Monatshefte für Chemie 137, 567–581 (2006)
DOI 10.1007/s00706-006-0450-z

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

EXAFS Spectroscopy of the Alkoxide Precursor $Zr(O^nBu)_4$ and its Modification in Solution[#]

Matthias Bauer[1,*], **Christoph Gastl**[1], **Christoph Köppl**[1],
Guido Kickelbick[2], and **Helmut Bertagnolli**[1]

[1] Institute of Physical Chemistry, University of Stuttgart, D-70569 Stuttgart, Germany
[2] Institute of Materials Chemistry, Technical University Vienna, A-1060 Wien, Austria

Received December 16, 2005; accepted February 13, 2006

Summary. The molecular structure of the transition metal alkoxide $Zr(O^nBu)_4$ in toluene and its modification by addition of *i*-propanol, tetrahydrofurane, and the coordinating ligand pentane-1,3-dione (H*acac*) were investigated by extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectroscopy. $Zr(O^nBu)_4$ dissolved in toluene forms dimers. It was proved that cluster size is a function of the number of added equivalents ligand. In contrast, the addition of *i*-propanol or tetrahydrofurane caused no structural changes observable by EXAFS spectroscopy. A detailed discussion of the structural models is given in terms of possible alternatives and errors within the EXAFS analysis.

Keywords. EXAFS spectroscopy; Transition metal alkoxides; Aggregation; Structure elucidation.

Introduction

The sol–gel process [1] has been extensively studied as a route to high-purity oxides [2], thin-film coatings [3], fibres [4], multicomponent ceramics [5], or even completely new mixed organic-inorganic materials [6, 7]. Key steps in this process are hydroxylation and accompanied condensation reactions of molecular precursors, such as alkoxides [8]. One essential parameter that influences the relative reaction rates of the condensation reactions is the chemical constitution of the molecular precursors, determined by the metal and the alkoxides and their aggregation in solution. While in case of silicon alkoxide sol–gel reactions the precursors are simple monomers of the type $Si(OR)_4$ or organically substituted derivatives thereof, metal alkoxides regularly form aggregated compounds in solution. These

---

[*] Corresponding author. E-mail: m.bauer@ipc.uni-stuttgart.de

[#] Dedicated to Prof. *U. Schubert* on the occasion of his 60th birthday oligomers of the type $[M(OR)_n]_x \cdot y HOR$ often determine the kinetics of the sol–gel process. Reaction rates can be influenced, *e.g.*, by the addition of chelating ligands like acetylacetone (H*acac*) that reduce the possibility of nucleophilic attack by H_2O through blocking coordination sites at the metal ion. On the other hand, the oligomerization degree itself is influenced by the competition between chelating ligands and bridging alkoxide groups or by addition of more bulky *Lewis* bases like *i*-propanol or cyclic ethers. Thus, the structure of the alkoxide precursors and its modification by various coordinating groups that are different from the alkoxide group of the precursor are of special interest for the preparation of taylor-made materials. In general, alkoxides of transition metals tend to saturate their coordination sites in non-polar solvents by alkoxide bridging, in polar solvents by association of free solvent molecules [9–11]. Several molecular structures of metal alkoxides were obtained from single crystal X-ray data in the solid state. In many cases oligomerization was observed, for example for $Zr(O^iPr)_4$ [12], which can be found as a dimer. A tetrameric structure can be found for $Zr(O^nPr)_4$ [13]. Whether the molecular structures found in the solid state are similar to those found in solutions is questionable. Especially additional *R*OH molecules present in commercially available precursors used in sol–gel chemistry limits the value of these studies of purified alkoxides for practical applications [12, 13]. Usually the molecular complexity of metal alkoxides is estimated from ebullioscopic or cryoscopic measurements, which suffer from unstable reproducibility [9]. Mass spectrometry is another method often applied, but has the disadvantage of not being an *in-situ* method [10]. Various other spectroscopic methods (Raman-, IR-, ^1H NMR-, multinuclear NMR-spectroscopy) have been applied in order to identify the molecular structures of the alkoxides in solution [14]. These methods do not provide direct information on the local structure of the central atom. Only few X-ray absorption experiments on solutions of titanium- [15] and zirconium- [11] as well as mixed titanium–zirconium-alkoxides [16] are known. In this work, we want to extend the EXAFS (Extended X-Ray Absorption Fine Structure) investigations on zirconium alkoxides started in our group [11] to non-polar solvents.

In contrast to studies of purified alkoxides, here commercially available $Zr(O^nBu)_4$ as an important precursor for sol–gel process was investigated. This precursor usually contains 10–20 weight% of the natant ^nBuOH. Compared to all other methods already applied [17], EXAFS spectroscopy offers the chance to immediately visualize the local surrounding of an X-ray absorbing atom without respect of the state and crystallinity of the sample. It allows the determination of the bond distance, the coordination number, the *Debye-Waller* factor (*DWF*), the nature of scattering atoms surrounding the excited atom, and the degree of association can be estimated from the number of the metal atoms in the neighbourhood of an absorber. By taking into account the number of different oxygen shells constituted by terminal or bridging alkoxide (O*R*) and alcohol (*R*OH) groups, a particular molecular model of the formed structure can be proposed.

Results and Discussions

A large number of publications on the structure of zirconium alkoxides by the methods described above has been published in the past [17–23]. The molecular

Table 1. Structural parameters obtained from fitting the experimental data of $Zr(O^{n}Bu)_4$ dissolved in toluene with different equivalents of ligands with theoretical models (Abs: absorbing atom, Bs: backscatterer, N: coordination number, R: distance of the Bs, σ: *Debye-Waller* factor, ^{a} Quality of fit)

Sample	Abs–Bs	N(Bs)	R/Å	σ/Å	Fit index^{a}	k-range/Å^{-1}	E_f/eV
pure	Zr–O	1.8 ± 0.2	1.97 ± 0.02	0.032 ± 0.003	44.90	3.5–15.0	1.91
	Zr–O	1.4 ± 0.1	2.12 ± 0.02	0.022 ± 0.002			
	Zr–O	2.0 ± 0.2	2.25 ± 0.02	0.045 ± 0.005			
	Zr–C	1.8 ± 0.6	3.10 ± 0.03	0.059 ± 0.018			
	Zr–Zr	1.0 ± 0.3	3.55 ± 0.04	0.074 ± 0.022			
	Zr–C	3.9 ± 1.2	3.58 ± 0.04	0.074 ± 0.022			
1 eq ^{i}*Pr*OH	Zr–O	1.8 ± 0.2	1.99 ± 0.02	0.032	46.61	3.5–15.0	0.84
	Zr–O	1.9 ± 0.2	2.16 ± 0.02	0.022			
	Zr–O	1.7 ± 0.2	2.30 ± 0.02	0.045			
	Zr–C	1.3 ± 0.4	3.11 ± 0.03	0.059			
	Zr–Zr	0.9 ± 0.3	3.56 ± 0.04	0.074			
	Zr–C	4.5 ± 1.5	3.61 ± 0.04	0.074			
2 eq ^{i}*Pr*OH	Zr–O	1.8 ± 0.2	1.99 ± 0.02	0.032	40.86	3.5–15.0	−0.58
	Zr–O	1.9 ± 0.2	2.16 ± 0.02	0.022			
	Zr–O	1.9 ± 0.2	2.30 ± 0.02	0.045			
	Zr–C	1.8 ± 0.6	3.11 ± 0.03	0.059			
	Zr–Zr	0.7 ± 0.2	3.56 ± 0.04	0.074			
	Zr–C	3.2 ± 1.1	3.64 ± 0.04	0.074			
3 eq ^{i}*Pr*OH	Zr–O	2.0 ± 0.2	1.98 ± 0.02	0.032	44.7	3.5–15.0	2.73
	Zr–O	1.7 ± 0.2	2.13 ± 0.02	0.022			
	Zr–O	2.0 ± 0.2	2.26 ± 0.02	0.045			
	Zr–C	1.3 ± 0.4	3.10 ± 0.03	0.059			
	Zr–Zr	0.9 ± 0.3	3.54 ± 0.04	0.074			
	Zr–C	4.4 ± 1.2	3.59 ± 0.04	0.074			
1 eq *THF*	Zr–O	1.9 ± 0.2	1.99 ± 0.02	0.032	40.28	3.5–15.0	−0.02
	Zr–O	1.8 ± 0.2	2.16 ± 0.02	0.022			
	Zr–O	1.8 ± 0.2	2.30 ± 0.02	0.045			
	Zr–C	1.6 ± 0.5	3.10 ± 0.03	0.059			
	Zr–Zr	0.8 ± 0.3	3.57 ± 0.04	0.074			
	Zr–C	3.2 ± 1.1	3.64 ± 0.04	0.074			
2 eq *THF*	Zr–O	1.8 ± 0.2	2.00 ± 0.02	0.032	40.67	3.5–15.0	−1.31
	Zr–O	1.9 ± 0.2	2.17 ± 0.02	0.022			
	Zr–O	1.7 ± 0.2	2.31 ± 0.02	0.045			
	Zr–C	2.3 ± 0.7	3.11 ± 0.03	0.059			
	Zr–Zr	0.9 ± 0.3	3.56 ± 0.04	0.074			
	Zr–C	1.8 ± 0.6	3.62 ± 0.04	0.074			
3 eq *THF*	Zr–O	1.8 ± 0.2	1.98 ± 0.02	0.032	41.93	3.5–15.0	1.83
	Zr–O	1.3 ± 0.1	2.13 ± 0.02	0.022			
	Zr–O	1.8 ± 0.2	2.25 ± 0.02	0.045			
	Zr–C	1.8 ± 0.6	3.10 ± 0.03	0.059			
	Zr–Zr	1.1 ± 0.3	3.56 ± 0.04	0.074			
	Zr–C	3.9 ± 1.2	3.58 ± 0.04	0.074			
1 eq H*acac*	Zr–O	0.9 ± 0.1	1.95 ± 0.02	0.050 ± 0.005	22.50	3.5–15.0	1.58
	Zr–O	3.7 ± 0.4	2.20 ± 0.02	0.050 ± 0.005			
	Zr–O	1.3 ± 0.1	2.33 ± 0.02	0.045 ± 0.005			

(*continued*)

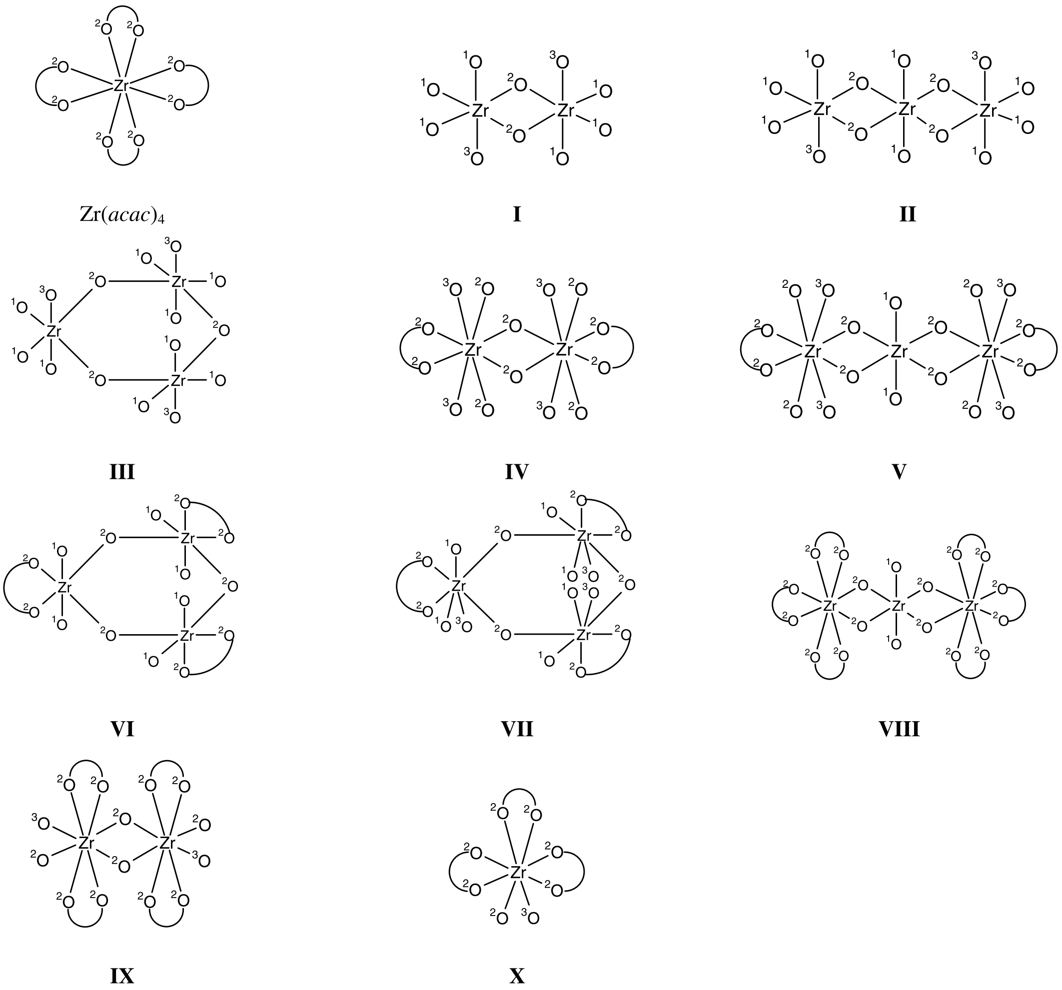
Table 1 (*continued*)

Sample	Abs–Bs	N(Bs)	R/Å	σ/Å	Fit index[a]	k-range/Å^{-1}	E_f/eV
	Zr–C	0.6 ± 0.2	3.16 ± 0.03	0.055 ± 0.012			
	Zr–Zr	2.2 ± 0.7	3.56 ± 0.04	0.067 ± 0.021			
	Zr–C	3.7 ± 1.2	3.58 ± 0.04	0.063 ± 0.019			
2 eq H*acac*	Zr–O	5.2 ± 0.5	2.22 ± 0.02	0.063 ± 0.006	33.44	3.5–15.0	−0.96
	Zr–O	1.3 ± 0.1	2.40 ± 0.02	0.045 ± 0.005			
	Zr–C	0.8 ± 0.2	3.18 ± 0.03	0.045 ± 0.015			
	Zr–Zr	0.6 ± 0.2	3.57 ± 0.04	0.050 ± 0.015			
	Zr–C	4.2 ± 1.2	3.62 ± 0.04	0.112 ± 0.033			
3 eq H*acac*	Zr–O	6.1 ± 0.6	2.21 ± 0.02	0.067 ± 0.007	33.95	3.5–15.0	2.03
	Zr–O	0.8 ± 0.1	2.37 ± 0.02	0.045 ± 0.005			

complexities of zirconium ethoxide have been recognized to be 3.6 in benzene and 2.5 in ethanol, while zirconium *i*-propoxide was found to be trimeric in benzene and dimeric in ^{i}PrOH by *Bradley et al.* [18]. Generally, the degree of association is found to decrease with increasing branching and bulkiness of the O*R* group, which is obvious from steric considerations [9]. Depending on the particular application as precursor, zirconium alkoxides have to be dissolved in their parent alcohol, *e.g.* in the sol–gel process, or in a hydrocarbon solvent like cyclohexane or toluene, *e.g.* in microemulsion preparation of nanoparticles [24]. The structure of $Zr(O^{n}Bu)_4$ (**1**) in ^{n}BuOH has been investigated in a first attempt [11], where it has been shown that it is possible to discern terminal alkoxy groups from axially bounded or bridging ones by means of EXAFS spectroscopy.

For the reference system $Zr(O^{i}Pr)_4$ dissolved in toluene, the found Zr–O bond distances were 1.96 Å for terminal, 2.09 Å for axial, and 2.19 Å for bridging *i*-propoxy groups. Coordinating *i*-propanol molecules *R*OH show a long Zr–O distance of 2.27 Å. By comparison with the solid state structure of $Zr(O^{i}Pr)_4$ [12], the applicability of EXAFS spectroscopy to such kind of systems could be proved. For $Zr(O^{n}Bu)_4$ (**1**) in ^{n}BuOH a dimeric structure has been detected [11]. Table 1 shows the numerical results of fitting our experimental EXAFS data for $Zr(O^{n}Bu)_4$ (**1**) dissolved in dry toluene with theoretical models. The data for solutions containing only the pure alkoxide as well as with one to three equivalents of ^{i}PrOH, *THF*, and H*acac* added are listed.

Three oxygen shells are necessary to fit the experimental data of **1** dissolved in dry toluene to obtain a good quality of the fit. The oxygen shells form approximately an octahedral coordination sphere, constituted of 1.8 backscatterers at 1.97 Å (terminal butoxy groups), 1.4 oxygens at 2.12 Å (bridging butoxy groups), and two O-atoms at 2.25 Å. As the last distance is longer than expected for an *axial* butoxy group, the coordination of one butanol molecule per zirconium center can be assumed. This is reasonable, as an 80 weight% solution of **1** in ^{n}BuOH contains 1.3 equivalents of *n*-butanol. Thus the obtained structural parameters suggest a dimeric structure similar to that found for solid $Zr(O^{i}Pr)_4$ [12]. The same complex was also found for solutions of **1** in butanol, which is shown as structure **I** in Fig. 1. Here, the octahedral coordination sphere is saturated by additional



Zr(*acac*)$_4$ **I** **II**

III **IV** **V**

VI **VII** **VIII**

IX **X**

Fig. 1. Structural models discussed in the text; the assignment of the different oxygen types is given in Table 2; an arc connects two oxygen atoms belonging to an *acac* group; for labelling the oxygen atoms see Table 2

coordination of two butanol molecules. The reduced coordination number in the second oxygen shell in comparison to the theoretical model structure will turn out to be a general feature found in the EXAFS analysis of **1** carried out here. One zirconium backscatterer determined at 3.55 Å confirms the conclusion of a dimeric species. A tetrameric species like the one found for Zr(O^i*Pr*)$_4$ [13] can be rejected as a zirconium coordination of two would be expected for such a structure. Due to the rather large error in the coordination number of shells at higher distances, the linear trimeric structure **II** (Fig. 1) or the cyclic trimeric structure **III** (Fig. 1) according to *Martin* and *Winter* [25] cannot be excluded. Structures following the suggestion of *Caughlan et al.* [26] for trimeric structures with three bridging O*R* groups connecting the metal centers can be neglected, since even in the case of titanium alkoxides with a small central atom it would force the metal centers to come too close together [27].

Table 2. Bond lenghts used for the calculation of possible structures formed by $\mathrm{Zr(O}^{n}Bu)_4$ with different equivalents of H*acac* in analogy to crystalline references; distances in parentheses show the spread within the given average value; labels give the assignment of the different Zr–O distances in the structures discussed (Fig. 1)

Coordination bond	Zr–O bond length/Å	Label
Zr–O*R* (terminal, 6-fold coordination of Zr)	~1.95 (1.9–2.0)	^{1}O
Zr–O*R* (terminal, 8-fold coordination of Zr)	~2.2 (2.1–2.3)	^{2}O
Zr–O*R* (bridging)		
Zr–O (*acac*)		
Zr–HO*R* (coordinated)	~2.35 (2.3–2.4)	^{3}O

Table 3. Theoretically calculated coordination numbers obtained by EXAFS spectroscopy of the structural models for only $\mathrm{Zr(O}^{n}Bu)_4$ dissolved in toluene, and with one to three equivalents of H*acac*; the numbering of the atoms is given in Table 2, the corresponding structures are shown in Fig. 1

Structural model	^{1}O	^{2}O	^{3}O	Zr
Zr(*acac*)$_4$	–	8.0	–	–
I	2.0	2.0	2.0	1.0
II	2.7	2.7	0.7	1.3
III	3.0	2.0	1.0	2.0
IV	–	6.0	2.0	1.0
3**I** + 4**IV** + 2 Zr(*acac*)$_4$ [11]	1.1	4.8	1.2	0.9
V	0.7	5.3	0.7	1.3
VI	2.0	4.0	–	2.0
VII	2.0	4.0	1.0	2.0
IV + Zr(*acac*)$_4$ [11]	–	6.7	1.3	0.7
VIII	0.7	6.7	–	1.3
IX	–	7.0	1.0	1.0
1**IV** + 4 Zr(*acac*)$_4$	–	7.3	0.7	0.3
X		7.0	1.0	–

But all these structures show characteristic combinations of coordination numbers and distances of the oxygen shells, as shown in Tables 2 and 3. The coordination numbers calculated in Table 3 for several zirconium complexes are those, which are expected to be determined by EXAFS spectroscopy. They are not identical with the average number of particular backscatterers present in the complex. In former studies [11], the average atom numbers have been used instead of the EXAFS coordination numbers, which are used in this work. The fitted carbon shells at 3.1 and 3.6 Å are also in agreement with the coordinated groups, and the inclusion of these shells improved the goodness of fit by 20%. Nevertheless, the number of carbon atoms found in the carbon shells throughout our study is less reliable than the oxygen and the transition metal shells. The reason for this can be found in the large spread of distances within the carbon shells, as well as interference effects and the weak backscattering amplitude of carbon, causing higher uncertainties in the coordination number at larger distances. Summarizing the results for **1** dissolved in toluene, the presence of a dimeric structure with octahedral coordination of the metal atom by three different oxygen shells is stated. This result is not in agreement with the association degree of 3.4 found in Ref. [9] for **1** dissolved in benzene. *Bradley et al.* have claimed from ebullioscopic measurements, that the molecular complexities of zirconium alkoxides are reduced to a large extent in their parent alcohol [18, 21]. For example, they propose an association of 2.5 for zirconium ethoxide in ethanol, whereas in benzene it exhibits an association of 3.6. On the contrary, our results and those of the previous study [11] reveal no difference in the association degree between **1** in butanol and toluene. This is even more surprising as the concentration in our study is higher than in the previous studies [11]. Applying the assumption of *Bradley et al.* [21], the difference between results in a non-polar and a polar solvent should be even higher than suggested by the ratio 3.6 to 2.5. But here, in both solutions the formed complexes are very similar despite the rather large error for the zirconium coordination. As in both studies the same value of the zirconium coordination number was determined, this value can be used as a relative probe for the changes induced by altering the polarity of the solvent.

The structure found for **1** dissolved in toluene forms the basis for further investigations into modifications, induced by adding complexing reagents in certain molar ratios. As it can be seen from Table 1, the addition of *i*-propanol or *THF* from one to three equivalents does not change the structural parameters, obtained for pure **1** dissolved in toluene. The small deviations of these samples in coordination numbers and distances are within the experimental errors. The *Debye-Waller* factors were fixed to the values obtained for **1** dissolved in toluene to ensure comparability. All other values were iterated.

The similarity of the samples containing *THF* and ^{i}*Pr*OH with the reference without any complexing agent is proved by inspection of the XANES spectra (Fig. 2).

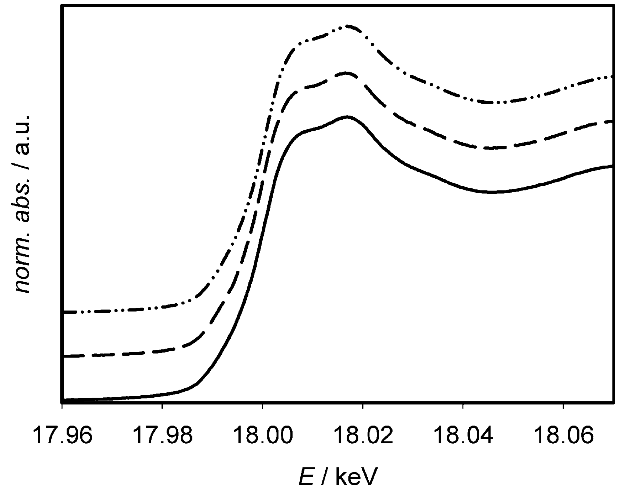


Fig. 2. XANES spectra of **1** dissolved in toluene (solid line), compared with the same solution containing one equivalent of ^{i}*Pr*OH (long dashed line) and one equivalent of *THF* (double dotted dashed line)

They also confirm the sixfold coordination of the zirconium center in these solutions. The first maximum of the absorption edge (white line) and its shape are due to s → p transitions and depend on the coordination of the X-ray absorbing zirconium atom [28]. Whereas octahedral coordination, *e.g.* in $BaZrO_3$, exhibits a splitting of the white line, only a broad band of non resolved s-p transitions is found in seven- or eightfold coordinated zirconium centers, *e.g.* in $Zr(acac)_4$ [29]. The similarity of the solutions containing **1** and one equivalent of ^{i}*Pr*OH or *THF* is again obvious in Fig. 3. It shows the experimental k^3-weighted $\chi(k)$-functions and the corresponding *Fourier* transforms. The spectra of the samples containing two and three equivalents of ^{i}*Pr*OH and *THF* were omitted for clarity.

These results strongly suggest that no structural change of the molecular complexity and coordination geometry at the metal center is induced by adding ^{i}*Pr*OH or *THF*. But it should be noted, that nothing can be said about possible exchanges

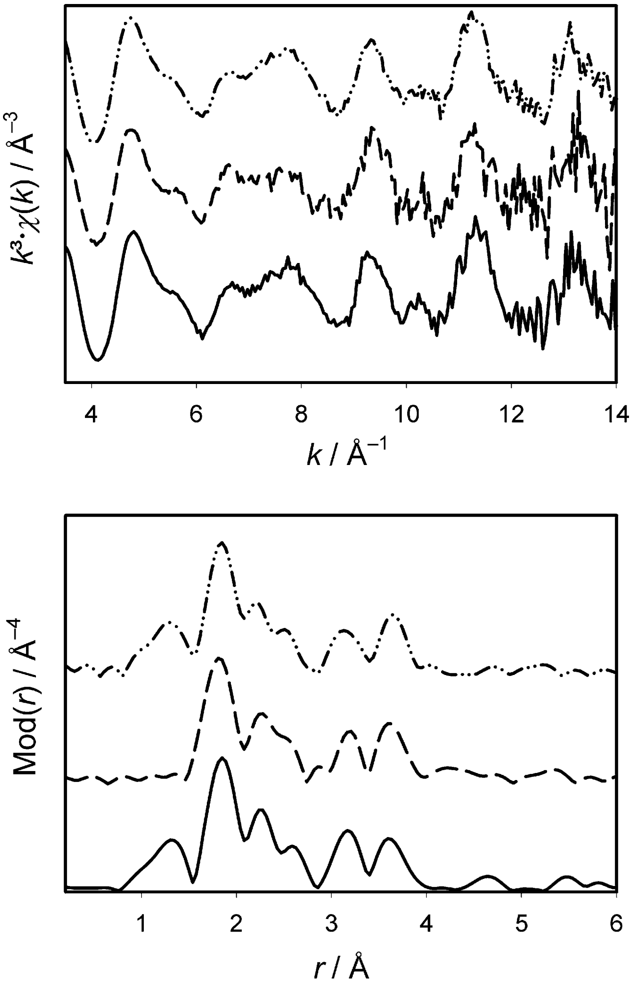


Fig. 3. Experimental $k^3 \cdot \chi(k)$-functions and the corresponding *Fourier* transforms of **1** dissolved in toluene (solid line), compared with the same solution containing one equivalent of ^{i}*Pr*OH (long dashed line) and one equivalent of *THF* (double dotted dashed line)

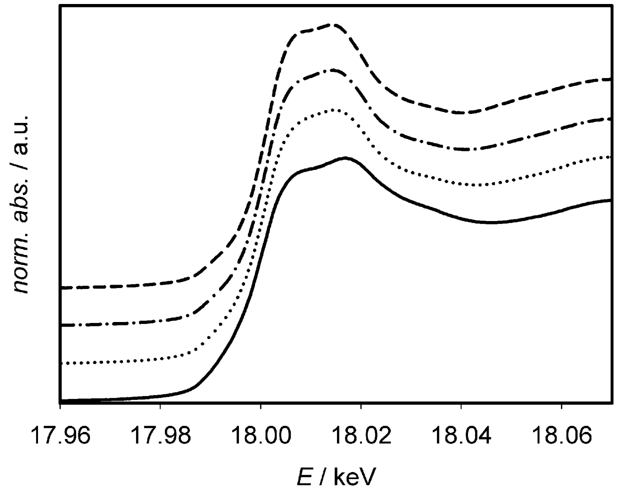


Fig. 4. XANES spectra of **1** dissolved in toluene (solid line), compared with the same solution containing one (dotted), two (dotted dashed), and three (short dashed) equivalents of H*acac*

of the coordinating butanol against *i*-propanol molecules, as carbon shells beyond the first two are not visible with EXAFS.

In contrast to the discussion above, the addition of acetylacetone causes significant structural modification of **1** in solution, which already can be observed in the XANES spectra (Fig. 4). Acetylacetone complicates the range of possible complexes formed, as the chelating effect of this ligand facilitates the formation of higher coordination geometries and thus makes coordination numbers of six, seven, or eight possible.

By adding one equivalent of H*acac*, the coordination geometry seems to change from six to seven or eight, as can be deduced from the diminished splitting of the white line. This finding is in agreement with previous observations and is visible from the EXAFS functions $\chi(k)$ and their *Fourier* transforms in Fig. 5.

In the *Fourier* transform the change in the first peaks that are due to oxygen shells is obvious. This first peak is reduced to a large extent, whereas the intensity of the second peak increases. This behaviour is reflected in the numerical results, where also a reduction of the coordination number in the third oxygen shell is observed. Thus, the average number of coordinating *R*OH groups is decreased compared to the pure solution of **1** in toluene. Still lacking is an explanation of the increase in the zirconium shell, which contains 2.2 backscatterers, with one equivalent H*acac*. In Ref. [11] this fact is not explained, as the values of the oxygen shells are already consistent with a mixture of the complexes **I**, **IV**, and Zr(*acac*)$_4$ (Fig. 1) with a molar ratio of 3:4:2. The bond lengths used for this and the following model calculations are shown in Table 2. The dimeric structure proposed by *Kessler et al.* [17] is also not able to reproduce the high zirconium coordination number. Considering only the smallest possible zirconium coordination number by including the maximum error and the change to a higher coordination number, a trimeric structure **V** as the only species in solution can be proposed. It contains mixed zirconium sites, two with eightfold and one with only sixfold coordination. In this case only two thirds of the added H*acac* molecules are coordinated to the

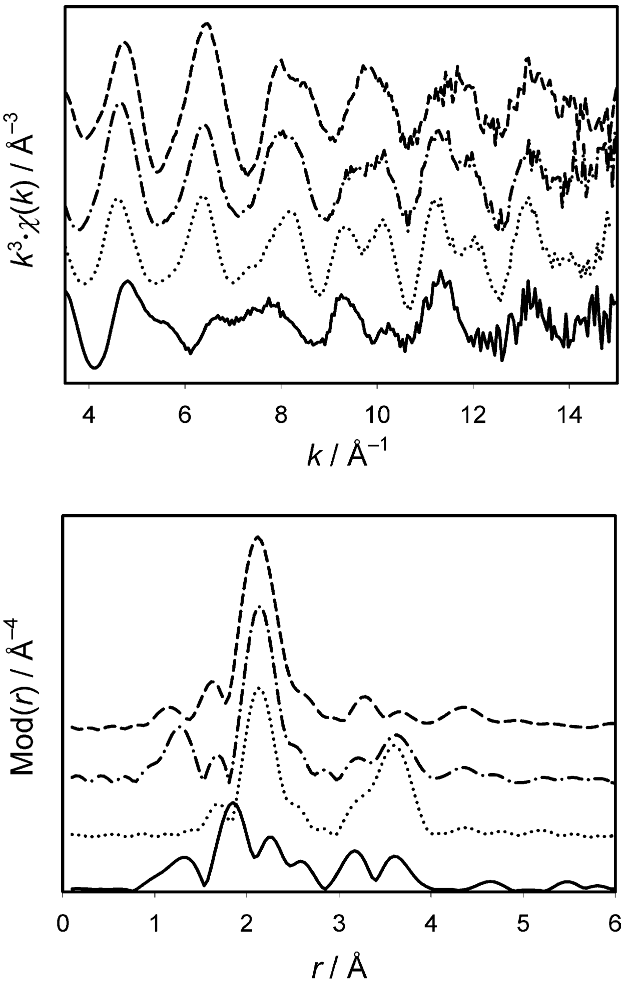


Fig. 5. Experimental $k^3 \cdot \chi(k)$-functions and the corresponding *Fourie*r transforms of **1** dissolved in toluene (solid line), compared with the same solution containing one (dotted), two (dotted dashed), and three (short dashed) equivalents of H*acac*

zirconium atoms. The theoretical coordination numbers calculated for this structure according to Tables 2 and 3 are one shell at about 1.95 Å containing two oxygen atoms, a second oxygen shell at around 2.2 Å with a coordination number of 5.3, and a third one with 0.7 oxygen at 2.35 Å. But only 1.3 Zr backscatterers are found in this structure. Thus, higher aggregates need to be considered in order to explain the determined coordination number of 2.2. From the proposed trimeric cluster for titanium alkoxides by *Martin* and *Winter* [25] the neutral cyclic complex **VI** can be constructed by adding one equivalent of H*acac* to each zirconium atom. As shown in Table 3, this structure does not reproduce the long oxygen distance found experimentally. Additionally, the XANES region indicates a seven- or eightfold coordination. Taking into account the 1.3 equivalents of *n*-butanol present in the starting material, a cyclic structure **VII** becomes possible with one ^{n}*Bu*OH coordinated to each metal center in the six-membered ring. The same construction is possible for a four-membered ring. In this case only two zirconium backscatterers would be found, as the distance of ~5 Å of the third one is too far to be detected by EXAFS. The obtained coordination numbers in the oxygen shell would be the same in such a tetrameric case. Such a tetramer is different from that proposed for the solid state structure of Zr(O^n*Pr*)$_4$ [13], as in this case the averaged oxygen coordination numbers are 2.5 at 1.94 Å, 1.0 at 2.11 Å, and 2.5 at 2.30 Å. These values are not consistent with the experimental data found in the present study.

Summarizing the results obtained for the precursor modified with one equivalent of H*acac*, at least two different structural models can be deduced. Whereas the mixture proposed in Ref. [11] fits the oxygen shells very well, the high coordination number in the zirconium shell cannot be explained even if the largest errors in the coordination number determination are assumed. Only the cyclic structure **VII** (or its four-membered equivalent) agrees with the determined structural parameters, despite the high strain.

With two and three equivalents of H*acac* the zirconium peak in the *Fourier* transforms of Fig. 5 decreases stepwise as it would be expected for a trend leading to monomeric Zr(*acac*)$_4$ [17]. The coordination numbers for two added equivalents H*acac* are in good agreement with a molar mixture of structure **IV** and Zr(*acac*)$_4$ in a ratio of 1:1. A related mixture was proposed in former NMR-studies [17], although the dimeric complex in this case was proposed to be structure **I**, which requires a short oxygen distance. Thus, to reproduce our experimental EXAFS data, it must be replaced by structure **IV**. Whereas such a mixture reproduces the obtained coordination numbers in the zirconium and the second oxygen shell with good quality, a complex obtained from **IV** by removing one *R*OH group from each zirconium center would give very good values for both oxygen shells. In contrast, the coordination number for the zirconium shell would be outside the experimental error. The experimentally not found short oxygen distance, the observed long one, and the zirconium coordination number of 0.6 exclude a trimeric structure similar to **V**, shown as compound **VIII**, where the added H*acac* is not homogeneously distributed over the zirconium centers present in the complex. Other simple models, for example structure **IX**, are not able to reproduce the low coordination number in the first oxygen shell as well as the low zirconium number without violating the results of the XANES region, which requires a seven- or eightfold coordination.

Concluding the discussion for solutions of **1** containing two equivalents of H*acac* the results can be interpreted as a 1:1 mixture of **IV** and Zr(*acac*)$_4$. Only the experimentally determined coordination number in the oxygen shell at about 2.2 Å seems to underestimate the real conditions. The same fact was already found for pure **1** dissolved in toluene and with one equivalent of H*acac*, where the coordination number in this oxygen shell was smaller than suggested by the best model, too. Thus, the proposed mixture and their molecular ratio is better fitting the reality in toluene than in *n*-butanol.

The same conclusion is valid for solutions containing three equivalents of H*acac*. In contrast to the measurements for *n*-butanol, two oxygen shells could be fitted with an increase in the first oxygen shell compared to solutions containing two H*acac*. All these findings are in accordance with a molecular mixture of structure **IV** and Zr(*acac*)$_4$ in a 1:4 molar ratio. Taking into account the experimental errors in the oxygen shells, the theoretical calculated coordination numbers are reproduced by the experimental results. Again, like in the case of one and two equivalents H*acac* the coordination number in the oxygen shell at about 2.2 Å is underestimated by EXAFS measurements. The backdraw of such a mixture is the required zirconium coordination of 0.3 backscatterers, which is not found experimentally. But it should be noted, that such a small number of zirconium atoms is at the limit of significance. The only other structural model that reproduces the determined experimental values better is shown in Fig. 1 as structure **X**. Because it is monomeric, no zirconium shell is expected to be found. Thus, no decision between the two proposed models can be made by means of EXAFS spectroscopy. But structure **X** is in agreement with ebulliometric molecular weight determinations in benzene, which support a monomeric character of zirconium β-diketonates, even if it is not clear from such measurements, whether only three H*acac* molecules can be added to zirconium alkoxides in simple solutions or all O*R* groups can be replaced by H*acac* to form $\mathrm{Zr}(acac)_4$ [30, 31]. Taking all these facts into account, structure **X** seems to be more likely than a mixture of one equivalent of **IV** and four $\mathrm{Zr}(acac)_4$. It should be noted, that also a mixture of all three species, which are connected by rearrangement reactions is possible, as suggested in recent NMR-studies [17].

As conclusion we can confirm, that the structure determined for $\mathrm{Zr(O}^n Bu)_4$ in *n*-butanol [11] is identical with the dimeric structure formed in toluene solution. The complex deduced from the experimental XANES and EXAFS data has an octahedral coordination geometry saturated by one additional butanol $^n Bu\mathrm{OH}$ per zirconium center. This finding is surprising inasmuch as former molecular weight determinations predict a drastic change in the degree of aggregation when the solvent is changed from the natant alcohol to benzene, or in our case to toluene. The question whether the unpredicted behaviour found in our studies is due to the 1.3 equivalents of *n*-butanol already present in the starting material – which is also used in the different applications mentioned – or whether the results of former cryo- and ebullioscopic measurements have to be reconsidered due to the high experimental errors of these methods cannot be answered in this work. Further experiments using the alcohol free alkoxide as starting material will clarify the situation. *i*-Propanol and *THF* are not able to change the structure of the alkoxide in solution. In the case of *THF* it can be concluded, that it is not coordinating to zirconium, as the bulky properties of *THF* would be expected to change the steric conditions at the zirconium center by coordination. For $^i Pr\mathrm{OH}$ the coordination cannot be excluded, as exchanging butanol for *i*-propanol is only affecting carbon shells that are beyond the detection ranges in EXAFS spectroscopy. If such a coordination would take place, it can then only be stated, that the structural parameters of the species present in solution are not altered. This situation changes in evidence when H*acac* is added. This effect has been described for *n*-butanol with the consecutive Eqs. (1)–(3) (cf. Ref. [11]).

$$1\,\mathrm{eq\ H}acac\mathrm{:}\ \ 8\mathbf{I} + 16\mathrm{H}acac \rightarrow 3\mathbf{I} + 4\mathbf{IV} + 2\mathrm{Zr}(acac)_4 + 10^n Bu\mathrm{OH} \qquad (1)$$

$$2\,\mathrm{eq\ H}acac\mathrm{:}\ \ 3\mathbf{I} + 12\mathrm{H}acac \rightarrow 2\mathbf{IV} + 2\mathrm{Zr}(acac)_4 + 10^n Bu\mathrm{OH} \qquad (2)$$

$$3\,\mathrm{eq\ H}acac\mathrm{:}\ 3\mathbf{I} + 18\mathrm{H}acac \rightarrow \mathbf{IV} + 4\mathrm{Zr}(acac)_4 + 20^n Bu\mathrm{OH} \qquad (3)$$

As can be seen from the previous discussion and more recent publications [17], these reactions are likely to oversimplify the situation. Especially for solutions containing one and three equivalents H*acac* a critical discussion of the possible neutral structures revealed, that better models can be found to explain the experimental data. In case of one equivalent H*acac* the puzzling fact of increased zirconium coordination numbers required a higher aggregated complex than proposed in earlier studies. The cyclic trimeric (or tetrameric) structure **VII** turned out to fit the structural parameters of *all* coordination shells to a larger extend than the mixture of Eq. (1). In contrast, Eq. (2) is in good agreement with the experimental results for two H*acac* added and only the dissociation of two *R*OH molecules of **IV** in a particular equilibrium might lead to a better description of the experimental results. For three equivalents H*acac* the experimental situation is almost as good explained by Eq. (3) as by a monomeric structure **X**. The improvement achieved by introducing **X** is an explanation of the missing zirconium atoms found in the EXAFS analysis. It also takes into account the controversial number of H*acac* molecules being able to coordinate to zirconium under the conditions applied here.

In conclusion, we showed that EXAFS spectroscopy is a valuable tool in the structural determination of metal alkoxides in solution. It offers the advantage of using the numbers of coordinating neighbouring atoms as a direct probe for the degree of aggregation. Despite the errors especially in coordination number determination it is more reproducible than ebullioscopic methods and thus better suited for this purpose. Still it is not possible to overcome the averaging drawback of the latter method, from which EXAFS suffers as well. The interpretation of the EXAFS data is not straightforward, as shown in this work, and the models to explain the experimental data need critical consideration. While doing this, the number of possible structures present in solutions as the investigated ones can be restricted to a large extend, but a final decision for one of these two or three remaining models cannot be carried out. The reason for this might be found in mixtures of these remaining structures, which can also be related to each other by exchange and rearrangement equilibria. To further elucidate the conditions present in such solutions, combined investigations on samples of the same concentration by EXAFS, IR, Raman, NMR, and mass spectrometry are necessary.

Experimental

Sample Preparation

The commercially available primary alkoxide zirconium tetra-*n*-butoxide $Zr(C_4H_{10}O)_4$ (**1**) (80 weight% in ^{n}BuOH) was purchased and used without further purification. Measurements were carried out in 0.2 mol dm^{-3} solution in dry toluene. Sample handling and addition of the dry ligands *THF*, ^{i}PrOH, and H*acac* were carried out under Ar. After adding the additional ligands, each solution was allowed to equilibrate for 2 h in order to ensure equivalent conditions in the measurements.

EXAFS Measurements

The EXAFS measurements were performed at beamline X1 of the Hamburger Synchrotronstrahlungslabor (HASYLAB) at DESY (Hamburg, Germany). They were performed at the Zr K-edge (17998.0 eV) using a Si(311) double crystal monochromator. The synchrotron beam current at HASYLAB (positron energy 4.45 GeV) was between 80–140 mA. All the experiments were carried out under ambient conditions at 25°C. The tilt of the second monochromator crystal was set to 40% harmonic rejection at beamline X1. Energy resolution was estimated to be about 5 eV for the Zr K-edge. All the spectra were collected in transmission mode with ion chambers, which were filled with Ar. The energy calibration of the transmission experiments was performed with the corresponding zirconium metal foil. A sealed liquid sample cell for handling air sensitive samples [32] was used in the EXAFS experiment to prevent hydrolysis. The path length for the samples of **1** was 6 mm in order to achieve an edge jump of approximately 1.5.

Four EXAFS scans of 30 min each were averaged. During the whole measurement time of 2 h no obvious changes could be detected in the EXAFS spectra, suggesting that no structural changes took part.

Data evaluation started with background absorption removal from the experimental absorption spectrum by subtraction of a *Victoreen*-type polynomial. Then the background subtracted spectrum was convoluted with a series of increasingly broader *Gauss* functions and the common intersection point of the convoluted spectra was taken as energy E_o [33, 34]. To determine the smooth part of the spectrum, corrected for pre-edge absorption, a piecewise polynomial was used. It was adjusted in such a way that the low-R components of the resulting *Fourier* transform were minimal. After division of the background subtracted spectrum by its smooth part, the photon energy was converted to photoelectron wave numbers k. The resulting EXAFS function was weighted with k^3. Data analysis in k space was performed according to the curved wave multiple scattering formalism of the program EXCURV98 with XALPHA phase and amplitude functions [35]. The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI was set to -4.00) and an overall energy shift (ΔE_o) was assumed. In all cases the Amplitude Reduction Factor (AFAC) was set to a value of 0.8.

Acknowledgements

We thank HASYLAB at DESY for provision of beamtime.

References

[1] Brinker CJ, Scherer GW, Brinker J, Scherrer G (1990) Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing, Academic Press

[2] Sequeira CAC, Hudson MJ (1993) Multifunctional Mesoporous Inorganic Solids, Kluwer Academic Publ

[3] Segal DL (1986) Alkoxide-derived Sol-gel Coatings, AEA Technology Plc

[4] Klein LC (ed) (1988) Sol Gel Technology for thin Films, Fibres, Preforms, Electronics and speciality Shapes, Academic Press

[5] Wu E, Chen KC, Mackenzie JD (1984) In: Brinker CJ, Clark DE, Ulrich DR (eds) Better Ceramics through Chemistry I, vol 32 Elsevier Science Publ, p 169

[6] a) Schubert U, Hüsing N, Lorenz A (1995) Chem Mater **7**: 2010; b) Schubert U (1996) J Chem Soc Dalton Trans 3343; c) Kickelbick G (2003) Progr Polym Sci **28**: 83

[7] Kickelbick G, Feth MP, Bertagnolli H, Puchberger M, Holzinger D, Gross S (2002) J Chem Soc Dalton Trans 3892

[8] Turova NY, Turevskaya EP, Kessler VG, Yanovskaya MI (2002) The Chemistry of Metal Alkoxides, Kluwer Academic Publ

[9] a) Bradley DC, Mehrotra RC, Gaur DP (1978) Metal Alkoxides, Academic Press, London; b) Bradley DC, Holloway CE (1964) Inorg Chem **3**: 1163

[10] Pfalzgraf LG (1987) New J Chem **11**: 663

[11] a) Peter D, Ertel TS, Bertagnolli H (1994) J Sol-Gel Sci Tech **3**: 91; b) Peter D, Ertel TS, Bertagnolli H (1995) J Sol-Gel Sci Tech **5**: 5

[12] Vaartstra BA, Huffmann JC, Gradeff PS, Yunhu K, Huber-Pfalzgraf LG, Dara JD, Paraud S, Caulton KG (1990) Inorg Chem **29**: 3126

[13] Day VW, Klemperer WG, Pafford MM (2001) Inorg Chem **40** (23): 5738

[14] a) Mehrotra RC, Batwara JM, Kapoor PN (1980) Coord Chem Rev **31**: 67; b) Gugliemi M, Carturan G (1988) J Non-Cryst Sol **100**: 16; c) Livage J, Henry M, Sanchez C (1988) Prog Solid State Chem **18**: 259

[15] a) Sanchez C, Babonneau F, Doeuff S, Leaustic A (1988) Ultrastructure Processing of Advanced Ceramics, J. Wiley & Sons, p 77; b) Babonneau F, Doeuff S, Leaustic A, Sanchez C, Cartier C, Verdaguer M (1988) Inorg Chem **27**: 3166

[16] Reinöhl U, Bertagnolli H, Ertel TS, Hörner W, Weber A (1998) Ber Bunsenges Phys Chem **102**: 144

[17] Spijksma GI, Bouwmeester HJM, Blank DHA, Kessler VG (2004) Chem Commun 1874

[18] Bradley DC, Mehrotra RC, Swanwick JD, Wardlaw W (1953) J Chem Soc 2025

[19] Bradley DC, Mehrotra RC, Wardlaw W (1952) J Chem Soc 2027

[20] Bradley DC, Mehrotra RC, Wardlaw W (1952) J Chem Soc 4204

[21] Bradley DC, Mehrotra RC, Wardlaw W (1952) J Chem Soc 5020

[22] Bradley DC, Carter DG (1961) Canad J Chem **39**: 1434

[23] Bradley DC, Holloway CE (1968) J Chem Soc A 1316

[24] Holzinger D, Kickelbick G (2004) J Mater Chem **14**: 2017

[25] Martin RL, Winter G (1960) Nature **188**: 313

[26] Caughlan CN, Smith HS, Katz W, Hodgson W, Crowe RW (1951) J Am Chem Soc **73**: 5625

[27] Russo WR, Nelson WH (1970) J Am Chem Soc **92**: 1521

[28] Ribot F, Tolédano P, Sanchez C (1991) Chem Mater **3**: 759

[29] Clegg W (1987) Acta Cryst C **43**(4): 789

[30] Puri DM (1970) Indian J Chem **47**: 535

[31] Saxena UB, Rai AK, Mathur VK, Mehrotra RC, Radford D (1970) J Chem Soc A 904

[32] Ertel TS, Bertagnolli H (1993) Nucl Instrum Methods Phys Res B **73**: 199

[33] Ertel TS, Bertagnolli H, Hückmann S, Kolb U, Peter D (1992) Appl Spectrosc **46**: 690

[34] Newville M, Livins P, Yacoby Y, Rehr JJ, Stern EA (1993) Phys Rev B **47**: 14126

[35] Binsted N, Hasnain SS (1996) J Synchrotron Radiat **3**: 185