Journal of ELECTRICAL ENGINEERING, VOL 66. NO 7/s, 2015, 128-133

FROM MACRO-SCALE MAGNETIC MEASUREMENTS TO NANO -SCALE IMAGING OF SUPERPARAMAGNETIC SYSTEMS

Artur Chrobak* ─ Grzegorz Haneczok ─ Grzegorz Ziółkowski***

The paper refers to magnetic characterization of superparamagnetic systems. The analysis consists in determination of distributions of cluster magnetic moments. Furthermore, the distribution can be connected with average sizes on the clusters, giving their picture in nano/micro scale. The proposed procedure is based on macro-scale magnetic measurements as well as a proper numerical analysis. The used models allow performing the analysis above and below the blocking temperature.

Keywords: superparamagnetism, magnetic clusters, simulated annealing

1 INTRODUCTION

During recent ten years, one may note a spectacular progress in the so-called nanotechnology and consequently nano-sciences. It is clear that researches related to nano-sized objects require special characterization techniques. In many cases, direct observations are possible using different microscopy methods like SEM, HRTEM, AFM or MFM. However, especially for bulk nano-materials, their characterization can be carried out using macro-scale measurements supplemented by a proper model and numerical analysis. A material that can be considered as such case is a magnetic system consisting of non-interacting ferromagnetic single-domain objects (clusters).

The paper refers to a kind of nano-scale characterization of superparamagnetic materials based on standard magnetic measurements. In this subject the two problems can be defined. The first one consists in a creation of magnetic curves (*ie*, magnetic isotherms, hysteresis loops *etc*) based on a microstructure of the analyzed magnetic system. The characterization method should include basic parameters of the magnetic objects such as (i) their total magnetic moment, (ii) magnetic anisotropy represented by the so-called blocking energy and (iii) temperature state *ie*, below or above the so-called blocking temperature. In the case of superparamegnetic materials, it is propose to apply the Stoner-Wohlfarth model of nanoparticles magnetization supplemented by the two-lewel kinetic model. This approach allows simultaneously including magnetic moment, magnetic anisotropy and temperature. The second, more complex, problem lies in determination of distribution of magnetic moments and energetic barriers of magnetic objects based on magnetization curves. It is possible to solve this problem using experimental $M(H)$ dependences (determined at different temperatures) and a special numerical procedure based on the mentioned two models [1,2]. In many cases, the determined distribution of magnetic moments can be recalculated into average size of the magnetic objects giving finally a nano/micro -scaled picture of the material. The proposed approach was successfully used in characterization of diluted magnets (alloys and natural samples), nanocomposites, powders and even for human hemoglobin. For examples see [3, 4]

The aim of this paper is a consistent presentation of our recent development of the models and their application to numerical methods, allowing nano-scale imaging of superparamagnetic systems by means of macro-scale magnetization curves.

2 MAGNETIZATION PRECESSES OF SIMPLE SUPERPARAMAGNETIC SYSTEM

Superparamagnetic systems consist of a set of non-interacting ferromagnetic single-domain clusters. Similarly to classical paramagnets, magnetization of such system can be described by the Langevin function with the reservation that magnetic moments of atoms should be replaced with total magnetic moment of the cluster. The value of magnetic moment of the clusters can be in the order of 10^3 – 10^6 μ_B (Bohr magneton), or even more.

According to the Langevin theory, magnetization as a function of temperature and external magnetic field is expresses by the following formula

$$M(H,T) = N\mu(\coth(x) - 1/x) = N\mu L(x)\,, \tag{1}$$

where N is the number of clusters per volume unit, $L(x)$ is the Langevin function, $x=(\mu\mu_0 H)/(k_B T)$, H is the applied magnetic field and T is the temperature. Saturation magnetization M_S odiously equals $N\mu$. In real materials, a distribution of different clusters, with different magnetic moment, is expected. The possible distribution can be included into the Langevin equation by introducing a distri-bution function. The obvious generalization of equation (1) is

$$M(H,T) = \int_0^\infty \rho(\mu)\mu L(x)\mathrm{d}\mu\,, \tag{2}$$

$$M_S = \int_0^\infty \rho(\mu)\mu\,\mathrm{d}\mu\,, \tag{3}$$

where $\rho(\mu)$ is the distribution function of clusters with the magnetic moment μ.

Different approach consists in approximation of real distribution function by a set of boxes (or channels)

* University of Silesia, Institute of Physics, 40-007 Katowice, Uniwersytecka 4, Poland : artur.chrobak@us.edu.pl ** University of Silesia, Institute of Materials Science, 41-500 Chorzów, 75 Pułku Piechoty 1A, Poland

ISSN 1335-3632 © 2015 FEI STU

describing a number of objects with magnetic moment associated with the channel. Equation (2) takes the form

$$M(H,T) = \sum_i N_i \mu_i L(x_i) , \quad (4)$$

and (3) is

$$M_S = \sum_i N_i \mu_i , \quad (5)$$

where index i is the counter of channels (boxes) with magnetic moment μ_i, N_i is the number of clusters with magnetic moment μ_i per unit volume.

3 THE STONER-WOHLFARTH MODEL

The Stoner-Wohlfarth (SW) model, elaborated in 1948 [5,6], describes the magnetic properties of the non-interacting nanoparticles. In this model, it is assumed that temperature is equal to zero and the single domain particle is an ellipsoid with the main axis as well as the easy magnetization axis along the z-direction. This situation is presented in Fig. 1 with an external field H, magnetization M and angles Ψ, φ and θ.

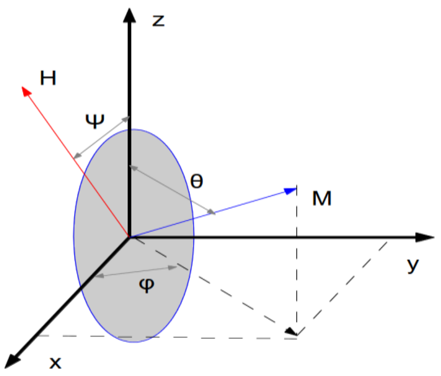

Fig. 1. The Stoner-Wohlfarth particle

Moreover, the coherent rotation of all magnetic moments (uniform magnetization in whole volume) is also assumed. In the case when demagnetization is neglected, the total energy of such system can be expressed as

$$\frac{E}{V} = K_1 \sin^2\theta - \mu_0 MH\left(\cos\theta\cos\Psi + \sin\theta\sin\Psi\cos\phi\right) , \quad (6)$$

where the first term is related to the magnetocrstalline anisotropy (K_1 is a coefficient of uniaxial anisotropy) and the second one expresses the magnetostatic energy.

The problem is to find the angle θ for which the density energy E/V has a minimum. This angle determines the position of magnetization vector in the conditions of the applied external magnetic field and the anisotropy. The described model can be used for simulations of magnetization processes of superparamagnetic cluster below the blocking temperature, *ie*, when an energetic barrier, caused by the magnetic anisotropy, plays an important role. In a simply case, this barrier can be described as the energy difference between parallel and anti-parallel alignment of magnetization to the external magnetic field. Figure 2 shows the energy of the system in a function of the angle θ for the case of $\Psi = 0$. As can be seen, for $H = 0$ the system have two equivalent minima of energy, *ie*, the alignment of magnetization to the field can be parallel or antiparallel with the same probability. Increasing external field causes an increase in energy between these two states. Finally, for $\mu_0 MH/K_1 > 2$ only one energy minimum, related to parallel directions of magnetization and field, is observed. In temperatures $T > 0$, the cluster magnetization can have the two directions attributed to these two energy minima. Probability of the states depends on temperate as well as the energy barrier dividing the minima.

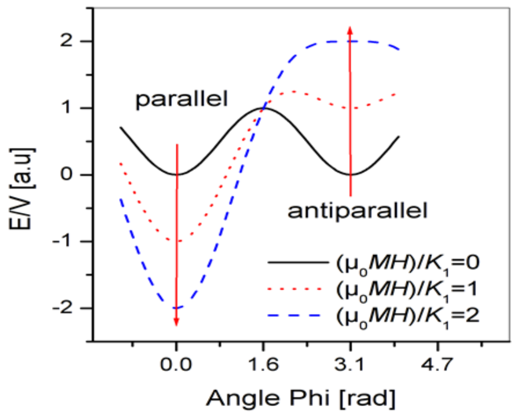

Fig. 2. Density energy for the Stoner-Wohlfarth particle

4 THE TWO-LEVEL KINETIC MODEL

The Stoner-Wolhrath model is valid only for $T = 0$ which causes some difficulty in analysis of real systems. However, it can be supplemented by the so-called two-level kinetic model allowing extending the SW model to higher temperatures. Fig. 3 shows a diagram of energy for two states dividing by an asymmetric barrier.

Dynamics of the system at $T > 0$ is described by the kinetic equations

$$\frac{\mathrm{d}n_X}{\mathrm{d}t} = W_{YX} n_Y - W_{XY} n_X , \qquad \frac{\mathrm{d}n_Y}{\mathrm{d}t} = W_{XY} n_X - W_{YX} n_Y \quad (7)$$

where n_X is the number of objects (per volume unit) in state X (antiparallel), n_Y is the number of objects (per volume unit) in state Y (parallel), W_{XY} and W_{YX} is the transition frequency from X to Y, and from Y to X, respectively.

The quantities W_{XY} and W_{YX} may be written as

$$W_{XY} = W_0 \exp\left(-\frac{E_A - h}{k_B T}\right), \qquad W_{YX} = W_0 \exp\left(-\frac{E_A + h}{k_B T}\right) \quad (8)$$

where W_0 is the jump frequency for $T = \infty$.

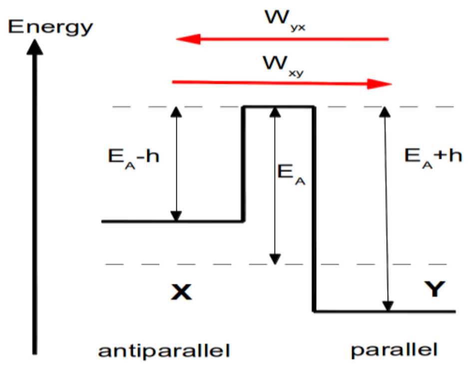

Fig. 3. Energy diagram of the two-level model

Solution of the equations (7) is

$$n_X = n\tau W_{YX} + (n_{X0} - n\tau W_{YX})\exp\left(-\frac{t}{\tau}\right), \qquad (9)$$
$$\tau = \frac{1}{W_{XY} + W_{YX}}$$

where $n = n_X + n_Y$, $n_{X0} = n_X$ (t = 0) and τ is the time constant. The main advantage form the described model is determination of the numbers of objects with magnetization directions, related to the two energy minima, at higher than zero temperatures.

5 MODEL OF MAGNETIZATION PRECESSES USING THE STONER-WOHLFARTH AND TWO-LEVEL MODELS

In case of materials, for which the so-called pinning mechanism (*ie* jumping of magnetic moments direction over an energetic barrier) plays the main role, application of the both described above models is necessary. Considering a cluster with unidirectional magnetic anisotropy and using the SW model one can determine the following quantities:

- angle positions of energy minima, regarding to magnetization of the cluster, external magnetic field and direction of the easy magnetization axis,
- values of the minima and the energy barrier between them.

This allows applying the two-level model in order to determine how many clusters take the positions, related to the energy minima, at a defined temperature. Therefore, the magnetization at $T > 0$ should be determined in two steps. Firstly, for a given particle shape, angle Ψ and H, one can determined θ_Y, θ_X and energy barriers using the Stoner-Wohlfarth model. Secondly, at a given T, using (8) and (9), one can calculate the numbers of clusters n_X and n_Y in the sates X and Y, respectively. Finally, magnetization of the considered system can be defined as:

$$M^* = \mu(n_Y \cos\theta_Y - n_X \cos\theta_X)V \qquad (10)$$

In many cases, magnetic materials consist of different objects with different magnetic moment and different anisotropy, therefore, a distributions of μ and E_A are expected. In the frame of the discreet approach, ranges of μ and E_A are divided into equally spaced channels with widths $\delta\mu$ and δE_A, respectively. The distribution n_{ij} is the number of objects (per unit volume) with magnetic moment $\mu_i = i\cdot\delta\mu$ and activation energy $E_j = j\,\delta E_A$. Magnetization can be expressed as

$$M* = \sum_i \sum_j i\delta\mu\left(n_Y^{ij}\cos\theta_Y^{ij} - n_X^{ij}\cos\theta_X^{ij}\right), \qquad (11)$$

where i and j numbers channels of μ and E_A, $n^{ij}_X + n^{ij}_Y = n_{ij}$ are related to (9) and (8).
An obvious normalization condition is

$$M_S = \sum_i \sum_j i\delta\mu n_{ij}\,. \qquad (12)$$

Simulations of magnetization processes can be carried out using the following scheme:

1. Designing of the considered magnetic system including the distribution of objects as well as their alignment (directions of the easy magnetization axes). We have the ranges of i, j, $\delta\mu$, δE_A, n_{ij}, Ψ_{ij}.
2. Calculation, for each object, the angles θ_Y^{ij} and θ_X^{ij} by searching the minima of energy describing by (6) including external magnetic field H.
3. Additionally, the energy barrier E_a^{ij} dividing these minima should be determined.
4. Using (9), the values of n^{ij}_X and n^{ij}_Y, including the value of T, can be calculated.
5. Magnetization of the system can be determined using (11).
6.

For example, hysteresis loops can be simulated using the initial condition of n_{X0} (in eq. 9) from previous step, *ie*, n_{X0} is equal to n_X after time t and with previous filed H. Figure 4 shows examples of hysteresis loops calculated for two magnetic phases with different mean values of anisotropy constants K_1V = 0.7 and 1.1 eV (at 200 K, 300 K and in ±1T range of magnetic field). In this example, Gaussian distributions with random orientation of the objects are used. It should be underlined that the proposed approach allows simulating magnetization curves with good quantitative agreement with real hysteresis loops. The assumption of the pinning mechanism leads to the statement that the presented method is valid rather for hard magnetic materials.

6 DETERMINATION OF MAGNETIC OBJECT (CLUSTER) DISTRIBUTION ABOVE THE BLOCKING TEMPERATURE

As it was mentioned in the introduction, more complicated is the opposite problem *ie*, determination of distribution of magnetic objects based on measured magnetization curves [1, 7]. In this point, one may define two cases: (i) the system above the blocking temperature, when the thermal energy allows spontaneous jumping over the energy barrier and (ii) the system below this temperature. In the first case, the searching distribution concerns only magnetic moment, while for the second case the distribution refers to the both magnetic moment and blocking energy.

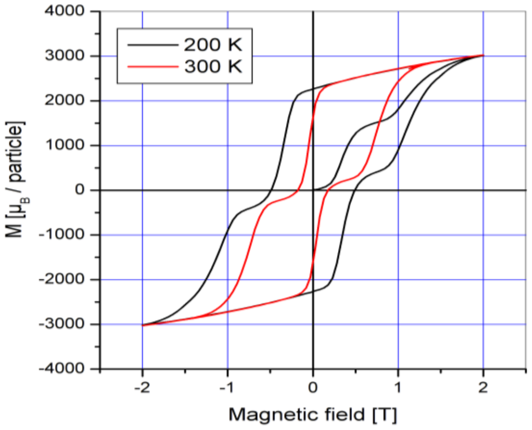

Fig. 4. Examples of simulated hysteresis loops calculated based on the two-level model (see in text)

When the system can be described by the classical Langevin equation, the problem can be solved by minimization of the expression

$$\chi^2 = \frac{1}{m}\sum_{i=1}^{m}\frac{(y_i - M_i)^2}{\sigma^2{}_i}, \tag{13}$$

$$y_i = M_S \sum_{j=1}^{n}\frac{N_j\mu_j}{\sum_{k=1}^{n}N_k\mu_k}L\left(\frac{\mu_0\mu_j H_i}{k_B T}\right), \tag{14}$$

where m is the number of experimental points of measured magnetic isotherm, y_i is the magnetization calculated from the cluster distribution procedure (theoretical curve), M_i is the measured magnetization at H_i (magnetic field), σ is the experimental error and n is the number of considered channels. The N_j is the number of objects with magnetic moment μ_j. Obviously, the minimization should give the searched distribution *ie*, proper values of N_j for which theoretical $M(H)$ curve fit to the empirical one. Shortly say, this is an optimization problem that can be solved using the so-called simulated annealing algorithm supplemented by the local entropy condition (for details see [1]).

Efficiency of the method is presented in Fig. 5. The dark line is the assumed distribution and the red bars are the calculated distribution based the $M(H)$ curves generated from the assumed one. As shown, the applied procedure well recreates original distributions especially mean values and, with lower accuracy, their width. It should be stressed that the algorithm does not require any preliminary assumption about a number of separated components (in our case - Gauss functions) which is the main advantage of the proposed approach.

7 DETERMINATION OF MAGNETIC OBJECT (CLUSTER) DISTRIBUTION BELOW THE BLOCKING TEMPERATURE

The presented above characterization of superparamagnetic systems is based on classical Langevin theory, which means that anisotropy of the clusters is not taken into account. When the anisotropy energy (or energy barrier E_B) is comparable with the thermal energy k_BT, it is necessary to include into consideration the both cluster parameters: magnetic moment μ and the barrier E_B, simultaneously characterizing the magnetic cluster distribution. As a consequence of the two-level model, the barrier between the two states depends on external magnetic field which causes the main difficulty in determination of the cluster distribution in E_B-μ space.

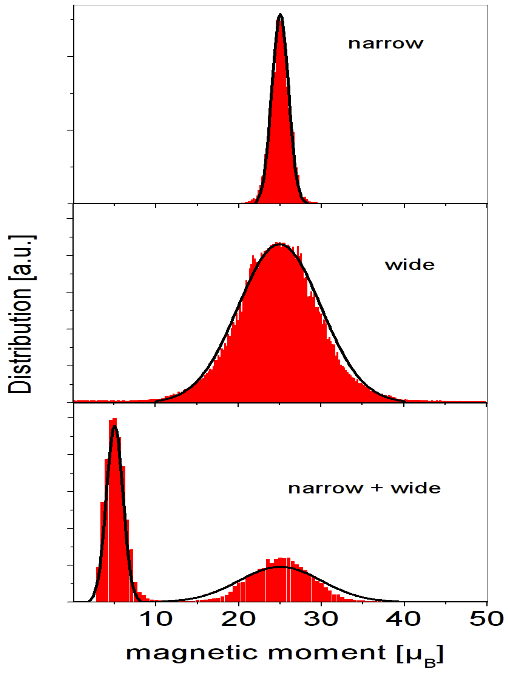

Fig. 5. Calculated distributions of the cluster magnetic moment (see the text)

This leads to some indistinguishability of two kind on magnetic objects, let say α and β, for which $E_B{}^\alpha - \mu_0\mu^\alpha H = E_B{}^\beta - \mu_0\mu^\beta H$. Furthermore, one can assume that for a typical measurement time 100 s, without external magnetic field and at a given temperature T, all objects that satisfy the condition $E_B < 25k_BT$ change their magnetization over the barrier E_B. Accounting the above the indistinguishably of magnetic objects is expressed by the line $25k_BT = E_B - \mu_0\mu H$, called H-line. In E_B-μ space, all objects with parameters below the H-line contribute to change of magnetization, see Fig. 6. Let us analyze the experiment consisting in reversal magnetization after saturation. Increasing field causes that more magnetic objects jump over the energetic barrier changing overall magnetization of the measured sample. This pinning effect is schematically depicted in Fig. 6 as the $M(H)$ curve. Determination of distribution of magnetic objects in E_B-μ space needs to overcome the described indistinguishability along the H-lines *ie*, we do not know where along this line the distribution points are placed – they are equivalent. The solution is to determine of the H-lines related to some homological points of the distribution at two different temperatures and calculate the parameters (*ie* magnetic moment and energetic barrier) from their intersection using simple geometric relations, as shown in Fig. 7. We have only one problem – how to determine the *H*-lines based on the empirical *M*(*H*) curves. The proposed solution consists in application of the simulated annealing algorithm with the additional maximum entropy condition (see [2]). The procedure gives a proper cluster distribution (values of n_{ij}), minimizing the following expression:

$$\chi^2 = \frac{1}{m}\sum_{k=1}^{m}\frac{\left(M(H_k)-M_k^{\exp}\right)^2}{\sigma^2_k} \tag{15}$$

where m is the number of experimental points, σ_k is the error, M_k^{exp} is the experimental magnetization measured at field H_k (at a given temperature) and $M(H_k)$ is the calculated magnetization using the SW and two-level models with random orientation of the clusters. The indistinguishability of the objects along the *H*-lines as well as the used calculation procedure allows determining, let say, some trace of the real distribution *ie*, some area in which the distribution is elsewhere placed.

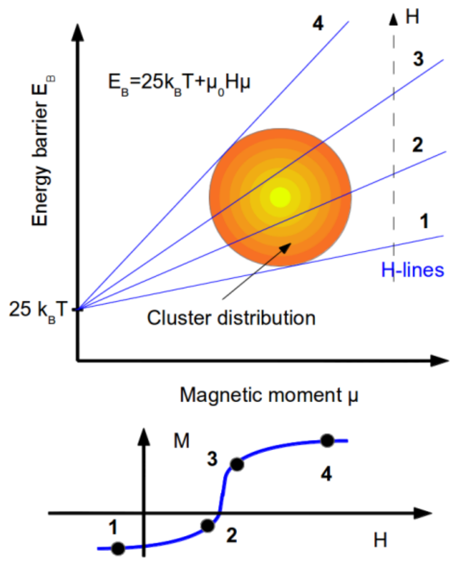

Fig. 6. The idea of the *H*-lines (see the text). Color reflects number of clusters with the E_B and μ parameters

The correctness of this approach can be easily confirmed by searching the cluster distribution based on generated magnetization curve for assumed distribution. Figure 8 shows an example for the Gaussian distribution with the mean values of μ and E_B equal to 5000 μ_B and 1 eV, respectively. The assumed temperature was 100 K. One can see the well-defined distribution trace, indicating area of a possible position of the cluster distribution. Real position, in E_B-μ space, of the mean values can be determined by performing similar calculations but at different temperature – in our case 300 K. In Fig. 9 such two traces are plotted. In order to determine the *H*-lines related to the mean values we proposed to count the calculated number of clusters along the *H*-line with varying *H*. This leads to creation of a kind of distribution profile, reflecting it real shape and homological points. Figure 10 presents the profiles determined at T_1 = 100 and T_2 = 300 K. The independent variable $a = \mu_0 H$ is the slope of the *H*-lines. Let us notice that the obtained profiles well recreated Gaussian shape with well-defined mean value. The real position of the distribution is calculated using the following equations

$$\mu = 25k_B\frac{T_2-T_1}{\mu_0H_1-\mu_0H_2},\quad E_B = 25k_BT_1+\mu\mu_0H_1 \tag{16,17}$$

where $\mu_0 H_1$ and $\mu_0 H_2$ refer to maxima of the profiles determined at T_1 and T_2, respectively. As shown, the real position of the mean distribution values perfectly fit to the assumed values. In a simple case, parameters of the *H*-lines, related to some homological points, can be determined form derivative of magnetization d*M*/d*H* vs. magnetic field. Thus, the intercept is $25k_BT$ and slope is $\mu_0 H$, where *H* is a field related to the homological point. From a shift of this field determined at T_1 and T_2, one may calculate a real position in E_B-μ space using the equations (16) and (17).

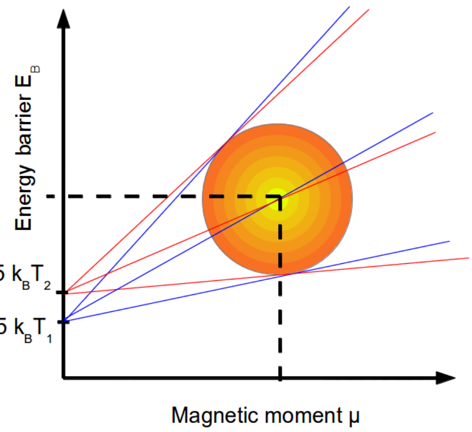

Fig. 7. Determination of positions of homological distribution points using the *H*-lines

Moreover, the presented approach can be used for materials containing interacting magnetic grains [8]. In this case the blocking energy can be ascribed to an apparent quantity including magnetic anisotropy as well as possible interactions.

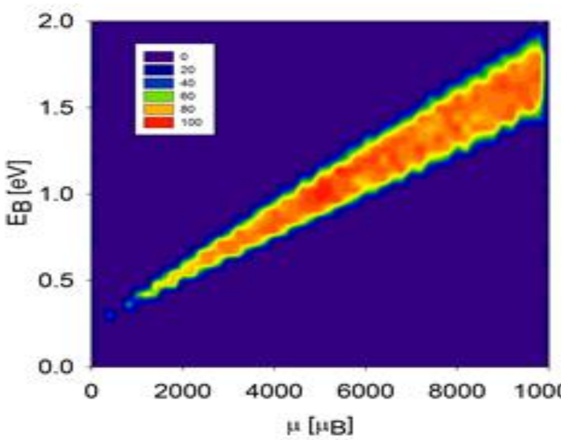

Fig. 8. The trace of the assumed cluster distribution at 100 K obtained using the simulated annealing algorithm

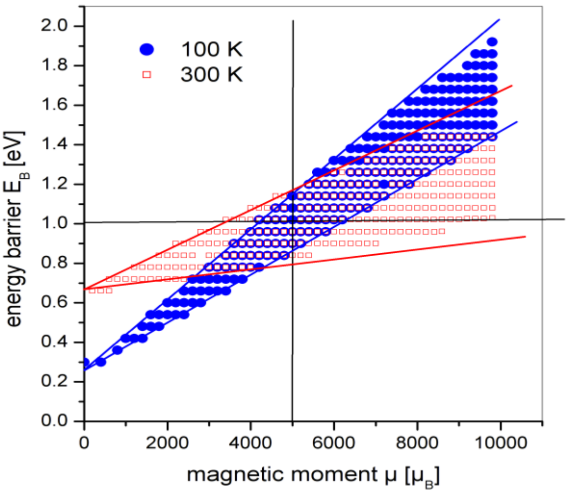

Fig. 9. The traces of the cluster distribution determined at 100 and 300 K

8 CONCLUDING REMARKS

The main aim of this paper is to collect theoretical background refers to characterization of superparamagnetic materials by a determination of distributions of cluster magnetic moments. In the case when magnetic anisotropy of the clusters can be neglected (the system is above the blocking temperature), the problem is quite easy, with this reservation that it requires application of simulated annealing algorithm modified by the maximum entropy condition. Such analysis can lead to determination of magnetic grain sizes of, for example, diluted magnets, natural rocks or biological specimens. The grains are usually of nano/micro size. Despite the fact, that such analysis is based on volumetric measurements, it can be considered as a kind of nano-scale imaging.

In the case when magnetic anisotropy cannot be neglected, the clusters are characterized by magnetic moment and energy barrier that, in a combination, causes the indistinguishability of the objects visible via macro-scale $M(H)$ curves. The solution consists in introduction the idea of the H-lines, allowing determination of some homological points of magnetic moment distribution. In nature, Gaussian like distributions are expected. Their mean values are also important and, with knowledge of magnetic and crystal structure of the clusters, allow characterizing the analyzed superparamagnets.

In conclusion, for materials in which the pinning of magnetic moments over the energy barrier is dominant, the determination of cluster distributions can be considered as additional characterization method.

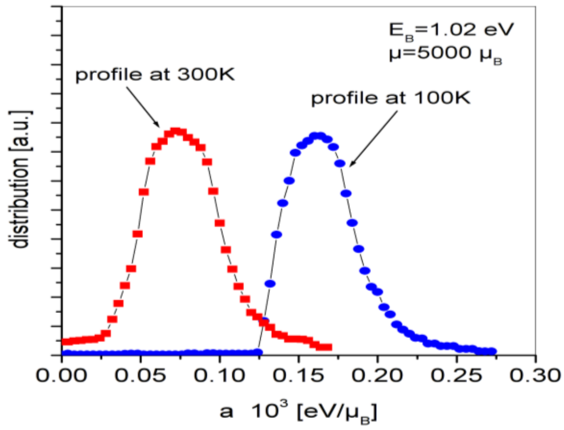

Fig. 10. The profiles of the cluster distribution determined at 100 and 300 K

REFERENCES

[1] CHROBAK, A. — HANECZOK, G. — CHEŁKOWSKA, G. — KASSIBA, A. — ZIÓŁKOWSKI, G: Phys. Stat. Sol.(a) 208, No. 11, (2011) 2692–2698.

[2] CHROBAK, A. — HANECZOK, G.: Phys. Stat. Sol.(a) 210, No. 8, (2013) 1584–1592.

[3] CHROBAK, A. — SLEBARSKI, G. — HANECZOK, G. — KOTUR, B.: Journal of Applied Physics 110, (2011) 113908.

[4] BÚĆKO, M. S. — MATTILA, O-P CHROBAK, — A. ZIÓŁKOWSKI, G. — JOHANSON, B. — CUDA, J. — FILIP, J. — ZBORIL, R. — PESONEN, L. J. — LEPPARANTA, M.: Geophysical Journal International, Volume 195, Issue 1, (2013) p.159-175.

[5] STONER E. C., — WOHLFARTH, E. P.: Philos. Trans. Roy. Soc. A 240, (1948) 599, reprinted in IEEE Trans. Magn. 27, (1991) 3475.

[6] GUIMARAES, A. P.: Principles of Nanomagnetism (Springer-Verlag, Berlin, Heidelberg, 2009), p. 82.

[7] KAKAY, A. — GUTOWSKI, M. W. — TAKACS, L. — FRANCO, V. — VARGA, L. K.: J. Phys. A 37, (2004) 6027.

[8] CHROBAK, A. — ZIÓŁKOWSKI, G. — RANDRIANANTOANDRO, — KLIMONTKO, N. J. — CHROBAK, D. — PRUSIK, K. — RAK, J.: Acta Materialia, 98 (2015) 318–326.

Received 30 November 2015