Vibrational Properties of Nanograins and Interfaces in Nanocrystalline Materials

S. Stankov,[1] Y. Z. Yue,[2,3] M. Miglierini,[4] B. Sepiol,[5] I. Sergueev,[1] A. I. Chumakov,[1] L. Hu,[2,3] P. Svec,[6] and R. Rüffer[1]

[1]*European Synchrotron Radiation Facility, BP220, 38043 Grenoble, France*
[2]*Section of Chemistry, Aalborg University, 9000 Aalborg, Denmark*
[3]*Key Laboratory of Liquid Structure and Heredity of Materials, Shandong University, 250061 Jinan, China*
[4]*Department of Nuclear Physics and Technology, Slovak University of Technology, 81219 Bratislava, Slovakia*
[5]*Faculty of Physics, University of Vienna, 1090 Vienna, Austria*
[6]*Institute of Physics, Slovak Academy of Sciences, 84511 Bratislava, Slovakia*

The vibrational dynamics of nanocrystalline $Fe_{90}Zr_7B_3$ was studied at various phases of crystallization. The density of phonon states (DOS) of the nanograins was separated from that of the interfaces for a wide range of grain sizes and interface thicknesses. The DOS of the nanograins does not vary with their size and down to 2 nm grains still closely resembles that of the bulk. The anomalous enhancement of the phonon states at low and high energies originates from the DOS of the interfaces and scales linearly to their atomic fraction.

The dynamics of nanocrystalline (NC) materials [1] has been a subject of intense investigations due to the striking differences of their atomic vibrations relative to the bulk counterparts. The observed anomalies are the enhancement of their density of phonon states (DOS) at low and high energies and broadening of the phonon peaks [2–9]. In addition, the functional dependence of the low-energy part of the DOS for systems with large surface-to-volume ratio [10] has been a source of long-standing debates. While the DOS of most NC materials does not deviate from the quadratic Debye behavior, a linear dependence is observed for NC Pd [11], and a power law with $n = 1.33$ is reported for Fe nanoclusters [12]. The unusual properties are commonly attributed to the nanograin component of the NC materials. Recent molecular-dynamics calculations indicate that they also may originate from the interfacial regions [13,14]. However, an experimental separation of the atomic vibrations of nanograins and interfaces has not been done so far.

In this Letter we report on the determination of the DOS separately for the nanograins and interfaces. The results show that the vibrational anomalies of the NC materials originate from the interface regions, whereas the DOS of the nanograins remains close to that of the bulk.

We studied $Fe_{90}Zr_7B_3$ NC material with 63% enrichment of iron in the ^{57}Fe isotope. A 20 μm thick ribbon was obtained by the melt-spinning technique. The first 783(1) K and the second 1017(1) K crystallization temperatures were determined by differential scanning calorimetry. Several NC samples composed of α-Fe nanograins and homogenous porosity-free intercrystalline (IC) regions [15] were prepared by annealing of the as-quenched ribbon in a vacuum of 1.6×10^{-6} mbar. We denote by *A*, *B*, *C*, and *D* the samples obtained by annealing for 10 min at 753 K, 10 min at 783 K, 30 min at 783 K, and 80 min at 893 K, respectively.

The mean nanograin sizes d (Table I) were determined by Rietveld refinement of the x-ray diffractograms (XRD) [Fig. 1(a)] measured with Cu K_α radiation. The obtained values were confirmed by transmission electron microscopy (TEM). In agreement with an earlier TEM study [16], the as-quenched material revealed the presence of nanograins with 2.2 nm size. The derived lattice constant a_L of the nanograins (Table I) is consistent with that of bulk α-Fe ($a_L = 2.8665$ Å). No traces of any oxides were detected. The presence of other crystalline phases was also not detected and is excluded because the annealing was performed at temperatures well below 1017 K.

The relative atomic fractions of nanograins and interfaces were determined by conversion electron Mössbauer spectroscopy (CEMS). According to the established model [17], the CEMS spectra were decomposed into three contributions [Fig. 1(b)]: The narrow sextet (dashed line) arises from the nanograins interior. The broader sextet (gray line) originates from atoms located at the surfaces of the nanograins. The third component (filled area) corresponds to the IC phase, which consists of grain boundaries and triple junctions (intersections of three and more grain boundaries). The determined atomic fractions X_{IC} of the interfaces are shown in Table I.

TABLE I. The derived lattice constant a_L and the mean size d of the nanograins, and the mean thickness δ and the atomic fraction X_{IC} of the interfaces.

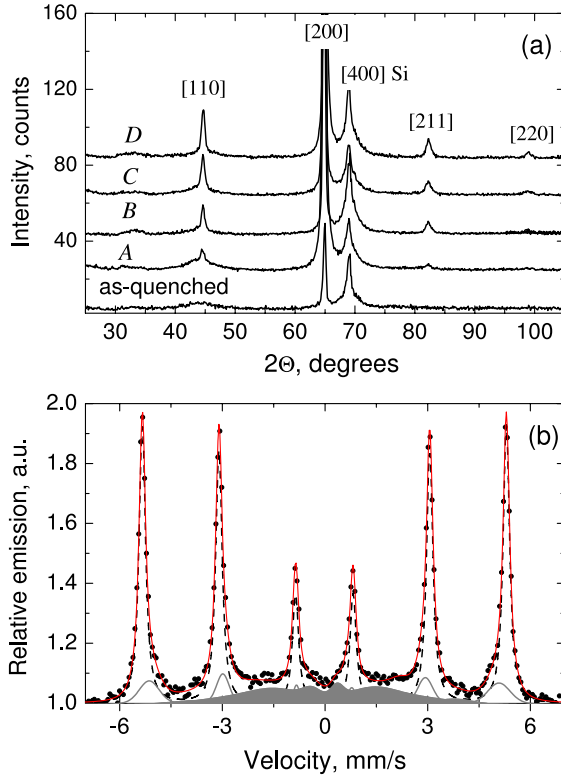| Sample	a_L (Å)	d (nm)	δ (nm)	X_{IC}
As-quenched	2.8661(1)	2.2(5)	1.0(5)	0.84(2)
A	2.8662(1)	10.9(5)	2.3(5)	0.51(2)
B	2.8660(1)	12.5(5)	1.5(5)	0.32(2)
C	2.8661(1)	13.4(5)	1.0(5)	0.21(2)
D	2.8659(1)	14.9(5)	0.6(5)	0.11(2)

FIG. 1 (color online). (a) XRD data with the assigned α-Fe peaks (Si peak arises from the holder); (b) CEMS spectrum of the sample C (circles) decomposed into the subspectra related to the grains interior (dashed line), the grains surface (gray line), and the interfaces (filled area). The red solid line shows the fit.

The pronounced decrease of the IC fraction from 0.51 to 0.11 and the relatively small increase of the grain size from 11 to 15 nm suggest that the annealing process increases mainly the number of nanograins and does not significantly affect their size. From the IC fraction and the mean grain size the mean interface thickness δ was calculated [18]. It gradually decreases with annealing [19], reaching the value of 0.6(5) nm for the sample D (Table I).

The iron-partial DOS were measured by nuclear inelastic scattering [20,21] at the Nuclear Resonance beamline (ID18) [22] of the European Synchrotron Radiation Facility. The measurements were performed at room temperature with 1.0 meV energy resolution. For comparison, the DOS of an α-Fe foil was also measured.

The DOS of the NC samples [Fig. 2(a)] reveal a significant enhancement of the vibrational states below 20 meV, a decreasing of the peaks at 27 and 36 meV, and a notable increase of the states above 38 meV. These are the known vibrational anomalies of the NC materials, which are usually explained by the small size of the nanograins [23]. Indeed, Table I shows that the gradual development of the DOS anomalies correlates with the continuous decrease of the grains size. However, one could also correlate the increase of the DOS anomalies with the increase of the IC fraction.
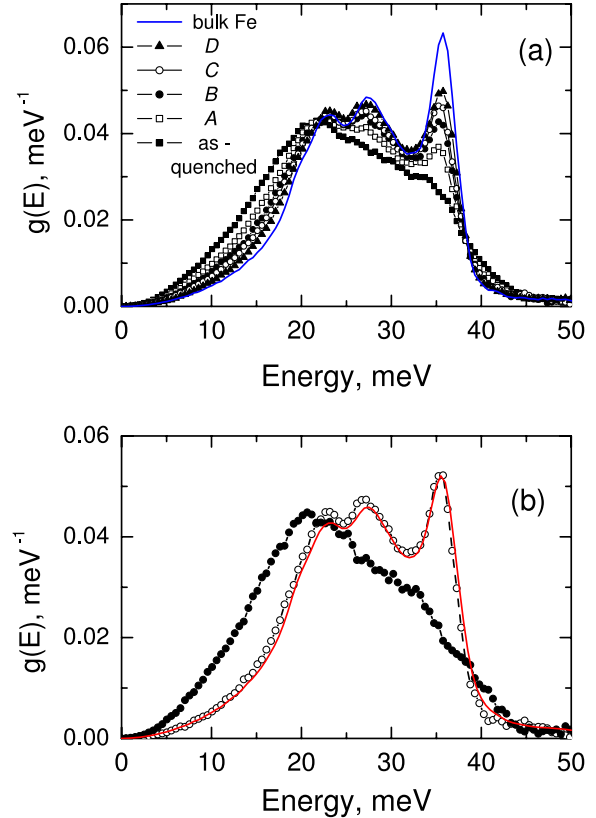

FIG. 2 (color online). (a) The DOS of $Fe_{90}Zr_7B_3$ at various phases of crystallization. The blue solid line shows the DOS of α-Fe foil. (b) The derived DOS of the nanograins (open circles) and of the interfaces (solid circles), see text. The red solid line shows the DOS of α-Fe convoluted with the damped harmonic oscillator function with a quality factor $Q = 36$.

The DOS $g(E)$ of each NC sample consists of the DOS of the nanograins $g_{NG}(E)$ and that of the interfaces $g_{IC}(E)$:

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

The relative weights $1 - X_{IC}$ and X_{IC} of the two components are known from CEMS (Table I). Assuming that $g_{NG}(E)$ and $g_{IC}(E)$ do not vary much with the grain size (as confirmed below), one can calculate them applying Eq. (1) to any pair of measured DOS. Figure 2(b) shows the DOS of the nanograins and the interfaces calculated from the DOS of samples A and C.

Figure 2(b) shows that the vibrational anomalies of the NC materials originate not from the nanograins but from the interfaces. Indeed, the DOS of the interfaces reveals an enhancement of the phonon states at low and high energies and vanishing of the peaks at 27 and 36 meV. On the contrary, the DOS of the nanograins resembles closely that of bulk iron. In order to estimate a proximity of the vibrational properties of the grains to the bulk iron, the DOS of the nanograins was compared to the α-Fe DOS convoluted with the damped harmonic oscillator function [24]. The best fit [Fig. 2(b)] was obtained with a quality

factor $Q = 36$, revealing only a slight difference between the DOS of nanograins and bulk α-Fe. This is in agreement with the quality factor $Q = 30$ obtained [4] for 10 nm grains.

In order to analyze the dependence of the DOS of the nanograins on their size, we subtracted from the measured DOS the contribution of the interfaces $X_{IC}g_{IC}(E)$. Figure 3 shows the obtained DOS of the nanograins for the as-quenched, B, and D samples. They are compared to the reference DOS of the nanograins $g_{NG}(E)$ obtained from the DOS of samples A, and C as discussed above.

Figure 3 shows that the DOS of the nanograins does not vary with their size and remains close to the DOS of bulk α-Fe. While this still could be expected for the samples $A - D$ with relatively big and similar grains sizes (Table I), it is quite surprising for the 2.2 nm grains of the as-quenched sample. In such small crystals where translational periodicity breaks after $\sim$8 atoms and where up to 65% of the atoms are located at the surface, one usually observes a significant damping of the DOS peaks [5]. However, in agreement with the molecular-dynamics calculations [13] Fig. 3(a) shows that the DOS of the 2.2 nm particles remains close to that of the bulk iron.

Figure 4 shows the DOS of the interfaces obtained by subtraction of the nanograin contribution $g_{NG}(E)$ from the measured DOS of the B, as-quenched, and D samples. They are compared to the reference DOS of the interface $g_{IC}(E)$ obtained from the DOS of samples A and C as discussed above. Figures 4(a) and 4(b) reveal that the DOS of the interfaces remains the same for the as-quenched, A, B, and C samples, i.e., for the interface thicknesses down to 1 nm. Most likely, the observed DOS is related to the triple junctions, which are characterized by high structural disorder and dominate the grain boundaries for grain sizes below 20 nm [25].

A further decrease of the interface thickness from 1.0 to 0.6 nm leads to a drastic transformation of the DOS: The DOS reveals distinct phonon peaks at 23, 27, and 36 meV, it loses significantly the vibrational states below 20 meV, and it becomes similar to the reference DOS of the nanograins $g_{NG}(E)$ [Fig. 4(c)]. This suggests that the interface with a mean thickness equal or less than two atomic layers acquires the vibrational properties of adjacent nanograins.

Finally, we analyze the functional dependence of the DOS at low energy. Figure 5(a) shows the DOS of all measured samples in a double logarithmic scale. The straight lines show parabolic fits $g(E) = \alpha E^2$ to the data within the 2–12 meV energy range. The vibrational states at low energy do not show any deviation from the Debye law.

In order to quantify the anomalous enhancement of the low-energy DOS, we plotted in Fig. 5(b) the ratio of the parabola coefficient α for the NC samples to that for the bulk Fe (α_0) as a function of the interface fraction X_{IC}. The
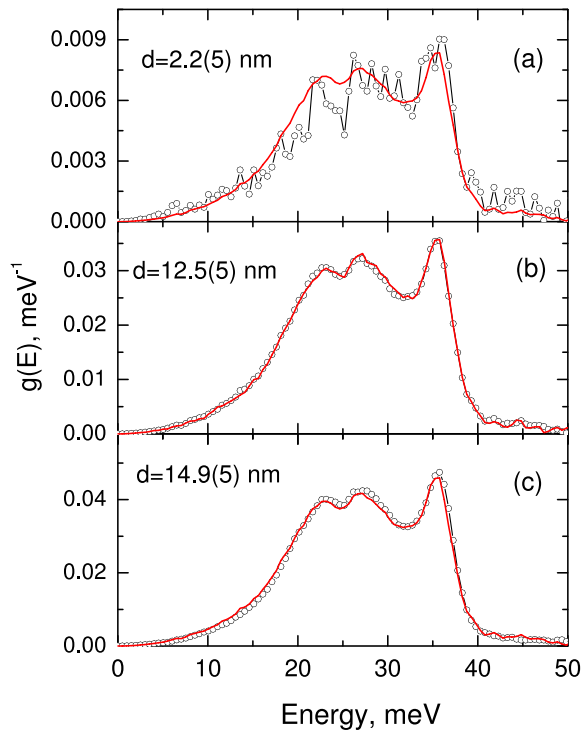

FIG. 3 (color online). The DOS of the nanograins (open circles) determined for (a) as-quenched, (b) B, and (c) D samples. The red solid lines show the reference DOS of the nanograins $(1 - X_{IC})g_{NG}(E)$.
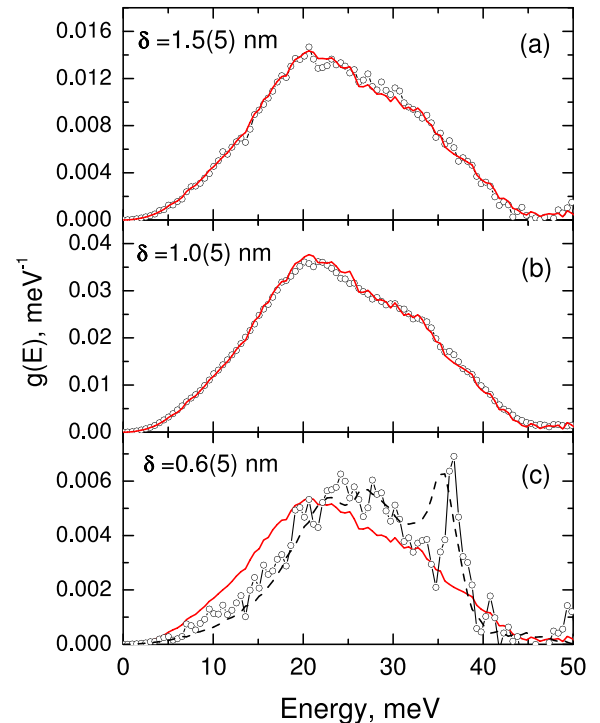

FIG. 4 (color online). The DOS of the interfaces (open circles) determined for (a) B, (b) as-quenched, and (c) D samples. The red solid lines show the reference DOS of the interfaces $X_{IC}g_{IC}(E)$. The dashed line in (c) shows the reference DOS of the nanograins $X_{IC}g_{NG}(E)$.
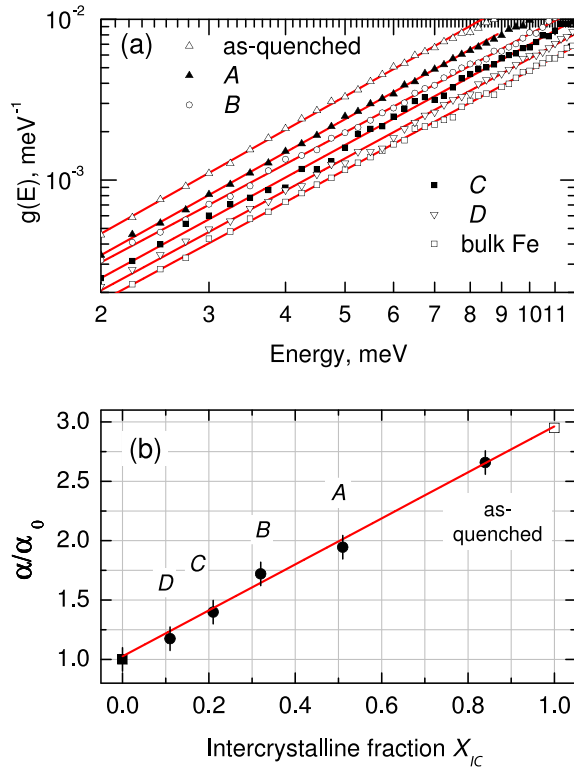
FIG. 5 (color online). (a) Double-log plot of the low-energy part of the DOS from Fig. 2(a). The solid lines show the fits by the Debye law $g(E) = \alpha E^2$; (b) the coefficient α/α_0 (see text) as a function of the interface fraction X_{IC}. The solid line is a linear fit to the data (solid circles). The solid square at $X_{IC} = 0$ is the value for the bulk Fe. The open square at $X_{IC} = 1$ is the value for the reference DOS of the interfaces $g_{IC}(E)$.

solid line is a linear fit to the data for the as-quenched and $A - D$ samples, which nicely follows the experimental points. Moreover, the extrapolation of the solid line to $X_{IC} = 0$ matches $\alpha/\alpha_0 = 1$ value for the bulk Fe (solid square), whereas the extrapolation to $X_{IC} = 1$ matches $\alpha/\alpha_0 = 2.9$ obtained for the reference DOS of the interfaces $g_{IC}(E)$ (open square). Similar linear dependencies are also valid for other thermoelastic quantities related to the DOS as vibrational entropy, mean-square displacement, average force constants, and specific heat.

The exact scaling of the enhancement of low-energy states to the IC fraction confirms that this anomaly originate solely from the interface atoms. Most likely, it is related to the lower sound velocity in NC samples with higher IC fraction due to the lower values of the force constants and their distribution typical for systems with a certain degree of structural disorder.

In summary, we determined separately the DOS of the grains and the interfaces in NC $Fe_{90}Zr_7B_3$ at various phases of crystallization. The DOS of the nanograins does not vary with the grain size and down to 2 nm grains remains close to that of the bulk. The DOS of the interfaces reveals an enhancement of the vibrational states at low and high energies, and is entirely responsible for the vibrational anomalies of the NC materials. As a practical implication the results suggest that tailoring of thermoelastic properties of the NC materials requires a control of the nanograin's fraction rather than of their sizes.

The developed approach can be applied to a large number of NC systems and constitutes a method to study separately the atomic vibrations of the nanograins and interfaces for various sample compositions or under extreme conditions like high pressures or plastic deformations, which are challenging fields of research.

[1] C. Suryanarayana and C. C. Koch, Hyperfine Interact. **130**, 5 (2000).
[2] J. Trampenau *et al.*, Nanostruct. Mater. **6**, 551 (1995).
[3] B. Fultz *et al.*, J. Appl. Phys. **79**, 8318 (1996).
[4] H. N. Frase *et al.*, Philos. Mag. B **75**, 335 (1997).
[5] B. Fultz *et al.*, Phys. Rev. Lett. **79**, 937 (1997).
[6] H. Frase, B. Fultz, and J. L. Robertson, Phys. Rev. B **57**, 898 (1998).
[7] E. Bonetti *et al.*, J. Appl. Phys. **88**, 4571 (2000).
[8] L. Pasquini *et al.*, Phys. Rev. B **66**, 073410 (2002).
[9] A. F. Yue *et al.*, Phys. Rev. Lett. **93**, 205501 (2004).
[10] A. Kara and T. S. Rahman, Phys. Rev. Lett. **81**, 1453 (1998).
[11] U. Stuhr *et al.*, Phys. Rev. Lett. **81**, 1449 (1998).
[12] B. Roldan Cuenya *et al.*, Phys. Rev. B **76**, 195422 (2007).
[13] P. M. Derlet *et al.*, Phys. Rev. Lett. **87**, 205501 (2001).
[14] P. M. Derlet and H. V. Swygenhoven, Phys. Rev. Lett. **92**, 035505 (2004).
[15] M. E. McHenry *et al.*, Scr. Mater. **48**, 881 (2003).
[16] T. Ohkubo *et al.*, Mater. Sci. Eng. A **312**, 274 (2001).
[17] M. Miglierini and J. M. Grenèche, J. Phys. Condens. Matter **9**, 2303 (1997).
[18] G. Palumbo, S. J. Thorpe, and K. Aust, Scr. Metall. Mater. **24**, 1347 (1990).
[19] X_{IC} depends on the ratio of d and δ; i.e., very small particles result in a small δ. Therefore the value of δ in the as-quenched sample is smaller than that of sample A.
[20] M. Seto *et al.*, Phys. Rev. Lett. **74**, 3828 (1995).
[21] W. Sturhahn *et al.*, Phys. Rev. Lett. **74**, 3832 (1995).
[22] R. Rüffer and A. I. Chumakov, Hyperfine Interact. **97−98**, 589 (1996).
[23] By definition the light B and heavy Zr atoms do not contribute to the measured partial Fe-projected DOS.
[24] B. Fåk and B. Dorner, Institute Laue Langevin Technical Report No. 92FA008S 1992 (unpublished).
[25] P. M. Derlet and H. Van Swygenhoven, Phys. Rev. B **67**, 014202 (2003).