

Effect of Grain Size and Crystalline Orientation on the Coercivity of Sintered Magnets

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Abstract: The coercivity of sintered magnets like barium ferrite (BaFe₁₂O₁₉), samarium-cobalt (SmCo₅) or neodymium-iron-boron (Nd₂Fe₁₄B) is largely affected by the grain size. A method to evaluate coercivity behavior as function of the crystalline orientation, including the effect of grain size, is presented. Expressions were deduced to estimate the critical size of nucleus for spontaneous reversion of magnetization. The model indicates that the nucleation in grains of materials with high magnetocrystalline anisotropy only can begin by domain rotation. The model also predicts that the surface condition of grains is very important for the coercivity. A qualitative explanation is offered for the fact that materials with higher coercivity (or with smaller grain size) tend to follow an angular dependence of the coercivity similar to that given by the Stoner-Wohlfarth model, while materials with lower coercivity (or with larger grain size) tend to follow an angular dependence of the coercivity similar to $1 / \cos \theta$.

1. Introduction

The effect of grain size on the coercivity of magnetic materials is a very controversial question. Cullity [1], for example, mentions this effect as “only partially understood”. Besides, the grain size effect has to be addressed for two different situations: soft and hard magnetic materials. For soft magnetic materials, this subject has been recently discussed [2].

Our objective now is tackling this problem in the case of permanent magnets. It is experimental fact that the coercivity of sintered magnets as Barium ferrite (BaFe₁₂O₁₉) [3], samarium-cobalt (SmCo₅) [4] or neodymium-iron-boron (Nd₂Fe₁₄B) [5] are strongly affected by the grain size.

A very important detail has been neglected on the attempts for establishing a connection between grain size and coercivity: the angular dependence of the coercivity [3,6,7]. Although some studies [6] have indicated such relationship, those relevant data have been neglected.

Experimental data show [3,6,7] that materials with larger coercivity (or smaller grain size) tend to follow an angular dependence of the coercivity similar to that given by the Stoner-Wohlfarth model [8], while materials with smaller coercivity (or with larger grain size) tend to follow an angular dependence of the coercivity similar to $1/\cos \theta$ (Kondorsky law) [9].

Thus, for evaluating the effect of grain size on coercivity, it is also necessary to include the effect of crystalline orientation or texture. This question is left for the end of this paper. Our starting point will be the relationship between particle size and magnetostatic energy.

2. Relationship between magnetostatic energy and grain size

2.1. Case of spherical grain

The magnetostatic energy is associated with the demagnetizing field, and can be found with the equation:

$$E_{magnet} = \frac{1}{8\pi} \int H_d^2 dV \quad (2.1)$$

where E_{magnet} is the magnetostatic energy, H_d is the demagnetizing field and dV is an volume element. Making $H_d = N M_s$, where N is the demagnetizing factor and M_s magnetization of saturation, the magnetostatic energy per volume unit is $E = \frac{1}{2} N M_s^2$ (for a sphere, $N = 4\pi/3$).

The reduction of magnetostatic energy due the magnetization reversal in a spherical cap with thickness x (Fig. 1) is directly proportional to the volume V of this cap [10,11].

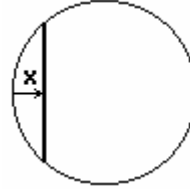


Figure 1. Spherical cap of thickness x in a sphere with radius R . It is assumed a ferromagnetic material with uniaxial anisotropy.

For a sphere with radius R the magnetostatic energy, as function of x , is (Fig. 1):

$$E = \frac{NM_s^2}{2} \left(\frac{4\pi}{3} R^3 + \frac{\pi}{3} x^3 - \pi R x^2 \right) \quad (2.2)$$

and the associated domain wall energy is (Fig. 1):

$$E = \pi(2Rx - x^2)\gamma_D \quad (2.3)$$

where γ_D , the domain wall energy is $\gamma_D = R_c \frac{4\pi}{9} M_s^2$ [12]. R_c is the single domain critical radius, as defined by Kittel [12].

By another hand, the classical expression [9] is:

$$H = \frac{1}{\cos\theta} \frac{1}{2M_s} \left(\frac{\partial E}{\partial x} \right)_{\max} \quad (2.4)$$

Adding Eq. 2.2 and Eq. 2.3, making $(\partial E/\partial x)$ and dividing by an area element equal to $\pi(2Rx - x^2)$:

$$\frac{\partial E}{\partial x} = \frac{(2R - 2x)}{(2Rx - x^2)} \gamma_D - \frac{NM_s^2}{2} \quad (2.5)$$

According to Eq. (2.5), $\frac{\partial E}{\partial x} \rightarrow \infty$ when $x \rightarrow 0$. This means that formation of nucleus near the surface - by domain wall movement - is a very unfavorable process. The nucleus should have origin by domain rotation, the process studied by Stoner and Wohlfarth [8]. Besides, Eq. 2.2 and 2.3 lead to another interesting result, as shown in Figure 2 where $E_{magnetostatic}$ is given by Eq. 2.2, E_{wall} is given by Eq. 2.3 and E_{total} is the sum of Eqs. 2.2 and 2.3.

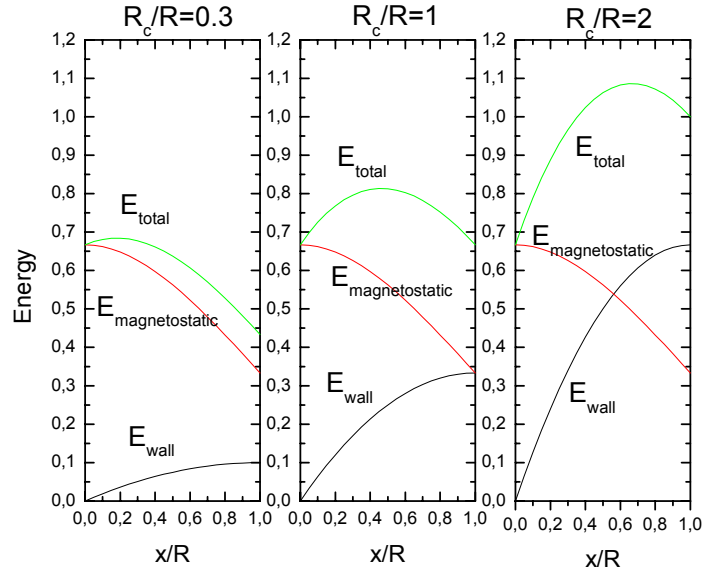


Figure 2. $E_{\text{magnetostatic}}$, E_{wal} and E_{total} , as function of x/R , for three values of R_c/R

Making $(\partial E/\partial x)=0$ for the curve $E_{\text{total}}(x)$ shown in Fig. 2, we get:

$$x_{\text{max}} = x_{\text{crit}} = \frac{4R_c + 6R - \sqrt{16R_c^2 + 36R^2}}{6} \quad (2.6)$$

$$V_{\text{crit}} = \pi R x_{\text{crit}}^2 - \frac{\pi}{3} x_{\text{crit}}^3 \quad (2.7)$$

Where x_{crit} is the “critical” length, when spontaneous reversal of magnetization occurs. The critical volume is the volume of the spherical cap with thickness x_{crit} , given by Eq. 2.7.

Fig. 2 provides a very important result: increasing R_c/R , the maximum E_{total} also increases. If thermal processes are considered, the energy variation ΔE , given by Eq. 2.8, can be related with the decrease of coercivity, when grain size increases.

$$\Delta E = \text{Maximum} \{ E_{\text{total}}(R) \} - (E_{\text{magnetostatic}}(x=0)) \quad (2.8)$$

According Aharoni [13], Micromagnetics – a theory that aims to predict the coercivity - fails when: i) surface roughness, ii) crystalline imperfections or iii) thermal fluctuations are not non-negligible. Statistical thermal fluctuations may overcome the barrier predicted by Eq. 2.8, since lattice defects are often present [14,15] and also collaborate for the magnetic reversal. Then, a nucleation theory like that by Turnbull and Fisher [16] could be adapted, predicting that the probability of nucleus reversal increases when the barrier ΔE , given by Eq. 2.8, decreases. This implies that, with such thermal fluctuations present, coercivity decreases with grain size. However, this does not violate the so-called Brown Paradox (that says coercivity does not depend on grain size) because, as Aharoni [13] pointed out, Micromagnetics does not deal with thermal fluctuations.

It also has to be noted that, when grain size is below the R_c , reduction of coercivity has already been attributed to thermal fluctuations [17]. Thus, similar phenomena may be occurring for grain size larger than R_c , where thermal fluctuations could be responsible for coercivity decrease.

2.2. Case of a grain with cubic shape

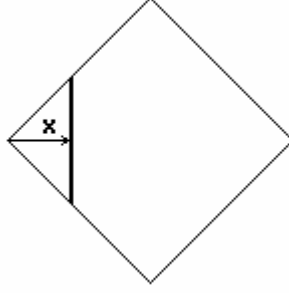


Figure 3. Corner with length x in a cube with side L . It is assumed a ferromagnetic material with uniaxial anisotropy.

Now, the nucleation in a corner of a grain with cubic shape will be discussed. This problem is analogous to that of section 2.1. Eq. 2.9 and 2.10 are analogous, respectively, to Eq. 2.2 and 2.3.

$$E = \frac{NM_s^2}{2}(L^3 - Lx^2) \quad (2.9)$$

$$E = 2Lx\gamma_D \quad (2.10)$$

After the sum of Eqs. 2.9 and 2.10, the $\partial E/\partial x$ per surface unity is:

$$\frac{\partial E}{\partial x} = \frac{1}{x}\gamma_D - \frac{1}{2}NM_s^2 \quad (2.11)$$

In the same way as predicted by Eq. 2.5, Eq. 2.11 indicates that $\frac{\partial E}{\partial x} \rightarrow \infty$ when $x \rightarrow 0$.

Thus, also for a corner, the formation of a nucleus near the surface – by domain wall movement – is a very unfavorable process, in agreement with Eq. 2.5.

3. The angular dependence of coercivity

Substituting Eq. 2.5 in the Eq. 2.4, another result is obtained:

$$H = \frac{1}{\cos \theta} \frac{1}{2M_s} \left(\frac{(2R - 2x)}{(2Rx - x^2)} \gamma_D - \frac{NM_s^2}{2} \right) \quad (3.1)$$

Eq. 3.1 predicts that the coercivity follows a law of type $1/\cos \theta$, and also that the coercive field is directly proportional to the domain wall energy, γ_D . By another hand, if the coercive mechanism is coherent rotation, it is predicted that coercivity should be described by Eq. 3.2.

$$H_c(\theta) = \frac{1}{((\cos \theta)^{2/3} + (\sin \theta)^{2/3})^{3/2}} \frac{2K_1}{M_s} - NM_s \quad (3.2)$$

Eqs. 3.1 and 3.2 offer a qualitative explanation for the experimental fact that that materials with larger coercivity (or smaller grain size) tend to follow an angular dependence of the coercivity similar to that given by the Stoner-Wohlfarth model [8], while materials with lower coercivity (or with larger grain size) tend to follow an angular dependence of the coercivity similar to $1/\cos \theta$.

Thus, there is a “competition” between the two mechanisms: resistance against domain wall displacement (Eq. 3.1) and between coherent rotation (Eq. 3.2). The reversal of magnetization will happen by the mechanism that is the most favorable.

4. Analysis for SmCo₅ magnets

Magnets of SmCo₅ type will be used as practical example for discussing the meaning of Eqs. 3.1 and 3.2. A typical SmCo₅ magnet has grain diameter ~10 μm. A graph of Eq. 3.1, for R=5 μm is shown in Fig. 4. Typical SmCo₅ magnets can have coercive field > 30 kOe after heat treatment [14]. Without heat treatment, coercivity (iH_c) is only a few kOe [14].

For R=5 μm, $x_{crit}=0.62$ μm (Eq. 2.6). After $x=0.62$ μm, the reversal of magnetization should extend spontaneously in the grain. Figure 4 shows that, for magnets with larger coercivity, for example $iH_c=30$ kOe, there is no competition between mechanisms assumed in Eqs. 3.1 and 3.2, and the mechanism should be coherent rotation [8], with angular dependence given by Eq. 3.2.

However, for lower coercivity magnets, for example $iH_c=5$ kOe, the calculation indicate “competition” between the two possible mechanisms (because they have approximately the same magnitude order in the range $0.2 < x < 0.62$ μm, see Fig. 4), and this leads to an angular dependence intermediate between those predicted by Eqs. 3.1 and 3.2.

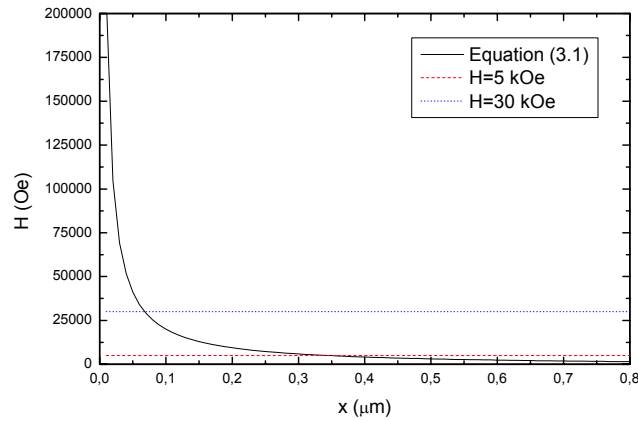


Figure 4. Graph of Eq. 3.1 for a typical SmCo₅ magnet, with R= 5 μm ($x_{crit}=0.62$ μm). For SmCo₅, $R_c = 1$ μm [18], $\gamma_D = 120$ ergs/cm² [18] and $4\pi M_s = 11.2$ kG [18]. Calculation for $\theta=0$.

The experimental values of 30 kOe and 5 kOe shown in Fig. 4 should be interpreted as “reduction” of anisotropy field, probably due to crystalline defects that have their effect included by means of the non-dimensional α factor, as shown in Eq. 3.3:

$$iH_c = \frac{2\alpha K_1}{M_s} - NM_s \quad (3.3)$$

Eq. 3.3 is a modification of Eq. 3.2 (for $\theta=0$). According Eqs. 2.5 and 2.11, nucleation only can start by rotation. Although domain rotation is necessary to begin the process, reversal by domain wall displacement can also happen, in special for larger x (before x_{crit}), see Fig. 4.

The model indicates (as showed by Eqs. 2.5 and 2.11) that the surface condition of the grains is essential for coercivity. The existence of lattice defects in the region near the surface favors domain rotation (reducing α in Eq. 3.3), decreasing coercivity.

An experiment to verify this theory would be measuring the angular dependence of coercive field as function of temperature (T). Eq. 3.2 is function of K_1 (T) and M_s (T), while Eq. 3.1 is function of γ_D (T) and M_s (T). This would allow to separate reversal contributions by rotation and by wall displacement.

This model only can be applied for very specific situations, which are the same where Domain Theory [12] holds. It was supposed that the domain wall thickness can be considered

negligible, typical condition of phases with high magnetocrystalline anisotropy. This is true for SmCo₅, where $\delta=60\text{\AA}$ [18] and $R_c = 1\ \mu\text{m}$ [18]. Thus, $R_c / \delta > 100$.

Conclusions

Expressions to evaluate the coercivity as function of crystalline orientation, including grain size considerations, were presented. It was obtained an equation to find the nucleus critical size. After this critical size, reversal spontaneously occurs.

The model indicated that, in grains of phases with high magnetocrystalline anisotropy, the beginning of nucleation only can happen by domain rotation. But, although rotation is necessary to start the process, reversal by domain wall displacement also may occur at same moment.

A qualitative explanation is offered for the fact that materials with higher coercivity (or with smaller grain size) tend to follow an angular dependence of the coercivity similar to that given by the Stoner-Wohlfarth model, while materials with lower coercivity (or with larger grain size) tend to follow an angular dependence of the coercivity similar to $1 / \cos \theta$.

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