Magnetic behavior of metastable fcc Fe-Cu after thermal treatments

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(Received 29 March 1993; revised manuscript received 30 April 1993)

A ferromagnetic and supersaturated fcc $Fe_{51}Cu_{49}$ solid solution has been obtained by mechanical alloying. After subsequent thermal treatments the fcc phase undergoes a spinodal decomposition which finally, at 780 K, yields a mixture of fcc and bcc phases. In this work, a systematic magnetic study is carried out on samples at different decomposition states in order to determine the process of transformation into the stable phases. We observe a 20% maximum diminution on the magnetic moment with increasing temperatures of the thermal treatment. The Mössbauer spectrum taken at 8 K shows that 20% of the Fe atoms are in a nonferromagnetic state. On the other hand, upon heating up to 723 K the room-temperature coercive field increases dramatically to 640 Oe, and after cooling down to 10 K it decreases to 270 Oe. Deviations from the $T^{3/2}$ law in the temperature dependence of the magnetization have been observed. This behavior is explained by fluctuations in composition due to the spinodal decomposition, which lead to fluctuations of the magnetic order parameters, i.e., magnetic moment and Curie temperature.

I. INTRODUCTION

Although iron and copper are almost immiscible in the equilibrium state, Uenishi *et al.*,[1] Yavari, Desré, and Benameur[2] and Eckert *et al.*[3] have recently produced fcc Fe-Cu solid solutions by mechanical alloying. Thin films were previously obtained by vapor deposition (Chien *et al.*[4]).

Several authors have reported magnetic measurements on as-milled samples in a broad compositional range. Uenishi *et al.*[1] have shown that the magnetic moment for the Fe atom is around $2.2\mu_B$ for Fe contents higher than 50% Fe, but it falls to zero for less than 20% Fe. Chien *et al.* have shown that the Curie temperature is very sensitive to the composition.[4] For Fe contents higher than 70% the solid solution is bcc, while for contents lower than 60% it is fcc. For intermediate compositions both phases coexist.

Yavari, Desré, and Benameur[2] show a near equality of the magnetic moment at room temperature for both the fcc phase and its decomposed state. By considering the difference in Curie temperatures between the fcc Fe-Cu phase and α iron, which are, respectively, about 500 and 1040 K, the reported equality of magnetic moments at 300 K suggested to us the existence of crossover in the magnetization curves at lower temperatures. In order to analyze a possible leakage of iron magnetic moment at intermediate states of the fcc Fe-Cu decomposition process, a study of the magnetization behavior of fcc Fe-Cu after thermal treatment is performed in this work.

II. EXPERIMENTAL TECHNIQUES

Samples were prepared by mechanical alloying of pure Cu in thin foil form and Fe powder in a Fritsch vibrating ball mill modified to allow vacuum levels of 10^{-5} torr in the vial before introducing an operating pressure of 1.5 atm of argon. Milling was done in a stainless-steel vial with a 6-cm steel ball. The milling process was monitored by x-ray diffraction (XRD). After milling for 360 h, only Bragg peaks of the fcc solution remain.

In order to avoid overlapping of peaks, high-resolution x-ray-diffraction patterns were obtained at very low scale velocity using Cu $K\alpha$ radiation. Additional information is obtained from the peak widths. Grain size was estimated using Scherrer's formula, from the Cu (111) and Fe (110) peaks.

The thermal stability was examined by differential scanning calorimetry (DSC), at a scanning rate of 20 K/min up to 923 K, under pure argon flow; treatments at different temperatures were carried out in the DSC in the same conditions. The heat treatments of samples for magnetic measurements were performed in the same calorimeter by heating up at 20 K/min to 423, 523, 623, 723, and 923 K and cooling down to 300 K.

Low-temperature magnetic measurements and hys-

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teresis loops have been performed in a superconducting quantum interference device magnetometer from 5 to 300 K and in a Faraday magnetometer for higher temperatures. In order to determine the environments of Fe atoms, Mössbauer spectroscopy was performed at 8 and 300 K.

Microstructural studies and analysis were done by means of a scanning electron microscope (SEM) equipped with energy dispersion x ray (EDX), on samples without preparation as well as on samples set up in resin and polished. Thermogravimetric measurements were carried out to check for possible oxidation during the thermal treatments.

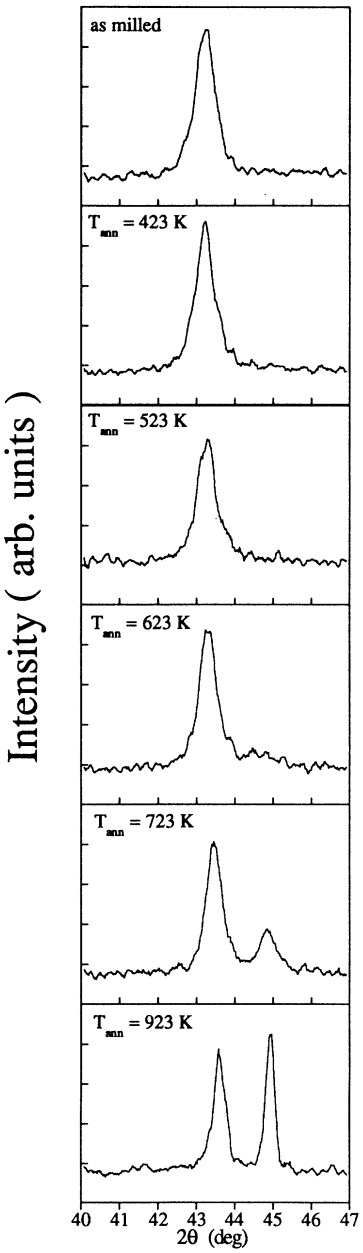

FIG. 1. XRD patterns of as-milled and heat treated samples.

III. RESULTS

The sample milled for 360 h has a composition of $Fe_{51}Cu_{49}$ (at. %), according to EDX analysis, and a fcc structure with Bragg peaks shifted towards lower angles than those of pure Cu indicating an expansion of the Cu lattice probably due to magnetovolume effects[2] (the bcc Fe atomic size is smaller than that of Cu). Figure 1 shows the (111) peak of the fcc phase. The evolution of the coherent domain size from an initial value of 25 nm (crystal size) with the thermal treatment temperature is shown in Fig. 2. SEM observations show a microstructure typical of mechanical alloyed materials.

The Curie temperature of the alloy was 513 K, and the temperature dependence of the magnetization follows a perfect $T^{3/2}$ Bloch law up to 200 K, as shown in Fig. 3, with an exchange stiffness constant of 96.9 meV Å^2, which is roughly three times smaller than that of pure Fe.[5] The hysteresis loops obtained at 10 and 300 K show that the average susceptibility does not change in the temperature range from 10 to 300 K and indicate that the fraction of nanocrystals exhibiting superparamagnetic behavior is negligible. The small hysteresis, with remanence values below 0.06 times the saturation magnetization and coercive field H_c of 30 Oe at 10 K and 8 Oe at 300 K, points out a negligible structural anisotropy. The lack of structural anisotropy might be a consequence of the disordered distributions of Fe and Cu atoms in the fcc structure. The Mössbauer spectrum at room temperature [Fig. 4(a)], shows a sextet corresponding to a ferromagnetic disordered Fe alloy with a Poisson distribution of neighboring Fe atoms. The fitting of the Mössbauer spectrum has been performed in a similar way to that used by Billard and Chamberod[6] for Fe-Ni disordered alloys, and results in an average hyperfine field of 22.30 T, see Table I.

The DSC trace in Fig. 5 shows an irreversible exothermic reaction with onset at 610 K and peak at 720 K. The enthalpy of this process is 9.7 kJ/mol and it corresponds to the decomposition of the solid solution. Thermogravity showed that oxidation affects to less than 2% of the Fe atoms (the weight increased 0.8% during an-

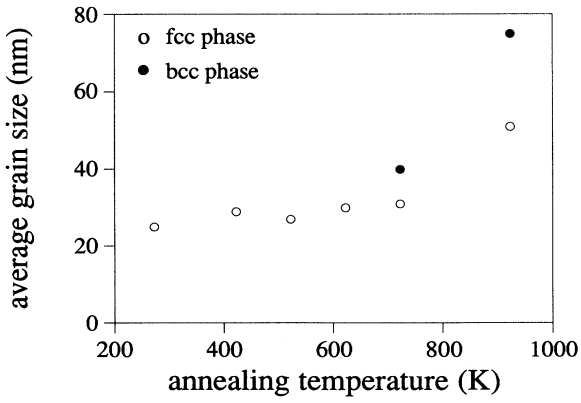

FIG. 2. Average grain size vs temperature of treatment for the fcc phase (○), and the bcc phase (●).

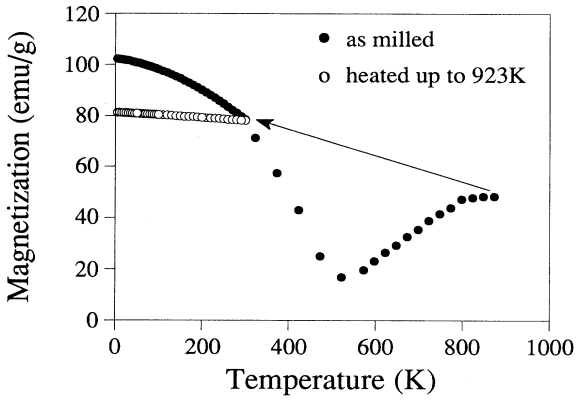

FIG. 3. Low- and high-temperature magnetization measurements of an as-milled sample showing the Curie temperature at 513 K (○), as well as the crossover at room temperature and the lower magnetic moment (○) after the precipitation of bcc Fe.

nealing). To follow the transformation the material was heated up to different temperatures ranging from 420 to 925 K.

The XRD pattern (Fig. 1) of the sample annealed at 423 K shows the same 111 peak than the as-milled state, with the same lattice parameter. For samples annealed at 523 and 623 K, only fcc peaks are present with a slight shift toward higher angles with respect to the as-milled material. The grain size increases up to about 30 nm with these thermal treatments. Materials annealed at 423, 523, and 623 K show a similar soft magnetic behavior to as-milled material, following a $T^{3/2}$ Bloch

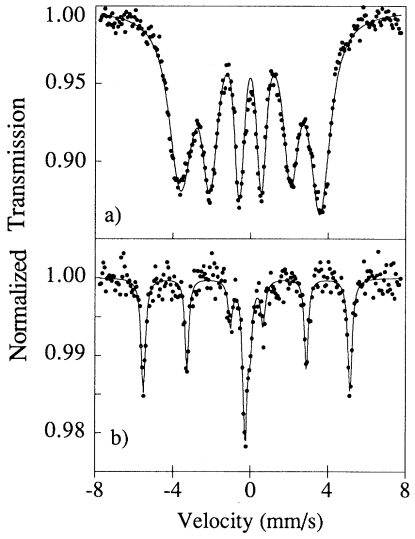

FIG. 4. Room-temperature Mössbauer spectra for (a) as-milled and (b) heated samples. The spectrum in (a) shows a broad distribution of hyperfine fields. The shoulder in the central peak in spectrum (b) shows the existence of a number of nonmagnetic Fe atoms with Cu in the neighborhood (See text).

TABLE I. Mössbauer parameters of the Fe-Cu alloys at room temperature.

	Phases	B_{HF} (T)	IS (mm s^{-1}) (a)	QS (mm s^{-1})
As-milled	fcc Fe-Cu	22.3±0.2	+0.11±0.02	
Annealed At 823 K	bcc Fe	33.0±0.2	−0.002±0.004	
	(b) fcc Fe		−0.06±0.01	
	(c)		+0.01±0.3	0.33±0.04

[a]Relative to α-Fe standard.
[b]Single peak component.
[c]Quadrupole doublet.

law up to 200 K (Fig. 6) with similar Curie temperatures and exchange stiffness constants. However, a decrease in the magnetic moment measured at 5 K with the temperature of treatment is observed. This decrease is about 7% for the material annealed at 623 K.

The XRD pattern for the material treated at 723 K shows an evident shift of the fcc peaks toward higher angles, with a crystal size of 30 nm. A peak corresponding to a bcc phase appears now with an approximate crystal size of 40 nm.

For the material treated at 723 K the dependence of the magnetization with the temperature follows a $T^{3/2}$ behavior up to 200 K (Fig. 6). Magnetic measurements above 300 K (Fig. 7), show a distribution of Curie temperatures up to a maximum of $T_c = 400$ K, and another ferromagnetic phase with T_c higher than 700 K. The latter shows a magnetic behavior similar to that of bcc Fe. The magnetic moment at 5 K is much lower now, being 20% less than the value of the as-milled material. Figure 8 shows the anomalous variation of the coercive field with the temperature of the material annealed at 723 K, showing a high coercive field of 640 Oe at 300 K, a minimum value at 50 K, and a further increase to 260 Oe at 10 K. This value is one third of the value at 300 K, which is not an usual behavior.

For the material treated at 923 K the XRD pattern al-

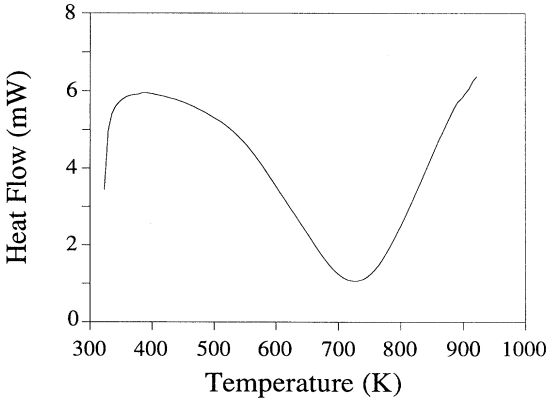

FIG. 5. DSC trace up to 923 K for an as-milled sample.

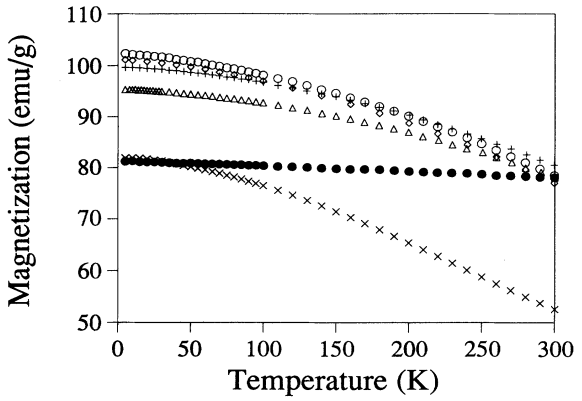

FIG. 6. Temperature dependence of the magnetization for an as-milled sample (○) and after heating up to 423 (◇), 523 (+), 623 (△), 723 (×), and 923 K (●), measured with an applied magnetic field of 5 T.

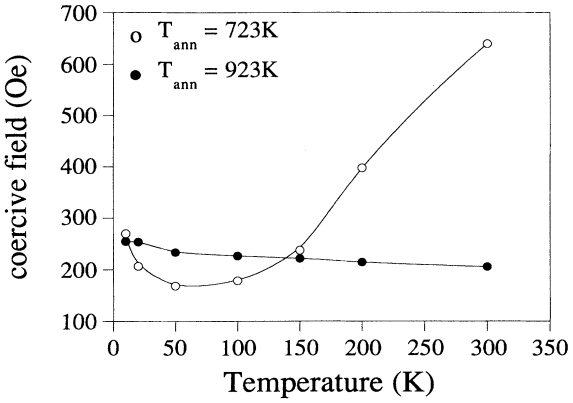

FIG. 8. Temperature dependence of the coercive field for the sample heated up to 723 K (○) and 923 (●).

ready shows the clear presence of bcc Fe, with a crystal size of 75 nm compared to about 50 nm for the fcc phase (Fig. 2). The dependence of the magnetization on the temperature does not show a $T^{3/2}$ law. Instead we found a nearly linear behavior with a variation of only 4% between 5 and 300 K and with an extrapolated Curie temperature which can lie close to that of bcc Fe. The magnetization remains about 20% smaller than the as-milled material. Meanwhile the coercive field does not present any anomalous behavior, decreasing monotonously from 250 Oe at 10 K to 200 Oe at 300 K (Fig. 8).

In order to clarify the anomalous moment reduction found in the material annealed at higher temperatures, Mössbauer spectroscopy, illustrated in Fig. 4(b), was carried out on a sample annealed at 823 K. The spectrum obtained at room temperature shows a perfect pattern of crystalline bcc Fe, with a hyperfine field of 33 T, and a nonmagnetically ordered phase which corresponds to 20% of the resonant area. To elucidate the possible magnetic ordering of this phase at low temperature, Mössbauer spectroscopy was also carried out at 8 K (Fig. 9), without observing any broadening of the nonmagnetic peak, which indicates that this Fe has no magnetic ordering at this temperature. Only a change in the isomer shift (IS) of about 0.1 mm/s is observed on cooling. This change is almost the same for both phases and is related to the second-order Doppler effect.[7]

IV. DISCUSSION

As reported in the literature, mechanically alloyed Fe-Cu solid solutions are ferromagnetic. Probably this behavior is due to the fact that Fe atoms in the fcc lattice adopt an atomic size and *d* band structure, which allow ferromagnetism.[8]

In this work the magnetic characterization of the phases obtained after subsequently annealing of the fcc Fe-Cu phase has been carried out. Three noticeable effects have been observed. (1) The magnetization of 0 K decreases when increasing the temperature of the thermal treatments, (2) The high value of the coercive field at room temperature observed in the sample heated at 723 K, together with their temperature dependence, which makes it three times higher at 300 K than at 10 K, and

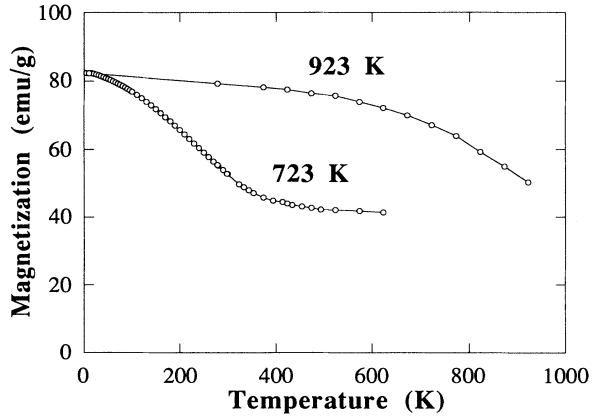

FIG. 7. Low- and high-temperature magnetization measurements for samples heated up to 723 and 923 K.

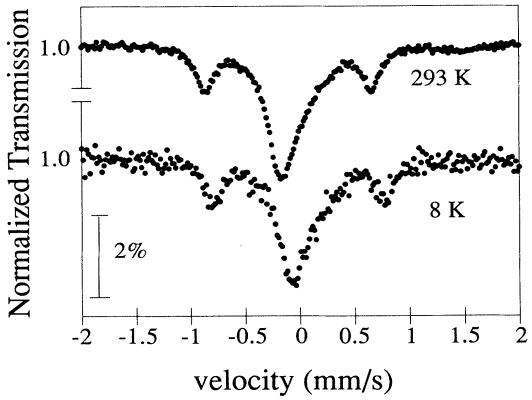

FIG. 9. Low- and room-temperature Mössbauer spectra for sample heated up to 823 K.

(3) The complex behavior of $M_S(T)$, deviating from the $T^{3/2}$ law, for the sample treated at 923 K. These results are not in agreement with a simple decomposition of the fcc Fe-Cu solid solution into bcc Fe+fcc Cu upon heating.

A plausible explanation is found by assuming a spinodal decomposition of the solid solution. For annealing temperatures below 723 K the homogeneous fcc Fe-Cu solid solution will suffer fluctuations of composition prior to a further decomposition into two regions, one fcc Fe rich, which does not change its magnetization, and the other fcc Cu rich, which exhibits lower atomic moment for the Fe. According to Uenishi *et al.*[1] the decay of the magnetic moment of Fe occurs for iron contents lower than 20 at %. The possibility that some Fe atoms could be isolated in a fcc structure in the Cu-rich region, giving no contribution to the magnetization, cannot be left aside.[9]

For higher annealing temperatures the Fe-rich phase will enrich in Fe, and relax into a bcc phase. The fcc-bcc transformation occurs when the Fe content reaches a value of around 70%, according to Uenishi *et al.*[1] and Chien *et al.*[4]. Meanwhile, the Fe-poor phase will still lose more Fe, decreasing its magnetic moment and Curie temperature. If 20 at % of the iron remains in the fcc lattice, its composition will be $Fe_{17}Cu_{83}$, close to the nonmagnetic limit.

The spinodal decomposition could take place in the following way, for the early stages:

$$\text{fcc } Cu_{50}Fe_{50} \rightarrow \text{fcc } Cu_{poor}Fe_{rich} + \text{fcc } Cu_{rich}Fe_{poor} ,$$

and with further decomposition

$$\begin{aligned}&\text{fcc } Cu_{poor}Fe_{rich} + \text{fcc } Cu_{rich}Fe_{poor} \\ &\quad \rightarrow \text{bcc } Cu_{poor}Fe_{rich} + \text{fcc } Cu_{rich}Fe_{poor} \\ &\quad \rightarrow \text{bcc Fe} + \text{fcc Cu} + \text{fcc Fe} .\end{aligned}$$

The coincidence of the x-ray-diffraction peaks corresponding to Cu and fcc Fe, due to the very close lattice parameters of Cu ($a = 3.616$ Å) and γ-Fe ($a = 3.666$ Å), does not allow one to elucidate the presence of fcc Fe.

The structure of the central peak exhibited by the Mössbauer spectrum is compatible with the corresponding γ-Fe analysis of Macedo and Keune[10] obtained by deposition of a few Fe layers on a Cu substrate. In both cases Fe atoms with a certain number of Cu neighboring atoms give rise to a quadrupole-split (QS) component in addition to the single-line one. The IS of the single component line varies with the number of Fe atomic layers in the sample. In our case the value of IS becomes -0.055 ± 0.015 mm/s and will correspond, by extrapolation, to 5–7 atomic distances in the crystallites. Since 20% of Fe atoms behave as nonmagnetically ordered even at 8 K, it is reasonable to assume that these para- or nonmagnetic atoms are responsible for the 20% reduction of the saturation magnetization observed at low temperatures.

However, as can be deduced from the magnetization curves, there is no paramagnetic contribution at low temperature, with more than $0.4\mu_B$ per Fe atom, associated with this central Mössbauer peak. Both observations suggest that the thermal treatments give rise to two types of Fe clusters: (1) α-Fe, bcc, which is ferromagnetic and (2) either nonmagnetic iron on the fcc Cu or γ-Fe. The latter is not antiferromagnetically ordered even at 8 K, but this behavior has been observed in small size γ-Fe precipitates in Ref. 7, and is also likely to be present in our case.

The absence of other crystalline phases in x-ray diffraction, the Mössbauer spectra, and the reported appearance of γ-Fe in other Fe-Cu alloys obtained by sputtering or other techniques suggest the idea of a 20% of γ-Fe segregation, as it seems likely that Fe clusters with small size retain the fcc structure coherent with the surroundings. The sluggish transformation of γ-Fe to bcc Fe in a Cu matrix, which only reaches completion after cold working, was already pointed out by Smith in 1940.[11]

The anomalous behavior of H_c with the temperature for the sample annealed at 723 K, as well as the dramatic increment of the coercive field at room temperature, 640 Oe, which is three orders of magnitude higher than that of the as-milled sample, and its decrease to 260 Oe at 10 K are justified by means of the spinodal decomposition. For this annealing temperature the spinodal decomposition gives rise to the appearance of a bcc Fe-rich phase, as XRD shows, plus some undetected γ-Fe (Ref. 12). Meanwhile the fcc Cu-rich phase, whose average grain size remains unchanged from that of the alloys annealed at lower temperatures, presents fluctuations of composition. The high value of the coercive field can be explained by a structure of single domain bcc Fe-rich phase particles of small size embedded in a fcc Cu-rich phase, mainly paramagnetic at room temperature, which avoids the ferromagnetic coupling between the bcc Fe particles. The increase in the coercive field with temperature is due to the broad distribution of Curie temperatures of the fcc regions. For low enough temperatures the different Cu-rich regions are ferromagnetic, allowing coupling between the bcc nanocrystals; therefore, H_c decreases with increasing temperature (Fig. 8). For $T > 50$ K, H_c increases with temperature, indicating that some regions are becoming gradually paramagnetic and isolating the single domain bcc Fe particles.

Upon annealing at 923 K the grain size of the bcc phase grows up to 75 nm, while the fcc phase gets poorer in Fe, behaving as paramagnetic in all the temperature ranges and isolating the Fe grains. Therefore, the temperature dependence of H_c does not present any anomalous behavior because the particles are not any more single domains, allowing the formation of domain walls inside each bcc Fe grain.

An alternative explanation of the high H_c observed in the samples treated at 723 K is related to the size of the α-Fe precipitates appearing at this temperature, being similar to the thickness of the ferromagnetic walls in the material. This critical size hinders the wall movement and increases the coercivity. Other treatments result in either no precipitates or in larger grains which interact less with the ferromagnetic domain walls.

Concerning the deviation of the $M_S(T)$ behavior from

the $T^{3/2}$ law, two explanations are also possible. In the first one, the fluctuation of exchange parameters and Curie temperatures can add up different contributions, giving rise to an anomalous temperature dependence of the average spontaneous magnetization. On the other hand, the linear dependence observed is typical of bidimensional magnetism, which can be related to the laminar shape of the Fe crystals obtained as a result of the spinodal decomposition of the Cu-Fe alloy.

V. CONCLUSIONS

The spinodal decomposition of the soft magnetic fcc $Fe_{51}Cu_{49}$ solid solution gives rise to three important phenomena: the possible appearance of 20% fcc Fe, the obtention of samples which cover a wide range of magnetic behaviors, from the magnetically soft as-milled sample to a hard magnetic behavior, with H_c of the order of that of the Al-Ni-Co alloys, for intermediate stages of the decomposition, and the observed deviations from the $T^{3/2}$ law. These phenomena are due to the compositional fluctuations, which lead to fluctuations of the magnetic order parameters, such as magnetic moment and Curie temperature, giving rise to noticeable changes in the exchange-correlation length.

ACKNOWLEDGMENTS

The authors wish to thank Professor N. García for useful comments, the Spanish CICYT for financial support under Grant Nos. MAT92-0491, MAT92-0405, and MAT90-0877, and Comunidad de Madrid C175/91.

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