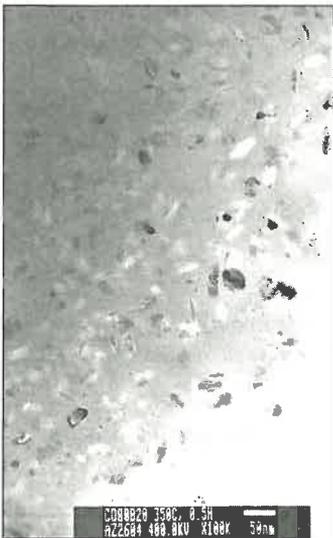


Magnetism in nanocrystals

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Physics of magnetic materials portends the improvement of the magnetic properties useful for applications. These can be roughly classified in two big groups [1], i) magnetic flux multiplication (magnetic cores) and ii) magnetic storage of either energy (magnets) or information (magnetic recording). There also exist other sophisticated devices as sensors and actuators that, being based on magnetic properties of materials as magnetostriction or giant magnetoresistance, GMR, are widely used in electronic and microelectronics circuits [2]. For flux multiplication soft magnetic materials characterised by low losses and coercivity, H_c , are required; whereas, high H_c and energy product are the relevant properties of hard magnetic materials used for storage. Control of coercivity has been carried out by playing with the parameters that governs the magnetic anisotropy i.e. composition and structure [3]. The possibility of tailoring anisotropy has allowed us to spread nowadays the available spectrum of coercivities over seven orders of magnitude. But what is really remarkable is that the softest materials $Fe_{79}Zr_7B_9$ ($\mu_0 H_c = 10^{-7} T$) as well as the hardest material $Fe_{79}Nd_7B_9$ ($\mu_0 H_c = 10 T$) known in 2000 are obtained from amorphous alloys with closely related compositions. Notice that only a difference of 7 at. % in content gives rise to a difference of seven orders of magnitude in coercivity. This enormous difference is due to the nanocrystalline structure obtained by partial devitrification of the initial amorphous state. Both types of samples consist of a soup of nanograins embedded in a softer matrix [4]. Therefore, it can be concluded that nanocrystalline materials form an outstanding group of magnetic materials as concerns applied magnetism [5].

In this review the basic definitions and classification of nanocrystalline materials as well as their more remarkable intrinsic characteristic are introduced. Finally two examples of nanocrystalline magnetism related to pure Fe ferromagnetic grains are described. The first example deals with the amazing magnetic behaviour observed at low temperature in nanocrystalline Fe and the second one is related to the anomalous thermal dependence of the spontaneous magnetization in nanosized Fe ribbons embedded in a Cu matrix. It is shown that such anomalous thermal dependence can be explained by



◀ **Fig. 1:** Nanocrystalline system formed by Co nanograins embedded in a Co rich CoB amorphous ribbon as observed by TEM (Zern *et al.* [4])

taking into account the combined effect of size and shape on the spin wave thermal excitation. These two examples are expected to be useful to illustrate the relevance of nanocrystals not only on technical magnetism but also on more fundamental aspects of magnetism.

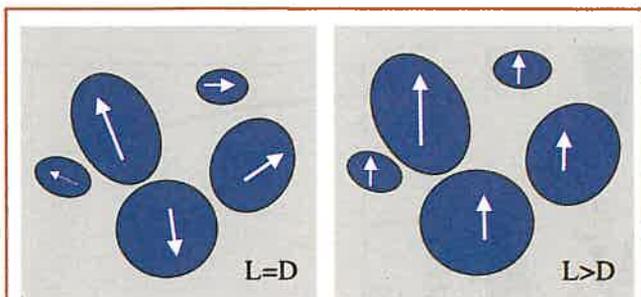
A polycrystalline solid formed by an isotropic distribution of nanometric sized grains is known as a nanocrystalline material. Figure 1 shows an assembly of Co nanograins embedded in a Co rich amorphous matrix. The structure corresponds to the partial devitrification of amorphous $Co_{80}B_{20}$ obtained after annealing at 630 K for 30 minutes. In general nanocrystals are connected between them by either grain boundaries or a different matrix. In the case of ferromagnetic nanocrystals, the matrix can be magnetic or non magnetic. The strength of the exchange coupling between the magnetization of the adjacent ferromagnetic grains strongly depends on the average thickness, d , and the magnetic nature of the matrix. It is important to remark that the macroscopic properties of nanocrystalline ferromagnetic samples are governed by the

nanometric dimensions of the grains and also by the degree of ferromagnetic coupling between grains. Hence, the matrix nature becomes an extremely important parameter.

The relevance of nanocrystals in magnetic research is associated with the control of the magnetic and magneto-transport (magnetoresistance [6] and tunnel magnetoresistance [7]) properties. Before going into deeper details, let us state the two outstanding physical aspects of nanocrystalline materials. First, is the high value of the ratio, N_s/N_v , between the atoms at the interface, N_s , and the total number of atoms N_v . If we call D the average grain size and a the inter-atomic distance, N_s/N_v varies roughly as a/D that, when D is a nanometric distance, can reach values as high as 30%. Second, there is coincidence between the grain size scale with the exchange correlation length, L_0 , or domain wall width of the bulk ferromagnetic materials with the same composition as that of the nanocrystals [8]. In fact L_0 is the distance at which any local disturbance in the collinear ferromagnetic order propagates through the material.

The actual exchange correlation length in the nanocrystalline sample, L , can be either larger or shorter than L_0 , depending on the magnetic nature of the matrix interconnecting the grain. Let us restrict the discussion to those nanocrystalline materials with grain size D very close to L_0 and average distance between grains, d of the order or smaller than D . The following two cases, described in Figure 2, can be distinguished

- i) First case: $L < D$. This happens always for $L_0 < D$ [9], as, for example, is the case of nanocrystalline $Fe_{79}Nd_7B_9$. But, even if $L_0 > D$, it is also possible that $L < D$ if the matrix does not transmit exchange between grains (non magnetic matrix). For this case the grains are ferromagnetically decoupled and should closely behave as isolated magnetic single domains [10]. In general, the systems for which $L < D$ would exhibit high temperature superparamagnetism, low temperature hard magnetic behaviour



▲ Fig. 2: Schematic magnetization arrangement in A) a decoupled nanocrystalline system ($L=D$); the magnetic moment of each crystallite align along the easy axis and B) in a coupled system ($L \gg D$) in which the ferromagnetic arrangement is achieved by exchange interactions that overcome anisotropy.

and giant magnetoresistance, GMR [6]. The particles are only coupled through magnetostatic interactions whose strength depends on the particle dilution or average intergrain distance, d [11].

ii) $L > D$. This case only holds under two independent conditions, a) $L_0 > D$ and b) the matrix is a good exchange transmitter (soft ferromagnetic matrix). In this case all the grains contained in L^3 are exchange coupled among them. The magnetization process is collective and the average anisotropy falls from the anisotropy of an isolated nanograin k down to $k^* = k/N^{1/2}$. Under the alignment effect of the exchange interaction between grains the magnetic moments tend to arrange in a ferromagnetic structure. Since the easy axis fluctuates in orientation from one grain to the adjacent (random anisotropy), the exchange effect is counterbalanced by the misalignment tendency exerted by the anisotropy at each nanograin. When the exchange is stronger than the local anisotropy, k , the average anisotropy, k^* , decreases as expected from random walk considerations [12]. Therefore, it can be concluded that the extremely soft magnetic character of nanocrystalline $Fe_{79}Zr_{17}B_4$ is due to the effect of random anisotropy.

In order to illustrate the influence of the nanostructure in the magnetic properties pure iron has been found to be an excellent example. In fact it is somehow amazing that Fe, the oldest known ferromagnetic metal that has been considered the archetype of a ferromagnetic material, exhibits new and singular magnetic properties when it is in the form of nanostructures. Indeed, recent

experiments performed on nanocrystalline Fe systems obtained by different methods have shown that intrinsic properties, such as the thermal dependence of the spontaneous magnetization, and technical aspects, as magnetic softness, are strongly modified by the nanometric scale of the Fe grains.

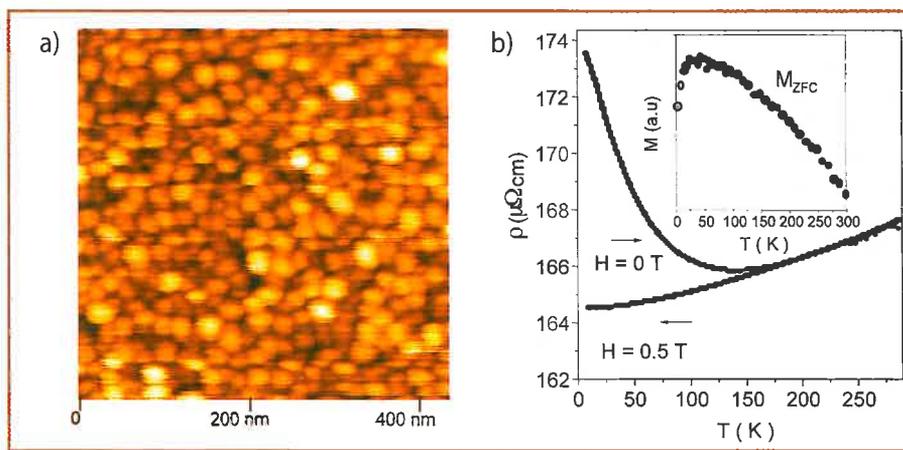
Let us start with the case of pure nanocrystalline Fe in which the contact between grains takes place through the grain boundaries that act as matrix. After measuring the thermal dependence of the magnetization under weak applied fields after field cooling, FC, and zero field cooling, ZFC, processes, a dramatic hardening of the samples was observed for temperatures below 70 K. The hardening was detected by the decrease of the real component of the susceptibility and the dramatic drop of the thermoremanence. It is important to remark that this low temperature anomaly has been observed in nanocrystalline Fe obtained by two very different methods such as ball milling [13] and sputtering [14]. Mössbauer spectroscopy carried out on strongly milled Fe powders with average grain size of

Fe, the oldest known ferromagnetic metal... exhibits new and singular magnetic properties

12 nm indicated that 13 at% of the Fe atoms were subjected to a hyperfine field different to that of regular α -Fe, ie. 33 T. This result suggested that 13 at% was the percentage of atoms located at the grain boundaries that, due to fluctuations of interatomic distances and coordination angles, exhibited a broad spectrum of hyperfine fields. Since magnetism is known to be extremely sensitive to short range order,

the hardening was suggested to be due to spin disorder being frozen-in within the boundaries at low temperature. Spin disorder must drastically decrease the ferromagnetic exchange connection between grains giving rise to a shortening of L that promotes magnetic hardening. In order to confirm this suggestion electrical resistivity measurements were performed in thin films formed by (110) Fe islands grown by sputtering onto Al_2O_3 (0001) substrates in an ultrahigh vacuum triode sputtering system at 980 K. Figure 3-a shows the structure of the film observed by Atomic Force Microscopy and Figure 3-b illustrates the thermal dependence of resistivity measured during field cooling and zero-field cooling processes. The enormous increase of resistivity observed at low temperature under the zero-field cooling procedure and not observed when the cooling is achieved under a field can be explained by the proposed spin disorder at the boundary that also

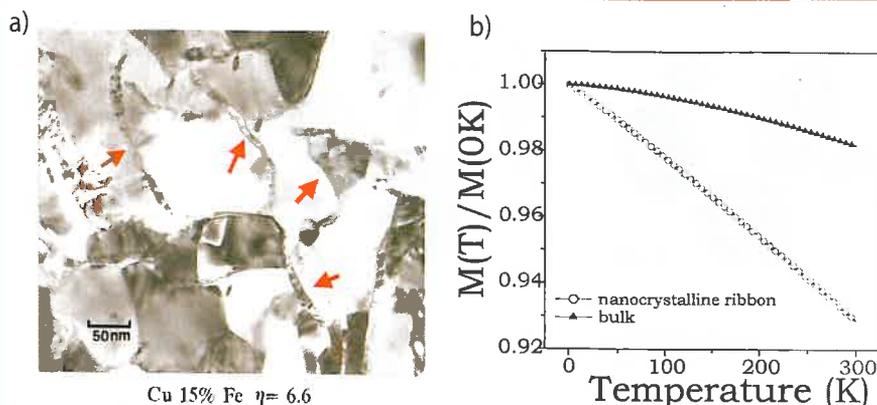
features



◀ Fig. 3: a) AFM image of the Fe grains; b) Electrical resistivity measured during zero-field cooling and field cooling. The dramatic increase of resistivity observed at low T in the zero-field cooling curve is originated by the disorder spin structure frozen in the grain boundaries.

► Fig. 4:

a) Scanning Electron Microscopy image of the composites. The nano-ribbon of Fe can be observed at the grain boundaries of Cu grain;
 b) Thermal dependence of the reduced magnetization for bulk and nanocrystalline ribbon shaped Fe.



contributes to increase the scattering with conducting electrons and therefore to enhance resistivity. Therefore, at low temperatures the exchange correlation length and the electron mean free path are remarkably reduced in nanocrystalline Fe. These effects are consequences of the low temperature disordered distribution of those spins located at the structurally disordered grain boundaries. It is obvious that this effect is not appreciable in polycrystalline Fe for which the percentage of atoms at the boundaries is negligible and the exchange connection between grains does not have any significant influence on the macroscopic magnetic properties.

Finally let us discuss the effect observed in Fe ribbon shaped nanocrystals embedded in a Cu matrix. Wire Cu-15 vol%Fe composite alloys have been produced by heavy working of spray-deposited billets. With the cold working proceeding the spheroidal Fe particles, about 1 μm in size, become drawn into elongated, flattened ribbons with progressively smaller cross section and (1,1,0) texture [15]. Figure 4-a shows the microstructure of the composite and Figure 4-b summarises the experimental thermal dependence of the reduced spontaneous magnetization, $M(T)/M(0K)$, for bulk Fe and that measured in Cu-Fe composites formed by Fe grains with 3.5 nm thickness, 27 nm width and 5×10^3 nm length. The nanocrystalline sample exhibits an almost linear decrease of magnetization with temperature, T , instead of the usual $T^{3/2}$ behavior predicted by the Bloch law and experimentally observed in bulk samples. This effect can be understood by considering that spin waves with wavelength larger than the nanocrystals dimensions can not be excited. At low temperatures the Planck distribution indicates that only large wavelengths are excited to a considerable extent. Thus, in nanometric spheroidal particles the magnetization is stable at low T up to that T at which spin waves of the sample dimensions are allowed to be excited. However, in the case of ribbon shaped nanocrystals, the spin waves excited at low T can only be those with wave vector oriented along the particle length. But, as is well known, the number of spin waves excited in one dimension diverges in the limit of very large wavelength. Therefore, the number of spin waves excited within the T interval in which all of them are one dimensional is enormous. Such T interval increases with the aspect ratio.

We have shown two examples that illustrate the sensitivity of Fe magnetism to short range order. The spin disorder at grain boundaries of Fe nanocrystals indicates the dependence of the magnetic structure on the topological short-range order. The shape influence, at the nanometric scale, on the spin-wave excitation rate also emphasises the relevance of nanocrystalline structure for controlling the intrinsic magnetic properties of the materials.

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