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Shifting the Superparamagnetic Limit of Nanosized Copper Iron Spinel

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Abstract. Using a co-precipitation method, a system formed by nanocrystalline Cu–Fe spinel, grain size $D = 6$ nm, and CuO (15 wt.%) was obtained. A Mössbauer blocking temperature (T_B) of the spinel particles that lies between 100 and 200 K was observed. T_B progressively increases as the sample is subjected to high-energy ball milling, being higher than 298 K after milling for 10 hours. The magnetic results also showed the increment of T_B. The maxima of the in-phase component of the AC susceptibility at T_{max} shift toward higher temperatures with the milling. After 4 hours, this shift is $\approx$70 K for all the AC field frequencies. Simultaneously, the increase in the mean grain sizes (up to $D = 13$ nm) and the decrease of the microstrain level indicate that the degree of crystallinity of the spinel phase increases with the milling. After milling for 10 h, the sample is only composed by copper iron spinel with cubic structure.

Key words: ferrites, spinel, ball milling, nanostructures, Mössbauer spectroscopy.

1. Introduction

Assemblies of ferrimagnetic nanoparticles are systems of great complexity due to the simultaneous presence of competing factors, which display different trends in the system's magnetic response. Because of their use as recording media and other technological applications, they have been intensively studied over the last years [1–4]. Notwithstanding, the relation between the surface effects, the interparticle interactions, the surface spin disorder, the degree of inversion or the exchange coupling to the inner ordered grain cores, are still a matter of controversy. This is probably the reason why the precise response of a particular system cannot be assessed *a priori*, and different methods are used semi-empirically to tailor the desired response of a certain material.

High-energy ball milling has been successfully employed to obtain nanostructured ferrites from the material in its bulk state [1–4], which afterwards displays unusual magnetic behavior. In this work, exploring the reverse way, i.e., starting with nanocrystalline copper ferrite and subjecting it to ball milling, we have care-

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fully analyzed its structural, hyperfine and magnetic properties to investigate the influence of each parameter on the overall behavior of the system.

2. Experimental

Copper nanoferrite was synthesized by a co-precipitation method [6] and a subsequent annealing at 300°C (AP sample). Afterwards, the AP sample was milled in a vibratory horizontal miller (Retsch) with stainless steel vial and ball for different times up to 12 hours. The mass-to-powder ratio was 10 : 1 and the frequency of operation 40 Hz. The vial was opened after selected times $t_m = 2, 4, 8, 10$ and 12 h, to take out sample for analyses. The XRD diffraction patterns were taken in a Philips PW 1710 diffractometer using Cu$K\alpha$ radiation. The Mössbauer spectra in the 25 to 300 K range of temperature were taken in transmission geometry with a nominal 25-mCi ^{57}Co source in a Rh matrix using a Displex closed cycle cryogenic apparatus. Isomer shifts (δ) were calibrated with an α-Fe foil at room temperature. The spectra were fitted using the NORMOS program [5]. The absorbers were prepared with 18 mg/cm^2 of sample. The magnetic measurements were carried out using a commercial SQUID magnetometer and a LakeShore 7130 AC susceptometer.

3. Results and discussion

XRD results showed that the AP sample is composed of copper iron spinel nanograins (mean crystallite sizes $D \approx 6$ nm) and an amount of $\approx$15 wt.% of CuO. The percentage of CuO decreases and, in addition, the spinel line-widths become slightly narrow with the milling. After $t_m = 10$ h, copper iron spinel in its cubic phase is the only phase detected [6]. After $t_m = 12$ h there is a segregation of α-Fe_2O_3. We observe that D increases with t_m, reaching $\approx$13 nm after milling for 10 h. At the same time, the average microstrain level $\varepsilon = \Delta d/d$ (d is the interplanar distance) decreases. For $t_m = 12$ h, D and ε deviate from the general trend [6].

We observe a broad Fe^{3+} doublet in the room temperature (RT) Mössbauer spectrum of the AP sample (Figure 1). As the measurement temperature is lowered, its relative area decreases while an asymmetric broadened magnetic signal starts to be resolved (Figure 2). At 25 K the magnetic signal accounts for the main part of the Mössbauer spectrum (Figure 3). This thermal evolution is typical of a superparamagnetic (SPM) relaxation behavior, which reveals the small size of the particles. Indeed, at RT the thermal energy is high enough to overcome the anisotropy barriers, and causes the direction of the magnetic moment of the particle to fluctuate between the easy directions of magnetization averaging the hyperfine field to zero within the Mössbauer timescale ($\approx 10^{-8}$ s). As the thermal energy is reduced the relaxation time diminishes and a blocked state of particle magnetic moments is attained, which corresponds to the resolved magnetic signal at 25 K. In this case, the large line-widths as well as the asymmetric line-depths

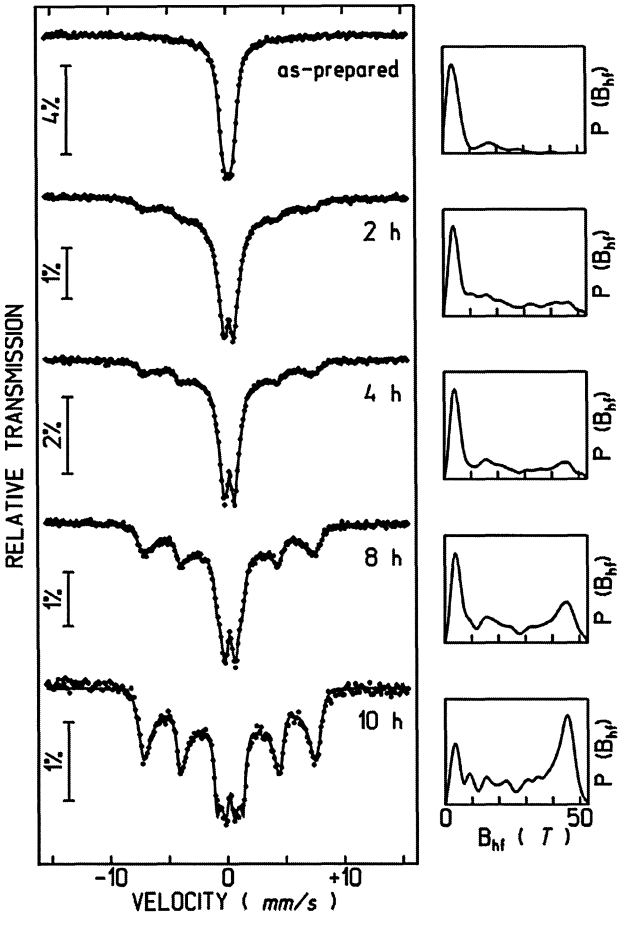

Figure 1. Mössbauer spectra at room temperature for AP sample and after milling during the times indicated (*right*). The solid lines represent the fitting by assuming a distribution of hyperfine fields H_{hf} (*left*).

suggest the presence of at least two different magnetically resolved subspectra I and II. Their hyperfine parameters, assuming Lorentzian line-shapes, are similar to those reported for the B and A spinel sites in cubic $CuFe_2O_4$, respectively ($H_{\mathrm{I}} = 49.6$ T, $\delta_{\mathrm{I}} = 0.41$ mm/s, $2\varepsilon_{\mathrm{I}} = -0.02$ mm/s; $H_{\mathrm{II}} = 52.4$ T, $\delta_{\mathrm{II}} = 0.48$ mm/s, $2\varepsilon_{\mathrm{II}} = -0.02$ mm/s) [7].

After milling the AP sample, a magnetic signal comes out in the RT spectra, which co-exists with the SPM doublet (Figure 1). The relative area of this signal increases with t_m, taking up to $\approx$60% of the total spectrum area for $t_m = 10$ h. For simplicity, we have considered a distribution of static hyperfine fields H_{hf} to fit these spectra. The distribution initially centered at $H_{\mathrm{hf}} \approx 10$ T represents the SPM relaxation of the particles with the smaller energy barriers. As the milling advances there is an increasing probability to have contributions from higher H_{hf}, which arise from iron ions in magnetically ordered oxides whose particle magnetic moments

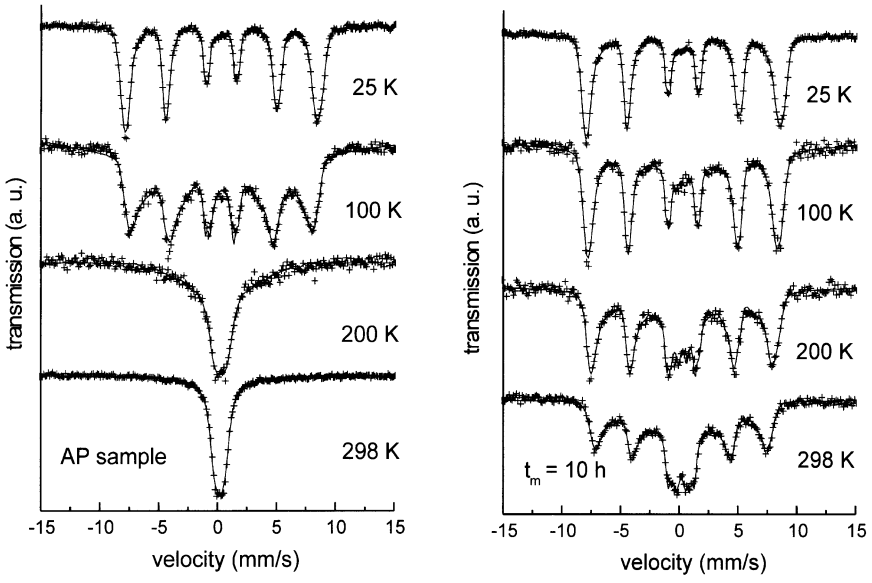

Figure 2. Thermal evolution of the Mössbauer spectra for the copper nanoferrite (AP) and for $t_m = 10$ h. The solid lines correspond to the fitting.

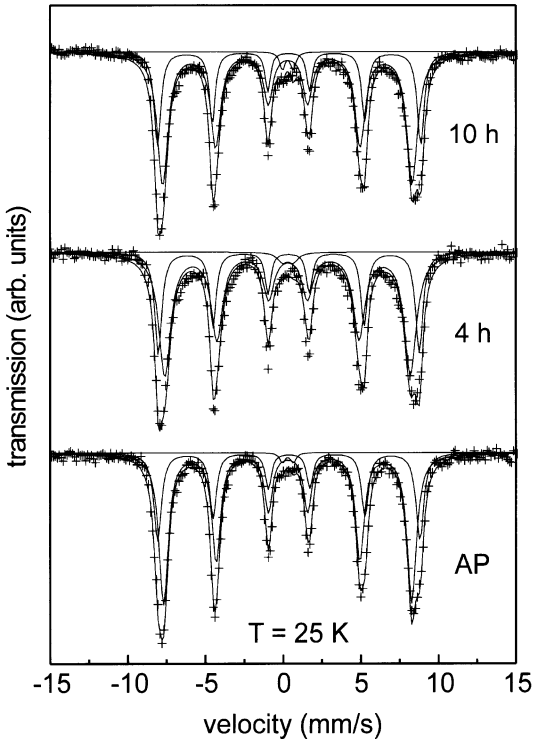

Figure 3. Mössbauer spectra taken at 25 K for the samples shown on the labels. The solid lines are the results of the fittings as described in the text.

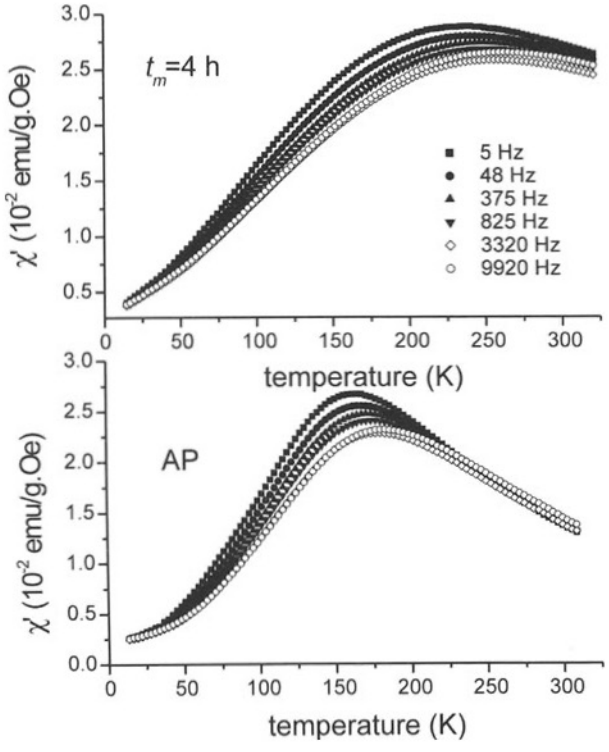

Figure 4. Thermal dependence of the in-phase AC susceptibility, χ', for AP and $t_m = 4$ h samples for different frequencies ν of the AC field H_{AC} of amplitude 1 Oe.

are in a blocked state. The thermal evolution of the spectra of milled samples also displays a SPM behavior (Figure 2). At 25 K we observe that the hyperfine parameters and the relative area ratio of the resolved signals remain almost unchanged with the milling. ($H_I = 49.9$ T, $\delta_I = 0.41$ mm/s, $2\varepsilon_I = -0.02$ mm/s; $H_{II} = 52.6$ T, $\delta_{II} = 0.48$ mm/s, $2\varepsilon_{II} = 0.03$ mm/s.) This would indicate that neither the spinel structure nor the Fe distribution amongst the A and B spinel sites have changed significantly.

The mean Mössbauer blocking temperature T_B, taken as the temperature at which the relative area of the blocked state corresponds to 50% of the total spectrum area, shifts to higher temperatures with t_m. Indeed, T_B is in the 100–200 K interval for AP, while is above 298 K for the 10-h milled sample (Figure 2).

The magnetic results also show an increment of the blocking temperatures. The ZFC maximum of the M vs. T curves (not shown), which is related to the mean T_B, is at 140 K for the AP sample, and shifts to 174, 190, 268 for $t_m = 2$, 4 and 8 h, respectively. The same trend is observed for the temperature at which the ZFC-FC irreversibility starts (T_{irr}), which represents the blocking of particles with the highest energy barriers [6].

The thermal dependence of AC susceptibility χ (Figure 4) shows maxima at T_{max}, which shifts toward higher temperatures when the frequency of the applied

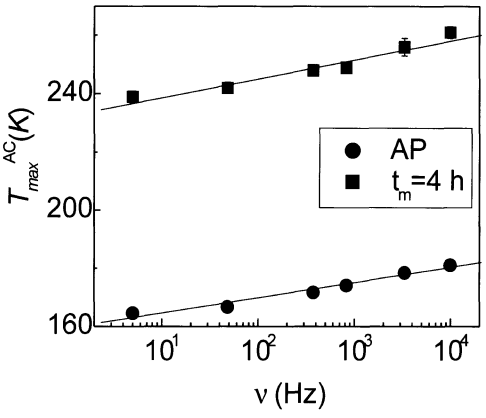

Figure 5. Temperature of the maximum of the in-phase component of the AC susceptibility χ' as a function of the frequency, for AP and 4 h samples.

field, ν, increases. The $T_{\max}$ of the in-phase χ is related to T_B, the latter defined as the temperature at which the relaxation time τ of the nanoparticles equals the measurement time $\tau_m = 1/2\pi\nu$. We observe that the $T_{\max}$ shifts ≈70 K for all ν after milling for 4 h. For $t_m = 10$ h, $T_{\max} > 300$ K.

In addition to the growth of T_B there is an increase in the magnetic response with the milling; e.g., we observe that the saturation magnetization M_S at 5 K increases from 17 to 45 emu/g after 10 h.

The present results show that milling nanocrystalline iron–copper spinel induces an important shift in its superparamagnetic limit toward higher temperatures. The poorly crystalline initial state of the AP sample (a mixture of spinel and 15 wt.% CuO) originates a high degree of spin disorder, as evidenced by its relatively low M_S value. The high-energy milling generates an increment of the spinel crystallinity, by increasing D (although remaining in a nanometric scale) and decreasing ε. In addition, the increment of the T_B denotes that the crystallinity improvement causes an increment of the apparent magnetic size. The magnitude of the magnetic response also progressively increases. After $t_m = 10$ h, the Cu–Fe spinel stabilizes in its otherwise metastable cubic phase, which has the larger magnetic moment per formula unit [8].

4. Conclusions

The present results show that the blocking temperatures of nanocrystalline copper ferrite spinel can be shifted to higher temperatures by high-energy ball milling. This process induces an increment of the mean grain size and of the apparent magnetic one. After 10 h of milling the copper nanoferrite stabilizes in the cubic phase. Further milling originates the segregation of hematite.

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