*Hyperfine Interactions* **141/142:** 175–179, 2002.



# Superparamagnetic Relaxation in Nanocrystalline $Fe_{80}Zr_7B_{12}Cu_1$ Alloys

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**Abstract.** Nanocrystalline $Fe_{80}Zr_7B_{12}Cu_1$ alloys with different amounts and sizes of *bcc* precipitates were prepared by appropriate annealing of amorphous ribbons. The 6–10 nm ferromagnetic *bcc* granules are embedded in a residual amorphous tissue with a thickness at least 4 nm. Above room temperature superparamagnetic relaxation characteristic for small magnetic particles was observed with increasing temperature, as indicated by a significant increase in the width of the Mössbauer lines belonging to the *bcc* precipitates. It shows the absence of magnetic coupling which is stronger than the dipole–dipole interaction between the ferromagnetic nanoparticles.

**Key words:** nanocrystal, superparamagnetic relaxation, magnetic coupling.

Nanocrystalline Fe–Zr–B–Cu alloys prepared by partial crystallization of amorphous ribbons containing nanosize crystalline *bcc* precipitates in a residual amorphous matrix are good soft magnetic materials [1]. Interphase exchange interaction or magnetic exchange interactions between the adjacent ferromagnetic grains mediated by the intergranual amorphous matrix may cause the averaging out of particle anisotropies. In this work the magnetic coupling of granular materials is investigated by Mössbauer spectroscopy.

Temperature dependent Mössbauer measurements of partially and fully nanocrystalline $Fe_{80}B_{12}Zr_7Cu_1$ alloys will be reported. The amorphous precursors were prepared by melt-spinning in vacuum. Crystallization of the amorphous $Fe_{80}B_{12}Zr_7Cu_1$ alloy takes place in two steps. The first differential scanning calorimetry (DSC) peak corresponds to the formation of nanosize iron-rich *bcc* precipitates and the second step is the crystallization of the residual amorphous phase. The nanocrystalline ribbons were produced by partially or fully annealing out the enthalpy of the first DSC peak. X-ray diffraction has confirmed the nanocrystalline state and was used to determine the size of the grains [2]. The Mössbauer measurements were made with a 50 mCi $^{57}$Co in Rh source by a constant acceleration spectrometer.

At and above room temperature the contributions of the *bcc* and the residual amorphous phases are well separated in the Mössbauer spectra as shown in Figure 1. The narrow sextet with slightly asymmetric lines observed at room temperature is attributed [3] to the *bcc* granules, the broad magnetic components be-

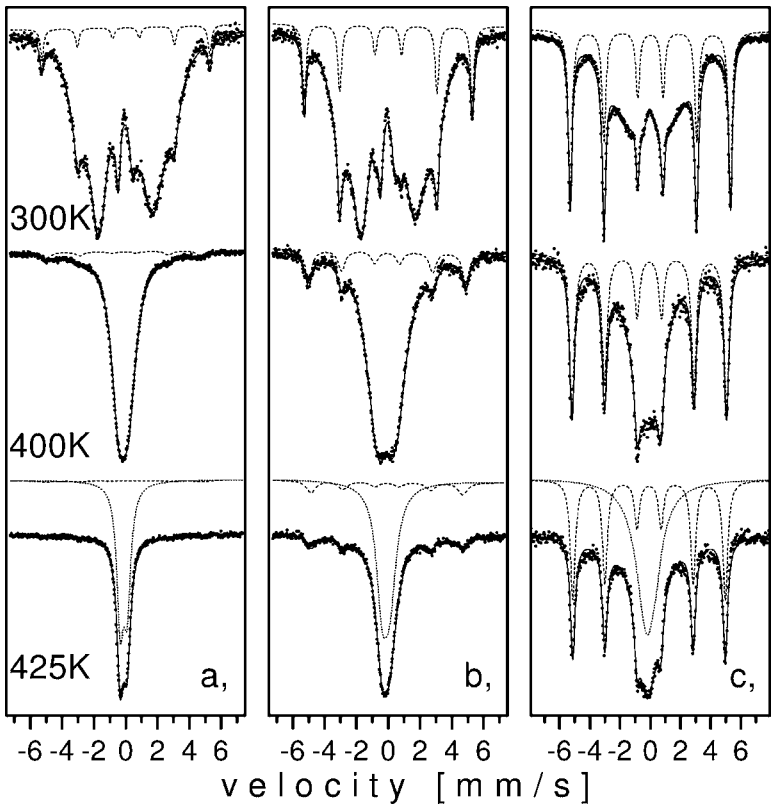


*Figure 1.* Mössbauer spectra in the vicinity of the Curie temperature of the residual amorphous phase of nanocrystalline $Fe_{80}B_{12}Zr_7Cu_1$ annealed to a degree of 10% (a), 33% (b) and 100% (c) of the nanocrystalline state. The full line is the fitted curve, dashed lines show the component of the *bcc* phase described with a single six-line pattern. At 425 K dotted lines show the components of the residual amorphous phase.

long to the residual amorphous phase which is characterized by its hyperfine field distribution. At higher temperatures both the average value and the width of this distribution decreases signaling the Curie temperature of the residual amorphous matrix. An approximately constant value was extrapolated from the average hyperfine field versus temperature curves [3] as 387, 404 and 396 K for the 10%, 33% and 100% nanocrystallized samples, respectively.

The low-field side asymmetry of the Mössbauer lines of the *bcc* granules is caused by the remaining Zr and B impurities in the *bcc* phase [3]. Its proper description involves at least two six-line patterns corresponding to the iron atoms without and with impurity neighbours, respectively. Resolution of the two *bcc* components is increasingly difficult when they have small intensities corresponding to a low degree of nanocrystallization and at low temperatures when they strongly overlap with the spectrum components of the residual amorphous phase.

At higher temperatures significant line broadening of the *bcc* components characteristic of superparamagnetic relaxation is observed (Figure 1). This affects the proper evaluation of the linewidth of the *bcc* components as a function of temperature, their correlation may result in significant underestimation of the linewidth of the stronger, narrower component corresponding to the iron atoms without impurity neighbours [3]. Under these circumstances a single six-line pattern describes better the temperature dependence of the average linewidth of the *bcc* components, despite the improper description of the line-asymmetry and the resulting systematic underestimation of the *bcc* intensity. The *bcc* grain size obtained from X-ray and its relative amount from Mössbauer measurements allow the estimation of the average thickness of the residual amorphous phase, $d$ [3]. With the present underestimated *bcc* fraction $d = 12.9$, 8.7 and 5.2 nm values are deduced for the 10%, 33% and 100% nanocrystallized samples. These values are in line with the progress in the nanocrystallization, but somewhat overestimated if compared to the former, more proper $d = 3$ nm value of the fully nanocrystallized sample [3].

Temperature dependences of the average linewidths of the *bcc* components, $2\Gamma$ for the 10%, 33% and 100% nanocrystallized samples are shown in Figure 2a. $2\Gamma$ is increasing for all samples above room temperature. The increase is faster for the smaller *bcc* granules (Figure 2b) and the Curie temperature of the residual amorphous phase does not play any special role. Such a reversible line broadening is the finger-print of superparamagnetic relaxation of small magnetic particles. The characteristic doublet of the paramagnetic amorphous phase is only observed when the *bcc* contribution is almost completely smeared out because of the fast relaxation (Figure 1: 425 K). At lower temperatures but still above the Curie temperature of the residual amorphous phase, the effect of the fluctuating dipolar magnetic fields of the *bcc* grains can be seen in the spectrum of the residual amorphous phase as a significant line broadening.

In the simplest evaluation of the excess line broadening, $\Delta\Gamma$ ($\Gamma = \Gamma_0 + \Delta\Gamma$, where $\Gamma_0$ is the low temperature value of $\Gamma$) is proportional to the inverse superparamagnetic relaxation time, $\tau^{-1}$ [4]. It is given for non-interacting uniaxial particles by the Néel–Brown expression as $\tau = \tau_0 \mathrm{e}^{\Delta E/k_\mathrm{B}T}$, where $\tau_0$ is of the order of $10^{-10}$s, $\Delta E$ is the energy barrier separating the two orientations of magnetization and $k_\mathrm{B}$ is Boltzmann's constant. $\Delta E = KV$, where $K$ is the magnetic anisotropy constant and $V$ is the volume of the particle. The expression $\Gamma = \Gamma_0 + \mathrm{const} \cdot \mathrm{e}^{-\Delta E/k_\mathrm{B}T}$ describes reasonably well the temperature dependence of the average *bcc* linewidth for the 100% nanocrystallized sample as shown by the full line in Figure 2a. A strong correlation between the parameters prevents a similar fit for the 10% and 33% nanocrystallized samples. In these cases the relaxation is observed in a relatively narrow temperature range and the influence of the magnetic field of the residual amorphous matrix below its Curie temperature may not be excluded. However, the observed line broadening in the vicinity of this Curie temperature when this magnetic field should be small follows the trend expected from the volume dependence (Figure 2c).

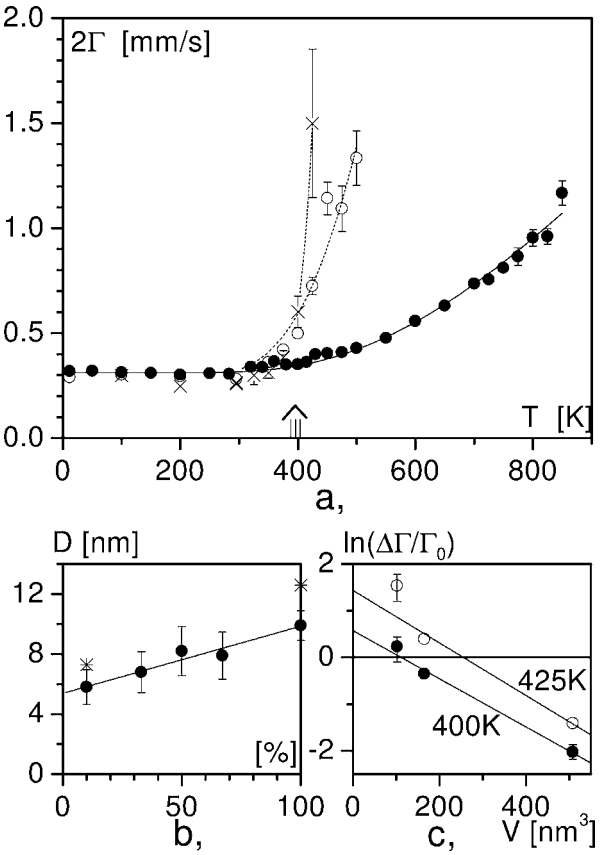


*Figure 2.* Temperature dependence of the full linewidth of the six-line pattern used for the description of the *bcc* phase of nanocrystalline $Fe_{80}B_{12}Zr_7Cu_1$ annealed to a degree of 10% (crosses), 33% (empty circles) and 100% (full circles) of the nanocrystalline state (a). The full line is fitted curve, dashed lines are guides to the eye. Curie temperatures of the residual amorphous phases are marked by arrows. The average diameter, $D$ of the *bcc* grains determined from X-ray measurements are shown as a function of the annealing degree (b), stars correspond to the sizes obtained from the usual Langevin-type evaluation of magnetic measurements [5]. The logarithm of the relative excess line broadening as a function of the volume of the *bcc* grains is shown in (c) at 400 and 425 K (full and empty circles), respectively.

$\Delta E = (2335 \pm 119)$ K was deduced from the fit of Figure 2a for the 100% nanocrystallized sample, substantially lower than the former overestimated value [3]. $K = 6 \cdot 10^5$ erg/cm$^3$, which is somewhat larger than the room temperature value for pure iron ($4.8 \cdot 10^5$ erg/cm$^3$), is obtained with the particle volume determined from X-ray measurement. A lower value, $K = 3 \cdot 10^5$ erg/cm$^3$ was calculated from the $(-K/k_B T)$ slope of Figure 2c.

Superparamagnetic relaxation of the *bcc* grains can also be seen in the magnetization measurements at high temperatures [5]. Figure 2b shows the deduced cluster sizes obtained from the usual Langevin representation. The magnetic grain

size seems to be systematically larger than the atomic (X-ray) grain size. It reflects strong magnetic dipole–dipole interaction between the particles. The larger magnetic volume gives lower anisotropy constants: $3 \cdot 10^5$ erg/cm$^3$ for the 100% nanocrystallized sample and $1.5 \cdot 10^5$ erg/cm$^3$ extrapolated from the volume dependence. Low-temperature spin freezing showing the gradual magnetic blocking of a fraction of nanocrystals decoupled from the ferromagnetic matrix was also detected [6].

The present observation of superparamagnetic relaxation shows that qualitative trends are in line with the expected volume dependence of small magnetic particles without invoking any additional exchange interaction effects and further investigation is necessary to reach more quantitative description.

## Acknowledgements

We are grateful to Prof. T. Ungár for fruitful suggestions on particle size determination and financial support of the Bolyai Research Grant (D.K.) and of the Magyary Zoltan postdoctoral program of the Foundation for Hungarian Higher Education and Research (J.G.) is acknowledged. This work was supported by the Hungarian Research Fund (OTKA T 0030753).

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