Are Nanophase Grain Boundaries Anomalous?

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Abstract

The grain boundary regions of nanophase Cu metal are investigated using the x-ray absorption fine structure (XAFS) technique. Typical such samples made by standard techniques need to be greatly thinned if measured in transmission in order to eliminate experimental artifacts which erroneously lower the apparent coordination number. To avoid this problem the samples were measured by the total electron yield technique. The results indicate conventional grain boundary structure, contrary to previous XAFS measurements made in transmission which indicated a lower coordination number.

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The properties of nanocrystalline materials have engendered much interest recently. Nanocrystalline materials, also called the nanophase, have such fine grains (1-100 nm) that the volume of the interfacial region between grains, i.e., in the grain boundary (GB), is an appreciable fraction of the total volume. They have been found to have different properties from ordinary polycrystalline materials, e.g., metals become stronger and more brittle and ceramics more ductile [1]. One obvious important factor that must be understood to explain their differences from conventional grain-size materials is the properties of their grain boundaries. Unfortunately, the structure of such interfaces is controversial [1–5]. One exciting claim has been that the GB region is completely disordered, as in a gas, without even the short range order of liquids or amorphous solids [6]. The experimental basis for this claim was founded on a diffraction analysis [7] of a 6 nm grained Fe sample and an x-ray absorption fine structure (XAFS) analysis of 10-24 nm grained Cu [8]. On the other hand, atomic resolution imaging in the transmission electron microscope [9] (TEM) and another diffraction study on Pd [10] indicate that the grain boundaries in the nanophase are not anomalous. Since a knowledge of the structure of the GB region is so crucial to an understanding of the properties of the nanophase, it is important to clarify this controversy.

In this Letter we revisit the GB structure determination by XAFS. XAFS is the premier technique to investigate the local structure of the GB, since its interpretation is most direct [11]. The interpretation of the diffraction pattern of the nanophase is not unique, but depends on the assumption one uses for modelling. Thus, two different diffraction studies can come to different conclusions. TEM requires thinning the sample to thickness of the order of grain size, drastically modifying the surface stresses and contamination, which leads to questions regarding possible structural changes. In contrast, XAFS is noninvasive.

Copper was chosen as the material of choice because it has a special place in the development of the XAFS technique. It is the hydrogen atom of XAFS, the standard against which the accuracy of any theory of XAFS is first tested. Samples were prepared by inert gas condensation [12] and warm compaction. High purity Cu shot (99.999%) were evaporated from alumina lined boats into an atmosphere of 650Pa of high purity He (99.9999%). The processing was done within a UHV system to prevent contamination of the particles and the GB regions of the compacted material. After collection on a liquid-nitrogen temperature cold finger, the resulting powder was warmed and compacted with 1.4 GPa of pressure for 10 min. at 150°C into a roughly circular disk about 9 mm in diameter and 100μm thick.

Such samples thicknesses are typical for the compacted nanophase and introduce a challenge for accurate XAFS measurements. The samples are too thick for accurate transmission XAFS measurements, which require films about one absorption length thick (4.4μm) or else the signal is distorted by the "thickness effect" [13]. This distortion usually lowers the apparent coordination number. It was the measurement of a lowered coordination number by the original XAFS investigation [8] that led to the conclusion of an anomalous GB structure. The original XAFS investigators were aware of this thickness effect and, thus, milled their sample into a fine powder about one absorption length in diameter. Such a drastic mechanical milling may modify the properties of the nanophase. Moreover, a more serious problem is that for a powder to have a negligible thickness effect distortion, particles must be significantly less than one absorption length in size [14]. The requirement for particles is more stringent than for a film, since the particle has a variation in its thickness through which the x-ray beam passes. It is not clear that such fine powder was employed in the original investigation, leaving the possibility open that the conclusion of reduced coordination number is not real but an experimental artifact.

To avoid this problem we did not measure XAFS in transmission, but used the total electron yield (TEY) method [15]. In this method the absorption of the x-rays is monitored by detecting the total number of electrons emitted from the surface into which the x-rays impinge. It has been shown that about 100 nm depth of the sample from the surface contributes to this signal. The TEY was detected in a chamber filled with 1 atmosphere of He gas with 300 V across the sample and the planar collector plate, which was at a positive potential and a centimeter distant. Because 100 nm is very much smaller than an absorption length the TEY is not affected by any thickness effect distortions, nor by self-absorption effects which are present for Cu metal when XAFS is detected in the fluorescence mode [11].

To minimize any contribution from a Cu-oxide surface layer, the sample was dipped into a concentrated HCl solution, which attacked only the oxide, just before the sample was placed into the chamber with its He environment. Three samples were measured, one an annealed polycrystalline film with large 20μm grains and two nanophases, one with 13 nm and the other with 34 nm diameter grains, as measured by x-ray line broadening (Warren-Averbach method corrected for stacking faults and twins) [16]. The two nanophase samples had densities of 94% of a fully-dense standard. Measurements were made at room temperature on beamline X11A at the National Synchrotron Light Source at Brookhaven National Laboratory. A (111) Si double crystal monochromator was detuned about 20% to minimize the harmonic content of the beam, though harmonics do not cause any distortion in the signal in the TEY method.

Figure 1 shows a plot of $k\chi(k)$ of (a) the 34 nm and polycrystalline samples and (b) the 13 nm and polycrystalline samples. Here $\chi(k)$ is the XAFS normalized by the absorption edge step as a function of the photoelectron wavenumber k. Plotted in Fig. 2 are $|\chi(R)|$, the magnitudes of the Fourier transforms into R-space of $k\chi(k)$, for (a) the 34 nm and polycrystalline samples and (b) the 13 nm and polycrystalline samples. Fig. 2(c) shows the $k^3\chi(k)$ transform for both the 13 nm and polycrystalline samples. Note that the difference in the first peak height between the coarse-grained and 13 nm samples depends on the k-weighting. The difference is enhanced with a k^3-weighting. This illustrates one mistake made in the original XAFS interpretation [8], namely drawing conclusions on the coordination number by looking at the magnitudes of the Fourier transforms. The magnitude of the first peak depends on both the coordination number, N, and the disorder about the average distance. The disorder introduces typically a Debye-Waller factor which multiplies the XAFS by $e^{-2k^2\sigma^2}$ where σ^2 is the mean square disorder. The Debye-Waller factor thus lowers the signal at large k-values, and the Fourier transform of larger n-weighting in k^n is more sensitive to disorder and will show a larger disorder by a greater decrease in its peak. To obtain the actual structural parameters of the sample requires a detailed analysis which is by now quite standard [11]. The original XAFS paper [8] did recognize that a detailed analysis is required to obtain the correct coordination number and this analysis found a decrease in N of 10% instead of the 30% decrease of the transform peak. Curiously, the conclusions of that paper ignored the correct analysis and used the incorrect 30% figure so that agreement could be made with the estimated fraction of GB regions!

Such an analysis gives the results listed in Table I. Within the uncertainty of 3% all three samples have the same coordination number in the first shell. The only significant difference between the three samples is the mean squared displacement, σ^2, with a trend of increasing disorder with smaller grain size. This result is just as expected for a conventional grain boundary. It indicates that the Cu atoms in the grain boundary have approximately the same coordination number as the bulk but are somewhat more disordered. A 13 nm nanophase sample has about 20% of its volume composed of GB regions and if the gaseous model of Gleiter et al [6] were correct the coordination number of this sample should be 20% less than that of the polycrystal, clearly not the case.

A recent XAFS investigation on nanophase Pd metal also disagrees with the anomalous character of the GB regions [10]. This study based its conclusion on the fact that the XAFS signal was the same for a nanograined powder as for the compacted powder, arguing that the powder does not have any GB contribution. In this study the coarse-grained sample still had a larger XAFS signal than the nanostructured Pd metal and no detailed analysis was made to verify that the difference with the coarse-grained sample was due only to disorder and not coordination. Another complication was that the method of measurement of the XAFS was different on the powder than on the compact. The powder was done in transmission while the TEY method was employed for the compact, possibly adding a systematic uncertainty.

Since the TEY technique samples the first 100 nm from the surface, one must argue that this region is characteristic of the rest of the sample and is not composed of larger grains. The method of fabrication is done at a temperature well below that which would induce significant grain growth during the compaction [16]. Diffraction line broadening measurements, which average over the penetration depth of about 10μm, and scanning tunneling and atomic force microscopy which measure the surface only [17] together show that the nanophase has the same size of grains at the surface as in the bulk, and thus the sampling of the TEY is characteristic of the nanophase.

The XAFS measurements verify that the TEY sensitive depth including its GB regions of our samples, is not significantly contaminated by oxide or other impurities. Any GB contamination would cause a deviation in the transform of Fig. 2(a) and (b) between the nanophase and the polycrystal. There appear to be no significant differences besides disorder. The differences around R = 1Å are due to background subtraction errors and are not structural differences. We estimate that the oxide contamination in the GB is less than 15%, the sensitivity of the XAFS measurement. Also, x-ray diffraction from these samples indicated no contamination within its accuracy (ca. 5%).

If the assumption is made that the nanophase consists of a bulk region inside the grains and a GB region, which change their relative amounts but not their properties as the grain size varies, then the results of Table I can be used to determine the coordination number N_{gb} and mean square disorder σ^2_{gb} of the first shell in the GB. The result is $\sigma^2_{gb} = 0.0108 \pm 0.0016$Å^2 and N_{gb} is 11.4 ± 1.2, i.e., the GB has somewhat more disorder (σ^2 increase of 0.003 Å^2) and, within uncertainty, the same coordination as the interior of the grains. On the other hand, the uncertainties indicate up to a 15% decrease in coordination is reasonable. For comparison, a Cu sample, cold-worked by rolling, has an increased $\Delta\sigma^2$ of 0.00018 ± 0.00025 Å^2. The increase of disorder in the GB is much greater than cold working causes but is still a modest increase. For example, just heating the sample by 100°C above room temperature will cause a similar increase of disorder. It should be noted that XAFS gives a result averaged over all Cu atoms. Thus, the GB contribution is averaged over all types of boundaries in the sample.

In conclusion, by taking care to eliminate experimental artifacts, XAFS is in agreement with other measurements that the grain boundaries in the nanophase are not unusual [18]. They have the short range order of grain boundaries in conventional materials and are not gas-like. The interesting properties of the nanophase arise in the presence of conventional grain boundary structures.

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FIGURES

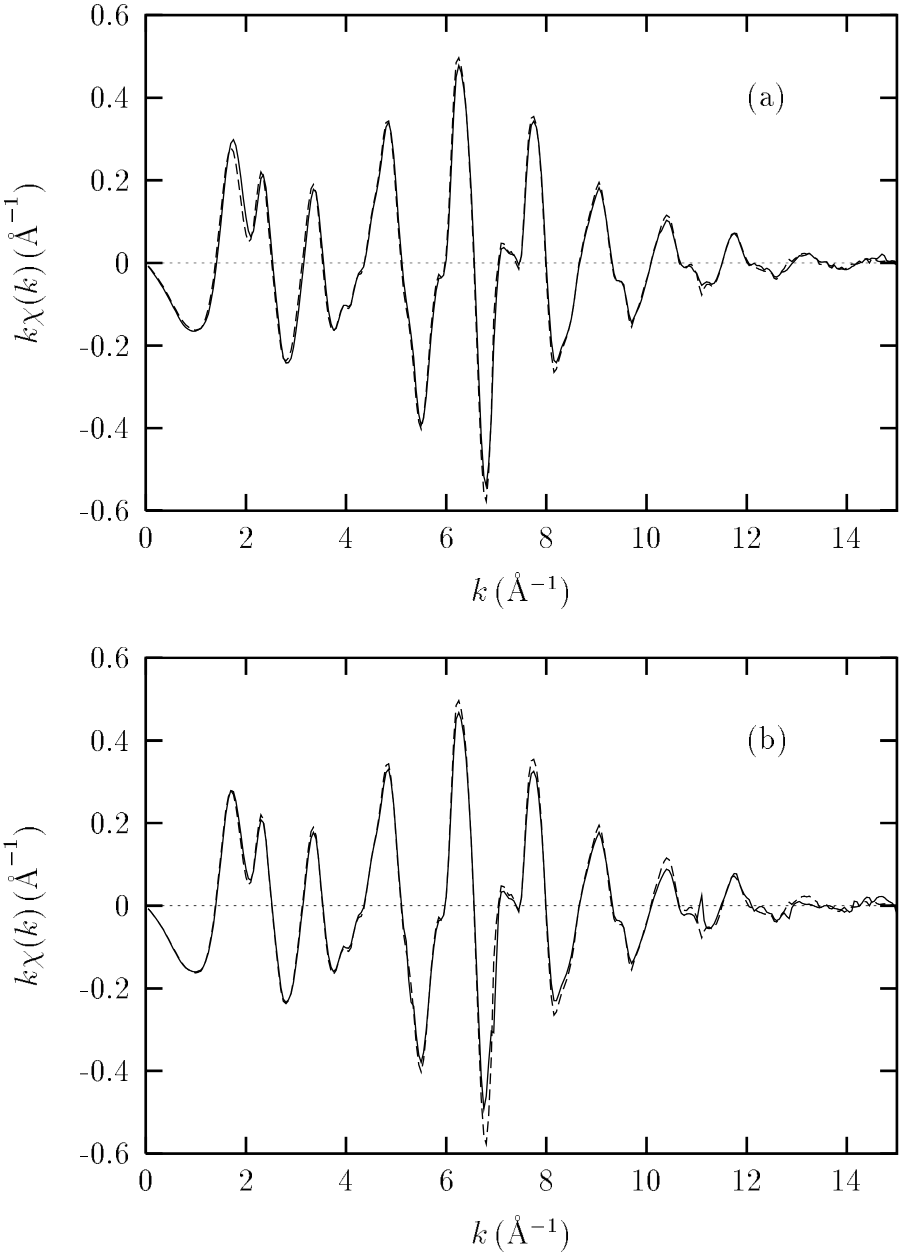
FIG. 1. $k\chi(k)$ for nanocrystalline (solid) and bulk polycrystalline (dashed) phases of Cu. (a) shows the 34 nm nanocrystal with the bulk and (b) shows the XAFS of the 13 nm nanocrystal with the bulk.

FIG. 2. The Fourier transform (FT) $|\chi(R)|$ for nanocrystalline (solid) and bulk polycrystalline (dashed) phases of Cu. (a) shows the 34 nm nanocrystal and polycrystal FT of $k\chi(k)$. (b) shows the 13 nm nanocrystal and polycrystal FT of $k\chi(k)$. (c) shows the 13 nm nanocrystal and polycrystal FT of $k^3\chi(k)$. All Fourier transforms were done between $k = [2.0, 14.5]\,\text{Å}^{-1}$.

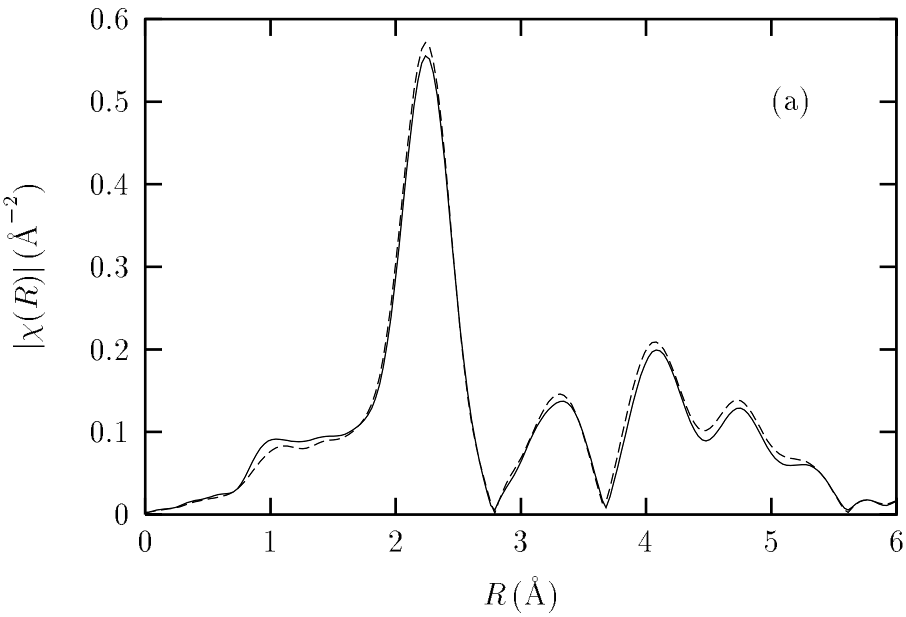
TABLES

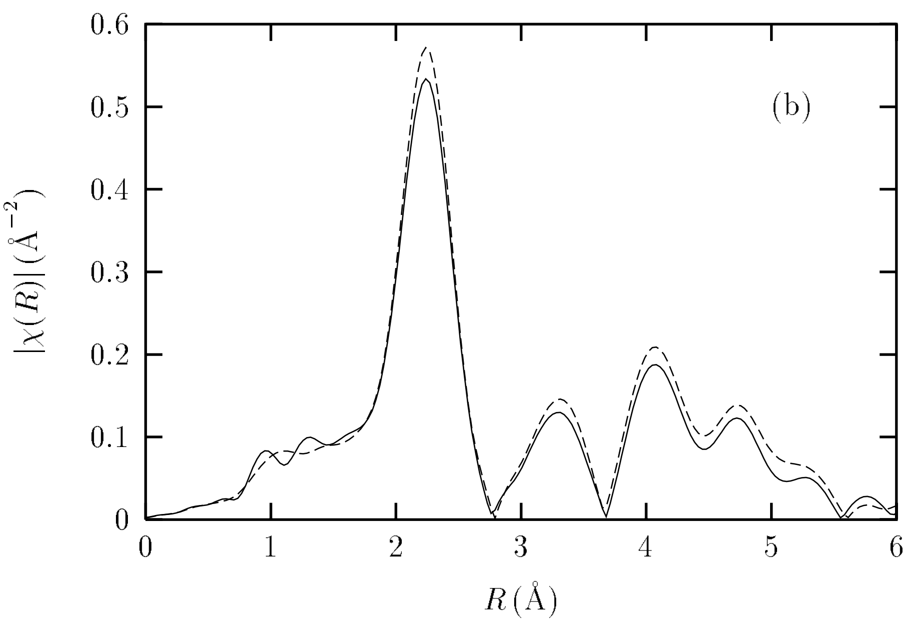
TABLE I. Results of fits to Cu nanocrystal samples. The scale in the fitting routine was set so as to give the correct coordination of 12 in the first shell of coarse-grained (bulk) Cu foil. σ_1^2 is the mean square disorder at room temperature in the first coordination shell of Cu metal and N is the coordination number in that shell.

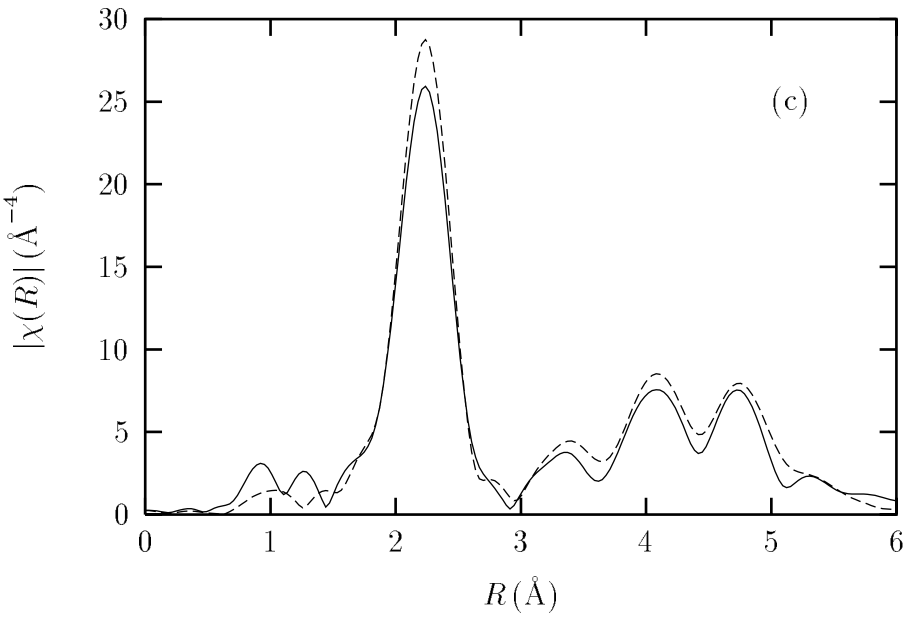
Sample	N	σ_1^2 (Å^2)
Bulk foil	12	0.00810 ± 0.00027
34 nm	11.8 ± 0.3	0.00824 ± 0.00021
13 nm	11.9 ± 0.3	0.00864 ± 0.00023



0.6
0.4
0.2
0
-0.2
-0.4
-0.6
0
2
4
6
8
10
12
14
(a)
$k\chi(k)\,(\text{Å}^{-1})$
$k\,(\text{Å}^{-1})$
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
0
2
4
6
8
10
12
14
(b)
$k\chi(k)\,(\text{Å}^{-1})$
$k\,(\text{Å}^{-1})$


(a)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
$|\chi(R)|\,(\mathrm{\AA}^{-2})$
$R\,(\mathrm{\AA})$


(b)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
$|\chi(R)|\,(\mathrm{\AA}^{-2})$
$R\,(\mathrm{\AA})$



(c)
$|\chi(R)|\,(\text{Å}^{-4})$
$R\,(\text{Å})$
0
5
10
15
20
25
30
0
1
2
3
4
5
6