Partial Vibrational Density of Phonon States in $Fe_{90}Zr_7B_3$ Nanocrystalline Alloy Studied by Nuclear Inelastic Scattering of Synchrotron Radiation

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Motivation

Vibrational properties of nanocrystalline materials have been a subject of intense investigations in the last decade due to the observed striking differences of their density of phonon states (DOS) compared to that of bulk counterparts. The anomalous features include a significant enhancement of the phonon states at low and high energies, and broadening of the phonon peaks. In addition, the functional dependence of a low-energy part, which is expected to deviate from the quadratic Debye-like behaviour for systems with large surface-to-volume ratio, has been a subject of long-standing debates.

Aim

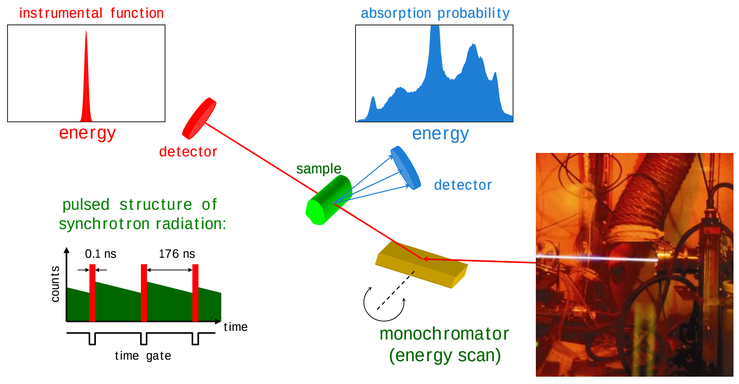
- To reliably identify DOS of the intercrystalline material and to investigate its vibrational properties as a function of the volume content of nanocrystallites.
- A systematic study of the interfaces which, as recently suggested by molecular-dynamics calculations, are the origin of the unusual vibrational properties of nanocrystalline materials. Such studies have not been done so far.

Experiment

Synchrotron

- ID18 @ ESRF, Grenoble
- high resolution monochromator with an energy bandpass of 1 meV
- 14.41 keV energy of synchrotron radiation
- energy scan over DE = 70 meV

- nuclear resonance
  - nuclear forward scattering
  - nuclear inelastic scattering



Samples à preparation

amorphous and nanocrystalline
- $Fe_{90}Zr_7B_3$ enriched to 63% in ^{57}Fe
- prepared by the melt-spinning technique
- ribbons about 20 mm thick
- annealing of the as-quenched ribbons in a vacuum furnace (1.6×10^{-6} mbar) at:
  - 753 K/10 min à sample A
  - 783 K/10 min à sample B
  - 783 K/30 min à sample C
  - 893 K/80 min à sample D

crystalline (bulk crystals)
- 10 mm thick bulk a-Fe foil enriched to 95% in ^{57}Fe

Results

Samples à characterization

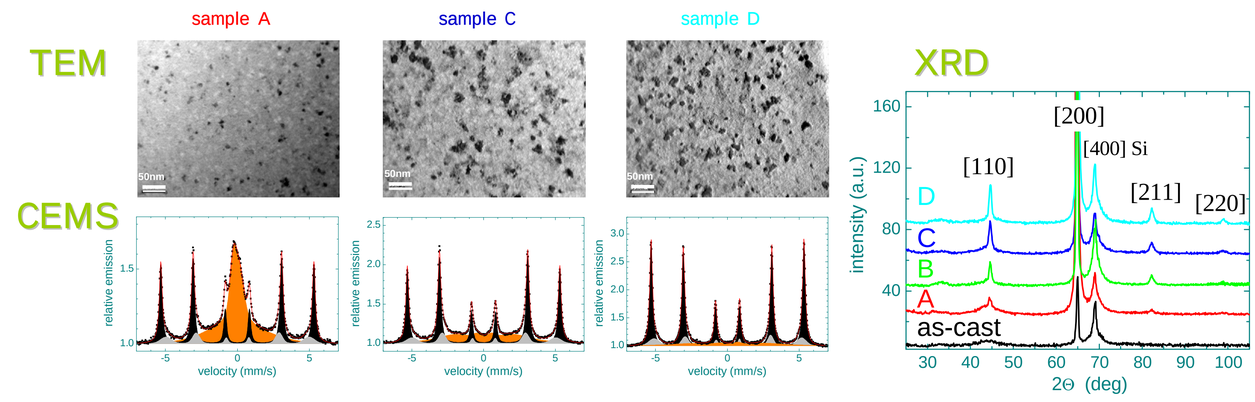
- XRD – x-ray diffraction (Cu K_a radiation)
- TEM – transmission electron microscopy
- CEMS – conversion electron Mössbauer spectrometry (^{57}Co/Rh source)

- synchrotron radiation à nuclear inelastic scattering

Table I.

sample	*a* (Å)	*d* (nm)	*d* (nm)	X_{IC}
as-quenched	2.8661(1)	2.2(5)	1.0(5)	0.84(2)
A	2.8662(1)	10.9(5)	2.3(5)	0.51(2)
B	2.8660(1)	12.5(5)	1.5(5)	0.32(2)
C	2.8661(1)	13.4(5)	1.0(5)	0.21(2)
D	2.8659(1)	14.9(5)	0.6(5)	0.11(2)

a – lattice parameter; *d* – average size of nanocrystals; *d* – width of intercrystalline layer; X_{IC} – relative intercrystalline content obtained from CEMS



structural arrangement:
- nanocrystalline grains à bcc-Fe: bulk (CEMS: B_{hf} = 32.99 T, XRD: *a* = 2.8665 Å)
  surface of nanocrystalline grains
- intercrystalline regions à amorphous residual matrix (glass-like behaviour)

Density of phonon states - DOS

$$g(E) = (1 - X_{IC})\,g_{NG}(E) + X_{IC}\,g_{IC}(E) \qquad \text{(Equ. 1)}$$

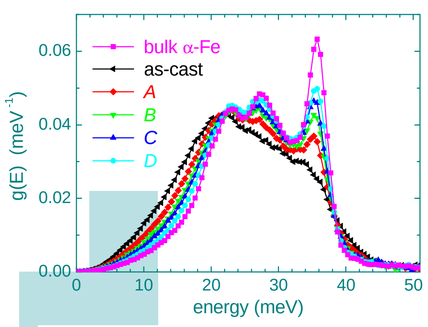


Fig. 1. DOS of $Fe_{90}Zr_7B_3$ in as-quenched state and at different states of nanocrystallization. The magenta line represents the DOS of α-Fe crystalline foil.

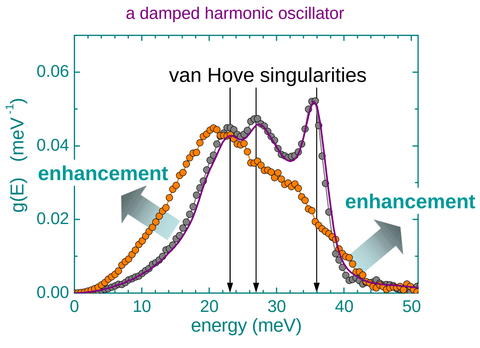


Fig. 2. Reference DOS of nanograins and internal surfaces $g_{NG}(E)$ and that of intercrystalline phase $g_{IC}(E)$. Both functions are derived as solutions of two linear equations system obtained by applying Eq. (1) to DOS of samples A and C and the corresponding X_{IC} values from Table 1. The purple solid line represents DOS of α-Fe convoluted with a damped harmonic oscillator (quality factor Q = 36).

quantification:
- from the low energy part of the phonon spectra
- Debye law: $g(E) = a \cdot E^2$
- a: enhancement factor (a_0 – for bulk a-Fe)

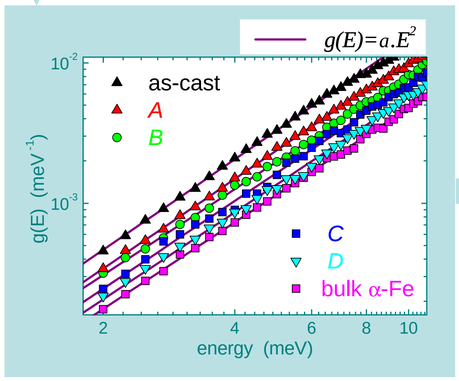


Fig. 5. Double-log plot of the low-energy region of the DOS displayed in Fig. 1. The purple solid lines are fits according to the Debye law $g(E) = a \cdot E^2$.

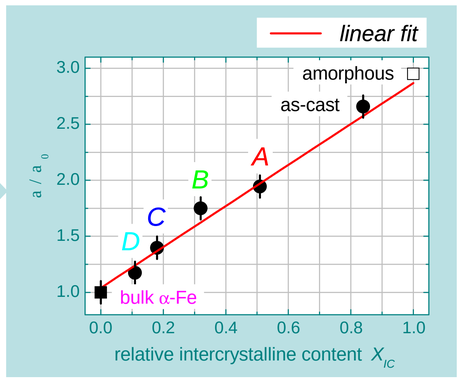


Fig. 6. Enhancement coefficient α/α_0 as a function of the intercrystalline content X_{IC} (α_0 is obtained from the DOS of α-Fe foil). The red solid line results from a linear fit to the experimental points (solid circles). The solid square at X_{IC} = 0 marks the value derived from DOS of bulk α-Fe, while the open square at X_{IC} = 1 corresponds to the reference intercrystalline DOS $g_{IC}(E)$.

contributions from:
nanocrystalline grains

$$(1 - X_{IC})\,g_{NG}(E) = g_{\exp}(E) - X_{IC}\,g_{IC}(E)$$

intercrystalline regions

$$X_{IC}\,g_{IC}(E) = g_{\exp}(E) - (1 - X_{IC})\,g_{NG}(E)$$

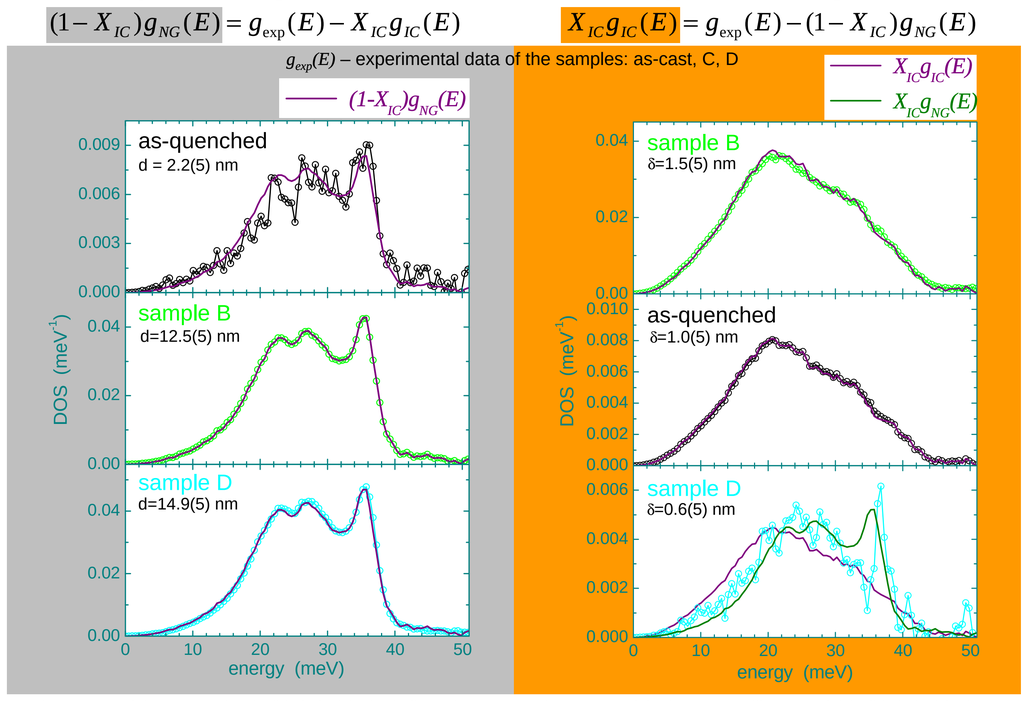


Fig. 3. DOS of the nanograins (solid circles) in the indicated samples obtained by subtracting the reference intercrystalline DOS weighted by the corresponding volume contribution, i.e. $X_{IC}g_{IC}(E)$ from the experimental DOS. The purple solid lines show plots of $(1\text{-}X_{IC})g_{NG}(E)$.

Fig. 4. DOS of the interecrystalline material (solid circles) in the indicated samples obtained by subtracting the reference nanograin DOS weighted by the corresponding volume content, i.e. $(1\text{-}X_{IC})g_{NG}(E)$ from the experimental DOS. The purple solid lines show plots of $X_{IC}g_{IC}(E)$ while the green solid line corresponds to $X_{IC}.g_{NG}(E)$.

An excellent fit with DOS of the nanograins in the as-quenched sample (d = 2.2 nm) suggests that the DOS of the nanograins and belonging surfaces is essentially bulklike and independent on the grain size.

Better fit with DOS of the nanograins (green solid line) implies that the residual regions belong to the nanograin surfaces rather than to the IC regions as a consequence of high degree of crystallization in sample D.

Conclusions

- Density of phonon states (DOS) was studies independently for intercrystalline regions and for nanograins in the $Fe_{90}Zr_7B_3$ alloy with different content of nanocrystallites.
- The enhancement of phonon states at low and high energies originates from the vibrational modes of the intercrystalline phase, which exhibits a substantially glasslike spectrum.
- The low energy enhancement of phonon states scales linearly with the volume content of the intercrystalline material and perfectly obeys the Debye law.
- DOS of the nanograins and belonging surfaces resembles closely that of a bulk material, assuming a certain lifetime broadening, being to a large extent independent of the grain size.

Synchrotron Facilities for the Development of Science and Technology in the Central and Eastern Europe
November 20-21, 2007
Brno, Czech Republic

Acknowledgement: Contributions from Y. Yue, I. Sergueev, A. I. Chumakov, L. Hu, P. Švec, and R. Rüffer.
Support by the Austrian Ministry grant bm:bwk GZ 45.529/2-VI/B/7a/2002.