Local Structure and Size Effects in Nanophase Palladium: An X-Ray Absorption Study

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Abstract

The connection between local structure and the grain size distribution in nanophase palladium is studied by X-ray absorption spectroscopy (XAFS) and X-ray diffraction. XAFS shows that there is a reduced average coordination number in all samples; this reduction is compatible with a size effect, contradicting previous XAFS measurements.

1. Introduction

The interest in the local structure of nanophase materials [1,2] stems from the high density of grain boundaries (GBs) present. One may try to study the structure of such defects by volume sensitive methods but this is impossible in coarse grained materials due to their low volume fraction. It is essential to clarify what is the local structure of a GB and whether it is different in a coarse grained or nanophase material. An early X-ray diffraction study [3] on nanophase Fe reported a large diffuse scattering background which was interpreted as arising from a structure having no long-range or short-range order in the GB; this was proposed to lead to a GB radial distribution function (RDF) lacking either short-range or long-range order. Two effects could contribute to this phenomenon: atomic relaxations in the GB, due to the different environment than in the bulk, and the different local environment of each GB which, when averaged over all the GBs present could lead to a disordered average RDF. This result has initiated a controversy fed with results from different techniques either supporting or ruling out this model [4–11].

X-ray absorption spectroscopy (XAFS) [12] has played an important role in this debate [13]. In fact, all measurements reported to date [14–19] have

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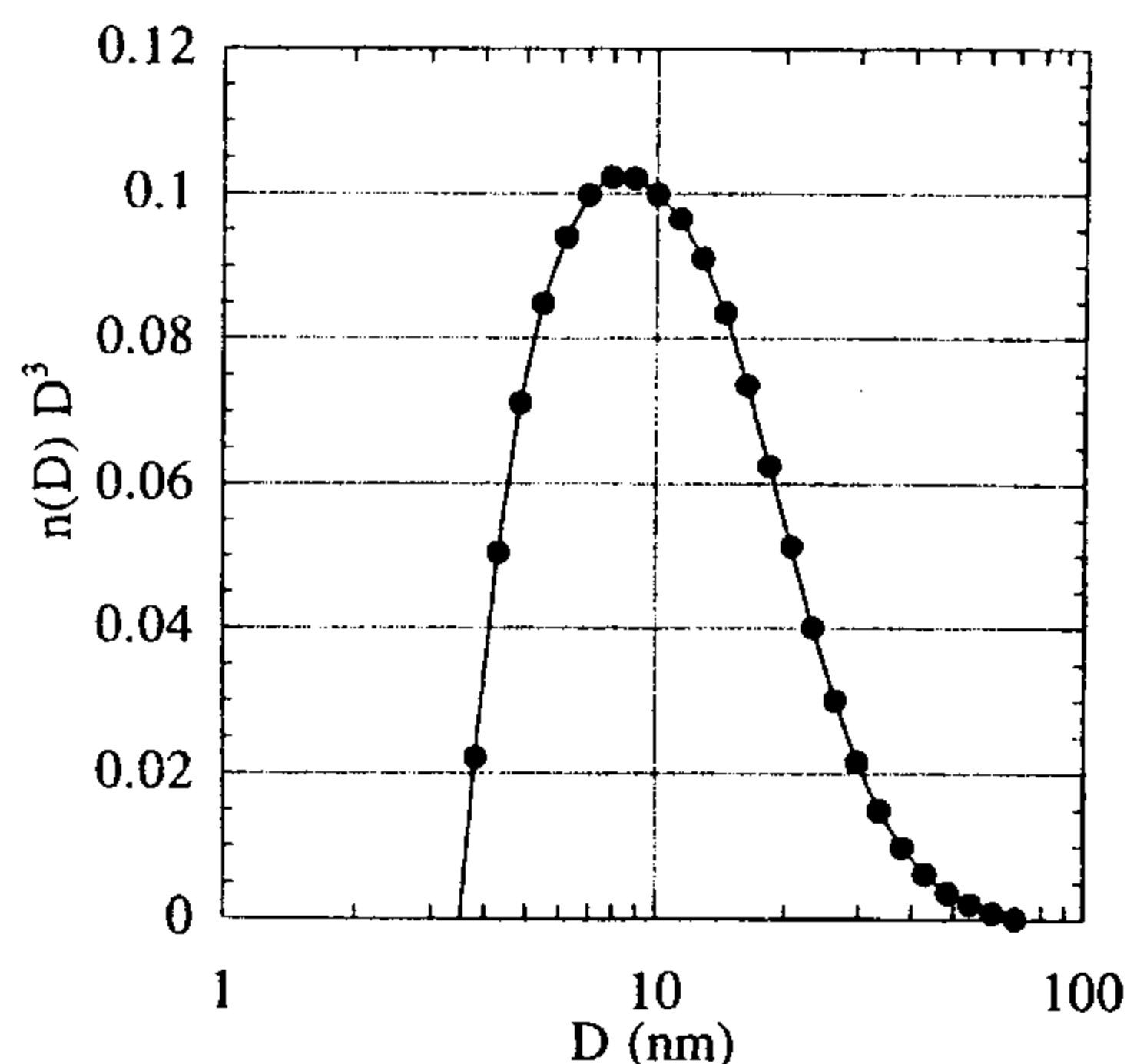* Corresponding author. E-mail: boscherini@lnf.infn.it.

Fig. 1. Volume-weighted grain size distribution function for sample 4 determined from the (111) and (222) Bragg reflections.

shown a reduction of average coordination numbers in the first few coordination shells. A reduction in the average coordination number is expected for an aggregate of nanometer sized clusters due to the reduced coordination of surface atoms and the high average surface-to-bulk ratio (SBR). A similar reduction is expected also for compacted nanophase materials in which free surfaces are replaced by incoherent grain boundaries. However, the reduction in coordination numbers reported so far by XAFS was greater than compatible with a simple estimate of the SBR and most measurements were interpreted as compatible with the disordered grain boundary model [14–17] or with the presence of a high defect density [19].

A recent X-ray diffraction (XRD) study [20] of nanophase Pd (n-Pd) has reported reduced average coordination numbers in the first few shells for all samples studied. This reduction was satisfactorily explained by the SBR for all samples except for those investigated within 10 days of preparation; for the latter samples it was concluded that 10% of atoms are off lattice sites.

In the present paper we report XAFS measurements of n-Pd samples which have been carefully characterized as those studied by XRD by Löffler and Weissmüller [20]; of particular importance is the determination of the particle size distribution [21]. We note that XRD and XAFS are complementary in that they probe different parts of wave-vector space: 0 to 17 Å^{-1} for XRD and 6 to 40 Å^{-1} for XAFS. Results in qualitative agreement with those reported here have been already published by other authors [18], but no quantitative analysis or interpretation has been detailed.

2. Sample preparation and experimental

Six samples of n-Pd were prepared by inert gas condensation with different treatments following the deposition. One sample (no. 1) was not consolidated, in order to serve as a reference for an ensemble of clusters with a negligible grain boundary density. All other samples were consolidated in situ under high vacuum for 5 to 10 minutes at 1–2 GPa; at this stage samples have a density from 84% to 87% of coarse grained Pd. Following room temperature consolidation one sample was kept at liquid nitrogen temperature (LNT) up to 1 week before measurements in order to reduce room temperature (RT) grain growth. Two samples were stored at RT for different periods of time and the remaining two samples were submitted to annealing and hot-pressing procedures.

The size distribution of materials prepared by inert gas evaporation has been proposed to be a log-normal distribution function [22]. For compacted

Table 1
Sample characteristics; $\langle D \rangle_A$ is the area weighted average particle size

Sample	Preparation/Treatment	$\langle D \rangle_A$ (nm)
1	not compacted	8.4
2	stored at LNT	11.5
3	stored at RT for 1 month	16.7
4	stored at RT for 2 weeks	12.2
5	hot pressed for 2 days, 3.2 GPa, 100°C	11.5
6	as No. 5, then annealed for 1 hour at 160°C	13.0

materials, however, a bimodal distribution provides a better description, due to the details of the grain growth kinetics [21]. The particle size distribution functions, $n(D)$, for all our samples has been determined by indirect deconvolution of Bragg peaks [21]. An example $n(D)$ for sample 4 is shown in Fig. 1.

The average grain size can be determined from this and it is listed in Table 1, together with the sample history. The rms strain values lie between 0.03% and 0.3%.

In order to perform reliable XAFS experiments, a thin (≈ 10 μm), homogeneous sample is required;
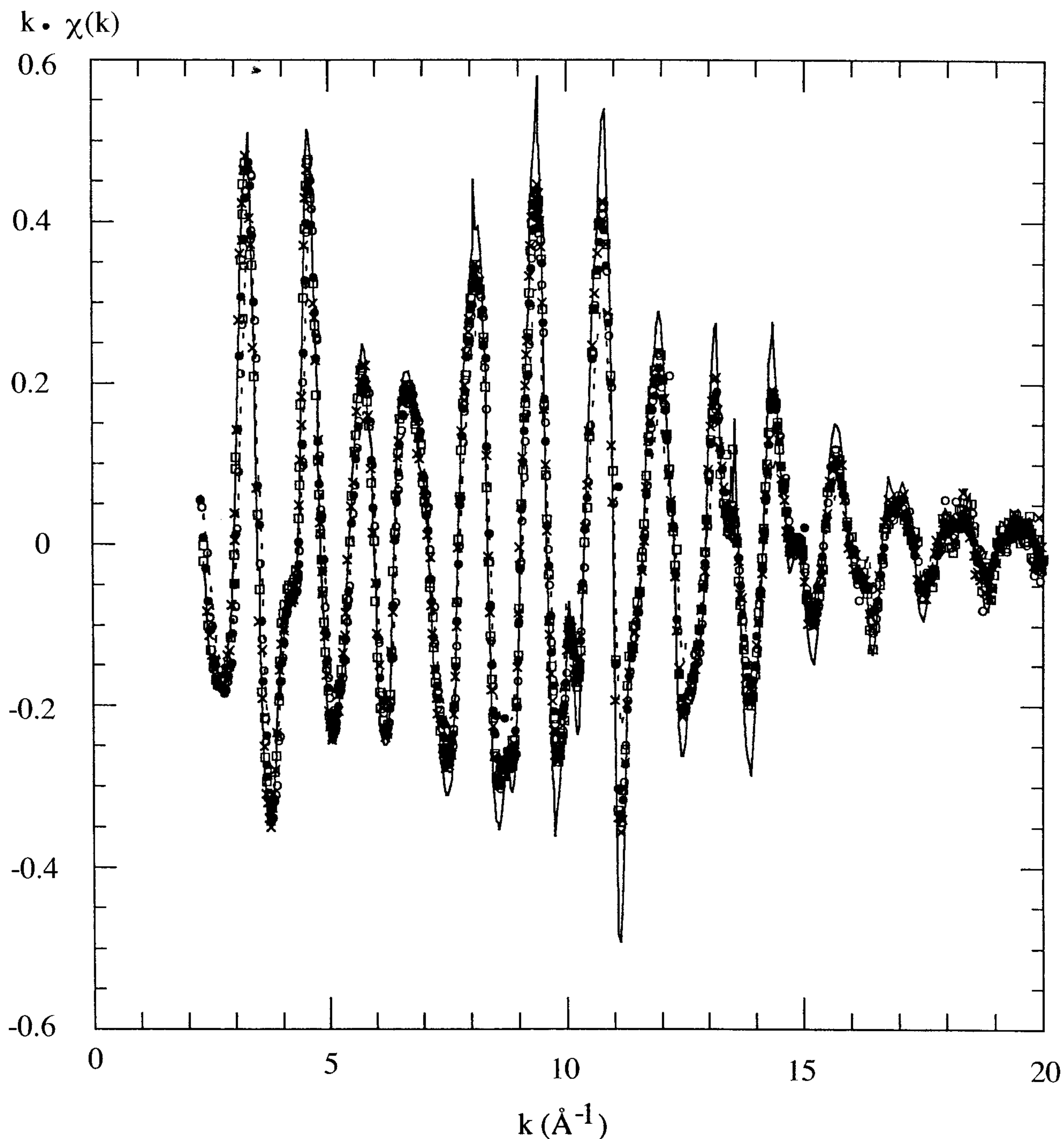

Fig. 2. Background subtracted raw XAFS data for all samples. Solid line: reference foil; dashed line: sample 1; (○) sample 2; (×) sample 3; (□) sample 4; (●) sample 5; (▲) sample 6.

inhomogeneity in the sample thickness distribution is a major source of experimental artefacts [23,24], which systematically lower the apparent coordination numbers. Consequently much care was devoted to the preparation of homogeneous samples. Note that all known experimental artefacts tend to reduce the measured coordination numbers, not to enhance them. The samples were lightly ball milled at LNT in order to produce a powder which was then dispersed in toluene using an ultra-sound bath. Only the finest particles (those forming a fine suspension at the top of the test tube) were then deposited on a cellulose membrane forming a homogeneous sample. Homogeneity at the sub-micron level was checked optically and by measuring spectra on samples of different thicknesses, from 1 to 15 μm, which showed
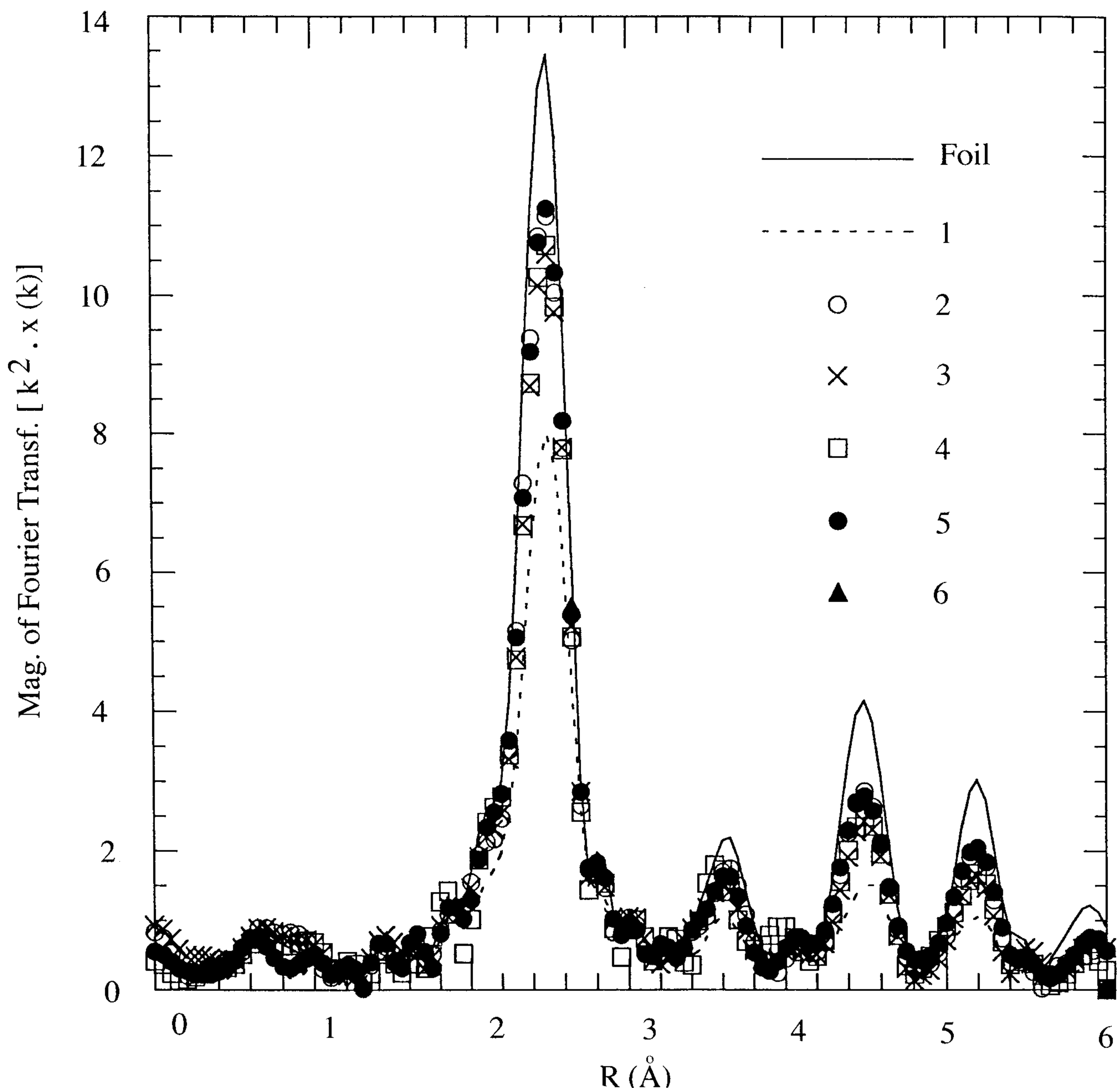

Fig. 3. Magnitude of the Fourier transform of the data presented in Fig. 2.

identical values of the coordination numbers. We found that samples prepared by using all particles produced by ball milling (without dispersion in toluene and subsequent selection of finest particles) exhibited artificially reduced coordination numbers. In fact, samples of coarse grained powder prepared in the same way showed the same artificially low coordination numbers. This experimental artefact might be the origin of the low coordination numbers reported previously at least for materials produced by inert gas evaporation.

XAFS measurements were performed at the GILDA CRG (D8) bending magnet beamline of the European Synchrotron Radiation Facility, Grenoble, France. We used a double crystal monochromator equipped with Si(311) crystals and with sagittal focussing. Harmonics rejection was achieved by detuning the crystal to 1/3 of the rocking curve maximum using a closed loop feedback controller; the absence of harmonics was checked with a Si(Li) detector and multi-channel analyzer. XAFS spectra were measured in the transmission mode with Ar filled ionization chambers in the energy range 24–26 keV; all spectra were measured at 77 K in order to increase the available k-space. Temperature dependent measurements were performed only for a few samples and no variation of the determined average coordination numbers was found, but only an increase of the thermal disorder factor in accordance to the known vibrational behaviour [25]. A coarse grained Pd foil was measured as a reference sample.

3. Results and discussion

Spectra were analyzed according to standard procedures [12]. All near-edge structures were found identical to the reference foil, indicating that no appreciable oxidation had taken place. The raw XAFS functions, reaching 20 Å^{-1}, are reported in Fig. 2 and the good signal-to-noise is apparent. These functions were Fourier transformed in the range 3 to 20 Å^{-1} and the result is displayed in Fig. 3. From the figures it is apparent that the spectra show different amplitudes and can be roughly grouped in three sets in order of decreasing amplitude: the coarse grained foil, samples 2 to 6 (i.e. all the compacted samples) and sample 1 (the uncompacted sample).

In order to quantitatively analyze the spectra an inverse Fourier transform was performed in the range 1.8–3.2 Å to probe the nearest-neighbour environment; the result was fitted to a model function using a non-linear least squares routine and experimental amplitudes and phases from the coarse grained Pd foil. Average coordination numbers, $\langle N \rangle_{\text{EXP}}$, and variations of the mean square relative atomic displacement (MSRD), $\Delta \sigma^2$, determined in this way are reported in Table 2; for both parameters the model is the coarse grained foil. The estimated errors [26] are one standard deviation and include the effect of correlation between $\langle N \rangle$ and $\Delta \sigma^2$ which is, in fact, the major source to error bars; the errors on these two parameters should be interpreted in the following way: if $\langle N \rangle$ is increased (decreased) to its maximum (minimum) value then $\Delta \sigma^2$ must also be increased (decreased) in the same manner. The interatomic distances in all nanophase samples were found to be identical to those of the coarse grained reference; this seems most reasonable as size-dependent variations in interatomic distances set in at much smaller dimensions [27,28]. Finally, we found no evidence for anharmonic effects justifying the use of any Gaussian damping of the signal [29].

In order to interpret the data we have calculated in

Table 2
Experimental variation of first shell MSRD with respect to Pd foil, average first shell coordination number and two estimates of the latter quantity, as described in the text

Sample	$\Delta \sigma^2$ (10^{-3}Å^2, ±0.5)	$\langle N \rangle_{\text{EXP}}$ (atoms, ±1.0)	$\langle N \rangle_{n(D)}$ (atoms)	$\langle N \rangle_\alpha$ (atoms)
1	1.2	9.7	11.33	11.41
2	0.8	11.7	11.50	11.57
3	0.9	11.5	11.60	11.70
4	1.0	12.0	11.52	11.59
5	0.7	11.8	11.50	11.57
6	0.8	12.0	11.57	11.62

two independent ways the average coordination number expected for the samples considering only the SBR. The FCC structure can be built by adding successive layers of atoms to form cubo-octahedrons. Atoms at the surface have a reduced coordination compared to those in the bulk and the average coordination of a single particle constituted by n atomic layers around the central atom, $N(n)$, can be calculated [30],

$$N(n) = \frac{40n^3 - 96n^2 + 80n - 24}{\frac{1}{3}(10n^3 - 15n^2 + 11n - 3)}. \tag{1}$$

The size, D, of the particle is taken to be twice the edge length, so that $D = 2R_1(n-1)$, where R_1 is the nearest neighbour distance. The average coordination number for the cluster was calculated as being the volume weighted average of the particle size distribution, $n(D)$, which was determined as described above,

$$\langle N \rangle_{n(D)} = \frac{\int_0^\infty N(D) \times n(D) \times D^3 \, dD}{\int_0^\infty n(D) \times D^3 \, dD}. \tag{2}$$

As an alternative estimate we have also used the relation [20]

$$\langle N \rangle_\alpha = 12 \left(1 - \tfrac{1}{2}\alpha R_1 \right), \tag{3}$$

where $\alpha = 3/\langle D \rangle_A$ which is the SBR, assuming spherical particles. Both estimates of $\langle N \rangle$ are quite similar and are reported in Table 2. The experimental values reported in Table 2 are compatible with the rough division of spectra based on visual inspection referred to earlier: sample 1 shows a greatly reduced $\langle N \rangle_{EXP}$ while samples 2 to 6 exhibit similar values for this parameter. We will discuss first the results for the compacted material and then for sample 1.

$\langle N \rangle_{EXP}$ values for samples 2 to 6 are all quite close to the estimates of $\langle N \rangle$ based on the SBR. The present measurements indicate, therefore, that the reduction of $\langle N \rangle$ for compacted materials can be simply explained by a size effect with no evidence of further reduction, provided the particle size distribution is carefully determined. No evidence is found for disordered GB components. This is the main result of this paper, and is in contradiction with nearly all previous reports based on XAFS. We have already pointed out that for the samples deposited by inert gas evaporation at least a partial contribution to

the enhanced reduction found in previous work may lie in the sample thickness inhomogeneity. A previous XAFS study on n-Fe particles prepared by ball milling [19] also reported a very big (30% to 50%) reduction in average coordination number. However, the particle size distribution was not determined and the authors relied on an average value of the particle size which might be misleading. Let us note that the improvements in our sample preparation procedures over the last few years now provide well characterized samples as to impurity content and particle size distribution.

The slight enhancement of σ^2 with respect to the coarse grained foil indicates that the process of evaporation and compaction produces a slight distortion of the first shell environment which is insensitive to further hot pressing or annealing. It is interesting to compare the present result with the determination of disorder by XRD. In a real space analysis of XRD data [20] the slight increase of σ^2 was not found. However, we believe that the present results are more reliable as a greater proportion of reciprocal space is probed by XAFS than by XRD. In a k-space analysis of XRD [10] an (isotropic) increase of 3×10^{-3} Å^2 in the mean square displacement (MSD) was found which is to be compared with the 0.8×10^{-3} Å^2 we find for the increase in MSRD: In this case the two techniques measure different quantities, XAFS being sensitive to the relative atomic displacements (hence only to uncorrelated atomic displacements), while XRD measures the atomic displacements from the lattice positions. By comparing the numerical results of the two techniques we conclude that the increase in MSD is due mostly to atomic displacements which are correlated in the first coordination shell.

Sample 1 (with a negligible grain boundary density) shows a greatly reduced $\langle N \rangle_{EXP}$. This fact alone clearly suggests that the origin of the reduction of average coordination number for the compacted samples must be found in a size effect and cannot be attributed to the presence of GBs [10]. The reduction of $\langle N \rangle_{EXP}$ is not, however, reproduced by either of our estimates. There may be a number of reasons for this, including that our model of the size distribution is not correct for uncompacted samples. It may well be that there are many more small diameter grains than presently estimated and that they coalesce dur-

ing compaction; in fact it has been noted that the determination of $n(D)$ by XRD may neglect small diameter grains [21]. The slight increase in σ^2 may have both a structural and a dynamic [27] component, which cannot be decoupled from the present measurements alone. The small reduction of σ^2 upon compaction indicates that atoms in the outermost layer of each crystallite have greater constraints of motion in grain boundaries than on a free cluster surfaces and/or reduced static disorder.

In conclusion we have presented a XAFS study of local order in n-Pd samples submitted to various treatments. By considering the distribution of particle sizes we have shown that the observed reduction in average coordination number can be explained as a size effect originating from the reduced coordination of the atoms present of the surface of the particles, with no evidence of further reduction. As additional information on the disorder was available, the results were compared to the local structure in an un-compacted sample.

Acknowledgement

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