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# Magnetic Structure of $Fe_xCu_{100-x}$ Magnetoresistive Alloys Produced by Mechanical Alloying

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**Abstract.** $Fe_xCu_{100-x}$ magnetoresistive alloys were produced by mechanical alloying. X-ray diffraction shows fcc structure. The room-temperature Mössbauer spectra evolves from an asymmetrical doublet below $x = 25\%$, to a broad magnetic hyperfine field distribution above this concentration. Quadrupole splitting of the doublet varies between 0.48 and 0.57 mm/s, and its isomer shift from 0.16 to 0.29 mm/s. Low-temperature Mössbauer spectroscopy displays a $B_{hf}$ distribution. Magnetization measurements display different features depending on concentration, from mictomagnetism to ferromagnetism. Low-temperature magnetoresistance is measured. Samples with $x \sim 20\%$ exhibit larger magnetoresistivity ratios. Bulk and hyperfine magnetic properties are correlated in order to explain magnetoresistivity features of these samples.

**Key words:** Mössbauer spectroscopy, mechanical alloying, magnetoresistive alloys.

## 1. Introduction

Granular giant magnetoresistive materials were produced for the first time in 1992 by Xiao *et al.* [1], who proposed that such systems would exist if magnetic entities were dispersed in an electrically conductive, nonmagnetic matrix. In such systems, total spin in every magnetic entity aligns with an external applied magnetic field, diminishing scattering of conduction electrons, lowering in this way the electrical resistance of the alloy.

Mechanical alloying (MA) is a set of techniques which are able to produce chemical scale mixtures of different elements trough the conversion of macroscopic mechanical energetic events (for example, ball-vial impacts) into atomic movements and crystal plane sliding [2].

Fe and Cu do not form compounds, due to their positive enthalpy of mixing. By means of non-equilibrium production techniques, such as MA, Fe–Cu solid solutions were produced in the whole concentration range [3]. Some works on mechanically alloyed GMR systems have been reported [4], including the production of a multilayered system using MA techniques [5].

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## 2. Experimental procedure

Fe and Cu powders were ground together in a mill Nissin Gikken NEV-MA8. The blend was loaded under Ar atmosphere into stainless steel vials previously coated with the material to be ground. Powders obtained were pressed into small ingots and then magnetoresistivity was measured. Samples were measured at room temperature and 77 K. Mössbauer effect (ME) spectra, X-ray diffractograms (XRD) and zero-field-cooled (ZFC) magnetization were measured. Details on sample preparation were given in [6].

## 3. Results

XRD shows broadened fcc peaks for all the samples produced, with no distinguishable bcc structures [6]. This is in agreement with former works on this system [3]. Magnetoresistivity measurements performed at room temperature do not display GMR behavior. Same measurements done at 77 K are different: GMR is present in samples with an iron concentration between 10 and 45 at.%. The highest values of GMR ratio were reached at 20 at.% ($\Delta\rho/\rho = 1\%$ for as-prepared samples milled for 75 h, and 2.75% for as-prepared samples milled for 20 h).

Magnetization vs. temperature measurements show an iron concentration dependence. ZFC magnetization (Figure 1) reveals a change in the magnetic character of the sample: low Fe concentration samples ($x = 5$, 10, 18.8 at.%) have a mictomagnetic behavior; high Fe concentration samples features ferromagnetic behavior. Signal broadens with increasing iron concentration, as expected, although an inversion is observed for the 5 and 10% samples. From these graphs, glassy and Curie points ($T_g$ and $T_C$) are estimated. Calculation of these magnitudes is a difficult task, because we are dealing with a strongly disordered system, in which magnetic entities could be not similar, neither in size nor in shape. In order to obtain unambiguously $T_C$, we define it as the temperature at which second derivative nulls. This is because we consider that the ferromagnetic phase becomes the majority one at this point. These values agree reasonably well with previous work. We have plotted the so obtained $T_C$ on a magnetic phase diagram (Figure 2) with the values obtained by Chien *et al.* from a system prepared by sputtering [7]. Our paramagnetic–ferromagnetic phase-change line is situated at higher temperatures, but has similar shape.

Room-temperature ME measurements show a doublet for samples with $x$ between 10 and 25 at.%. For $x = 30\%$ the doublet broadens, and for higher $x$, a clear hyperfine field distribution appears. They are analyzed in terms of their Doppler velocity moments. First and second order moments, which are indicative of the average isomer shifts ($\delta$), and average magnetic hyperfine field $B_{hf}$ strength, are plotted in Figure 3. The isomer shift slightly decreases with $x$, but stabilizes around 20%. It would indicate that ferromagnetic entities become richer in iron, and above 20 at.% Fe, a stationary concentration of copper inside the clusters is

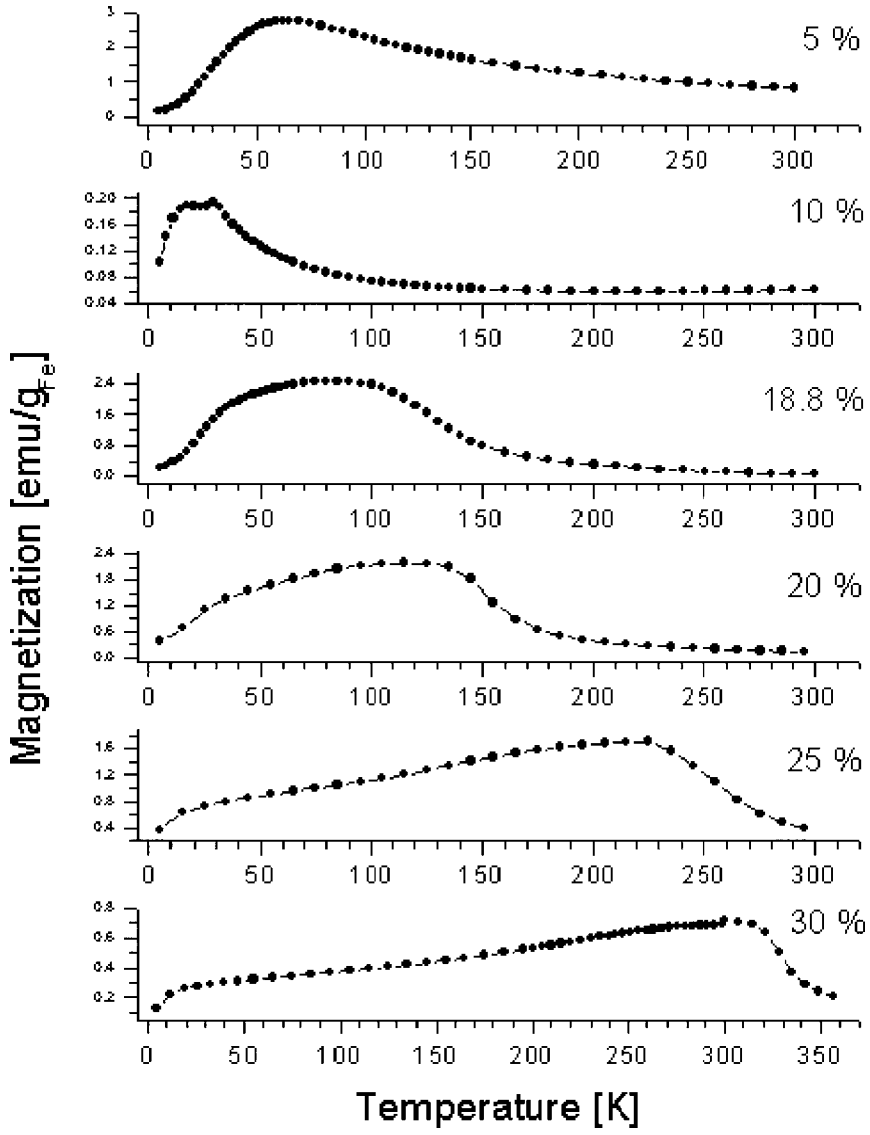


*Figure 1.* Zero-field cooled magnetization (whole sample) vs. temperature measurements. Mictomagnetic behavior is clearly seen in samples with an iron content of 5, 10 and 18.8 at.%. 20, 25 and 30 at.% shows a ferromagnetic character.

reached. The second moment has a steady value, up to a point located between 25 and 35%; from here to higher $x$, it increases indicating the development of a $B_{\mathrm{hf}}$.

Low temperature ME spectra correspond to a broad magnetic hyperfine field $B_{\mathrm{hf}}$ distribution with a maximum at around 20 T. No significant contribution comes from an iron-bcc-like component. Isomer shifts confirm the tendency shown for RT measurements.

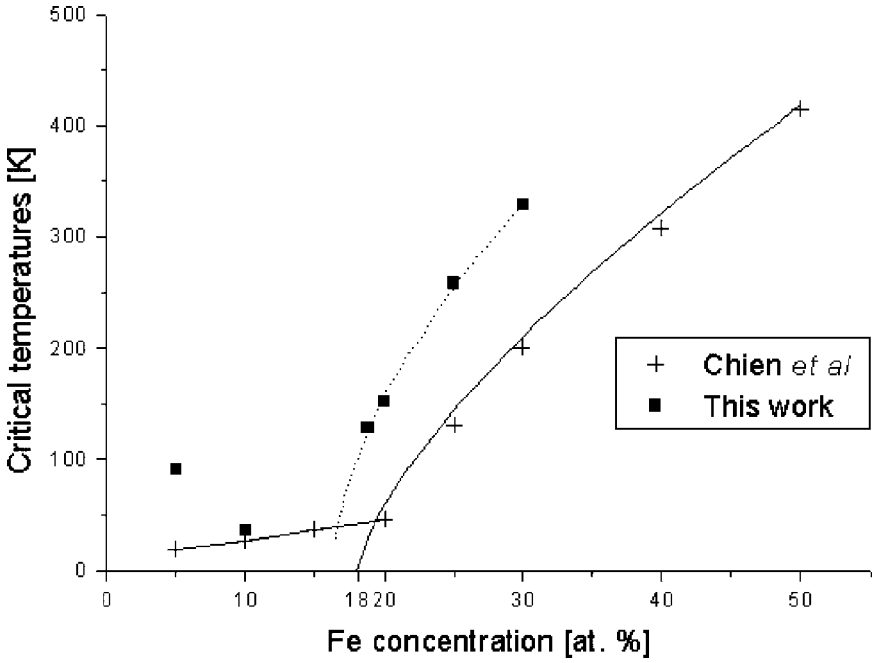


*Figure 2.* $T_C$ obtained in this work (■), plotted with the points (+) obtained by Chien *et al.* [7]. Lines indicate change of the magnetic phase.

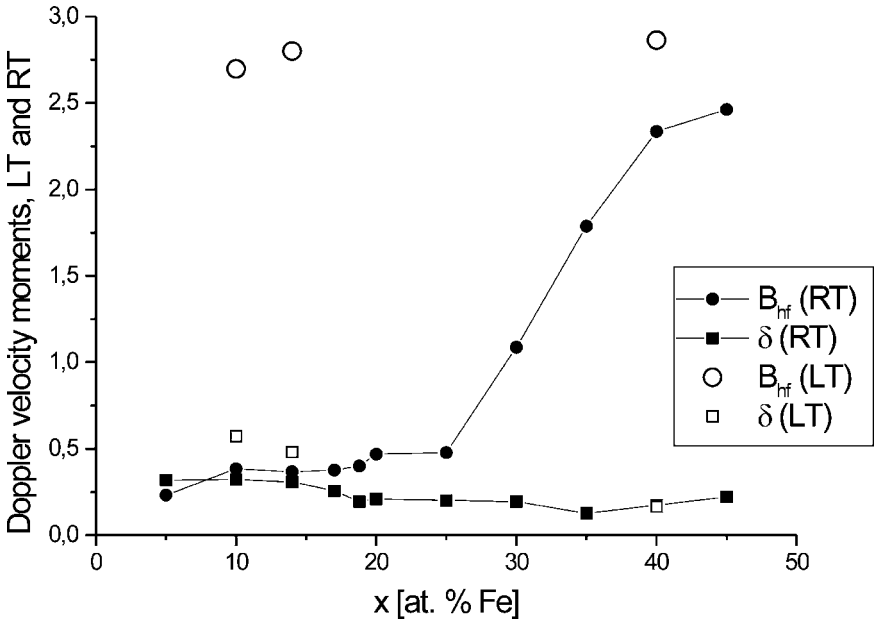


*Figure 3.* 1st and 2nd Doppler velocity moments (in mm/s and $mm^2/s^2$), indicative of isomer shift ($\delta$) and magnetic hyperfine field ($B_{hf}$), plotted against Fe concentration. Open symbols are those corresponding to low-temperature ME measurements (4.2 K for $x = 10, 14.1\%$; 15 K for $x = 40\%$).

## 4. Discussion

MA forces iron to occupy structural sites in the Cu lattice. This structure is severely damaged because of mechanical work. Bulk magnetic measurements show an evolution from a mictomagnetic structure to a ferromagnetic one. Iron atoms would arrange in small structures, which may be coherent with the fcc matrix, as indicated by XRD results and low-temperature Mössbauer spectroscopy. As indicated by isomer shifts, such arrangements are not composed purely by iron. Copper atoms are present inside these clusters. As the concentration increases, Fe-richer clusters are obtained, up to a limit evidenced by the steady value of $\delta$. This is an effect of milling, which provides limited amounts of energy to the system. The RT-ME results reflect a true paramagnetic-ferromagnetic transition behavior, as phase-change temperature is consistent with the magnetic behavior depicted in Firure 3.

## 5. Conclusions

Mechanical alloying mix the system at a level in which small iron-rich clusters are immersed in the copper matrix. Most probably, these clusters are fcc, and their total spin is able to follow an applied magnetic field, producing GMR effect. The composition of these clusters varies with iron concentration, up to a steady value. The Fe–Cu system changes from a mictomagnetic state to a ferromagnetic one, with increasing iron concentration. Bulk magnetic properties are consistent with the interpretation of hyperfine parameters obtained by Mössbauer spectroscopy.

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