Polydispersity and EXAFS simulations

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Abstract. EXAFS is an important experimental technique for determining the local atomic structure of nanoclusters embedded in a bulk material. In practical cases, nanocluster samples do not contain homogeneous clusters of just one size, and the average cluster size is strongly influenced by the specific distribution of cluster sizes. Combinations of different cluster sizes might provide very similar results; this issue is called polydispersity. The goal of this study is to understand if there are any principal limitations for EXAFS studies related to polydispersity. Here a new approach based on EXAFS simulations followed by linear combination of EXAFS spectra is presented. The simulations were performed on pure Cu and binary Cu-Fe clusters. The main result of this study concerns the proof that polydispersity does not affect XAFS studies on nano-clusters within a size of up to 140 atoms.

1. Introduction

Many elements, such as Cu and Ni, are not soluble in Fe even at low concentrations below approx. 1%, so that they segregate under special heat and/or mechanical treatments. The segregation leads to clustering, which may strongly modify the mechanical and physical-chemical properties of the material. Depending on the involved elements, their concentrations and the applied treatments, the clusters can be coherent, i.e. they have the same phase of the matrix, or incoherent, i.e. they crystallize in different phases. Furthermore, the size of the clusters can play an important role for materials properties, e.g. for the embrittlement of reactor pressure vessel (RPV) steels in nuclear power plants [1,2] or in completely different fields like catalysis or surface science. Due to its inherent sensitivity towards the local structure around an X-ray absorbing element, EXAFS spectroscopy is a powerful tool to investigate nanostructures like small clusters. As long as EXAFS is an element selective technique, it provides information from all the atoms of a chosen element, regardless whether these atoms belong to clusters or to the matrix. In real cases samples do not contain homogeneous clusters of just one size, and the determination of an average cluster size is strongly influenced by the specific size distribution of the clusters. Combinations of different cluster sizes can provide very similar results; this issue is called polydispersity. Moreover, it is known that polydispersity is a limit for EXAFS experimental analysis [3-5]. Here, only nano-clusters (with less than 225 atoms and with a radius less than 8.5 Å) are investigated, and their shape is always considered spherical. Cu is the main element investigated and it is reasonable to expect that comparable conclusions can be drawn for other fcc-metals such as Al, Ca, Ni, Pd or Ag.

Moonen et al. [6] already pointed out that fcc clusters of 147 atoms in vacuum have the same amount of atoms in the first and second shell (8.9 and 4) like a combination of clusters composed of 13 (32%) and 1415 atoms (68%), and, according to this study, experimental EXAFS data analysis cannot solve this issue. The first detectable difference appears in the 3rd shell where the linear composition shows 13.8 atoms and the 147 atoms cluster 13.0 atoms. However, this difference is hard to detect even if high quality experimental data is available. Here, a new approach based on EXAFS simulations followed by linear combination (LC) of EXAFS spectra is presented. The simulations were performed for pure Cu clusters and binary clusters composed of Cu in the inner core surrounded
by two outer layers of Fe. Such an interface is introduced because small Cu clusters might be embedded in an iron matrix [7], as it is the case for, e.g. RPV steels.

The main result of this study concerns the possibility to overcome the polydispersity issue for nano clusters with less than 140 atoms for the mono-elemental case. So, here the effect of the size is investigated regardless of the possible variation of the atomic distances. All the results found in this study have been gained by EXAFS simulations.

2. Experimental analysis

In order to have a correct evaluation of all the analysis program cards involved in the EXAFS calculations it has been mandatory to reproduce the EXAFS signal of a Cu foil. Once the EXAFS signal was properly reproduced, all the different card parameters have been frozen for all the cluster simulations. The sample analyzed is a Cu foil (99.999%) annealed and rolled to ~12 μm, prepared by M. Newville, and the used data, collected at 10 K, are delivered with the IFFEFIT package [8].

3. Applied model

The simulation of the Cu reference has been performed only for the central atom of a large cluster of 10 Å radius, while for the clusters, the simulations have been performed for all the individual shells. A shell is composed of all the atoms at the same distances with respect to the central atom; thus a cluster of two shells is composed of an atom at the centre, 12 atoms in the first shell (at 2.56 Å) and 6 in the second (at 3.62 Å), according to the fcc geometry. The total number of atoms involved is 19, as shown in table 1. The contributions of the shells are added by a weight factor according to the number of atoms in the respective shell. The contributions of the shells at or close to the cluster surface are very important, especially for small clusters. The experimental data of the Cu foil were collected at 10 K.

All simulations have been performed with FEFF8.4 [9]. In a first step, the Cu reference is reproduced by simulations. The proper value of the edge step is determined by comparing the peak amplitude of the experimental Cu foil EXAFS signals and the simulations. In the second step a series of pure Cu clusters composed by different numbers of shells as compiled in table 1 are simulated.

Table 1. Summary of the Cu clusters. All EXAFS simulations are performed for each shell and added according to their weight factors. Highlighted in bold are the clusters investigated here by LC.

| Shell per cluster | 1 | 2 | 3 | 4 | 6 | 7 | 8 | 11 | 12 |
|-------------------|---|---|---|---|---|---|---|----|----|
| Atom per cluster  | 13| 19| 43| 55| 87| 135| 141| 225| 249|
| Radius (Å)        | 2.56| 3.62| 4.43| 5.11| 6.26| 6.76| 7.23| 8.48| 8.86|

Furthermore, a series of binary Cu/Fe clusters is simulated (see table 2). These binary clusters are composed of two different parts: the core, composed by 4, 6, 7, 8, 17 and 24 shells of fcc-Cu with the typical structure of a Cu bulk, which is surrounded by two Fe shells as interface. These external Fe shells are assumed to have the same fcc structure as the Cu core.

Table 2. Polydispersity is tested on binary alloy fcc clusters composed by a Cu core and 2 outer Fe atomic layers as interface. Fe atoms are in a fcc Cu-like structure. Highlighted in bold is the cluster investigated here by LC EXAFS analysis.

| Shells in the Cu cluster core | 4 | 6 | 7 | 8 | 17 | 24 |
|--------------------------------|---|---|---|---|----|----|
| Atoms in the Cu cluster core   | 55| 87| 135| 141| 459| 767|
| Shells in the Fe interface     | 2 | 2 | 2 | 2 | 2 | 2 |
| Atoms in the Fe interface      | 32| 54| 42 | 60 | 96 | 120|
| Total atom per cluster         | 87| 141| 177| 201| 555| 887|
| Radius (Å)                     | 6.26| 7.23| 7.69| 8.08| 11.43| 12.78|

Two clusters from table 1, composed by 7 and 11 shells, and one from table 2, composed of 7 shells of Cu surrounded by 2 shells of Fe, have been investigated in detail. Their EXAFS signals $\chi(k)$
and $\chi_i(k)$ are reproduced by linear combination (LC) of different EXAFS spectra $\chi_i(k)$, where $i$ refers to the number of shells per cluster as described in table 1 and 2. The ATHENA software [10-12] allows performing linear combination fits with a maximum of 4 terms. In this study only 2 terms were used because the same results are found using combinations of 2 and 4 terms. So for example, $\chi(k)$ can be reproduced by LC using $\chi_1(k)$ and $\chi_{28}(k)$, giving

$$\chi(k) \equiv a_1 \chi_1(k) + a_2 \chi_{28}(k), \text{ with } a_1 + a_2 = 1 \text{ and } 0 \leq a_i \leq 1. \quad (1)$$

The symbol $\equiv$ is used here because some small differences are always expected even for the best LC-fit; $a_1$ and $a_2$ are factors used to weight the contributions of $\chi_i(k)$ and $\chi_{28}(k)$. In order to find the best LC to reproduce $\chi(k)$ and $\chi_{14}(k)$, combinations of all the clusters indicated in table 1 were tested.

The quality of the each LC-fit is assessed with the help of the $R$ quality factor as defined in ref. [13]. Concerning the example described above, the $R$ quality factor is defined as:

$$R \propto \left[ \frac{\sum_i \left| \chi_i(k) - (a_1 \chi_1(k) + a_2 \chi_{28}(k)) \right|^2}{\sum_i \left| (a_1 \chi_1(k) + a_2 \chi_{28}(k)) \right|^2} \right]^{1/2}. \quad (2)$$

Usually a fit is satisfactory if its $R$ quality factor is lower than 0.03, which means that the two simulations differ by only 3%. In the following pages this ‘tolerance limit’ will be represented by a dashed line in the respective graphs. Below this ‘tolerance limit’ (TL), the difference of two simulations is considered as ‘significant’ if their $R$ quality factors differ by more than a factor 2. This leads to the classification that all the simulations which have an $R$ quality factor smaller than twice the smallest $R$ quality factor can be considered as valid. This limit is called ‘quality limit’ (QL) and is represented by a solid line in the graphs. The quality limit is lower than the tolerance limit. Using these limits it is possible to correctly evaluate the best simulations and to rate simulations as valid or not. This limit cannot be universally defined because it is easy to find a wrong model with an rather small $R$ quality factor. Polydispersity occurs if many combinations, which involve clusters with very different sizes, are located below the QL. The TL has been fixed ‘a priori’ to 0.05 by experts [14] and herein is 0.03. Basically the TL is a simple way to judge whether the applied model is correct or not. Although this limit, as well as the TL, is not theoretically proved, it is important to point out that it is not used to verify the quality of the model (LCs of EXAFS simulations), but it is used to compare results obtained consistently (with the same model).

The $R$ quality factor increases if the signal is noisy. The influence of the noise can be reduced by performing the experiment at low temperature. Low temperatures are particularly suggested to avoid anharmonical corrections for the evaluations of the cluster size [15, 16]. It is reminded that our simulations are performed at low temperature and that the noise is not significant.

**Figure 1.** The magnitude of the Fourier-transform and the EXAFS signal of a Cu foil measured at 10 K and its simulations (k-range for the FT: $3 \leq k \leq 18$ Å$^{-1}$, $dk = 0.5$ Å$^{-1}$, Edge step = 0.96). The parameters of the simulation were optimized to obtain a good approximation up to 6 Å radial distance. Roman numbers are used to show the number of the different shells

**4. Results**

In this part all the results gained by EXAFS simulations are presented. The result for the simulated EXAFS Cu foil is shown in figure 1. This simulation has verified that $E_0$ is properly calculated even if a very small shift to lower energy is found. In the analysis program, the utilization of the SCF card was preferred here in contrast to the
The manual shift of the $E_0$. The edge step of the Cu reference simulation is varied in order to reproduce properly the amplitude of the experimental EXAFS signal of the Cu foil. The edge step is 0.96 and this value is used in all of the following simulations. Simulated EXAFS spectra for the clusters given in table 1 and their Fourier Transforms (FTs) are not shown here, but they are consistent with the number of atoms involved: larger peaks in the FT correspond to a larger number of atoms involved in the calculation.

The quality of the linear combinations of pure Cu clusters is shown in figure 2: The 7 shell Cu cluster is reproduced by LC, according to Eq. 1, and the $R$ quality factor of the resulting simulations, calculated by Eq. 2, is represented in figure 2(a). In figure 2(b) the same procedure is applied to the 11 shell Cu-cluster. An example: in figure 2(a), the red point, see arrow, is obtained by the linear combination of the EXAFS signal of 6 shell clusters (see x axis) and 26 shell clusters (see inset). The value on the y axis is the $R$ quality factor, according to equation 2, in our example replacing $\chi_6$ and $\chi_{26}$ with $\chi_6$ and $\chi_{26}$. Considering all the simulations obtained with 6 shell clusters, which lie on the same vertical line, it is worth to note that all the LCs give different results. Those simulations which involve ‘small’ clusters (of 13 and 18 shells) give a better result than those containing ‘larger’ cluster of 22, 26 and 28 shells. If two LCs have the same $R$ quality factors then their points. This behavior happens more often if the clusters involved are both larger than the 7 shell cluster (see, for instance, point surrounded by a circle in figure 2(a)). For example the LCs of $\chi_{13}$ with $\chi_{18}$ and $\chi_{13}$ with $\chi_{26}$ give the same result because the percentage of the 18 and 26 shell clusters is expected to be ‘zero’ in both cases. This behavior is obvious because the 7 shell clusters can be better simulated by the 13 shell cluster than by LCs of larger clusters. The quality limit is calculated from the best simulation which involves the 6 shells cluster (18.4 ± 0.6 %) and the 8 shells cluster (81.6 ± 0.6 %) with a small $R$ quality factor of 0.0014, thus the quality limit was fixed to 0.0028. In figure 2(b) the quality limit is found by a LC involving clusters of 4 shells (5.0 ± 0.6 %) and 12 shells (95 ± 0.6 %), with $R = 0.0012$.

It is emphasized that the quality limit is determined using all the possible cluster combinations from table 1, while the LCs shown in figure 2 only involve those combinations with a significant amount of ‘larger’ clusters containing 13, 18, 22, 26 or 28 shells. If many different combinations involving larger clusters result in a $R$ quality factor below the quality limit, polydispersity can occur.

![Figure 2](image_url)

**Figure 2.** $R$ quality factor versus the number of shells of the clusters involved in the linear combination of the 7 (a, left) and 11 shell clusters (b, right). Full and dashed horizontal lines represent the quality and the tolerance limit, respectively. The cyan-coloured lines indicate that in (a) there are no LCs below the quality limit, while in (b) there are several. Details see text.

From figure 2, two main differences can be noted: While none of the LCs shown in figure 2(a) for the 7 shells cluster is below the quality limit, there are several in figure 2(b) for the 11 shells cluster. Further, many LCs, especially those involving clusters with at least 18 shells, are beyond the tolerance limit in figure 2(a), while in figure 2(b) there are only few. This behaviour shows that it is easier to find simulations with $R$ quality factors below or near the quality limit for larger – i.e. in our case 11
shells – clusters than for smaller clusters. The cyan line helps to guide the eye indicating the behaviour of a series of LCs involving the 13 shells cluster, resulting in combinations with relatively good quality. Finally, figure 2(a) reveals that none of the simulations that involve large clusters can reproduce properly the EXAFS signal produced by a 7 shell cluster. This means that polydispersity in this case is not expected. On the other hand, in figure 2(b) there are many simulations with \( R \) factors below the quality limit, suggesting that in case of larger clusters polydispersity needs to be seriously considered.

In figure 3, the \( R \) quality factors for the LC-fits of the binary Cu/Fe-clusters are reported. It is noted here that many combinations give results similar to those reported for the larger Cu clusters in figure 2(b). However, the existence of few LCs below the quality limit shows that polydispersity may occur, due to the presence of the two layers of Fe. These surface/interface layers have a passive role since they scatter photoelectrons but they do not absorb. Moreover all of the Cu absorbers have the first and the second shell completed by these Fe atoms. So the effect of the surface is reduced compared to a larger elemental Cu cluster and polydispersity already occurs for smaller clusters. Basically the Fe surface/ interface layer reduces the difference between the EXAFS spectra. In figure 3 the best results are given by a combination of 5 shells cluster (68 ± 1 %) and 15 shell cluster (32 ± 1 %).

![Figure 3](image)

*Figure 3. \( R \) quality factor versus the number of shells of clusters involved in the linear combination for the 7 shells binary clusters of a Cu core surrounded by 2 shells of Fe at the surface.*

The amount of LCs with a \( R \) quality factor below the quality limit, between the quality and the tolerance limit and above the tolerance limit are normalized and shown in table 4. The second, the third and the forth row represents the amount of LCs whose \( R \) quality factor is above the tolerance limit (\( > TL \)), the amount of simulations between the tolerance and the quality limit (\( QL < R \) quality factor < \( TL \)), and those LCs whose quality factor is below the quality limit (\( < QL \)). Thus the latter row is the most important because it indicates if polydispersity can occur or not. If it is not equal to zero (as for the 11 shell cluster and the 7 shell cluster + the interface) this implies that there are several simulations with valid results. It is not explicitly shown here, but polydispersity is found to appear if pure clusters have a size of at least 8 shells (141 atoms) while smaller clusters appear polydispersity free. In the case of binary clusters (e.g. Fe-Cu) where the x-ray absorbing atoms are located in the core of the cluster and the second element on the surface, polydispersity seems to occur also for smaller cluster sizes.

| \( R \) quality factor | 7 Shell Cluster | 11 shell cluster | 7 shell cluster + interface |
|------------------------|----------------|----------------|-----------------------------|
| \( > TL \)             | 22 %           | 3 %            | 12 %                        |
| \( QL < \) \( R \) quality factor < \( TL \) | 78 %           | 81 %           | 68 %                        |
| \( < QL \)             | 0 %            | 16 %           | 20 %                        |

5. Conclusions
Many linear combinations of small and large clusters are tested in order to fit the EXAFS spectrum produced by pure Cu clusters of 7 and 11 shells containing 135 and 225 atoms respectively.

Furthermore, a binary cluster composed of 7 shells of Cu surrounded by two shells of pure Fe with a fcc structure is investigated. The main results derived here are: for pure clusters composed of 7 shells (135 atoms) or less, polydispersity does not seem to be an issue. For an 11 shell cluster the situation is different because many combinations of larger and smaller clusters can satisfactorily reproduce the EXAFS spectrum, and thus for clusters of this size and even larger, polydispersity is an issue. For binary clusters with a 7 shell core surrounded by two non-absorbing outer shells, polydispersity is an important issue also for smaller clusters because the atoms on the surface reduce the differences among clusters of different sizes. In conclusion, EXAFS simulations are suited to study the polydispersity effect on small clusters. The simulated spectra depend strongly on the details of the geometry of the clusters. The effect of the atoms that lie on the surface of the clusters is predominant for their EXAFS simulation.

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References
[1] Cammelli S, Degueldre C, Kuri G, Bertsch J, Lützenkirchen-Hecht D and Frahm R 2009 J. Nucl. Mat. 385 319
[2] Cammelli S, Degueldre C, Kuri G and Bertsch J 2008 Nucl. Instr. Meth. B 266 4775
[3] Bazin D, Lynch J and Ramos-Fernandez M 2003 Oil & Gas Sci. Technol. Rev. 58 667
[4] Bazin D and Rehr JJ 2003 J. Phys. Chem. B 107 12398
[5] Bazin D, Sayers DA and Rehr JJ 1997 J. Phys. Chem. B 101 11040
[6] Moonen J, Slot J, Lefferts L, Bazin D and Dexpert H 1995 Physica B 208&209 689
[7] Cammelli S, Degueldre C, Cervellino A, Abolhassani S, Kuri G, Bertsch J, Lützenkirchen-Hecht D and Frahm R 2009 Nucl. Instr. Meth. B, accepted.
[8] Newville M, Ravel B and Zhang Y; available on http://cars9.uchicago.edu/iffwiki/About
[9] Ankudinov AL, Nesvizhskii AI and Rehr JJ 2003 Phys. Rev. B 67 115120
[10] Newville M 2001 J. Synchrotron Rad. 8 322
[11] Ravel B and Newville M 2005 J. Synchrotron Rad. 12 537
[12] Ravel B 2001 J. Synchrotron Rad. 8 314
[13] Stern EA, Newville M, Ravel B, Yacoby Y and Haskel D 1995 Physica B 208&209 117
[14] See http://cars9.uchicago.edu/iffwiki/FAQ/FeffitModeling#head-a993eb2c8bd4a05db12e92fc7edc3d0794612921
[15] L.B. Hansen, P. Stoltze, J.K. Nørskov, B.S. Clausen and W. Niemann, Phys. Rev. Lett. 64, (1990) 3155.
[16] B.S. Clausen, H. Topsøe L.B. Hansen, P. Stoltze, J.K. Nørskov; Catalysis today (1994) 49-55