 T. The anisotropy field determined from the kink in the hard-direction curve amounts to 4 T at 250 K. A salient feature of the isothermal magnetization curves is the significant anisotropy of the magnetic moment: the magnetization in the hard direction does not fully approach the easy-axis one above the anisotropy field. The magnetization along the hard axis is 4.5% smaller than that along the easy axis, even in a field of 14 T. For comparison, in an isostructural compound Sm_2Fe_{17} [7], the difference is less, 3% at room temperature.

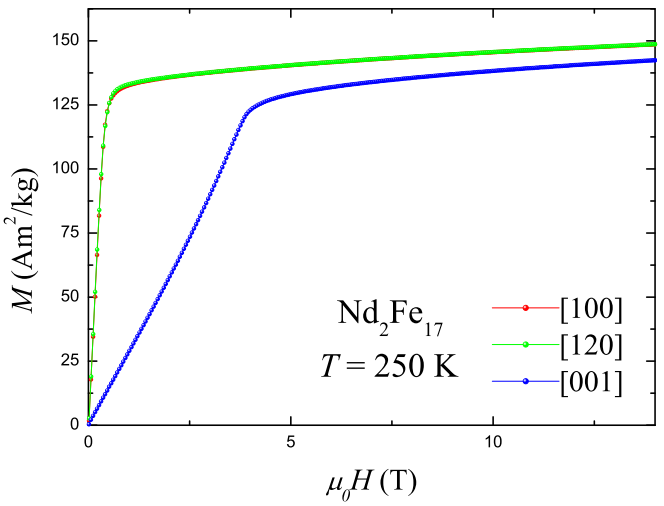

FIG. 1. Magnetization isotherms of Nd_2Fe_{17} single crystal, measured at $T = 250$ K in steady magnetic fields applied along the principal axes.

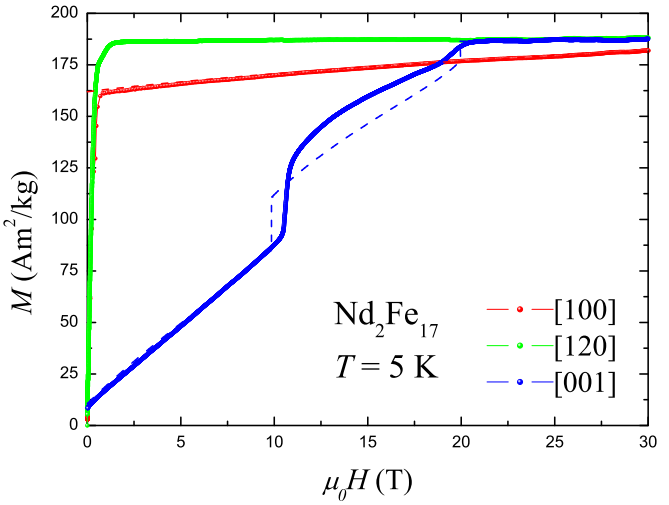

FIG. 2. Magnetization curves of Nd_2Fe_{17} single crystal, measured at $T = 5$ K in pulsed magnetic fields applied along the principal axes. Dashed lines represent the theoretical calculations of Sec. IV.

Figure 2 displays magnetization curves of Nd_2Fe_{17} taken along the principal crystallographic directions at $T = 5$ K. A very large magnetic anisotropy is present within the basal plane, as seen from the marked difference between the magnetization curves along the [100] and [120] axes. The ratio of the spontaneous magnetizations along the two principal axes in the basal plane, [100] and [120], is close to $0.865 = \cos(\pi/6)$, which reflects the high quality of the crystal and its proper orientation. The magnetization curve along the threefold symmetry axis [001] features two field-induced transitions, interpreted as FOMPs. At a critical field of $\mu_0 H_{cr1} = 10.4$ T the hard-axis magnetization experiences a stepwise increase to about 130 A m^2/kg, followed by a gradual growth (a type-II FOMP according to the nomenclature of Asti [8,9]). A further steplike rise at about $\mu_0 H_{cr2} = 20$ T brings the magnetization to saturation (a type-I FOMP). Moreover, a spontaneous component of the magnetic moment is observed along the hard axis, reflecting the deviation of the easy directions from the basal plane.

Spontaneous magnetization M_S was determined as the ordinate of the crossing point of the linearly extrapolated low- and high-field portions of the magnetization isotherms along the [120] axis. Near the magnetic ordering temperature the magnetization curve becomes essentially nonlinear and this simple way of determining M_S is no longer applicable. Therefore, at $T > 250$ K M_S was deduced from Arrott-Belov plots [10,11]. The spontaneous magnetization is plotted in

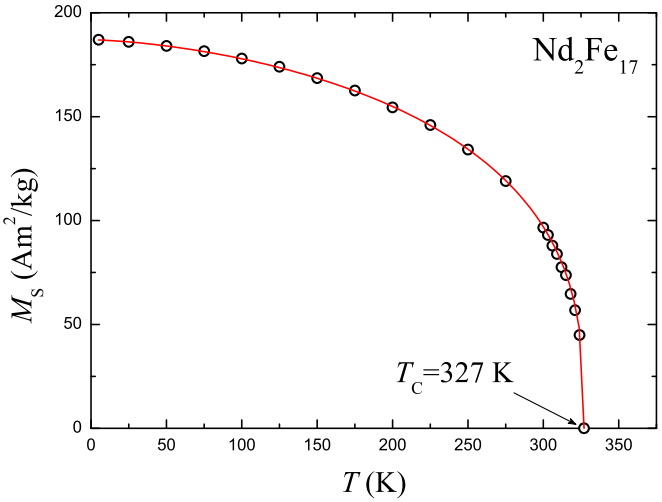

FIG. 3. Spontaneous magnetization of Nd_2Fe_{17} as a function of temperature.

Fig. 3 as a function of temperature. The solid line is a fit to the following expression [12]:

$$M_S(T) = M_0\left[1 - s\left(\frac{T}{T_C}\right)^{3/2} - (1-s)\left(\frac{T}{T_C}\right)^{5/2}\right]^{1/3}, \quad (1)$$

with $M_0 = 187\,\mathrm{A\,m^2/kg}$, $T_C = 327\,\mathrm{K}$, and $s = 0.75$. Such a shape of $M_S(T)$, with $s = 0.75$, is typical for Fe-based ferromagnetic compounds [7,12,13].

The sixth-order anisotropy constant K_3'' was determined as one-half of the area between the magnetization curves along [120] and [100] measured at the same temperature. The so-obtained K_3'' is presented as a function of temperature in Fig. 4. The low-temperature limit is $K_3''(0) = 220\,\mathrm{J/kg}$. The in-plane anisotropy decreases monotonically upon heating and disappears above 225 K.

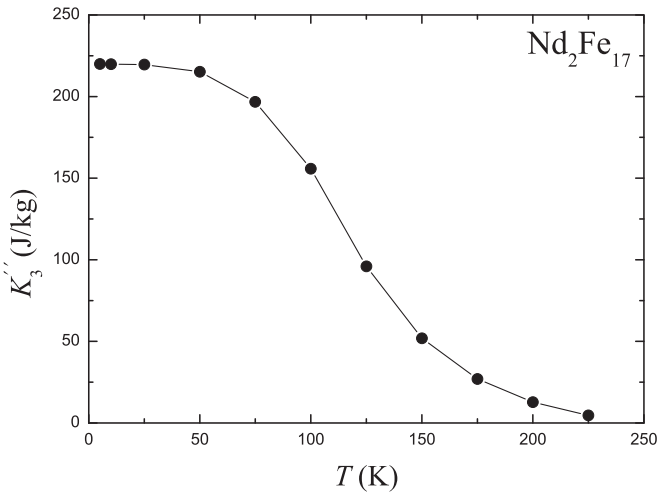

FIG. 4. Temperature dependence of the anisotropy constant K_3''.

IV. THEORY

Reflecting on the mechanism of the double FOMP, one should bear in mind that not just its presence in Nd_2Fe_{17} has to be explained but also its absence in an isostructural compound Sm_2Fe_{17}, where only one FOMP of type I is observed [7]. Moreover, the model of Ref. [7] insists that the type-I FOMP observed in Sm_2Fe_{17} should also take place in other rhombohedral magnets, including Nd_2Fe_{17}. So, it is the presence of the lower-field, type-II FOMP in Nd_2Fe_{17} (and its absence in Sm_2Fe_{17}) that needs to be explained. The most obvious peculiarity of samarium is that its sixth-order Stevens factor is zero and, consequently, the sixth-order anisotropy constants are small. For neodymium this is not the case, so the presence in Nd_2Fe_{17} of a strong sixth-order anisotropy term could be an explanation of the difference between the two compounds. Taking as the starting point the standard energy density expression characteristic of trigonal ferromagnets [14],

$$\begin{aligned} E = {} & K_1\sin^2\theta + K_2\sin^4\theta + K_2'\sin^3\theta\cos\theta\sin 3\varphi \\ & + K_3\sin^6\theta + K_3'\sin^3\theta\cos\theta(11\cos^2\theta - 3)\sin 3\varphi \\ & + K_3''\sin^6\theta\cos 6\varphi - \mu_0\,\boldsymbol{H}\cdot\boldsymbol{M}, \end{aligned} \quad (2)$$

we set to zero all the anisotropy constants except the leading one (K_1) and the sixth-order trigonal one (K_3'). The term in K_3' is the likely cause of the unusual double FOMP in Nd_2Fe_{17}; this term is weak in Sm_2Fe_{17} and strictly zero in hexagonal compounds.

Let us divide the resulting expression by K_1 ($K_1 < 0$) and denote

$$\kappa = |K_3'|/|K_1|, \qquad h = \mu_0\,H\,M_0/|K_1|. \quad (3)$$

Minimizing first with respect to φ, we get

$$E' = -\sin^2\theta \pm \kappa\sin^3\theta\cos\theta(11\cos^2\theta - 3) - h\cos\theta, \quad (4)$$

where the upper/lower sign corresponds, respectively, to the phase that is stable/metastable as $h \to 0$ (θ acute/obtuse). Now minimizing Eq. (4) with respect to θ, we find

$$h = 2m \mp 3\kappa(1 - 15m^2 + 22m^4)\sqrt{1-m^2}, \quad (5)$$

where $m = \cos\theta$ is reduced magnetization in the z direction. Setting Eq. (5) into Eq. (4) yields

$$E' = -1 - m^2 \pm \kappa m^3(55m^2 - 31)\sqrt{1-m^2} \quad (6)$$

Equation (5) describes the magnetization curves of both phases [Fig. 5(a)], while the conjunction of Eqs. (5) and (6) provides a parametric description of the energy-versus-field curves [Fig. 5(b)], the parameter m running between 0 and 1. The sole model parameter is $\kappa = 0.04$, as found directly from the experimental data. [The intercept of the reduced magnetization equals $(3/2)\kappa$, for κ small.]

As can be seen in Fig. 5(b), the energy curves of the two phases intersect at $h_1 = 1.037$: the phase that was stable at $h < h_1$ becomes metastable above h_1 and vice versa. Therefore, a first-order phase transition (a type-II FOMP, according to Asti) should take place at $h = h_1$. The observed magnetization curve consists of portions corresponding to different phases (where

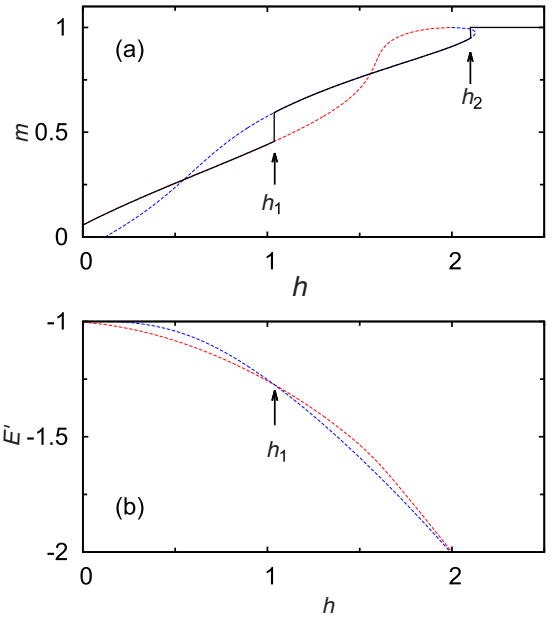

FIG. 5. (a) Construction of the magnetization curve along the c axis; (b) energy curves of the two phases.

those are stable), as shown by the bold line in Fig. 5(a). At the transition point, $h = h_1$, a jump of magnetization occurs.

On approach to saturation, the second (high-field) phase becomes first metastable and then unstable. The instability is manifest in the negative slope at $h \approx 2$. In this region a second FOMP takes place; this time it is a FOMP of type I. Above this FOMP, the axial phase is stable, with $\theta = 0$, or $m = 1$. The calculation yields $h_2 = 2.1$ for the critical field. The origin of the instability—like in the case of Sm_2Fe_{17}—is the presence of a radical in Eq. (5). This means that the discontinuity in the magnetization curve at h_2 will not disappear at any small but nonzero κ. Rather, the height of the discontinuity will tend to zero as $\kappa \to 0$ and it will eventually become imperceptible.

V. DISCUSSION

In Sec. III we demonstrated that the magnetic behavior of Nd_2Fe_{17} is most interesting at low temperature and in a magnetic field directed parallel to the hard axis [001]. Our main objective is to analyze hard-axis magnetization curves, for which a quantitative model has been developed in Sec. IV. According to the theoretical model, the magnetization curve should contain two jumps as shown in Fig. 5(a). These magnetization steps are first-order phase transitions. Taking this explanation as a working hypothesis, one comes to the following scenario of the magnetization process in the [001] direction. At zero field the magnetization has a spontaneous component which equals 9.5 A m^2/kg. This is followed by a progressive growth of the magnetization. Then a first magnetization step takes place around 10.4 T. A second and last step brings the system to saturation, with $M_0 = 187$ A m^2/kg as observed in Fig. 2.

Our main finding, that during its first jump the magnetization vector turns through 60°*around* the applied field, as well as turning slightly *toward* the field, is supported by theoretical calculations [5] for $Nd_2(Fe_{0.96}Al_{0.04})_{17}$. It would be interesting to see if the crystal-field parameters used in Ref. [5] result in a set of anisotropy constants dominated by K_1 and K_3'. Unfortunately, it is not entirely clear what kind of "un-normalized tesseral functions" were used by Koide *et al.* to expand the crystal field in Ref. [5]. Still, the fact that A_4^3 was set to zero, whereas A_2^0 and A_6^3 were given the highest values, suggests that Koide's earlier explanation of the double FOMP in the Al-doped compound was essentially equivalent to ours.

The spontaneous magnetization along the hard axis determines, together with the saturation magnetization, the angle δ_0 between the easy directions and the basal plane. The peculiarity of the binary compound Nd_2Fe_{17} is that the deviation of the easy directions from the basal plane is rather small, $\delta_0 = \tan^{-1}(9.5/187) \approx 2.9°$ at 5 K. Larger values of δ_0 were observed in isostructural compounds. In Sm_2Fe_{17}, the magnetization was found to deviate from the basal plane by 10° [7]. A deviation as high as 26° was reported for Pr_2Co_{17} [15].

Turning back to our model and contrasting the value $h_2 = 2.1$ with the experimental critical field at 5 K, $\mu_0 H_{cr2} = 20$ T, we obtain 9.5 T for the conversion factor between the dimensionless field h and the usual field in teslas. Thus, the computed magnetization curve of Fig. 5(a) can be rescaled and plotted together with the experimental data; see Fig. 2 (dashed curve). The vertical scaling factor corresponds to the saturation magnetization. The calculated magnetization curve reproduces the observed features well, including two successive jumps and spontaneous magnetization along the c axis. Setting into Eqs. (3) $h = h_2 = 2.1$, $\mu_0 H = \mu_0 H_{cr2} = 20$ T, and $M_0 = 187$ A m^2/kg, we get

$$K_1 = -1780 \text{ J/kg}, \qquad |K_3'| = \kappa |K_1| = 71 \text{ J/kg}.$$

Regrettably, we cannot quantitatively compare the anisotropy constants of Nd_2Fe_{17} single crystal (our work) with earlier data obtained on oriented powder. Nd_2Fe_{17} is unsuitable for making oriented powder samples because of its low ordering temperature and also due to the fact that the [001] direction is a hard magnetic axis. A comparison leads to significant discrepancies; for instance, at $T = 4.2$ K the leading anisotropy constant of Ref. [16], $K_1 = -483$ J/kg, is about one-quarter of ours, $K_1 = -1780$ J/kg. No information is available on the other anisotropy parameters. As regards the Curie temperature of Nd_2Fe_{17}, our value, $T_C = 327$ K, proves very close to that found in polycrystals, $T_C = 326$ K [17,18]. Once again, Ref. [1] reports a significantly larger value of $T_C = 348$ K and a noticeably lower value of $M_0 = 175$ A m^2/kg, despite the sample being a single crystal. It seems likely that the crystal studied in Ref. [1] was of poor quality.

Finally, let us consider a case where the field is applied along a hard direction in the basal plane, which is $\boldsymbol{H} \parallel a$ or [100]. The magnetization curve computed by means of Eqs. (20) and (21) of Ref. [7] is plotted in Fig. 2 (dashed line). The values of the parameters used in the calculation were deduced directly from the experiment: $K_3'' = 220$ J/kg at $T = 5$ K (see Fig. 4) and $M_0 = 187$ A m^2/kg. Inspecting the [100] curves, one observes good agreement between the experimental data and theoretical fit.

VI. SUMMARY

Magnetization of Nd_2Fe_{17} has been measured along the principal crystallographic directions in steady and pulsed magnetic fields. Our most interesting finding is a double FOMP in a field directed along the threefold symmetry axis [001]. In a field applied in the hard direction [001], a first-order transition at 10.4 T is observed, followed by another first-order transition at about 20 T. The magnetization behavior is explained by a simple model, which enables us to deduce the main anisotropy constants. The magnetization process along [001] can be described as interplay of just two anisotropy terms; the ratio of the corresponding anisotropy constants κ is the sole model parameter determining the shape of the hard-axis curve.

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[1] K. Koyama and H. Fujii, Phys. Rev. B **61**, 9475 (2000).
[2] Y. Skourski, M. D. Kuz'min, K. P. Skokov, A. V. Andreev, and J. Wosnitza, Phys. Rev. B **83**, 214420 (2011).
[3] M. D. Kuz'min, Y. Skourski, K. P. Skokov, and K.-H. Müller, Phys. Rev. B **75**, 184439 (2007).
[4] O. Isnard, A. V. Andreev, M. D. Kuz'min, Y. Skourski, D. I. Gorbunov, J. Wosnitza, N. V. Kudrevatykh, A. Iwasa, A. Kondo, A. Matsuo, and K. Kindo, Phys. Rev. B **88**, 174406 (2013).
[5] T. Koide, H. Kato, J. Shiomi, and T. Iriyama, J. Magn. Magn. Mater. **140–144**, 983 (1995).
[6] M. D. Kuz'min, Y. Skourski, K. P. Skokov, K.-H. Müller, and O. Gutfleisch, Phys. Rev. B **77**, 132411 (2008).
[7] L. V. B. Diop, M. D. Kuz'min, K. P. Skokov, D. Yu. Karpenkov, and O. Gutfleisch, Phys. Rev. B **94**, 144413 (2016).
[8] G. Asti, First-order magnetic processes, in *Handbook of Magnetic Materials*, Vol. 5, edited by E. P. Wohlfarth and K. H. J. Buschow (North-Holland, Amsterdam, 1990), Chap. 5.
[9] G. Asti and F. Bolzoni, J. Magn. Magn. Mater. **20**, 29 (1980).
[10] K. P. Belov and A. N. Goryaga, Fiz. Met. Metalloved. **2**, 3 (1956).
[11] A. Arrott, Phys. Rev. **108**, 1394 (1957).
[12] M. D. Kuz'min, Phys. Rev. Lett. **94**, 107204 (2005).
[13] M. D. Kuz'min, D. Givord, and V. Skumryev, J. Appl. Phys. **107**, 113924 (2010).
[14] A. V. Andreev, S. Yoshii, M. D. Kuz'min, F. R. de Boer, K. Kindo, and M. Hagiwara, J. Phys.: Condens. Matter **21**, 146005 (2009).
[15] R. Verhoef, J. J. M. Franse, F. R. de Boer, H. J. M Heerooms, B. Matthaei, and S. Sinnema, IEEE Trans. Magn. **24**, 1948 (1988).
[16] O. Isnard and M. Guillot, J. Appl. Phys. **87**, 5326 (2000).
[17] X. C. Kou, F. R. de Boer, R. Grössinger, G. Wiesinger, H. Suzuki, H. Kitazawa, T. Takamasu, and G. Kido, J. Magn. Magn. Mater. **177–181**, 1002 (1998).
[18] O. Isnard, S. Miraglia, J. L. Soubeyroux, D. Fruchart, and P. l'Héritier, J. Magn. Magn. Mater. **137**, 151 (1994).