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Jun Dong and Kunquan Lu

Institute of Physics, Chinese Academy of Sciences, Beijing, 100080, People's Republic of China

Abstract. In this paper, we investigate the effect of unequal distance coordination in a standard sample on EXAFS data analysis, particularly on structural results from a curve fitting procedure. We calculate analytically this effect for a simple model, and EXAFS spectra of rutile type GeO_2, α-quartz type GeO_2, Fe_3O_4 and $LaFeO_3$ are measured to demonstrate this effect experimentally. A simulation computation is also carried out. The results show that the sample in which the neighbouring atoms around the absorbing one form two coordination sub-shells, can be used as a standard only if the differences of interatomic distances and mean square radial displacements between these two sub-shells are less than 0.1 Å and 0.0015 Å^2 respectively. A simple and feasible method is developed to eliminate this effect quantitatively for accurate structural determination. Improvement of accuracy of results based on this method is obtained. The situation about this effect for a complex model is discussed.

1. Introduction

The extended x-ray absorption fine structure (EXAFS) refers to the oscillatory modulation of the x-ray absorption coefficient as a function of x-ray photon energy beyond the absorption edge. During the 1970s it was recognized that EXAFS contains local structural information, and is a useful probe of the immediate structure of the absorbing atom in materials. This technique is particularly well suited to studies of the local atomic environment in complex systems which may be impossible for x-ray diffraction study. At the same time, the availability of synchrotron radiation greatly improved the speed of data acquisition and the quality of data that could be obtained. These developments have gradually established EXAFS as a practical and widely used structural tool [1–4].

For extracting the local atomic structural information which EXAFS contains, many analytical methods have been developed [5]. One of the most widely used techniques is a curve fitting procedure from which the quantitative results can be conveniently obtained. In this case, the backscattering amplitude function $A(k)$ and phase shift function $\varphi(k)$ are needed. These functions can be obtained either from theoretical calculation or from the experimental EXAFS spectrum of a standard compound for which the structure is known. Using calculated $A(k)$ and $\varphi(k)$ is independent of the choice of standard samples and suitable for different kinds of scattering atoms in the same coordination shell. However, the systematic error in results is very difficult to eliminate because there are many experimental factors always affecting the EXAFS spectrum and

these cannot be compensated for precisely no matter what $A(k)$ and $\varphi(k)$ are used, e.g. approximate values calculated by Teo and Lee [6] or accurate ones calculated by McKale *et al* [7]. However, if experimental $A(k)$ and $\varphi(k)$ obtained from the EXAFS spectrum of a standard sample are used, systematic error is not a problem, since it can be eliminated naturally as long as the experimental conditions for the standard sample are the same as those for the unknown one because the same experimental factors result in the same systematic error. So, the standard sample method is still used frequently in EXAFS curve fitting procedures, especially for accurate structural determination.

The feasibility of the standard sample method depends upon the transferability of the backscattering amplitude function $A(k)$ and the phase shift function $\varphi(k)$, that is, $A(k)$ and $\varphi(k)$ obtained from the standard sample can be used for the unknown one without apparent deviation. The non-transferability of $A(k)$ and $\varphi(k)$ can be greatly ameliorated by making use of good standards. Generally speaking, a good standard sample should not only contain the same absorbing–backscattering atomic pair but also have about the same chemical environment and neighbouring atomic geometry. For such cases, the backscattering amplitude function $A(k)$ and phase shift function $\varphi(k)$ are transferable between the standard and unknown samples [8–10]. On the other hand, for extracting $A(k)$ and $\varphi(k)$ from the EXAFS spectrum of the standard sample, it is required that the neighbouring atoms should have equal bond lengths, i.e. the neighbouring atoms should be in a single coordination shell with as small as possible static and thermal disorder. However, this requirement is difficult to satisfy in practice. The neighbouring atoms in the standard sample usually have different interatomic distances or large disorder in a shell, split up into several sub-shells.

Unfortunately, these sub-shells cannot be resolved experimentally because of the limit of the EXAFS resolution unless the difference of distances is greater than 0.6 Å. We have to treat these neighbouring atoms as a single coordination shell with an average interatomic distance $\bar{R}$. The $A(k)$ and $\varphi(k)$ extracted from the standard sample under this treatment will have some deviations from the actual values. Thus, a certain effect must arise with the accuracy of structural results derived by using a curve fitting procedure. This effect is referred to as the effect of unequal distance coordination in the standard sample. Sometimes, the error in results due to this effect is negligible, but sometimes not, especially for the mean square radial displacement of the order of interatomic spacing (about 0.003 Å² deviation).

What is even worse is that if this effect is very significant, the backscattering amplitude function $A(k)$ and phase shift function $\varphi(k)$ obtained from this sample cannot be used for the unknown one because the deviation of these functions from the actual ones is very large. In this case, a sample with this effect cannot be used as a standard one even though the other criteria for the standard sample mentioned above are satisfied. Since it is impossible in many cases to select a standard sample in which the neighbouring atoms form a single coordination shell, this effect is inevitable in the standard sample method. To study this effect on EXAFS data analysis, particularly on structural results from curve fitting procedures, is of benefit in at least two aspects. One is that it enables us to establish a criterion to estimate the quality of a given standard sample in order to select a good one; the other is that it is possible to develop a method to eliminate this effect quantitatively for improving the accuracy of structural results from the EXAFS technique.

In this paper, the effect of unequal distance coordination in the standard sample on structural results is discussed both analytically and experimentally. It is shown that this effect should be considered if a standard sample with unequal distance coordination is

applied in the EXAFS curve fitting procedure. A criterion is established to select a good standard sample, and a simple and feasible method is developed to eliminate this effect quantitatively for accurate structural determination.

2. Analytical consideration

The standard EXAFS equation can be presented as [10]

$$\chi(k) = -\sum_j \frac{N_j S_0^2}{kR_j^2} |F_j(k)| \exp(-2k^2\sigma_j^2) \exp(-2R_j/\lambda) \sin[2kR_j + \varphi(k)] \tag{1}$$

where $|F_j(k)|$ is the backscattering amplitude from each of the N_j coordination atoms in the jth shell which are located at a distance R_j from the absorbing atom. The exponential containing factor σ_j (the root mean square radial displacement of the atoms about R_j) is a Debye–Waller type term. $\varphi(k)$ is a phase shift function which is composed of the contributions from absorbing and backscattering atoms. k denotes the wavenumber of the photoelectrons calculated from

$$k = [2m/\hbar^2(E - E_0)]^{1/2} \tag{2}$$

where E represents the x-ray photon energy and E_0 is the threshold energy for absorption events.

In equation (1), the terms $\exp(-2R_j/\lambda)$, λ being the electron mean free path, and S_0^2 account for inelastic scattering processes and many-body effects, respectively. Because these two terms have no influence on the effect of interest in this paper, we shall incorporate them into $|F_j(k)|$ below.

For a standard sample without the effect of unequal distance coordination, that is the neighbouring atoms around the absorbing one form a single coordination shell, the backscattering amplitude function $A(k)$ and phase shift function $\varphi(k)$ extracted from it can be described as

$$A(k) = |F_s(k)| \exp(-2k^2\sigma_1^2) \tag{3a}$$

$$\varphi(k) = \varphi_s(k) \tag{3b}$$

where s denotes the standard sample, and σ_1^2 is the mean square radial displacement of the neighbouring atoms.

For simplicity, we consider only a standard sample in which neighbouring atoms are the same, and can be divided into two sub-shells. The conclusion obtained from this simple model can be expanded to a complex one, which will be discussed in section 3.

Assuming that N_1, N_2; R_1, R_2; and σ_1, σ_2 are coordination numbers, interatomic distances and Debye–Waller factors for first and second sub-shells respectively, the EXAFS function for such a case is

$$\chi_s(k) = -\frac{N_1}{kR_1^2} |F_s(k)| \exp(-2k^2\sigma_1^2) \sin[2kR_1 + \varphi_s(k)]$$

$$-\frac{N_2}{kR_2^2} |F_s(k)| \exp(-2k^2\sigma_2^2) \sin[2kR_2 + \varphi_s(k)]. \tag{4}$$

We define the total coordination number $\bar{N}$, average interatomic distance $\bar{R}$, $\Delta\sigma^2$, α, and β as follows:

$$\bar{N} = N_1 + N_2 \tag{5a}$$

$$\bar{R} = (N_1 R_1 + N_2 R_2)/(N_1 + N_2) \tag{5b}$$

$$\Delta\sigma^2 = \sigma_2^2 - \sigma_1^2 \tag{5c}$$

$$\alpha = N_2/N_1 \qquad (\text{assuming } N_2 \geqslant N_1) \tag{5d}$$

$$\beta = \Delta R/R_1 = (R_2 - R_1)/R_1 \qquad (\text{assuming } R_2 \geqslant R_1). \tag{5e}$$

Then, we can rewrite equation (4) as

$$\chi_s(k) = -(\bar{N}/k\bar{R}^2)|F_s(k)| \exp(-2k^2\sigma_1^2)A'(k) \sin[2k\bar{R} + \varphi_s(k) + \delta(k)] \tag{6}$$

with

$$A'(k) = \left(\frac{1}{1+\alpha}\right)\left(1 + \frac{\alpha\beta}{1+\alpha}\right)^2 \left(1 + \frac{\alpha^2}{(1+\beta)^4} \exp(-4k^2\Delta\sigma^2)\right.$$

$$\left. + \frac{2\alpha}{(1+\beta)^2} \exp(-2k^2\Delta\sigma^2) \cos(2k\Delta R)\right)^{1/2} \tag{7a}$$

$$\delta(k) = \tan^{-1}\left\{\left[\frac{\alpha}{(1+\beta)^2} \exp(-2k^2\Delta\sigma^2) \sin\left(\frac{2k\Delta R}{1+\alpha}\right) - \sin\left(\frac{2k\alpha\Delta R}{1+\alpha}\right)\right]\right.$$

$$\left. \times \left[\frac{\alpha}{(1+\beta)^2} \exp(-2k^2\Delta\sigma^2) \cos\left(\frac{2k\Delta R}{1+\alpha}\right) + \cos\left(\frac{2k\alpha\Delta R}{1+\alpha}\right)\right]^{-1}\right\}. \tag{7b}$$

According to equation (6), if we treat these neighbouring atoms as a single shell with an average $\bar{R}$, the $A(k)$ and $\varphi(k)$ extracted from equation (6) are

$$A(k) = |F_s(k)| \exp(-2k^2\sigma_1^2)A'(k) \tag{8a}$$

$$\varphi(k) = \varphi_s(k) + \delta(k). \tag{8b}$$

Comparing equations (8) and (3), it can be noted that $A(k)$ and $\varphi(k)$ extracted from the standard sample with unequal distance coordination will have additional factors $A'(k)$ and $\delta(k)$ respectively. If we use these functions to fit the EXAFS spectrum of a single coordination shell in the unknown sample with equation (1), and define N_c, N; R_c, R; and σ_c, σ to be the correct coordination numbers, interatomic distance and difference of Debye–Waller factors and fitting values, respectively, the following equation should be valid as long as a good fitting curve can be obtained:

$$(N_c/kR_c^2)|F_s(k)| \exp(-2k^2\sigma_c^2) \sin[2kR_c + \varphi_s(k)]$$

$$= (N/kR^2)|F_s(k)|A'(k) \exp(-2k^2\sigma^2) \sin[2kR + \varphi_s(k) + \delta(k)]. \tag{9}$$

Assuming that $R_c/R \approx 1$ (this approximation is reasonable because $|R_c - R|/R$ is usually about 1%), then the following equations can be derived from equation (9):

$$A'(k) = (N_c/N) \exp[-2k^2(\sigma_c^2 - \sigma^2)] \tag{10a}$$

$$\delta(k) = 2k(R_c - R). \tag{10b}$$

According to equations (9) and (10), it is shown that the dependences of $A'(k)$ and

$\delta(k)$ on k should be exponential and linear respectively, provided that $A(k)$ and $\varphi(k)$ extracted from the standard sample can be used to obtain a good fitting curve for the unknown sample, in other words, that $A(k)$ and $\varphi(k)$ are transferable to the unknown sample. In fact, equation (10) can be applied as a criterion to estimate the quality of a given standard sample with unequal distance coordination. It is directly shown that the sample cannot be used as a standard if $A'(k)$ and $\varphi(k)$ significantly deviate from exponential and linear functions, respectively, because no good fitting curve can be obtained.

We calculated several curves for $A'(k)$ and $\delta(k)$ using equation (7). The results showed that the dependences of $A'(k)$ and $\delta(k)$ on k are insensitive to R_1 or R_2, and not affected by α significantly because α is about 1–3 in many cases. It is expected that contributions from ΔR and $\Delta \sigma^2$ to $A'(k)$ and $\delta(k)$ are important. In fact, equation (10) is equivalent to adding a requirement for ΔR and $\Delta \sigma^2$. This requirement can be derived quantitatively by evaluating equation (7). The conclusion is that if $\Delta R \leqslant 0.1$ Å and $\Delta \sigma^2 \leqslant 0.0015$ Å^2, the dependences of $A'(k)$ and $\delta(k)$ on k do not apparently deviate from exponential and linear functions respectively, indicating that a sample with unequal distance coordination can be used as a standard one, but the effect of unequal distance coordination in the standard sample will be increased with increasing ΔR and/or $\Delta \sigma^2$. The critical values, $\Delta R \approx 0.1$ Å and $\Delta \sigma^2 \approx 0.0015$ Å^2, which were obtained based on analytical consideration need to be tested by experiment.

3. Experimental and simulated results

We have measured and analysed the Ge K-edge EXAFS of rutile type GeO_2 and α-quartz type GeO_2, and the Fe K-edge EXAFS of Fe_3O_4 and $LaFeO_3$ to demonstrate the conclusion derived in section 2. From crystallographic data we know that in α-quartz type GeO_2 and $LaFeO_3$, the neighbouring oxygen atoms form an equal distance coordination shell surrounding Ge and Fe respectively [11, 12], while the neighbouring oxygen atoms in rutile type GeO_2 and Fe_3O_4 are separated into two sub-shells around Ge and Fe with $\Delta R = 0.03$ Å and 0.16 Å respectively [13, 14]. Thus, rutile type GeO_2 and Fe_3O_4 can be used as standard samples with unequal distance coordination to extract the structural parameters of α-quartz type GeO_2 and $LaFeO_3$, respectively, and study the effect of unequal distance coordination in the standard sample experimentally.

All x-ray absorption measurements were performed at beam lines 10B and 7C of the Photon Factory Synchrotron Radiation Source in Japan with electron energy about 2.5 GeV and electron current from 150 mA to 300 mA. EXAFS spectra of the compounds were taken with the transmission mode, monochromized by channel-cut Si(311) for 10B and Si(111) double crystals for 7C. Appropriate gas and length of ion chamber were chosen for 10B and double crystals were detuned with a reflected mirror for 7C to eliminate harmonic effects. Ge K-edge EXAFS of α-quartz type GeO_2 was measured at 80 K, and others were measured at room temperature (300 K). The Cu K-edge was used to calibrate the energy scale. The energy resolution is about 1 eV. All samples were fine powders (about 10–20 μm particles) smeared on Scotch tape of appropriate thickness (edge jump, $\Delta \mu_0 x \leqslant 1.0$) to avoid EXAFS amplitude reduction. All EXAFS spectra were analysed by using the standard EXAFS data analytical procedure [10] to isolate the contribution from neighbouring atoms around the absorbing one. Then, the non-linear least square curve fitting procedure was applied to obtain the structural parameters.

We can extract $A'(k)$ and $\delta(k)$ experimentally from the $A(k)$ and $\varphi(k)$ of rutile type GeO_2 and Fe_3O_4 by using $A(k)$ and $\varphi(k)$ of α-quartz type GeO_2 and $LaFeO_3$. We define $A^n(k)$ and $A^s(k)$ to be $A(k)$ for compounds with unequal distance coordination and equal distance coordination, and $\varphi^n(k)$, $\varphi^s(k)$ to be $\varphi(k)$ respectively. Then, $A'(k)$ and $\delta(k)$ can be derived from equations (8) and (3):

$$A'(k) = [A^n(k)/A^s(k)] \exp[2k^2(\sigma_{1n}^2 - \sigma_{1s}^2)] \tag{11a}$$

$$\delta(k) = \varphi^n(k) - \varphi^s(k) \tag{11b}$$

where $(\sigma_{1n}^2 - \sigma_{1s}^2)$ is $\Delta\sigma^2$ for the first sub-shell in the sample with unequal distance coordination. It can be obtained from a curve fitting procedure by using $A^s(k)$ and $\varphi^s(k)$.

In figures 1 and 2, experimental values of $A'(k)$ and $\delta(k)$ obtained by using equation (11) for rutile type GeO_2 and Fe_3O_4, respectively, are shown with the calculated values obtained by using equation (7). It can be seen that the calculated $A'(k)$ and $\delta(k)$ are in good agreement with experiment, indicating that it is suitable to calculate $A'(k)$ and $\delta(k)$ using equation (7). For rutile type GeO_2 with $\Delta R = 0.03$ Å and $\Delta\sigma^2 = 0.0002$ Å^2, $A'(k)$ and $\delta(k)$ are apparently exponential and linear respectively. But for Fe_3O_4 with $\Delta R = 0.16$ Å and $\Delta\sigma^2 = 0.0042$ Å^2, $A'(k)$ and $\delta(k)$ significantly deviate from exponential and linear functions. In figures 3 and 4, EXAFS spectra of neighbouring oxygen atoms around Ge in α-quartz type GeO_2 and around Fe in $LaFeO_3$ are shown with their fitting curves by using $A(k)$ and $\varphi(k)$ extracted from rutile type GeO_2 and Fe_3O_4 respectively. The results and some crystallographic data for these compounds are presented in table 1. It appears that rutile type GeO_2 can be used as a standard sample to fit the EXAFS spectrum of α-quartz type GeO_2, but Fe_3O_4 cannot be used as a standard for $LaFeO_3$ because no good fitting curve can be obtained. This demonstrates experimentally that the sample cannot be used as a standard with large disorder $\Delta R > 0.1$ Å and/or $\Delta\sigma^2 > 0.0015$ Å^2.

For studying this effect at a critical situation ($\Delta R \approx 0.1$ Å, $\Delta\sigma^2 \approx 0.0015$ Å^2), the EXAFS curves were simulated for a single coordination shell and two coordination shells denoted by M^s and M^n respectively by using equation (1). The simulated data are also shown in table 1. The simulated $A'(k)$ and $\delta(k)$ of M^n are shown in figure 5 together with the calculated values. As illustrated in figure 5, not only are the simulated $A'(k)$ and $\delta(k)$ in agreement with calculation, but also $A'(k)$ and $\delta(k)$ can be approximated to exponential and linear functions except in the high-k region. The EXAFS curve of M^s is shown in figure 6 with its fitting curve by using $A(k)$ and $\varphi(k)$ extracted from M^n. The results are shown in table 1. It is shown that M^n can be used as a standard. This indicates that a sample with unequal distance coordination can still be used as a standard when $\Delta R = 0.1$ Å and $\Delta\sigma^2 = 0.0015$ Å^2, and critical values, $\Delta R \approx 0.1$ Å and $\Delta\sigma^2 \approx 0.0015$ Å^2, based on analytical considerations are quite reasonable. In combination with the results discussed above, it is concluded experimentally that if $\Delta R \leqslant 0.1$ Å and $\Delta\sigma^2 \leqslant 0.0015$ Å^2, a sample with unequal distance coordination can be used as a standard in EXAFS curve fitting procedures, confirming the analytical prediction presented in section 2.

From the results shown in table 1 (we assumed that results denoted by c, d, and * are accurate ones), it can be noted that the effect of unequal distance coordination in a standard sample on the structural results obtained from the curve fitting procedure is increased with increasing ΔR and/or $\Delta\sigma^2$, as expected. The deviations of results for α-quartz type GeO_2 from accurate ones can be neglected, but deviations for M^s are apparent, especially for mean square radial displacement (about 0.003 Å^2). This illustrates that even though samples with $\Delta R = 0.1$ Å and $\Delta\sigma^2 = 0.0015$ Å^2 can still be used
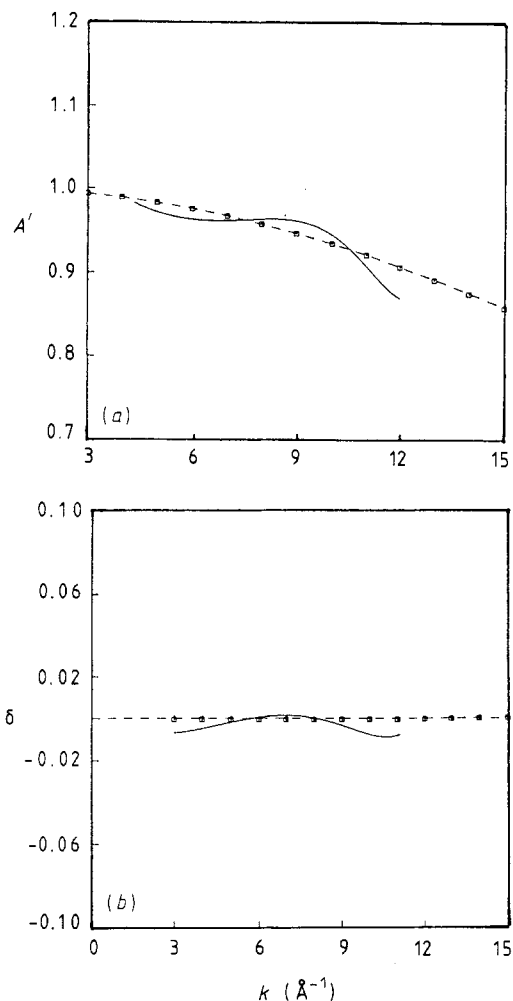
Figure 1. (*a*) Experimental $A'(k)$ (full curve) of rutile GeO_2 is shown with calculated values (open squares). The fitting curve for calculated $A'(k)$ is also shown (broken curve). (*b*) Experimental $\delta(k)$ (full curve) of rutile type GeO_2 is shown with calculated values (open squares). The calculated curve of $[\delta(k) - (0.263\Delta E_0 R)/k]$ with ΔE_0 about -0.025 eV is shown (+). Its fitting curve is denoted by the broken line.
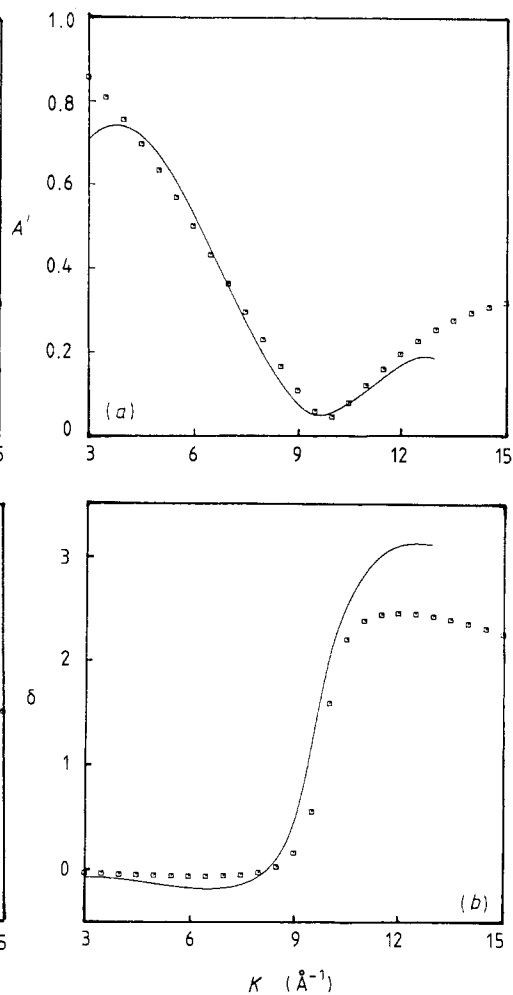
Figure 2. (*a*) Experimental $A'(k)$ (full curve) of Fe_3O_4 is shown with calculated values (open squares). (*b*) Experimental $\delta(k)$ (full curve) of Fe_3O_4 with calculated values (open squares).

as a standard, the effect of unequal distance coordination on structural results should be corrected to improve the accuracy of results, especially for accurate structural determination. To this end, a simple method can be developed according to equation (10). Since $A'(k)$ and $\delta(k)$ can be approximated to exponential and linear functions, respectively, in this case, they can be represented as follows:

$$A'(k) = a\exp(bk^2) + c \tag{12a}$$
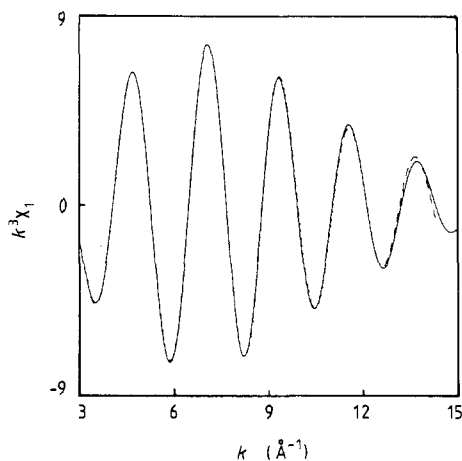
$$\delta(k) = dk + f \tag{12b}$$

Figure 3. The EXAFS spectrum $k^3\chi_1(k)$ for neighbouring oxygen atoms around Ge in α-quartz type GeO_2 is shown (full curve) with its fitting curve (broken curve) by using $A(k)$ and $\varphi(k)$ extracted from rutile type GeO_2.
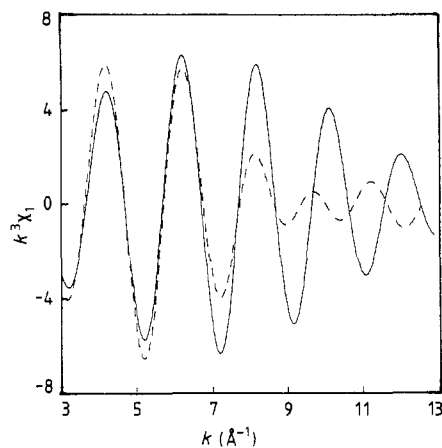
Figure 4. The EXAFS spectrum $k^3\chi_1(k)$ for neighbouring oxygen atoms around Fe in $LaFeO_3$ is shown (full curve) with its fitting curve (broken curve) by using $A(k)$ and $\varphi(k)$ extracted from Fe_3O_4.

Table 1. The results of experiments and simulation computation. CA represents the centre or absorbing atom; LT, RT indicate that experiments were made at low temperature (80 K) and room temperature (300 K) respectively; M denotes the simulated curve obtained by using the EXAFS equation; superscripts n and s indicate that neighbouring atoms form two and single sub-shells respectively; c represents crystallographic data; the data in square brackets are site occupancy; d represents simulated data; * means that the result is obtained by using the EXAFS technique without the effect of unequal distance coordination in the standard sample; the data in parentheses are the result denoted by ** with the effect of unequal distance coordination in the standard sample and the corrected value, denoted by a using the method described in the paper.

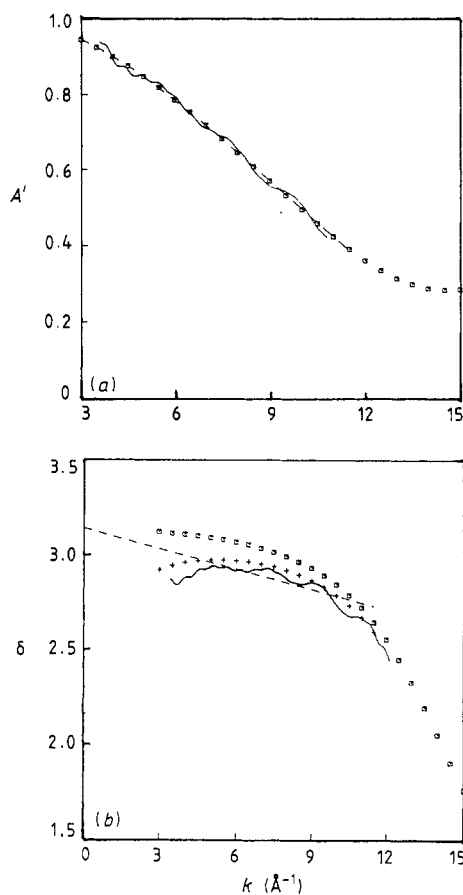| Sample	CA	N	R (Å)	$\Delta\sigma^2$ (Å^2)
GeO_2^n (RT) (rutile)	Ge	2^c 4^c	1.902^c 1.872^c	0.0011^* 0.0013^*
$Fe_3O_4^n$ (RT)	Fe	4^c [0.33] 6^c [0.67]	1.858^* 2.021^*	0.0000^* 0.0042^*
M^n		3^d 3^d	2.0^d 2.1^d	0.0000^d 0.0015^d
GeO_2^s (LT) (α-quartz)	Ge	4^c $(4.02^{**}, 4.02^a)$	1.739^c $(1.738^{**}, 1.738^a)$	-0.0011^* $(-0.0014^{**}, -0.0011^a)$
$LaFeO_3^s$ (RT)	Fe	6^c (9.34^{**})	2.006^c (1.997^{**})	0.0000^* (-0.0021^{**})
M^s		6^d $(5.92^{**}, 5.96^a)$	2.319^d $(2.333^{**}, 2.315^a)$	0.0000^* $(-0.0036^{**}, -0.0005^a)$

Figure 5. (*a*) The simulated $A'(k)$ (full curve) of M^n is shown with the calculated values (open squares). The fitting curve for calculated $A'(k)$ is also shown (broken curve). (*b*) The simulated $\delta(k)$ (full curve) of M^n is shown with the calculated values (open squares). The calculated curve of $[\delta(k) - (0.263\Delta E_0 R)/k]$ with ΔE_0 about 0.98 eV is shown (+). Its fitting curve is denoted by the broken curve.
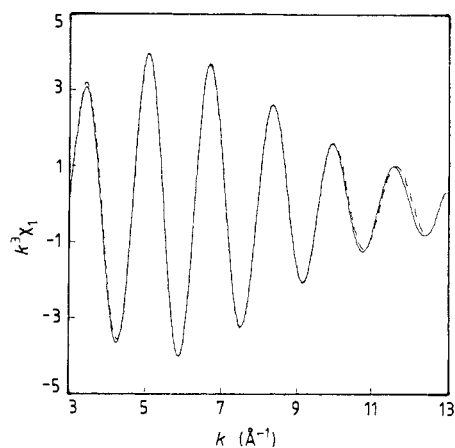
Figure 6. The simulated EXAFS spectrum $k^3\chi_1(k)$ of M^s is shown (full curve) with its fitting curve (broken curve) by using $A(k)$ and $\varphi(k)$ extracted from M^n.

where it is required that c and f should be zero according to equation (10). Usually, c is much smaller than unity as long as $\Delta R \leqslant 0.1$ Å and $\Delta\sigma^2 \leqslant 0.0015$ Å^2, but f is not. However, we can adjust E_0 to compensate for f, making $[\delta(k) - (0.263\Delta E_0 R)/k]$ zero at $k = 0$; in other words, the line of $[\delta(k) - (0.263\Delta E_0 R)/k]$ versus k crosses the origin. Here, ΔE_0 refers to the adjustment of E_0, R is a fitting value about the interatomic distance, and the term $0.263\Delta E_0 R/k$ is usually applied to compensate for non-transferability of the phase shift function between the standard and unknown sample [15]. Combining equations (12) and (10), we obtain:

$$N_c = (a + c)N \tag{13a}$$

$$\sigma_c^2 \approx \sigma^2 - \tfrac{1}{2}b \qquad (c \ll 1) \tag{13b}$$

$$R_c = R + \tfrac{1}{2}d \tag{13c}$$

where a, b, c and d can be obtained by applying equation (12) to fit $A'(k)$ and $\delta(k)$ and adjusting ΔE_0 to make $[\delta(k) - (0.263\Delta E_0 R)/k]$ zero at $k = 0$. By using equation (13), we can easily correct fitting values N, σ^2 and R to obtain accurate results, eliminating the effect of unequal distance coordination in the standard sample. The corrected results are shown in table 1 for α-quartz type GeO_2 and M^s. The fitting curves for $A'(k)$ and $\delta(k)$ of rutile type GeO_2 and M^n, respectively, are shown in figures 1 and 5. Comparing corrected and uncorrected results with the accurate ones, it is shown that an improvement in accuracy based on the method described above was obtained, especially for $\Delta R = 0.1$ Å and $\Delta\sigma^2 = 0.0015$ Å^2. This demonstrates that the method is simple and feasible to correct the effect of unequal distance coordination in standard samples.

Finally, it is worth discussing the effect for a complex system. As mentioned in section 2, the conclusion obtained in this paper from a simple model can be expanded to a complex one, where the neighbouring atoms around the absorbing one in the standard sample might form several coordination sub-shells, e.g. three or four sub-shells. The criterion derived above can still be applied to estimate the quality of the given standard sample in order to select a good one. In particular, if $\Delta R > 0.1$ Å and/or $\Delta\sigma^2 > 0.0015$ Å^2 for two arbitrary sub-shells of neighbouring atoms in a complex sample, it cannot be used as a standard, at least not a good one. The smaller the differences of R and σ^2 between two arbitrary sub-shells are, the better this sample is as a standard. On the other hand, if several sub-shells of neighbouring atoms in a complex model can be reduced equivalently to two sub-shells by using the fact that for very small ΔR and $\Delta\sigma^2$ the effect of unequal distance coordination can be ignored, as with rutile type GeO_2, the simple method described above will still be feasible to correct fitting results quantitatively. Otherwise, it is very difficult to correct this effect properly using a simple method.

4. Summary

We investigated the effect of unequal distance coordination in a standard sample on EXAFS data analysis, focusing on the structural results from a curve fitting procedure. We calculated analytically this effect for a simple model, and measured the EXAFS spectra of rutile type GeO_2, and α-quartz type GeO_2, Fe_3O_4 and $LaFeO_3$ to demonstrate this effect experimentally on structural determination. A simulation computation was carried out to study this effect further. It is clear from the results in this paper that this effect should be considered if a standard sample with unequal distance coordination is applied in the EXAFS curve fitting procedure. The criterion for selecting a good standard sample is that the differences in bond lengths (ΔR) and mean square radial displacements ($\Delta\sigma^2$) between two sub-shells should be less than 0.1 Å and 0.0015 Å^2 respectively. The smaller ΔR and $\Delta\sigma^2$ are, the better this sample is as a standard. A simple and feasible method was developed to correct this effect quantitatively for accurate structural determination. The accuracy of results improved based on this method. It was pointed out that the criterion and this simple method can also be used in a complex model, in other words, a real compound of interest.

Acknowledgments

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