Coercivity mechanisms in hard magnetic materials

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In permanent magnetic materials magnetization reversal does not take place by coherent and global rotation. No collective processes are involved when the energy barrier implicated in the reversal is of magnetocrystalline nature acting at the atomic level. The mechanism by which magnetization reversal occurs involves several events which are inherently linked to the presence of defects. These events, nucleation, propagation and pinning - depinning of a domain wall, are strongly linked to the microstructure. The liaison between magnetization reversal mechanisms and microstructure is still poorly understood. Four types of magnetic characterization are used (temperature dependence of the coercive field, angular dependence of the coercive field, magnetic viscosity and the direct evaluation of dipolar fields) where the analysis may or may not be based on a model.

Coercivity, the essential property which characterizes hard magnetic materials (generally in the saturated state) corresponds to the fact that magnetization reversal does not accompany the reversal of the magnetic field to which the material is subjected (figure 1). It is measured by the value of the coercive field H_c, the inverse field necessary to obtain this magnetization reversal.

From an experimental point of view the coercive field is deduced from the hysteresis cycle M_H (H), where M_H is the projection of the resultant magnetization in the direction of the applied field. It is defined as the field where dM_H / dH is maximum, and not, as is customary, as the field where the magnetization becomes zero. The two definitions give the same result when one considers a magnet whose grains are well aligned, subjected to a field applied antiparallel to its magnetization direction. However they can differ strongly when, in addition to irreversible processes, reversible rotation comes into play (isotropic magnets for example -figure 2).
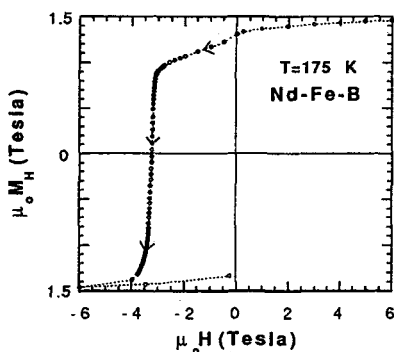

Figure 1   Figure 2
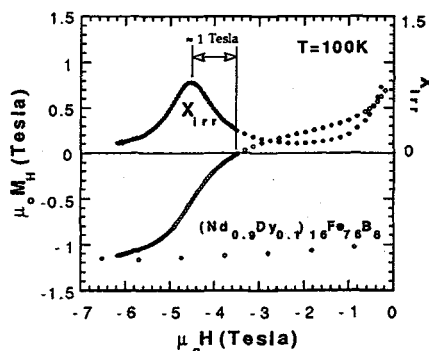Coercivity and the coercive field in anisotropic and isotropic magnets

I - The Coercive Field and Critical Fields

1 - Dipolar contribution

The applied field - in particular the coercive field H_c,- is not that which prevails in the magnet itself. Magnetic dipolar interactions, inherent in any magnetized material, either add to or subtract from the applied field an eminently inhomogeneous contribution which depends on the magnetization state. It is the combination of these two fields that gives the critical field actually felt by the magnetic moments, that which causes the reversal of $\vec{M}$.

$$\vec{H}_{crit} = \vec{H}_c + \vec{H}_{dip} \qquad\qquad (1)$$

Inversely, to estimate the value of $\vec{H}_c$ one needs to be able to evaluate $\vec{H}_{dip}$ and $\vec{H}_{crit}$.

2 - The processes involved in magnetization reversal

A magnet placed in an inverse field, inferior in modulus to H_c, is a stable system (since it remains magnetized antiparallel to the applied field) and its state corresponds to an energy minimum. Nevertheless a more stable state exists, that where the magnetization is parallel to the direction of the applied field, and this state corresponds to an energy well deeper than the former situation. A mandatory energy barrier exists between these two wells -figure 3- which is at the origin of the coercivity.

A material is thus coercive:
- if intrinsically it has a strong anisotropy energy linked to the orientation of the magnetic moments i.e. a magnetocrystalline anisotropy acting at the atomic scale,
- or if one can create an anisotropy acting on the resultant magnetization, typically a demagnetizing field anisotropy related to the shape of the grains.
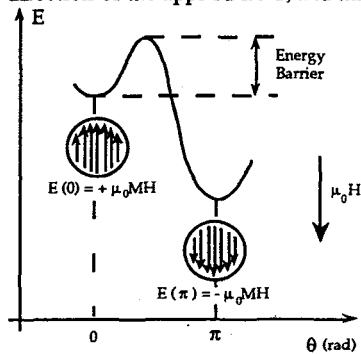

Figure 3 - The metastable coercive state for θ=0

a - Homogeneous materials
(i) Uniform Magnetization Reversal

The simplest process to pass from the metastable state to the stable state is to supply an energy to the system, equal to that of the energy barrier in an external field of zero; the critical field is then equivalent to the anisotropy field H_A,which measures this barrier. This is the model of Stoner and Wohlfarth [1] in which magnetization reversal is accomplished by coherent rotation of all the moments.

$H_{crit} \cong H_A$ constitutes the upper limit of the possible critical fields.

(ii) Non-Uniform Magnetization Reversal
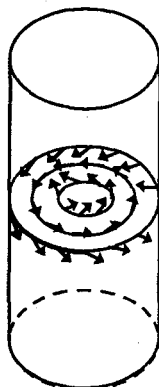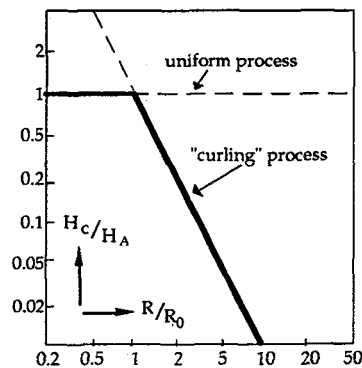

Figure 4 - Magnetization reversal by curling

Figure 5 - Comparison between the critical fields associated with both the uniform and "curling" processes as a function of the diameter of the elongated grain.

When the anisotropy results only from shape anisotropy reversal can take place via several collective processes - curling of the moments for example (figure 4) - during which the

resultant magnetization does not reverse. Thus it is not necessary to overcome the anisotropy energy; however such processes bring exchange energy into play. Depending on the diameter of the elongated grains concerned, these processes may be more economical than uniform rotation, in which case they lead to a critical field inferior to the anisotropy field H_A - figure 5.

When the anisotropy is created directly at the level of the atomic magnetic moments (magnetocrystalline anisotropy), any non-uniform process implies locally, a breaking away of one or more magnetic moments from the others (local deviation from saturation - figure 6)
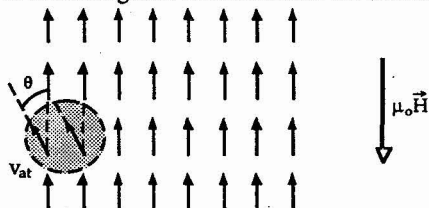

Figure 6 - A local deviation from the saturated state

In addition to the loss in anisotropy energy (existing at the level of each moment), one must consider a loss in exchange energy (due to the non uniformity created). Such a process, more costly than uniform reversal, leads to a critical field superior to that of the anisotropy field H_A and, therefore cannot be contemplated.

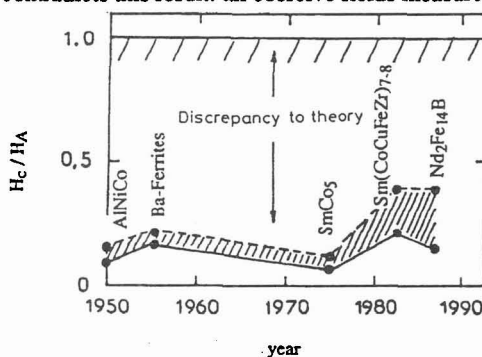Thus in theory $H_{crit} \equiv H_A$. However experience contradicts this result: all coercive fields measured are by far inferior to H_A (figure 7). This disagreement is known as the Brown Paradox [2]. It is proof that coercivity is not an intrinsic property of a homogeneous material and implies the existence, in hard magnetic materials, of heterogeneities with a preponderant role.

b - Heterogeneous materials : reversal processes by stages

In a saturated system where the coercivity is due to magnetocrystalline anisotropy, the understanding of coercivity is thus the understanding of the interplay between magnetic properties and microstructure (under the term "microstructure" one means the exact composition of the elements, their respective proportions, the way in which they are arranged, etc).

Figure 7 - Critical fields of principal magnets referred to their anisotropy field H_A (after Kronmüller [3])

The magnetization reversal under the effect of an inverse applied field is an event concerning simultaneously both the defects present and the principal phase which surrounds them. This event which begins in a grain with the nucleation of a domain of inverse magnetization in a defect, is completed when the domain wall created by this nucleation disappears having traversed the whole grain.

The successive processes which come into play during this time are the following:
• Nucleation of an inverse domain and the emergence of a domain wall, in the defect where the anisotropy barrier is the lowest.
• Passage of the domain wall from the defect to the principal phase.
• Progression of the domain wall in the principal phase.
• The eventual pinning (and subsequent de-pinning) of the domain wall on defects - pinning sites encountered.

For each of these processes, at each of these stages, there is an associated specific critical field which allows one to proceed to the subsequent. The microstructure is the key link producing and controlling the nucleation and pinning sites.

II- Coercive Field and Microstructure

The relationship between the coercive field and the microstructure is still very poorly understood illustrated by the lack of effective progress in this domain over the past 40 years, (figure 7). The analysis of this relationship (the determination of dimensions, of magnetic properties and of the role of defects, the evaluation of dipolar fields, etc.) is conducted with the aid of four types of experiment compared , or not, with models.

1 - Temperature dependence of the coercive field analysed with models

Two types of approach have been developed over several years to take into account the thermal variation of H_c. The first aims to differentiate between the two principal mechanisms,

nucleation and pinning - de-pinning of domain walls, whilst the second, more phenomenonological in nature, considers the profound similarities existing between all the possible mechanisms and additionally takes into account the effects of thermal activation.

a - Microscopic approach differentiating the mechanisms

The basis of this approach is the description at the microscopic scale of the two main types of defect using micromagnetic equations [4,5]. As a rigorous treatment would be extremely difficult (micromagnetic theory contains non linear differential equations) several assumptions must be made to simplify the problem:
- representation of the physical system by a single chain of atoms (one dimensional approach)
- nucleation is assumed to occur at the first local deviation from saturation (enabling the linearisation of the equations)
- simple analytical profiles of the anisotropy defect, for instance, step-like profile [6], linear variation [5], or quasi-harmonic anisotropy perturbation, figure 8 [3].
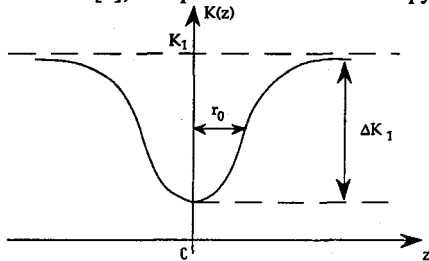
Figure 8 - Schematic representation of a quasi-harmonic anisotropy defect, after Kronmüller [3]. Depth of the perturbation:ΔK_1. Width of the defect: $2r_0 = d$

As part of this model, the coercive field is expressed by Kronmüller et al [3,7] as:

$$H_c = \frac{2K_1}{\mu_o M_s} \alpha_K \, \alpha_\psi - N_{eff} \, M_s \qquad (2)$$

where the second term describes dipolar interactions via the average parameter N_{eff}, while the first represents the critical field which depends on the actual mechanism involved in the magnetization reversal. Two parameters are used to quantify the critical field:

(1) The mechanism parameter α_K whose value depends on the defect (its type and dimension). The expected variations of α_K for nucleation sites and pinning sites are both presented in figure 9:

α_K^{nucl} varies regularly from 1 (i.e. $H_{crit} = H_{crit}^{main\ phase}$), when the width of the defect, d, is much smaller than δ (the domain wall width in the main phase), to the ratio $H_{crit}^{defect} / H_{crit}^{main\ phase}$ when $\delta \ll d$. The critical field in the latter case is the critical field of the nucleation site (and magnetization reversal is assumed to occur by coherent rotation in the defect): The defect which becomes the nucleation site is the one whose anisotropy field is minimum.
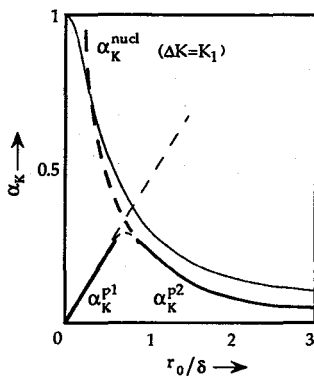
Figure 9 - Expected variations for α_K depending on the type of defect and its dimension. After Kronmüller [7]
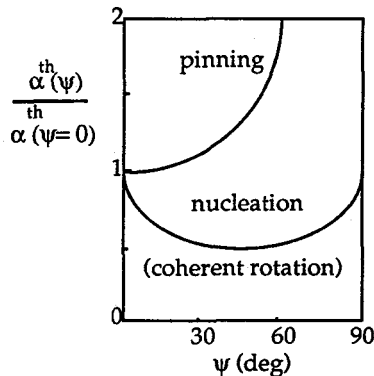
Figure 10 - Pure effect of angular dependence depending on the process involved after Kronmüller [7]

In contrast two regimes exist in the case of pinning, the pinning efficiency varies as d / δ for narrow heterogeneities and as δ / d for wide heterogeneities (d = $2r_0$). When d ≈ δ , a maximum value is obtained for α_K^{pin} , it corresponds to α_K^{pin} ≈ 0.3. A domain wall which sweeps across the entire sample meets all the different pinning sites, but it is those where the pinning is strongest, i.e. where α_K^{pin} is maximum, that determine the coercivity of the system. Different pinning sites may be involved at different temperatures so that α_K^{pin} ≈ 0.3 remains constant.

(2) α_ψ represents the effect of the angular dependence of the coercive field convoluted with the

angular distribution of the crystallite orientation. In the case of pinning the critical field is far inferior to that of the anisotropy field of the main phase and the angular dependence of the coercive field follows a $1/\cos\psi$ behaviour (where ψ is the angle between the applied field and the c-axis of the magnet). For a nucleation mechanism, magnetization reversal is assumed to occur by coherent rotation within the defect (figure 10).
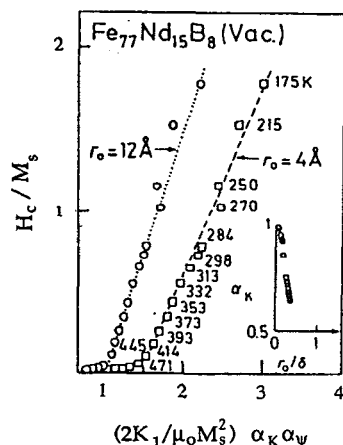

Figure 11 - Analysis of a classical NdFeB magnet after Kronmüller [7].

This model has been applied to sintered [7] and melt spun [8] NdFeB magnets. In both cases the mechanism of pinning - de-pinning appears inadequate as the mechanism governing coercivity, and magnetization reversal has been attributed to a mechanism of nucleation.

As an example, the analysis of sintered magnets with a composition of $Nd_{17}Fe_{77}B_8$, implies that the size of the defects is very small indeed [7] ($r_0 \approx 10\text{Å}$). (figure 11)

The dipolar interactions evaluated via this model were found to be very important: $N_{eff} \approx 1.6 - 1.8$.[7]. This corresponds in the latter magnet to a reduction of about 2.7T at 300K of the coercive field.

b - Phenomenological and global approach

This second approach, developed in parallel to the preceding one since 1988 [9,10], considers in a more global sense, what the various possible processes of magnetization reversal have in common with one another.

Whatever the mechanism involved (figure 12), i.e. a defect acting as a nucleation site, the expansion up to its critical volume of an already reversed nucleus in the main phase, or the break-away of domain walls from their pinning sites after swelling, the formation of a nucleus with an inversed magnetization occurs and it is from this that magnetization reversal in the magnet begins.

Figure 12 - Stages in magnetization reversal bringing into play a critical volume v

The cost of this operation is proportional to the increase of the associated domain wall energy which has the form $\gamma\, s$, where s measures the surface (or the growth of the surface) of the nucleus of volume v.

Supposing that the ratio s/v is not favoured by anomalies in the geometry of the grains, the domain wall energy can be written as:

$$\gamma\, s = \alpha\,\gamma\, v^{2/3}$$

α, a critical field parameter, takes into account the dimensional correspondence between s and v, but in addition quantifies the relationship between the domain wall energy in the principal phase and in the activation volume. Within the hypothesis that these two relationships are simply proportional, α is independent of the temperature.

The expression for the coercive field in this model is the following [9,10]:

$$H_c = \alpha\,\frac{\gamma}{\mu_o M_s v^{1/3}} - N_{eff}M_s - \frac{25kT}{\mu_o M_s v} \qquad (3)$$

the second term measuring, as in the earlier case, the effects of the dipolar interactions, and the third, the effect of thermal activation. The volume v can be identified with the activation volume v_a which can be directly calculated from magnetic viscosity measurements.

In the case of the composition $Nd_{17}Fe_{75}B_8$ the comparison of the variation of the calculated and experimental variations of $H_c(T)$ are presented in figure 13. Figure 14 yields the two parameters α (the slope of the line) and N_{eff} (the intersection with the y-axis) thanks to the use of the reduced variables:

$$\left|\frac{H_o}{M_s}\right| \quad \text{and} \quad \left|\frac{\gamma}{\mu_o M_s v^{1/3}}\right|$$

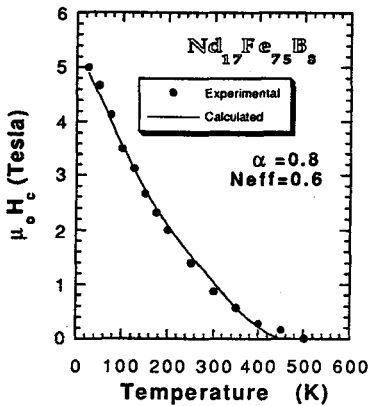where $H_0 = H_c + 25\, S_v$ is the absolute coercive field in the absence of thermal activation.

Figure 13

Figure 14

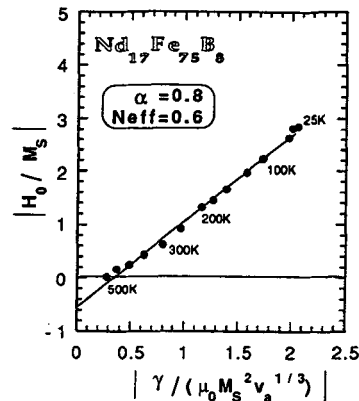Experimental $H_c(T)$ points fitted to the phenomenological model with the constant parameters α and N_{eff}

In most RFeB magnets α is found to be of the order of 1, which does not correspond simply to the dimensional factor alone and thus must contain a contribution which one can attribute to the microstructure.

N_{eff} differs strongly from one material to another: From low values for magnets produced by the technique of melt spinning, it rises to the order of 1 for magnets produced by sintering. In the case of $Nd_2Fe_{14}B$ this corresponds to a dipolar field of about 1.6 T at room temperature. This high value (although less than that derived in the first approach) will be corroborated later on by direct measurements.

2 - Magnetic viscosity and the activation volume

At a given temperature magnetization reversal can occur in one of two ways:
- by a lowering of the energy barriers by Δ, due to the effect of the applied field, giving rise to the experimentally derived irreversible susceptibility $\chi_{irr} = dM\,/\,dH$
- or by jumping these energy barriers of Δ, due to the effect of thermal activation, after a characteristic time, t, which can be linked to Δ via $\Delta = kT\, Ln\, t\,/\,\tau_0$ where $\tau_0 \approx 10^{-11}$s is the characteristic time for magnetization reversal when no barrier is present. The corresponding experimental parameter is the viscosity S of the magnetic system, defined by $S = dM\,/\,dLnt$.

The field acts through the magnetic moment of a critical volume, v, which is assumed to be equal to the activation volume v_a. One can then deduce this volume v_a from the relation [11]:

$$v_a = \frac{kT}{\mu_o M_s}\frac{\chi_{irr}}{S} = \frac{kT}{\mu_o M_s S_v}$$

where $S\,/\,\chi_{irr} = S_v$ is the coefficient of magnetic viscosity characterizing a given material at a given temperature.

Thus it is possible, providing certain precautions are taken [12,13,14,15], to determine v_a experimentally as a function of temperature

In this sense the activation volume corresponds to the creation of a non uniform state of magnetization. It is thus comparable with the characteristic dimension of a non uniform state of magnetization in a ferromagnetic material i.e. the width of a domain wall, δ.

Hence the comparison between the values obtained for v_a and δ via the ratio $v_a\,/\,\delta^3$ (figures 15 and 16), give an insight into the discrepancies existing between the intrinsic magnetic parameters of the main magnetic phase and those of the defect involved, or between different defects.

As an example the defects involved in the magnetization reversal are very similar in $Pr_{17}Fe_{75}B_8$ and $Pr_{17}Fe_{53}B_{30}$ (figure 15), but they are of a different nature in $Nd_{17}Fe_{75}B_8$

$Nd_{17}Fe_{53}B_{30}$ and NdFeB(V) UGISTAB (figure 16). In each case the intrinsic properties of the defects differ from those of the main phase $R_2Fe_{14}B$. [15]
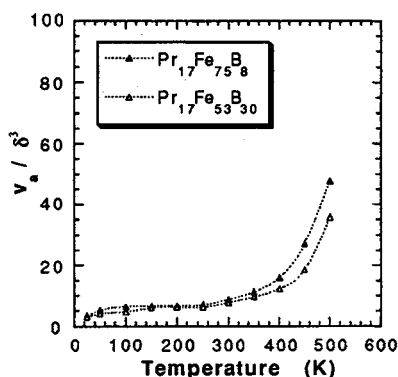

Figure 15

Figure 16
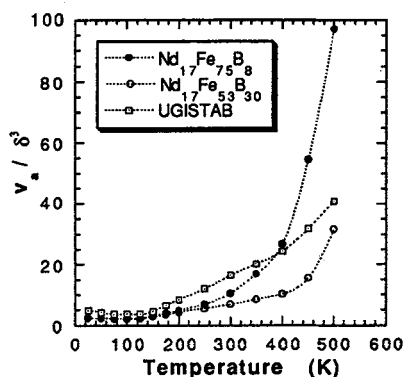
Thermal variation of v_a/δ^3 for some RFeB magnets.

3 - Direct evaluation of the dipolar contribution to magnetization reversal

Permanent magnets are very heterogeneous systems in which dipolar interactions are above all local and strongly variable from one point to another within the material, and even within a grain itself. Furthermore the situation which determines the reversal of a grain's magnetization is that where the inverse dipolar field is the most extreme when averaged out over an element the size of the activation volume.

The experimental method developed is direct [15,16,17,18], hence avoiding the use and perhaps contestable interpretation of a model. It is based on the following idea:

A grain, initially thermally demagnetized, in which the efficiency of the eventual defects - pinning sites can be neglected, becomes coercive at the moment it attains a state of complete saturation; this state is reached when the applied saturation field (uniform) compensates exactly that of the local dipolar field throughout the entire grain, in particular where it is at its strongest.

As a consequence, the applied saturation, once sufficient to render a grain coercive, measures the highest value of the local dipolar field existing in the grain.
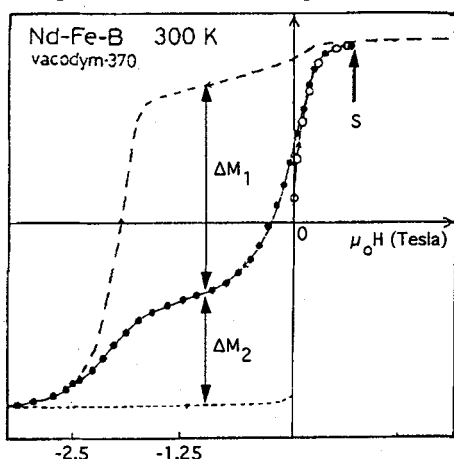

Figure 17 - Principle of the determination of the effective dipolar fields existing in the grains.

The hysteresis loop for a magnetic material (sintered Nd-Fe-B) which has been completely saturated in the positive field direction is illustrated by the dashed line in figure 17. If one applies a positive field of say 0.7 T (point S in the figure 17) to a thermally demagnetized sample of a magnetic material, one can then compare the minor loop obtained when the field direction is inversed at S with that of the major loop. Only a proportion of the grains, n_g, have been saturated by this field of 0.7 T, and thereby rendered coercive. This proportion can thus be deduced by :

$$n_g = \frac{\Delta M_2}{\Delta M_1 + \Delta M_2}$$
figure 17

The variation of n_g as a function of the applied saturation field for a sintered Nd-Fe-B magnet, (always using a sample which has been initially thermally demagnetized) is presented in figure 20 at 175 K.

The distribution of the dipolar fields obtained is evidently strongly dependent on the statistical environment of the grains considered. A grain whose environment is one of saturated grains in the same sense as itself (figure 18), is subjected to a very different situation when surrounded by grains in which half are saturated in one direction, half in the other (figure 19).
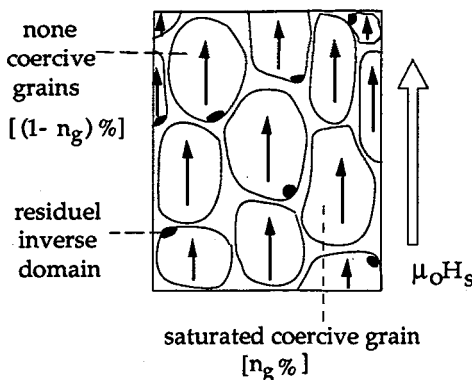
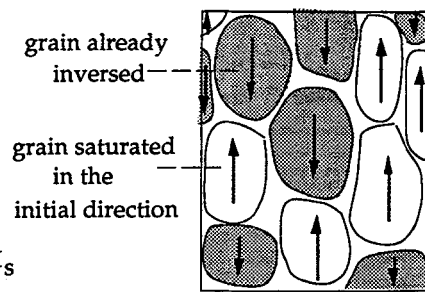Figure 18 - a fully saturated configuration   Figure 19 - a "coercive" configuration

The latter configuration (figure 19) corresponds to a situation where the overall resulting magnetization is around zero, which is similar to the situation in the region of the coercive field. It can be obtained by the careful choice of the initial positive saturation field acting on a population of grains thermally demagnetized. It is sufficient to saturate half of them, their distribution being, a priori, randomly distributed. The application of an inverse field, inferior to the coercive field of the saturated grains, saturates progressively the non-coercive population of grains, giving the distribution of the dipolar fields in this chosen configuration (n'_g). Figure 20 presents the variation of n_g aswell as n'_g as a function of H_{sat} for a sintered Nd-Fe-B magnet.
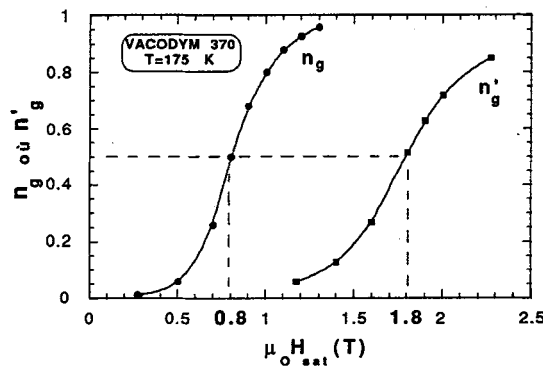

Figure 20 - Amount of saturated grains in both the magnetic configurations considered

In this configuration, one which reflects the situation of the grains in the region of the coercive field, the average dipolar field involved in the magnetization reversal was found to be much larger (see figure 20). For both NdFeB or PrFeB sintered magnets this corresponds to $N_{eff} \approx 1$ as obtained in the latter model.

4 - Angular dependence of the coercive field

The usual experimental conditions for the measurement of the coercive field is that of an applied field antiparallel to the magnetization direction. When the field is applied at an angle θ_{gh} from the easy axis, the value of H_c differs. On one hand the coupling energy between the magnetization and the applied field is reduced by a factor of $\cos\theta_{gh}$, on the other, due to the non-colinearity between M_s and H, a coupling force is exerted which induces a certain rotation of the moments towards the field direction modifying the physical system and thereby affecting the value of H_c.

The analysis of these variations can help in giving an insight into the mechanisms of magnetization reversal.

One can define a function $g(\theta_{gh})$ representing the angular dependence of H_c as:

$$H_c(\theta_{gh}) = H_c(0) \, g(\theta_{gh})$$

For a mechanism involving coherent rotation, the function $g(\theta_{gh})$ was calculated by Stoner and Wohlfarth [1]:

$$g(\theta_{gh}) = \frac{1}{[\sin^{2/3}(\theta_{gh}) + \cos^{2/3}(\theta_{gh})]^{3/2}} \qquad (\theta_{gh} \text{ corresponds to } \psi \text{ used by Kronmüller [7]})$$

When θ_{gh} is varied between 0 and $\pi/4$, the critical field decreases from H_A to $H_A/2$ and then rises to its initial value at $\pi/2$ (figure 21a). In the case where nucleation takes place in a defect one can suppose that coherent rotation of the moments takes place in the activation volume when the critical field reaches H_A of the defect and the angular dependence of $H_c(\theta_{gh})$, to a first approximation, is thereby given by the previous relationship. However, if domain wall formation is taken into account we obtain a divergence at higher angles -figure 21a.
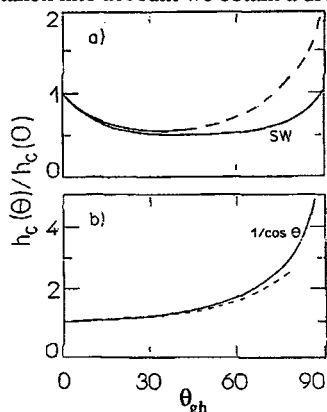

Figure 21 - Calculated angular dependence of the coercive field a) Full Line - SW, dashed line - SW + domain wall formation b) Full line - pinning, dashed line - allowing for moment rotation. After [19]
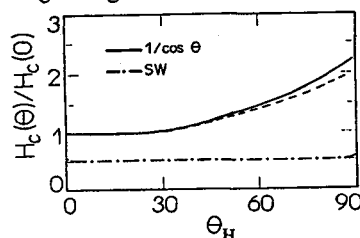

Figure 22 - Effect of the distribution of c-axes in a magnet on the coercive field.

In the case of pinning - de-pinning, one can suppose that the coercive field is considerably smaller than the anisotropy field. The rotation of the moments towards the field direction can thus be neglected and the coercive field varies simply as $1/\cos\theta_{gh}$ (figure 21b). If H_c manages to reach a significant fraction of H_A, the moments at both extremes of the domain wall turn towards the field direction hence the resulting angular dependence of H_c is less marked (in particular at large angles) than that which corresponds to $1/\cos\theta_{gh}$ (figure 21b)

In a magnet the easy axes of the grains are more or less distributed about the average magnetization direction. This distribution has an important effect on the angular dependence of H_c [19] as can be seen in figure 22: In the case of coherent rotation H_c remains roughly constant and independent of θ_H (the angle between the applied field and the c-axis of the magnet), whilst in the case of a $1/\cos\theta_{gh}$ variation of the individual grains, H_c increases with θ_H by a factor of 2 between 0 et $\pi/2$, slightly less if one considers a small rotation of the moments.

The results which have been obtained with NdFeB, SmCo5, and Ferrite magnets, seem to be in better agreement with the $1/\cos\theta$ law rather than with the models considering coherent rotation of the magnetization. This seems to indicate that nucleation might be a process for which the schematic description (simple coherent rotation of the magnetization in a small volume) is inadequate.

Conclusion

Over the last few years, many studies have been carried out on the mechanisms of coercivity in permanent magnetic materials, in particular within Europe thanks to the Concerted European Action on Magnets programme (CEAM).

These studies are primarily based on experiment. The various approaches have resulted in a certain consensus on several points such as: the fundamental role of the microstructure and therein the importance of defects, the existence of an activation volume which is a critical nucleus, acting as a seed for magnetization reversal and the large contribution of the dipolar interactions to the critical field, without which coercive fields could be almost twice as large in the case of Nd-Fe-B magnets at room temperature.

However there remain many points still to be unravelled: One important one is to understand in what way the mechanisms implicated in magnetization reversal bring into play intrinsic properties different (or non-proportional) to those of the principal phase. In any case one is led to consider that the temperature dependence of the coercive field is not a method appropriate for the discrimination between the models.

The analysis of the angular dependence of the coercive field, considering the different behaviours observed, remains today poorly understood and thus little exploited. The use in particular of model systems could lead towards a better understanding.

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