ESRF	**Experiment title:** Density of phonon states of grain boundaries in NANOPERM $Fe_{90}Zr_7B_3$ nanocrystalline alloy at high pressure measured by Nuclear Inelastic Scattering of synchrotron radiation	**Experiment number**: MA-291
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Names and affiliations of applicants (* indicates experimentalists):

*Svetoslav Stankov, Nuclear Resonance Group, ESRF, Grenoble, France

*Ulrich Ponkratz, Nuclear Resonance Group, ESRF, Grenoble, France

*Marcel Miglierini, Slovak University of Technology, Bratislava, Slovakia

*Bogdan Sepiol, Institut für Materialphysik, Universität Wien, Austria

Report:

In this experiment we have studied the density of phonon states (DOS) in NANOPERM-type nanocrystalline (NC) alloy at high pressure via nuclear inelastic scattering (NIS) spectroscopy. The aim was to apply the recently developed approach of separation of the DOS of the nanograins from DOS of the grain boundaries (GB) [1] and to investigate their high-pressure dependencies. An amorphous ribbon with stoichiometric composition of $^{57}Fe_{90}Zr_7B_3$ enriched to 65% in the resonant isotope ^{57}Fe was prepared by rapid quenching in a vacuum by the melt-spinning technique. The controlled annealing of the amorphous precursor results in formation of nano-crystals of α-Fe having homogeneous and porosity-free grain boundaries. NIS scans, employing monochromator with energy bandpass of 1.0 meV, have been performed on 3 samples: as-cast, annealed at 510º C for 10 min. (sample A), and at 620º C for 80 min. (sample B). The samples were loaded in a diamond anvil cell to pressure of 8.9 GPa. This particular pressure was selected in order to avoid the onset of α-to-ε phase transition in nanocrystalline Fe, which starts at about 11 GPa [2]. The pressure was controlled before and after the NIS experiments and proved to be very stable during the time of measurement (about 24 h.). The size of the synchrotron beam was reduced to about 20x20 µm using Kirkpatrick-Baez focussing mirror.

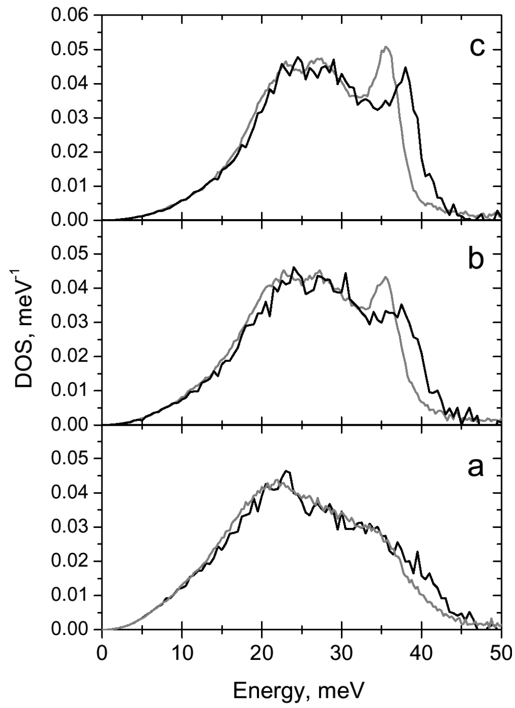

Fig. 1 DOS of $Fe_{90}Zr_7B_3$ at ambient pressure (grey) and at 8.9 GPa (black) of as-cast (a), annealed at 510º C for 10 min. (b) and at 620º C for 80 min. (c).

Fig. 1 summarises the extracted DOS of the NC samples at 8.9 GPa (black line), compared with the corresponding DOS at ambient pressure (grey line). One can notice the shift of longitudinal peak to higher energy, which results from the reduction of the volume of the unit cell. In the same time we observe a pronounced damping of this peak, which is a hint for reduction of the nanograin sizes.

In order to separate DOS of the GB from that of the nanocrystals the spectrum of sample *A* was fitted with the following function:

$$g_{fit}(E) = X_{CR}g_B(E)*D(E) + (1- X_{CR})g_{as\text{-}cast}(E)$$

where DOS of sample *B* $g_B(E)$ is convoluted with the characteristic spectrum of a damped harmonic oscillator $D(E)$ [3] and weighted by the relative volume content of nanocrystallites X_{CR}, while DOS of the as-cast sample $g_{as\text{-}cast}(E)$ is multiplied by the relative content of GB ($1\text{-}X_{CR}$) (see [1] for more details). The derived fits with this model, varying X_{CR} and the quality factor of the harmonic oscillator Q, are plotted in Fig. 2 with dashed lines to the DOS at ambient pressure and at 8.9 GPa. As one can notice from this figure the fits fairly well reproduce the experimental spectra. The partial DOS of the GB and nanograins are plotted in the same figure with black and grey solid lines respectively. The obtained values of Q and X_{CR} from this model are shown in Fig. 2 to each spectrum.

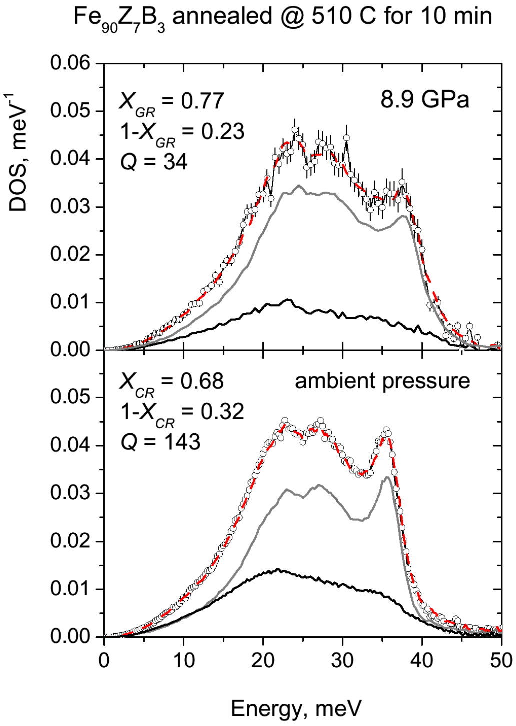

Fig. 2 DOS of sample *A* (open circles) at ambient pressure and at 8.9 GPa along with the partial contributions from the DOS of GB (black) and of nanograins (grey).

Comparing the corresponding values at ambient pressure and at 8.9 GPa one observes the following two effects:

I. Pressure-induced nanocrystallization.

The relative volume content of the nanograins in sample *A* at 8.9 GPa has increased by about 13% compared to the value at ambient pressure. This effect is described in the literature [4], where it was shown that the high pressure significantly reduces the temperature of nanocrystallization by promoting the short-range atomic rearrangement, which favours formation of nucleation centres.

II. Pressure-induced grain-size refinement.

Surprisingly the value of the quality factor Q has decreased by about 76% compared to the ambient pressure value. The pressure gradient in the cell, which would result in the same effect, we estimate to about 10%. Therefore the observed dramatic change of Q can be explained with reduction of the average nanograin sizes. However for detailed understanding of the observed effect, which could be of significant technological importance, more investigations are necessary. For example a measurement of DOS of sample *A* at ambient pressure after the high-pressure experiment will show if these effects are reversible. Complimentary high-resolution electron microscopy studies are in progress.

In conclusion:

- *The DOS of $Fe_{90}Zr_7B_3$ nanocrystalline alloy is measured at 8.9 GPa for the as-cast and two nanocrystallized states prepared by annealing at 510º C for 10 min. and at 620º C for 80 min.*
- *The previously developed approach of decomposition of the phonon spectrum to that of nanograins and grain boundaries is applied successfully for the DOS obtained at 8.9 GPa. This approach allowed to observe two phenomena, which take place at high pressures:*
  - *Pressure-induced nanocrystallization, which is described in the literature.*
  - *Pressure-induced size refinement, which could be of significant technological importance.*

[1] MA-83 Experiment report; S. Stankov et al., submitted to Phys. Rev. Lett..

[2] B. Chen et al., J. Appl. Phys. **89**, 4794 (2001)

[3] B. Fåk and B. Dorner, Institute Laue Langevin Technical Report No. 92FA008S, 1992.

[4] W. H. Wang et al., Appl. Phys. Lett. **75**, 2770 (1999)