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Spin-glass-like behaviour in ball milled $Fe_{30}Cr_{70}$ alloy studied by *ac* magnetic susceptibility

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ABSTRACT

Nominal nanostructured $Fe_{30}Cr_{70}$ obtained from ball milling during 110 h has been investigated from *dc* magnetization and *ac* magnetic susceptibility. The as-milled sample is not monophasic and is formed of two phases, $Fe_{20\pm2}Cr_{80\pm2}$ ($\sim$86 ± 2%) and iron ($\sim$14 ± 2%). The *ac* susceptibility measurements show evidence of a re-entrant spin-glass-like transition for the $Fe_{20}Cr_{80}$ phase below 30 K. The shift of the freezing temperature per frequency decade is moderate when compared to that found in conventional spin–glass alloys. A Vogel–Fulcher activation process can be used to explain the frequency variation. The results are also analyzed in terms of Cole–Cole formalism for extracting information of relaxation time ($\tau \sim 10^{-5}$ to 10^{-4} s).

For more than a century, the study of FeT iron with 3d metals (T = Cr, Ni and Cu) has been a fascinating field of research in *Condensed Matter Physics* [1]. Most of these materials owe their usefulness to a special combination of their crystal and symmetry properties. In particular, Fe_xCr_{100-x} solid solutions adopt a body centred cubic (bcc) crystal structure (at room temperature the lattice-cell parameters are close to those of Fe and Cr). In addition, these alloys display a rather complex magnetic phase diagram, showing the coexistence of several magnetic behaviours such as spin-glass, ferro- or antiferromagnetism [2–4]. In fact, the magnetic phase diagram of FeCr alloys was determined using small-angle neutron scattering and low-field magnetization [4]. Fe_xCr_{100-x} evolves from itinerant antiferromagnetism for Fe concentrations $x < 16$ to ferromagnetism for $x > 19$, and spin-glass behaviour was observed between the two critical concentrations [4]. Furthermore, Fe_xCr_{100-x} shows moment-volume instabilities and Invar properties in the compositional range around $x \approx 20$ [1].

Mechanical alloying technique is able to synthesize single-phase FeT (T = Cr, Cu and Ni) binary alloys with average crystalline size below 50 nm and exhibiting a variety of magnetic responses [5,6]. Among them, the most recent striking features are the observation of an Invar behaviour in Fe–Cu [7], and the enhancement ($\sim$150 K) of an intrinsic physical property such as the Curie temperature of mechanically stressed and thermally treated $Fe_{64}Ni_{36}$ Invar alloy [8,9], leading to an extension of the temperature range for having low- or near-zero thermal expansion coefficient in this material below the magnetic ordering temperature. In the case of ball milled Fe_xCr_{100-x}, the magnetic behaviour could be significantly modified by the disordered intergranular region [10,11]. In a previous work on the nominal $Fe_{30}Cr_{70}$ alloy it became clear that the as-cast material was multicomponent. The coexistence of bcc Cr-rich and Fe-rich phases was observed from a joined-analysis of X-ray absorption, X-ray and neutron diffraction experiments and dc magnetization measurements [12].

In this contribution, we present a systematic *ac* magnetic susceptibility study of the as-milled $Fe_{30}Cr_{70}$ alloy, which is close to the onset of ferromagnetism in FeCr alloys [4], to investigate the detailed dynamical magnetic processes. This work fills in the gap

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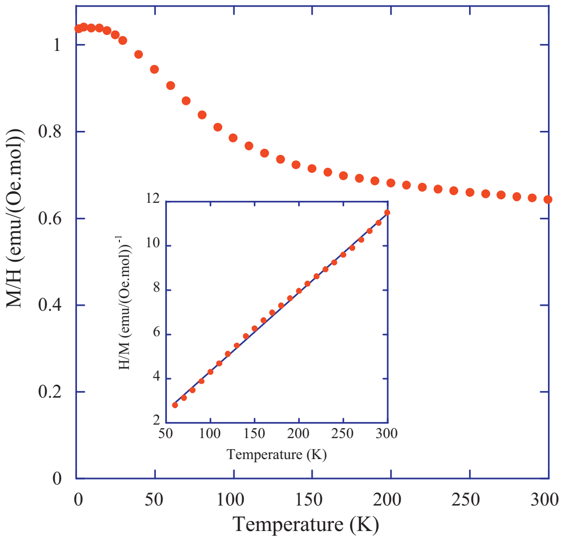

Fig. 1. Temperature dependence of the *dc* magnetic susceptibility for $Fe_{30}Cr_{70}$ powders measured in FC conditions under $H = 1$ kOe. The inset shows the temperature dependence of the inverse of *dc* magnetic susceptibility for $Fe_{20}Cr_{80}$. The solid line in the inset represents a fit to a modified Curie–Weiss law (see the text).

of the few examples in the literature of frequency-dependent reentrant spin-glass systems.

Powders of nominal $Fe_{30}Cr_{70}$ composition were mechanically synthesized for 110 h of milling time from chromium and iron powders (99.98% purity) using a commercial RETSCH PM-400 high-energy ball mill. Magnetization and *ac* magnetic susceptibility were measured in a PPMS-14T magnetometer (Quantum Design). In particular, the *ac* magnetic susceptibility data was collected using a *dc* magnetic field of 10 Oe and an amplitude for the *ac* magnetic field of 5 Oe at several frequencies (10, 40, 125, 400, 1000, 2000, 5000 and 10000 Hz) between 2 K and 350 K at a steady rate of 1 K/min, allowing the instantaneous recording of both real, χ', and imaginary, χ'', components.

In order to make a macroscopic magnetic characterization of the $Fe_{30}Cr_{70}$ alloy we have carried out also *dc* magnetization and susceptibility measurements. The temperature dependence of the *dc* susceptibility, M/H, for $Fe_{30}Cr_{70}$ powders under an applied magnetic field of 1 kOe (measured in field-cooled [FC] conditions) is shown in Fig. 1. According to our previous X-ray and neutron powder diffraction experiments, the nominal $Fe_{30}Cr_{70}$ powders are constituted of two phases, 86 ± 2% of $Fe_{20\pm2}Cr_{80\pm2}$ (hereafter denoted as $Fe_{20}Cr_{80}$) and 14 ± 2% of α-Fe. This feature means that the as-milled sample is not homogeneous after 110 h of milling time. Moreover, this fact explains the off-set signal of 0.64 emu/(Oe mol) seen in the magnetization at room temperature from which an estimation of the Fe phase of ~15% is obtained, in good agreement with that obtained from diffraction data. When the temperature is lowered below 150 K the *M*/*H* increases with decreasing temperature until a certain value is reached below 25 K, but with a trend to decrease below this temperature. The Curie ordering temperature, $T_C = 50 \pm 10$ K, has been determined as the inflection point of the M/H vs. temperature dependence. According to the FeCr magnetic phase diagram [4] this ordering temperature could be associated with a composition close to $Fe_{21}Cr_{79}$. At high temperatures a modified Curie–Weiss dependence accounting for the presence of the additional contribution to the magnetic susceptibility, χ_0, needs to be used for fitting the experimental data, $\chi = \chi_0 + \frac{C}{T-\theta_P}$, yielding to the values for the Curie constant, $C = 28.1 \pm 0.7$ emu K/(Oe mol) and the effective paramagnetic Curie temperature $\theta_P = -7 \pm 1$ K.

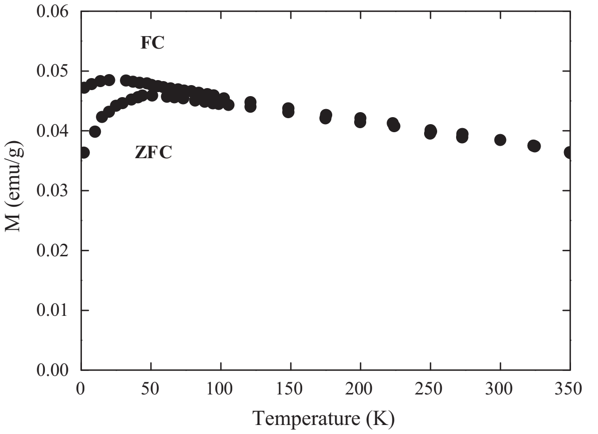

Fig. 2. Temperature dependence of the magnetization for $Fe_{30}Cr_{70}$ powders in ZFC and FC conditions, under an applied magnetic field of 5 Oe.

For $Fe_{30}Cr_{70}$, together with a rapid increase in M/H, below ~150 K there are differences in the temperature dependence of the magnetization measured either in zero-field-cooling (ZFC) and FC (see Fig. 2) regimes under a low magnetic field (~5 Oe). This behaviour could be related to a superparamagnetic character of the α-Fe and the existence of a disordered magnetic response of the $Fe_{20}Cr_{80}$ phase. On the latter case, one of the important signatures for a spin-glass behaviour, which characterizes the random freezing of the magnetic moments, is the appearance of a cusp in the *ac* magnetic susceptibility at the freezing temperature (T_f) that depends both on magnetic field and frequency. As a trademark of this behaviour found in $Fe_{20}Cr_{80}$ we present, in Fig. 3, the temper-

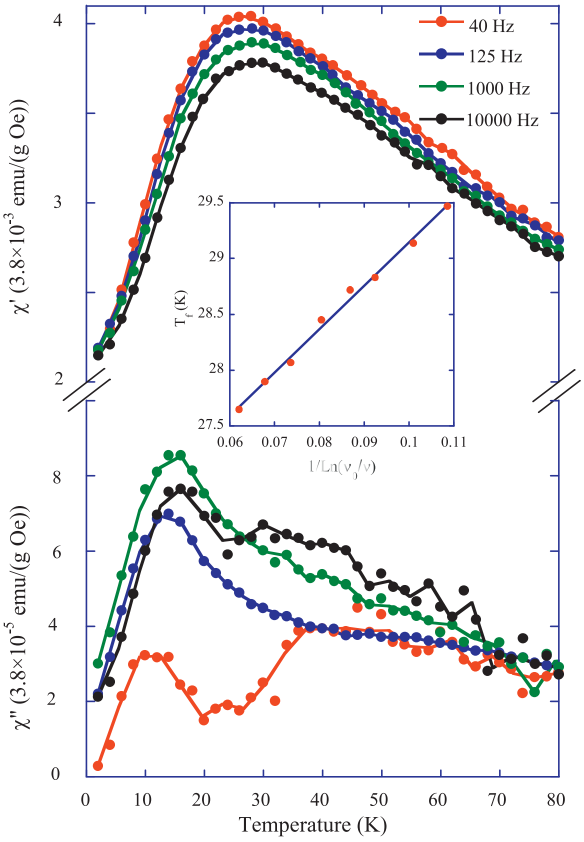

Fig. 3. Temperature dependence of the real (χ') and imaginary (χ'') *ac* magnetic susceptibility components. For the sake of clarity only the frequencies ν = 40, 125, 1k, 10k Hz for $Fe_{20}Cr_{80}$ alloy in the as-quenched state are represented.

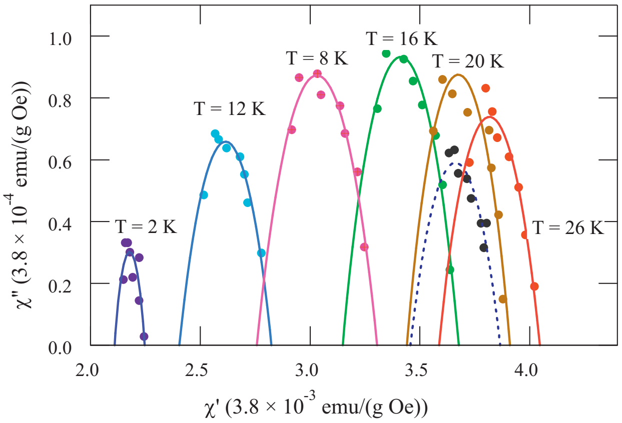

Fig. 4. Cole–Cole diagram in $Fe_{20}Cr_{80}$ for a selection of temperatures. Solid lines are fits obtained by using the expression based on the well-known phenomenological Cole–Cole model from Eqs. (4a) and (4b) in Ref. [15]. The dashed line corresponds to $T = 32$ K.

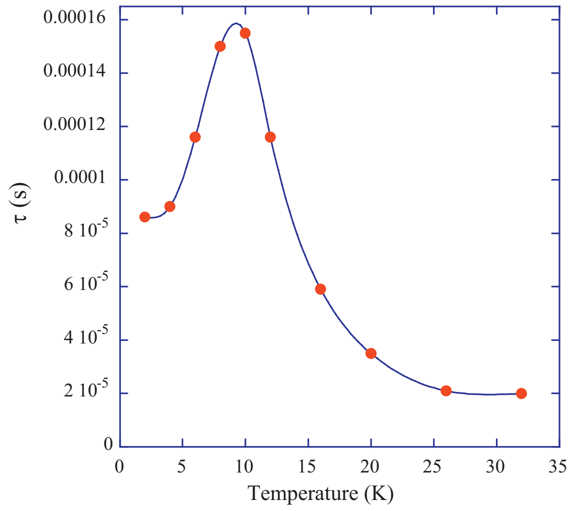

Fig. 5. Temperature dependence of the relaxation time, τ_c, in $Fe_{20}Cr_{80}$ derived from the Cole–Cole formalism used in Fig. 4. The solid line is a guide for the eyes.

ature dependence of the *ac* magnetic susceptibility. It can be seen a single broad anomaly in χ', while two are detected in χ'' (that found at lower temperature has no simple frequency dependence). The broad anomaly observed around 27–30 K in χ' is close to the re-entrant spin-glass transition [4], which was previously found in these $Fe_{20}Cr_{80}$ materials when prepared by induction techniques [4].

The position of the maximum of χ' at $T_f \approx 27.7$ K shifts to higher temperatures with increasing frequency (Fig. 3). The relative variation of T_f per frequency decade, $\Delta T_f/(T_f \Delta Ln\ \nu)$ is about 0.006–0.02 in agreement with the values usually reported in metallic spin-glasses [13,14]. In this way, we have plotted in the inset of Fig. 3, the spin-freezing temperature (defined as the cusp in the *ac* magnetic susceptibility, χ') as a function of $(Ln(\ \nu_0/\ \nu))^{-1}$. From this representation it can be seen that the slowing down of the dynamics in $Fe_{20}Cr_{80}$ follows rather well a Vogel–Fulcher law [13].

We now turn to an examination of the temperature dependence of the relaxation time, τ_c, which constitutes the principal result obtained from the Cole–Cole analysis of the *ac* magnetic susceptibility. Fig. 4 shows some representative Cole–Cole diagrams. The most noteworthy feature of this representation is that the circular arc is shifted with temperature between 2 K and 27 K, but almost having the same frequency dependence. This, in fact, corresponds with a τ_c evolving from 2×10^{-5} s (above 30 K), passing through a maximum of 1.6×10^{-4} s (around 10 K) to have a magnitude of 8×10^{-5} s (at 2 K).

Hence the relaxation time τ_c moves slowly through our experimental window, which covers slightly over 4 decades of frequency. Fig. 5 shows the temperature dependence of the relaxation time. Contrary to the typical spin-glass systems where the dynamics response slows down by as many as 16 decades in time, when crossing from the paramagnetic phase to the spin-glass regime, in $Fe_{20}Cr_{80}$ only one decade is observed. One likely source for such reduced slowing down range is clearly that the magnetic moments in this material at low temperatures are evolving from a ferromagnetic phase to an spin-glass one, and therefore it is not expected a divergence of the relaxation time crossing the transition temperature.

In summary, the *ac* magnetic susceptibility measurements in ball milled $Fe_{20}Cr_{80}$ have revealed the existence of a re-entrant spin-glass transition. The parameters characterizing this transition show no critical divergence dynamics, although a clear peak is observed in the real magnetic susceptibility, while the imaginary susceptibility has much more complex frequency dependence. Further experiments will be needed to elucidate this complex magnetic response of Cr-rich FeCr ball milled alloys in the immediacy of the 80 at.% in chromium when crossing through re-entrant spin-glass transition.

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