

Magnetically Ordered fcc Structure at the Relaxed Grain Boundaries of Pure Nanocrystalline Fe

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Pure Fe powders, milled down to 10 nm crystallite size, have been analyzed by a combination of Mössbauer spectroscopy, high resolution transmission electron microscopy, and magnetization measurements. After annealing the as-milled powders at 570 K for 1 hour, a new phase is identified with a hyperfine field of 21 T, a lower magnetic moment than bulk Fe, a magnetic order-disorder transition temperature of about 500 K, and a fcc crystal structure. It is tentatively interpreted as a new magnetically ordered phase of Fe. [S0031-9007(98)07721-7]

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The preparation of materials with unusual structures is one of the present challenges of the physics of small systems since modifying the atomic environment often results in substantial changes in the physical properties. Clusters, epitaxial layers, granular structures, and nanostructures are examples of systems whose crystalline structures can differ from the bulk [1]. Nanostructures, in particular, provide an excellent playground for the purposeful modification of atomic environments: When the size of a crystal is reduced to a few nanometers, the number of atoms located at the surface (or at the grain boundary, in the case of nanocrystalline materials) is comparable with that in the core [2].

Among those presenting different phases, Fe is one of the most investigated materials. Under normal conditions, up to about $T_0 = 1183$ K, ferromagnetic bcc Fe (α -Fe) is the only phase present. Above T_0 , a fcc phase (γ -Fe) appears, that remains stable up to 1663 K. The magnetic and structural properties of fcc iron at temperatures lower than T_0 are still an open question. It has been theoretically predicted [3] that fcc iron could exist in, at least, two different states: a high-moment, high-volume state [$\mu = (2.3-2.8)\mu_B$, lattice constant ≥ 3.6 Å] and a low-moment state ($\mu \leq 1.6\mu_B$) with a lower lattice constant (between 3.5 and 3.6 Å). Other calculations suggest a monotonic increase of the magnetic moment with the lattice constant [4]. The experimental situation is far from clear. An antiferromagnetic low-moment (around $0.7\mu_B$) state—denoted γ_1 —with a Néel temperature of about 67 K has been identified, for example, in small fcc Fe precipitates in supersaturated Fe-Cu alloys [5]. On the other hand, there is not yet experimental evidence for the existence of a ferromagnetic fcc Fe state (usually denoted γ_2), although hints of its presence may be obtained from the study of certain Fe solid solutions which adopt the fcc structure (such as Fe-Ni or Fe-Cu, with variable stoichiometry) or of thin iron films grown on fcc substrates [6–8]. In all the latter cases, relatively minor Fe volumes are forced to adopt the fcc structure by ex-

ternal constraints. In this Letter, we describe transmission electron microscopy (TEM), Mössbauer, and magnetization measurements on pure ball-milled Fe and we report the observation, at room temperature, of a magnetically ordered face-centered cubic phase. This phase forms at the interface between bcc crystals, following the thermally induced rearrangement of the grain boundary region. To our best knowledge, it is the first time that such a phase is identified in pure iron under solely internal constraints.

Nanocrystalline iron was prepared by ball milling 99.999% purity coarse-grained iron powders for 8 hours in a hardened tool steel vial with a SPEX mixer mill, model 8000. Milling was performed at room temperature in an Argon atmosphere, in order to minimize contamination (oxygen below 5 ppm). The final average grain size, evaluated by x-ray diffraction (XRD) through a Warren-Averbach analysis method, was 10 nm. Room temperature Mössbauer spectroscopy was carried out in a standard transmission geometry, using a ⁵⁷Co source in a Rh matrix. Magnetization (M) measurements were performed in argon atmosphere through a LDJ 9500 vibrating sample magnetometer (applied field $H = 10$ kOe). High resolution TEM, selected area diffraction (SAD), and energy-dispersive x-ray analysis were carried out in a Phillips CM200 FEG and a JEOL 4000 EX transmission electron microscope. Both as-milled powders and powders subjected to 1-h subsequent annealing in the 520–670 K range—in flowing Argon—were used as samples for Mössbauer and TEM analysis; they were compacted for easy handling for magnetic measurements. XRD and TEM analysis indicated that, as a consequence of the thermal treatment at 670 K, the average grain size had grown up to 20 nm, in agreement with published results on grain growth in nanocrystalline iron samples obtained under similar conditions [9]. For pure Fe samples, it is practically impossible to avoid some oxidation. Traces of oxide (characterized by TEM as Fe₃O₄) have been estimated to be of the order of 1%.

The collected Mössbauer spectra (Fig. 1) are fitted using one sextet with free hyperfine parameters and a distribution of magnetic hyperfine fields (HFF) in the 0–35 T range. The hyperfine parameters of the sextet correspond to those of bcc Fe (hyperfine field $B_{\text{hf}} = 33.0$ T, isomer shift, relative to a standard iron foil, $=0.00$ mm/s) and, therefore, this component is straightforwardly associated to the nanocrystals, whereas the HFF distribution component is attributed to the grain boundaries (interface) [10]. The error in the relative areas of both components is estimated in 2%. The bimodal character of the HFF distribution of the as-milled powders [Fig. 1(a)] is compatible with the existence of different environments for the Fe atoms at the interface. In particular, the contribution at 26 can be ascribed to a reduction of the coordination number [11], whereas the spreading of the distribution around 33 T suggests that for a number of atoms at the interface, the surrounding environment is not largely different from that of bcc bulk

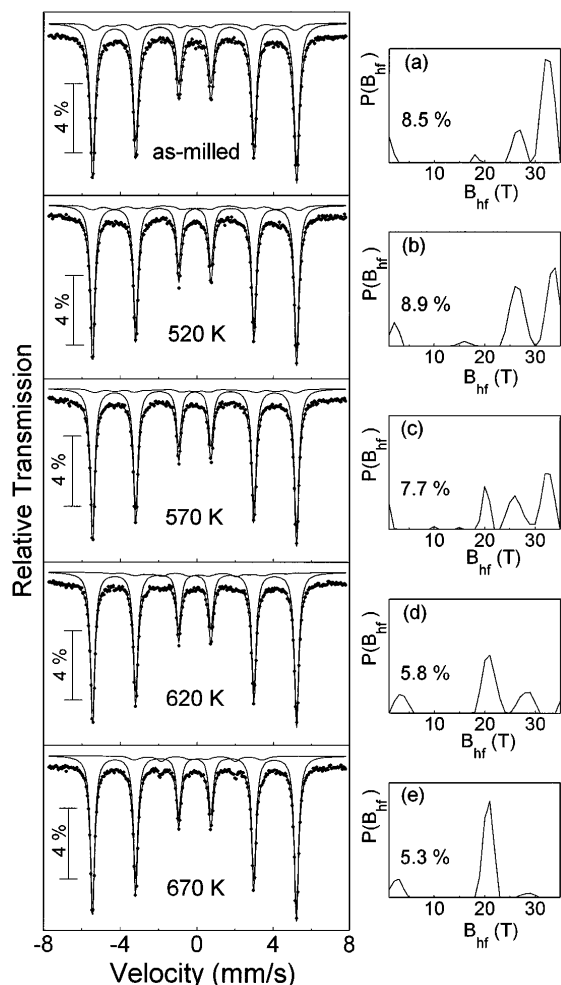


FIG. 1. Room temperature Mössbauer spectra (left-hand side) and relative hyperfine magnetic field distributions (right-hand side) corresponding to as-milled Fe and to milled powders subsequently subjected to 1-h thermal treatments at the indicated temperature. Percentages are relative to the resonant area linked to the hyperfine field distribution.

iron, probably due to a closer location to the core of the nanocrystals. In short, the Mössbauer results for the as-milled powder are consistent with a wide distribution of nearest-neighbor distances at the grain boundary together with a reduction of short range order [12].

Following the annealing treatments, the HFF distribution profile changes dramatically. After the thermal treatment at 570 K [Fig. 1(c)], a narrow peak centered on 21 T becomes visible. With increasing annealing temperature, its relative weight increases at the expense of the original contributions at higher fields [Figs. 1(c)–1(e)]. The values of the relative resonant area linked to the HFF distribution (which are assumed to be proportional to the interface volume fraction) are also reported in Fig. 1: They do not include the small contributions (of the order of 1%) at fields lower than 5 T, attributed to iron oxides. These data strongly suggest that a rearrangement of the atoms at the interface occurs mainly in the 570–670 K temperature range. As a Mössbauer sextet spectrum is characteristic of a magnetically ordered configuration, the appearance of the peak at 21 T in the HFF distribution indicates that, during grain boundary thermal relaxation, not only does the bcc configuration recover, but also a magnetically ordered Fe phase, unlike the usual α phase, is formed. After high temperature annealing—1 h at 920 K—only the bcc Fe sextet is observed, which implies a full recovery of the Mössbauer spectrum of Fe. At the same time the nanograins are seen to grow up to such a dimension (several tens of nanometers) that the interface volume fraction is no more comparable with that of the α -Fe nanocrystals.

We have monitored the transformation kinetics leading to the new phase by measuring the isothermal magnetization [13] at $T = 560$ K, as illustrated in Fig. 2. After 20 hours annealing, M has decreased about 13%, with respect to its value at $T = 560$ K, at the very beginning of the measurement. Once the sample is cooled down again to room temperature, the magnetization of the sample—at $H = 10$ kOe—is about 3% lower than before the annealing (Fig. 2, inset). When a magnetization measurement is performed in a further isochronal annealing of the same sample, a decrease of M is clearly observed at ~ 500 K, in agreement with an earlier report [10]. We attribute this decrease to the magnetic order-disorder transition of the new phase that is formed during the isothermal measurement and which, therefore, is interpreted as *ferromagnetic*. Accordingly, the considerable reduction of M —about 13%—in Fig. 2, can be explained assuming that the isothermal measurement has been carried out at a temperature higher than the Curie temperature of the new phase that is being formed in the course of the measurement. It is worth remarking that the volume fractions of the new fcc phase in both the Mössbauer and the magnetization samples cannot be directly compared because not only the techniques but also the thermodynamics conditions under which both samples have been prepared are different.

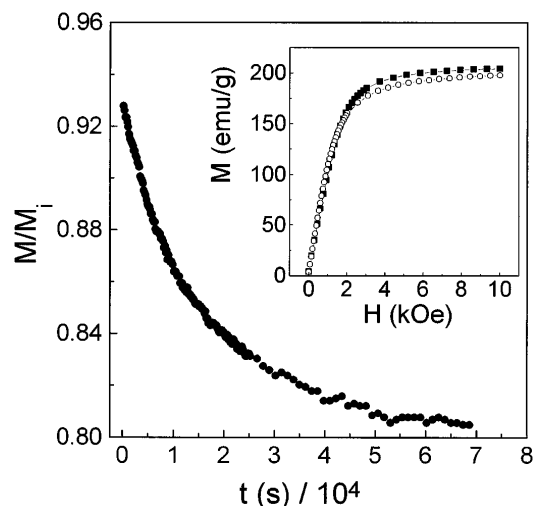


FIG. 2. Time dependence of the magnetization (M) at $T = 560$ K of nanocrystalline Fe (applied field $H = 10$ kOe). M_i is the room temperature magnetization value of the as-milled sample. In the inset: Room temperature M as a function of the applied magnetic field H for the nanocrystalline sample before (full squares) and after (open circles) the isothermal measurement.

In order to obtain structural information of the new Fe phase, a high resolution TEM analysis on annealed (1 hour at 670 K) and, for comparison, on as-milled powders was carried out. Figure 3 is a high resolution image of the annealed sample. Lattice and moiré fringes, due to the different grain orientations, are observed. The TEM contrast of the as-milled sample is very similar except that it has a smaller grain size (grain sizes are 6–10 nm for the as-milled sample and 10–20 nm for the annealed one, in good agreement with the XRD results). The crystal structure is determined from SAD patterns. Usually, one obtains a ring pattern which can be fitted with a random distribution of bcc and fcc crystals of lattice parameters of 2.87 ± 0.05 and 8.40 ± 0.05 Å, which are essentially the same as those of bulk bcc Fe

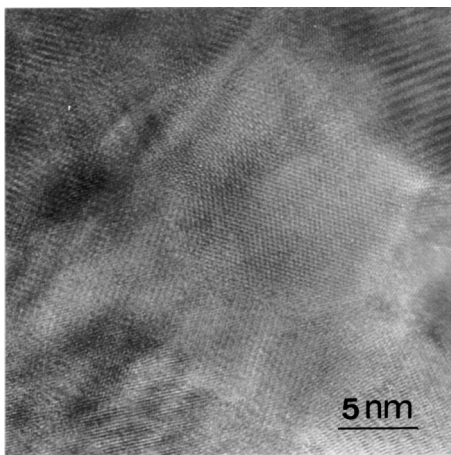


FIG. 3. High resolution image of the annealed sample. Lattice and moiré fringes due to the different grain orientations are observed.

and fcc magnetite (Fe_3O_4). The rings corresponding to the latter are weaker and, often, absent. It is likely that the Fe_3O_4 —when present—is in the form of very small crystallites, superparamagnetic at room temperature as suggested by the presence of the contributions at very low fields in the HFF distribution (Fig. 1).

In some thin regions of the annealed sample—free of oxygen traces—still another type of SAD pattern is observed. An example is shown as Fig. 4(a), where faint rings are visible along with spots corresponding to the superposition of two structures: One of them is the usual Fe bcc phase close to the (111) orientation and the other, as derived from the encircled spots of the figure, is identified as a fcc structure of lattice parameter 3.51 ± 0.05 Å,

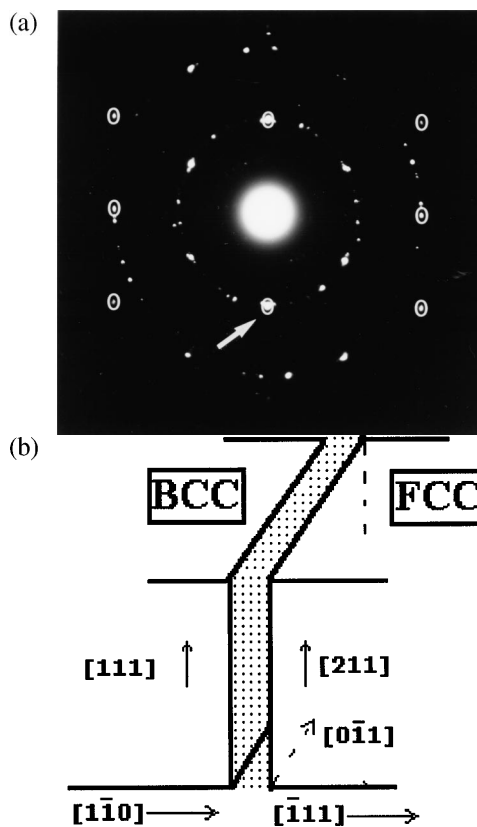


FIG. 4. (a) SAD pattern of the annealed sample. The rings correspond to the Fe bcc phase close to the $[111]$ zone axis orientation; the encircled spots can be indexed in terms of the $[211]$ zone axis electron diffraction pattern of a fcc structure of lattice parameter 3.51 ± 0.05 Å. The arrow points to the superposition of $(110)_{\text{bcc}} \parallel (111)_{\text{fcc}}$ reflections (b). Direct lattice construction associated to the geometry of (a). The shaded area corresponds to the plane of growth. The spreading of the distribution around 33 T suggests that for a number of atoms at the interface, the surrounding environment is not largely different from that of bcc bulk iron, probably due to a closer location to the core of the nanocrystals. The contribution observed at 26 T can be explained by a reduction of the coordination number [11], a wide distribution of nearest-neighbor distances at the grain boundary together and/or a reduction of short range order [12], although the experiments reported here do not allow a definite elucidation of the controlling mechanism.

close to the (211) orientation. Let us remark that the superposition of the two structures explains the apparent extra intensity of the first ring of bcc iron—compared to the one expected for this structure—as the interplanar distance of the {110} planes of the bcc phase is very near to the {111} of the fcc one. Note that, even in this case, the spots corresponding to both structures can be clearly separated [see arrow in Fig. 4(a)].

Further insight can be gained by observing—in the diffraction pattern—that both bcc and fcc structures are coherent with an orientational relationship of $[110]_{\text{bcc}} \parallel [111]_{\text{fcc}}$. A straightforward geometrical analysis [Fig. 4(b)] reveals that this relationship automatically implies that the two most-densely-packed planes of the two structures— $(110)_{\text{bcc}}$ and $(111)_{\text{fcc}}$ —superimpose on each other. It immediately suggests a simple mechanism by which bcc grains—bounded by compact planes—act as nucleation centers for fcc crystallites. Most epitaxial studies of bcc materials grown on fcc substrates (or v.v.) agree with this compact-on-compact rule. Moreover, calculations [14] predict some preferred orientational relationships at bcc-fcc interfaces. Our data are consistent with the so-called *R*-30 orientation, in which a compact direction of the bcc structure, for example $[111]_{\text{bcc}}$, lies halfway between the compact rows of the fcc, i.e., along $[211]_{\text{fcc}}$.

We propose that both the 21 T hyperfine component and the fcc spots originate from regions of ferromagnetic fcc Fe structure (γ_2 -Fe). This structure is orientationally related to bcc grains and results from grain boundaries rearrangements which occur in the 570–670 K temperature range. The reduced magnetization value (Fig. 2, inset), measured at room temperature, after the prolonged annealing at 560 K, indicates that the magnetic moment for Fe atom in the fcc configuration is lower than in the as-milled state. Preliminary SQUID measurements, now in progress, confirm this result and reveal also that the moment is lower than in the bcc configuration. Although the formation of fcc Fe is unexpected, recent work on ferromagnetic fcc Fe-Cu alloys produced by mechanical alloying yielded fields of 21–22 T [6,15] supporting the assignment of the 21 T peak observed here to ferromagnetic fcc Fe. Also, the observation of some unusual phases in grain boundaries have been recently reported, e.g., a bcc structure at the grain boundary of a Cu bicrystal [16].

In summary, we have shown that, following annealing of nanocrystalline Fe, along with the usual bcc grains, regions with a new structure consisting of magnetically ordered fcc Fe appear. This structure is rather stable and transforms into bcc Fe only after thermal treatments in the region of 900 K. Mössbauer data show that up to 5% of the volume fraction of the sample annealed for 1 h at 670 K can be related to this fcc phase.

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