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Critical analysis of the statistical method for the magnetocrystalline anisotropy constants determination of polycrystalline hard magnetic materials

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A computational analysis of the hard direction magnetization isotherms of polycrystalline materials with uniaxial symmetry, taking into account the angular statistical distribution of grain axis, is performed. By means of numerical method calculation the practical limits of the analytical description are established. The method determines by analytical way the magnetocrystalline anisotropy constants K_1 and K_2 and takes into account the misalignment degree of the grain *c* axis in magnetically oriented polycrystalline materials. By means of computational simulation the influence of theses parameters on the hard direction magnetization isotherms is analyzed. The results are used to define the magnetocrystalline anisotropy analysis of some R-T_{12} intermetallic compound.

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1. Introduction

The magnetocrystalline anisotropy is an important intrinsic property of hard magnetic materials, witch strongly influence their coercivity. With the singular point detection (SPD) method [1] it is possible to determine more exactly the anisotropy field H_A and consequently the total anisotropy constant $K = K_1 + 2K_2 + 3K_3 ...$ with $K = \mu_0 H_A M_S / 2$, where and M_S is the spontaneous magnetization. The second (K_1) and the forth (K_2) anisotropy constants of single crystal, can be determined by the classical Sucksmith-Thompson method [2]. Usually this method is applied to polycrystalline materials [3] using fine particles ($\leq 50\mu m$), oriented in a constant magnetic field (~ 1-2 T) and fixed in epoxy resin. However the values of K_1 and K_2 for these materials strongly depend of the degree of misalignment of the easy magnetization axis (EMA) of the quasi monocrystalline grains with respect to the orientation of the magnetic field. Durst and Kronmüller [4] have proposed a statistical model for the interpretation of hard direction magnetization isotherms, taken into account a discrete distribution of EMA with respect to the aligned direction (AD) of the grains. The application of this model supposed the determination of the distribution function of the EMA orientation. In uniaxial magnetic materials the EMA is parallel to the c axis and the distribution function of the EMA orientation follows the texture function. In order to determine the distribution function, the classical experimental procedure is the x-ray diffraction method [5]. Alternative direct magnetic methods [4, 6-8] were used. In the analytical methods [9-12] the misalignment of the grains is described a priori by means of continuous statistical Gaussian distribution with the assumption of an assembly of non-interacting particles. The variance of the Gaussian function reflects the misalignment degree of EMA.

In the present paper we present an accessible version of the analytical method [9] to determine the magnetocrystalline parameters of polycrystalline samples using a statistical model [4] developed with the computation facilities. The method has been applied to the simulation of the hard magnetization isotherms of polycrystalline $GdFe_{11-x}Si_xTi$ with $ThMn_{12}$ structure and uniaxial anisotropy.

2. Theoretical background

For single crystal with axial symmetry in an external magnetic field, the total magnetocrystalline and magnetostatic free energy density, is given by the well known expression

$$F == K_1 \sin^2\theta + K_2 \sin^4\theta + ... - \mu_0 H M_S \cos(\psi - \theta) \quad (1)$$

where, θ is the angle between the $\vec{M}_S$ direction and EMA (parallel to the c axis) and ψ is the angle between the EMA and the internal magnetic field $\vec{H}$.

$\vec{H} = \vec{H}_{ext} - N\vec{M}$, where N is the demagnetization factor and $\vec{H}_{ext}$ is the applied field. M_S is considered constant, by neglecting the magnetic field influence on the atom magnetic moments and the canting effect.

The preferential direction of the magnetization can be determined by minimizing the total free energy density with

respect to the θ variable. The equilibrium condition leads to

$$2K_1 \sin\theta\cos\theta + 4K_2 \sin^3\theta\cos\theta - \mu_0 H M_S \sin(\Psi - \theta) = 0 \quad (2)$$

The component of the magnetization parallel to the magnetic field can be written as

$$M = M_S \cos(\Psi - \theta) \quad (3)$$

The Equations (2) and (3) are the parametric equations of the magnetization dependence on H for a single crystal. In this case, from hard direction magnetization isotherms (Ψ=π/2) the Sucksmith - Thompson plot [2] leads directly to the anisotropy constants K_1 and K_2.

In the case of polycrystalline powder, aligned and fixed along AD, one must take into account the misalignment of the c axis or the EMA of grains with respect to AD. The misalignment is described by means of a statistical distribution around AD of the angles between the c axis and AD defined as θ_C [4]. In the assumption of non-interacting particles a Gaussian type continuous distribution over the θ_C angles can be used [6-12]. Consequently the distribution function is written as

$$f(\theta_C) = f_0 \exp\left(-\frac{\theta_C^2}{2\theta_{C0}^2}\right), \quad 4a)$$

with

$$f_0 = \left[2\pi \int_{\theta_C=0}^{\frac{\pi}{2}} \exp\left(-\frac{\theta_C^2}{2\theta_{C0}^2}\right)\sin(\theta_C)\ \ d\theta_C\right]^{-1}, \quad (4b)$$

where θ_{C0} is the variance of the Gaussian function, which reflects the degree of misalignment. In this assumption, the parametric equations of the magnetization M=f(H) become

$$\begin{aligned} &2K_1 \sin\theta\cos\theta + 4K_2 \sin^3\theta\cos\theta \\ &- \mu_0 H M_S\left(\cos\theta\cdot\overline{\sin\Psi} - \sin\theta\cdot\overline{\cos\Psi}\right) = 0 \end{aligned} \quad (5)$$

$$M = M_S\left(\cos\theta\cdot\overline{\cos\Psi} + \sin\theta\cdot\overline{\sin\Psi}\right). \quad (6)$$

The mean values of $\overline{\sin\psi}$ and $\overline{\cos\psi}$ were computed over $\psi = \pi/2 - \theta_C$ angle with the relations $\overline{\sin\psi} = \overline{\cos\theta_C}$ and $\overline{\cos\psi} = \overline{\sin\theta_C}$, using the distribution function (4). Eliminating the θ parameter from Equations (5) and (6) we can obtain the implicit form $\mu_0 H = f(M)$ of the expected relation M=f(H), as a function of five parameters M_S, K_1, K_2, $\overline{\sin\psi}$ and $\overline{\cos\psi}$:

$$\mu_0 H = \frac{2}{M_S}\frac{\left[K_1 + (K_1 + 2K_2)\cdot(\mathrm{tg}\theta)^2\right]\cdot \mathrm{tg}\theta}{\left[1 + (\mathrm{tg}\theta)^2\right]^{\frac{3}{2}}\cdot\left(\overline{\sin\psi} - \overline{\cos\psi}\cdot\mathrm{tg}\theta\right)}, \quad (7)$$

where

$$\begin{aligned} \tan\theta = &[(M/M_S)\sqrt{[(\overline{\sin\psi})^2 + (\overline{\cos\psi})^2] - (M/M_S)^2} \\ &- \cdot\overline{\sin\psi}\cdot\overline{\cos\psi}]/[(\overline{\sin\psi})^2 - (M/M_S)^2] \end{aligned} \quad (8)$$

The implicit function (7) of the magnetization M dependence versus H can simulate the hard magnetization isotherms by means of computational methods.

First, we have analyzed the theoretical limits of equations (7) and (8) for the simulation of hard magnetization isotherms of uniaxial polycrystalline materials. In order to establish the limits we have made an analysis of "$\mu_0 H$", "tan θ" and "θ" dependence on the reduced magnetization (M/M_S), using the numerical calculation method. As example, the result of this analysis for selected values of K_1=1MJ/m^3, K_2=0.1MJ/m^3 and θ_{C0}= 6^0 is presented in Fig. 1.

This analysis shows three analytical critical points.

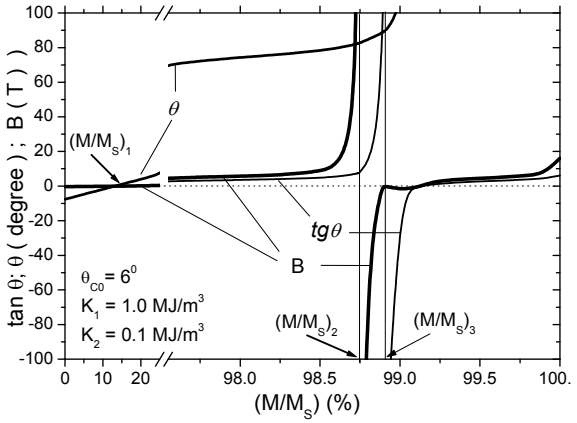

Fig. 1. The reduced magnetization dependence of "$\mu_0 H$" "tan θ", "θ" and the three analytical critical points $(M/M_S)_1$, $(M/M_S)_2$ and $(M/M_S)_3$.

i) The first critical point is observed for small values of the reduced magnetization at $M/M_S = (M/M_S)_1$, corresponding to the condition $\tan\theta = 0$ ($\theta = 0$). The condition $\tan\theta \geq 0$ ($0 \leq \theta < 90^o$) can be obtained only if $M/M_S \geq (M/M_S)_1$. From equation (6), at θ =0 results $(M/M_S)_1 = (M(0)/M_S) = \overline{\cos\psi}$.

ii) The second critical point at $(M/M_S)_2$ corresponds to the asymptotic behaviour of $B = \mu_0 H = f(M/M_S)$ (eq.7) at $\theta_{max} = \tan^{-1}(\overline{\sin\psi}/\overline{\cos\psi})$, then $\mu_0 H \to \infty$. This condition suppose that the eligible range of $M/M_S = f(\mu_0 H)$ values is limited at high values of reduced magnetization by the condition $\theta < \theta_{max}$ and consequently $M/M_S \leq (M/M_S)_2 < 100\%$ .The third critical point at $(M/M_S)_3$ corresponds to the asymptotic behaviour of $\tan\theta = f(M/M_S)$ (Equation 8), because for

$(M/M_S)_3 = \overline{\sin\psi}$, $\tan\theta \to \infty$ and $\theta = 90^0$. For $\theta_{C0} \geq 0$, $(M/M_S)_3 \geq (M/M_S)_2$. This critical point is not important, because it is excluded by the second critical point.

Concluding, for the simulation of the hard magnetization isotherms of axial polycrystalline textured materials the limits of eligible range are $0 < \theta < \theta_{max}$ corresponding to the condition $(M/M)_1 \leq M/M_S \leq (M/M_S)_2$. As an example, in Fig.2, the eligible range for the simulation of hard magnetization isotherms is represented by the plot of the reduced magnetization M/M_S versus variance θ_{C0}, for K_1 = 1.0 MJ/m^3 and K_2 = 0.1 MJ/m^3.

The second and more important application of the parametric Equations (7) and (8) is the fitting possibility of the hard magnetization isotherms, in order to determine the magnetic anisotropy constants. For this application it is important to outline that the two fitting parameters, $\overline{\sin\psi}$ and $\overline{\cos\psi}$, are not independent, because they depend of the variance θ_{C0}. In order to eliminate this difficulty we have made the numerical computation of $\overline{\sin\psi}$ and $\overline{\cos\psi}$ values. By least square numerical method we have given a very accurate linear dependence (correlation coefficient R = 0.99996 and standard deviation SD = 3.6·10^{-4}):

$$\left(\overline{\cos\psi}\right)^2 = 0.7665 - 0.7655\left(\overline{\sin\psi}\right)^2 \qquad (9)$$

Using this relation it is possible to eliminate as an example the $\overline{\cos\psi}$ parameter and to use only one parameter, $\overline{\sin\psi}$. It is possible to reduce by this way the fitting parameters of equations (7) at only four independent parameters: K_1, K_2, M_S and $\overline{\sin\psi} = f(\theta_{C0})$. On the other hand, the M_S is determined from the easy magnetization isotherms [8]. For the determination of K_1, K_2 and $\overline{\sin\psi}$ parameters we can use the least square numerical method. It can determine the variance θ_{C0} on the basis of the computed values of $\overline{\sin\psi} = f(\theta_{C0})$.

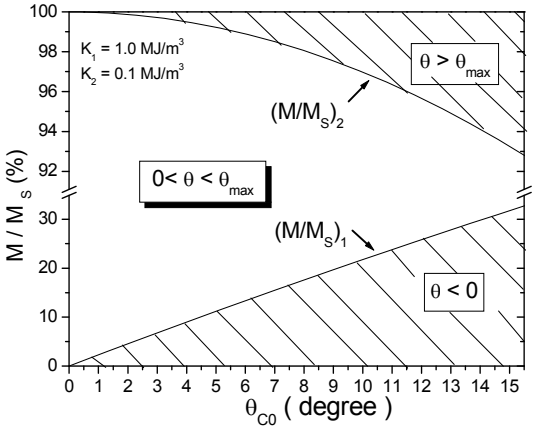

Fig. 2. An illustration of θ_C influence on the limits of eligible range for hard magnetic isotherms simulation.

Finally, can be given the anisotropy field with the well known relation

$$\mu_0 H_A = 2(K_1 + 2K_2)/M_S. \qquad (10)$$

3. Results of numerical simulation

With these assumptions presented in the previous section, we have performed the numerical simulation of the hard direction magnetization isotherms for various values of θ_{C0}, K_1 and K_2. For this simulation we have chosen the typical anisotropy constants for uniaxial anisotropy: $K_1 > 0$, $K_2 > 0$ or $K_2 < 0$ but $K_1 > 2|K_2|$ with different values of θ_{C0}. The obtained results for the first quadrant of the M/M_S - $\mu_0 H$ representation are presented in Figure 3. According to relation (7) a strong correlation between M/M_S and the θ angle is expected. In order to illustrate this correlation we have performed the numerical simulation of the influence of applied external magnetic field $\mu_0 H$ on the value of θ. The dependence of θ on $\mu_0 H$, for various values of variance θ_{C0}, K_1 and K_2 is reported in Figure 4. The results of these simulations suggest the following remarks.

- The reduced hard axis initial magnetization, $(M(0)/M_S)$ strongly depends on θ_{C0} (Fig. 3-a) according to Reference [7]. Only for the ideal case characterized by $\theta_{C0} = 0$, it results $(M(0)/M_S) = 0$. In this case it is very simple to determine also the anisotropy field $\mu_0 H_A$ using a graphical method and applying the condition $(M(H_A)/M_S) = 100\%$ (Fig. 3-a). On the contrary, for $\theta_{C0} \neq 0$ it results $(M(0)/M_S) \neq 0$. An asymptotically approach of M/M_S to the values 100% is observed. The evaluation of the anisotropy field $\mu_0 H_A$ using a graphical method is very difficult and practically impossible. It is possible to obtain satisfactory value of $\mu_0 H_A$ for polycrystalline samples only by analytical methods with Equation (10). For this purpose one can use the magnetocrystalline anisotropy constants K_i values, obtains by fitting of the hard direction magnetization isotherms and the saturation magnetization M_S obtained by fitting the easy direction magnetization isotherms. In the Fig. 4-a, we present the dependence of θ on the applied magnetic field for different values of the variance θ_{C0}.
- For constant values of θ_{C0}, the initial value of the reduced magnetization along the hard axis remains also constant, and independent of the anisotropy constants K_1 and K_2. However, these constants determine the shape of the hard magnetization isotherms. The anisotropy constant K_1 has a greater influence on the shape of hard magnetic isotherms (Fig. 3-b). This parameter changes not only the initial slope, of the hard magnetization isotherm at low magnetic field according to [12], but also the rate of asymptotical approach to saturation at high magnetic field, in correlation with the dependence $\theta = f(\mu_0 H)$ (Figure 4-b). This parameter changes not only the initial slope, of the hard magnetization isotherm at low magnetic field according to [12], but also the rate of asymptotical

approach to saturation at high magnetic field, in correlation with the dependence $\theta=f(\mu_0 H)$ (Fig. 4-b).

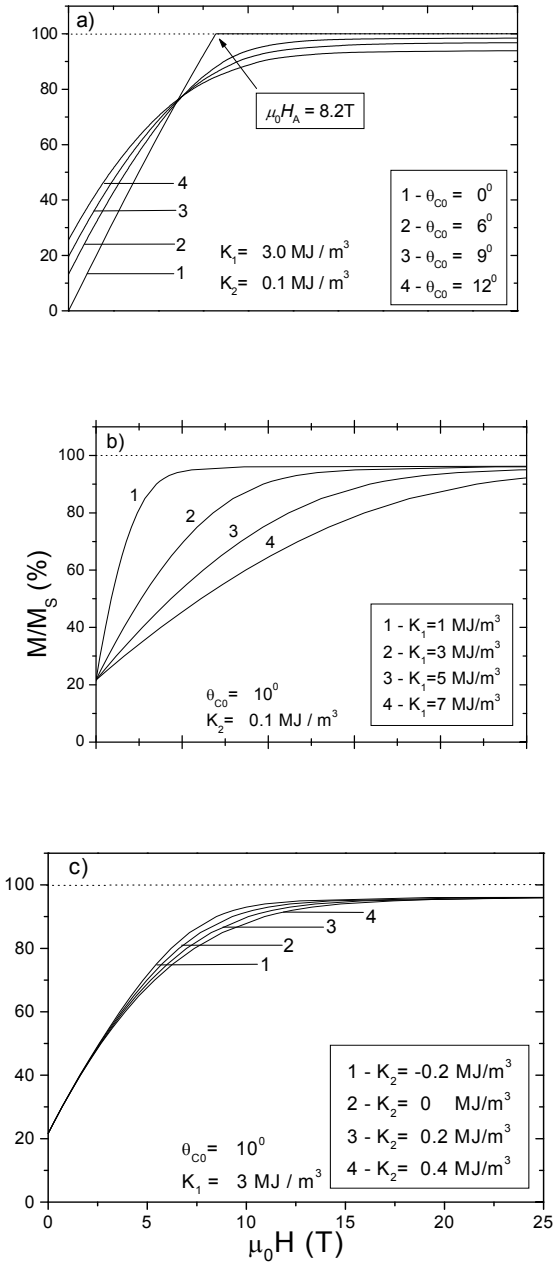

Fig. 3. The numerical simulation of hard magnetic isotherms for various values of the parameters a) θ_{C0}, b) K_1 and c) K_2.

- The K_2 anisotropy constant changes the shape of the isotherms only in the vicinity of the anisotropy field $\mu_0 H_A$ (Fig. 3-c), in correlation with the $\theta=f(\mu_0 H)$ dependence (Fig. 4-c).

The influence of this parameter on the shape of the hard direction magnetization isotherms at low and high magnetic field is negligible.

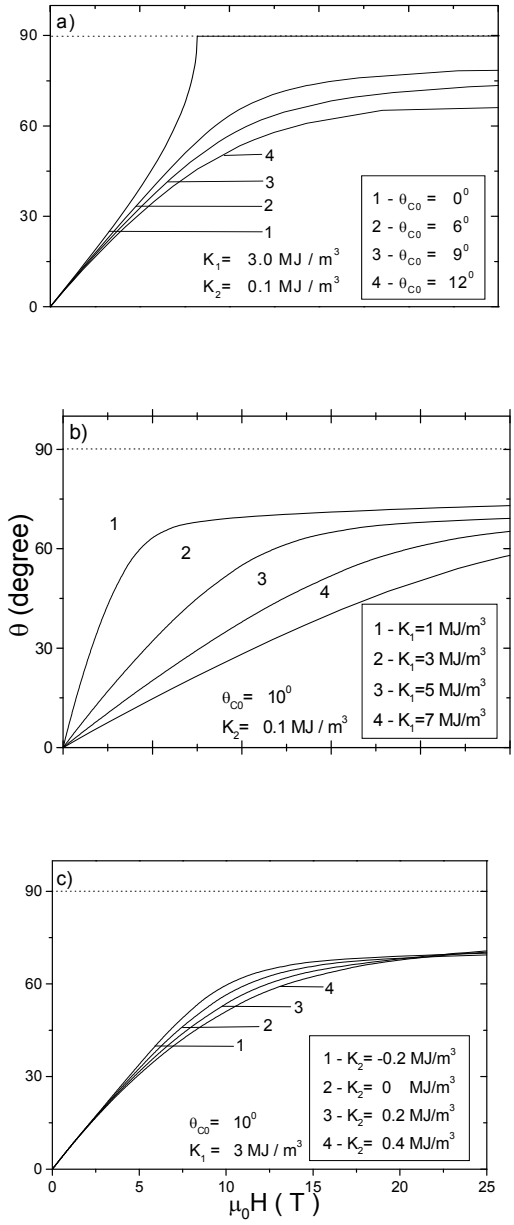

Fig. 4. The numerical simulation of the orientation θ angle between $\vec{M}_S$ and B for various values of parameters a) θ_{C0}, b) K_1 and c) K_2

4. Experimental results analysis

We present in this section an application of the method for the analysis of the magnetocrystalline anisotropy in $GdFe_{11-x}Si_xTi$ ($0 \le x \le 2$). The polycrystalline compounds were prepared by induction melting [13]. Both the crystal structure and the type of anisotropy were verified by X-ray diffraction (XRD) using a Brucker Cu-Kα diffractometer. The XRD patterns on random powder refined with the FULPROF computing code, based on the Rietveld method, shows the axial tetragonal I4/mmm structure of $ThMn_{12}$ type. The XRD patterns on magnetically oriented powder are relevant of a strong uniaxial anisotropy with EMA

parallel to c axis.

The isotherm magnetization data on magnetically aligned powders at 4.5K were obtained with SQUID magnetometer in an external magnetic field up to 5.5T (Fig. 5).

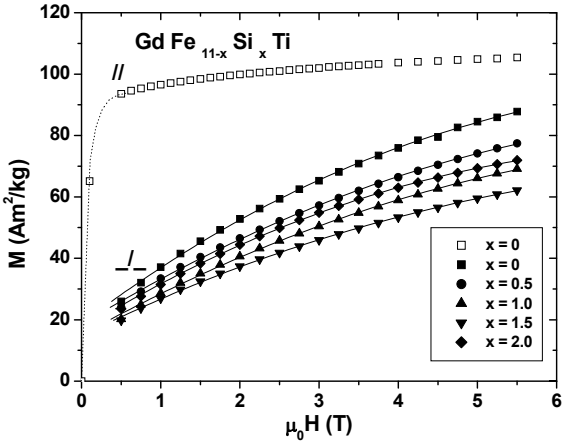

Fig. 5. Hard direction magnetization isotherms (solid symbols) of $GdFe_{11-x}Si_xTi$ compounds at 4.5K compared with easy direction magnetization for x=0 (open square). The solid lines represent the calculated data

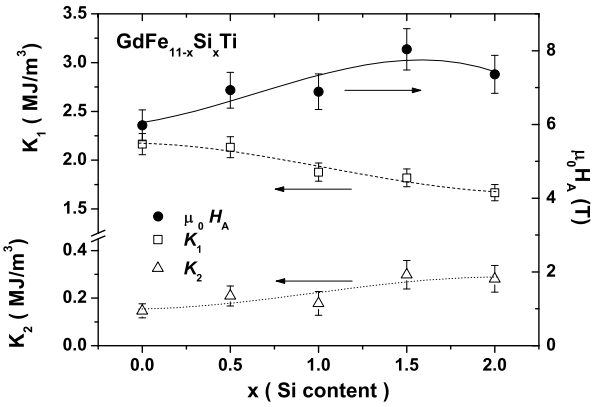

Fig. 6. Influence of Si content on the magnetocrystalline anisotropy constants K_1 (□), K_2 (Δ) and on the anisotropy field $\mu_0 H_A$ (●) of $GdFe_{11-x}Si_xTi$ compounds at 4.5 K

The parameters K_1, K_2, M_s, and $\overline{\sin\psi}$ depending of the misaligned θ_{C0} parameter were determined from the fit of $M_\perp(H)$ data with the parametric Equations (7) and (8), applying least square numerical method for $0.5T \le \mu_0 H \le 5.5T$, in the range of a magnetization process by coherent rotations. The anisotropy field $\mu_0 H_A$ was determined with Equation (10). The values of K_1, K_2 and $\mu_0 H_A$ are presented versus Si content in Fig. 6. The analysis of their composition dependence shows that the Si substitution for Fe in 8f and 8j sites changes the crystal field parameters and consecutively the anisotropy constant K_1, K_2. K_1 decreases from 2.16MJ/m^3 for x=0 to 1.67MJ/m^3 for x=2. On the contrary, K_2 increases with Si content from 0.15MJ/m^3 at x=0 to 0.28MJ/m^3 at x=2.

The composition dependence of the anisotropy field $\mu_0 H_A$ is more complex as is results from competitive changes of the magnetocrystalline constants with the Fe substitution for Si. It increases from 6.0T at x=0, up to 7.4T at x=2, with a maximum 8.0T around x=1.5.

5. Conclusions

Using the computation facility, the hard magnetization isotherms of polycrystalline magnetically textured samples were analyzed. In order to describe the misalignment of the easy magnetization axis of different grains with respect to the aligned direction, we have applied the statistical model in the assumption of non interacting particles. The theoretical limits of application of the method where analyzed by means of numerical calculation method. These limits are described by means of eligible range values of the θ angle between $\vec{M}_S$ and EMA, $0 \le \theta \le \theta_{max} < 90^0$.

The numerical simulation of hard magnetization isotherms shows that the misaligned degree described by θ_{C0} have a strong influence on the initial hard magnetization, $(M(0)/M_S)$ which increases with θ_{C0}. The anisotropy constant K_1 changes the initial slope of the hard magnetization isotherm at low magnetic field and the rate of asymptotical approach to saturation at high magnetic field. The anisotropy constant K_2 changes the shape of the isotherms only in the vicinity of the anisotropy field value.

This analytical method offers the possibility to fit the hard magnetization isotherms by least square numerical method. In order to determine the magnetocrystalline parameters the very simple way of reduction of the fitting parameters to three independent parameters K_1, K_2 and θ_{C0} is proposed. The method was successfully applied for the determination with a good accuracy of the magnetocrystalline parameters of intermetallic $GdFe_{11-x}Si_xTi$. The misaligned degree and the composition dependence of K_1, K_2 and $\mu_0 H_A$ at 4.5K have been determined.

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