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AQUEOUS SOLUTION BY XANES SPECTROSCOPY**

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AQUEOUS SOLUTION BY XANES SPECTROSCOPY**

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Abstract

The Jahn Teller distortion of the $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ cluster in aqueous solution has been studied by x-ray near edge structure spectroscopy. Theoretical calculations in the multiple scattering formalism have allowed us to identify in the XANES spectrum the characteristic feature of this distortion and to estimate from the energy separation between this feature and the main shape resonance a tetragonal distortion of about 0.3 Å. Accurate EXAFS analysis does not permit to distinguish between the distorted and undistorted cluster.

Introduction

Several techniques have been used to obtain information about the environment of a metal ion in solution, such as X-ray diffraction, neutron diffraction, N.M.R. studies and X-ray absorption spectroscopy. The peculiarity of this last technique is that information on the local environment

around the photoabsorber is obtained because of the finite mean free path of the ejected photoelectron. So the X-ray absorption spectroscopy can be used for crystals as well as amorphous material. ⁽¹⁾

In this paper, we present a study of the coordination of Cu^{2+} in aqueous solution by XANES spectroscopy. It is well known that Cu^{2+} in octahedral coordination presents a double degenerate ground state (ϵ_g). The Jahn Teller (J.T.) theorem states that a coupling between the electronic ϵ_g state with the normal vibrational modes of the same symmetry occurs and therefore the electronic degeneracy is removed ⁽²⁾ determining a distortion of the octahedral cluster site. Depending on the coupling strength and/or the temperature a dynamic or static regime of the J.T. effect occurs. For this last case, the complex is tetragonally distorted with four equatorial bonds at the same distance and two elongated or contracted axial bonds. In solids, different kinds of distortions have been found in CuL_6 complexes, where L is the ligand, the tetragonal one being the more common distortion with four Cu-L short bonds equivalent or approximately equivalent.⁽³⁻⁶⁾ The coordination of Cu^{2+} in solution is a controversial subject. In fact, the results of different experimental studies have been interpreted in terms of square planar, distorted and non-distorted octahedral arrangements in different concentrations. In particular, for CuCl_2 in solution a large distortion has been proposed from EXAFS studies⁽⁷⁾, but another EXAFS and x-ray radial distribution (XRD) by x-ray scattering experiments on CuCl_2 and CuBr_2 did not find evidence of distortion.^(8,9) On the other hand, XRD experiments on concentrated $\text{Cu}(\text{NO}_3)_2$ solutions suggest that Cu^{2+} is sixfold coordinated and probably in a tetragonal distorted configuration.⁽¹⁰⁾ Other studies on $\text{Cu}(\text{ClO}_4)_2$ and CuSO_4 solutions^(11,12) support the existence of a distorted coordination polyhedron around Cu^{2+} for these highly concentrated solutions. The elongation of the axial distance of the octahedral geometry found in these latest cases is about 0.3 Å.

Moreover, a neutron diffraction study of the CuCl_2 solution at 4.32 molar concentration shows that the axial distortion is about 0.5 Å.⁽¹³⁾

In this work we have studied the Cu^{2+} site symmetry in CuCl_2 solutions over a range of concentrations between 0.05 to 1M. The data have been analyzed on the basis of the multiple scattering theory for CuO_6 clusters. The effect of the tetragonal distortion on the XANES of copper octahedral cluster has been investigated by performing several calculations for symmetrical and distorted clusters of polarized and unpolarized spectra. The theoretical XANES results predict that when there is elongation of the axial distance the multiple scattering along that direction gives rise to a multiple scattering peak which appears as a shoulder on the low energy side of the rising edge of the main strong multiple scattering resonance (MSR) at the threshold of the Cu K-edge. This peak which is present in the XANES spectra of distorted copper sites in crystalline compounds ^(14,15) is identified as the main MSR peak for the photoelectron multiple scattering pathways in the direction of the longer bond which is shifted to lower energy because of the effect of the increased interatomic distance ⁽¹⁶⁾ in agreement with recent findings in angular resolved XANES of VO_6 bipyramidal clusters⁽¹⁷⁾. The predicted MSR peak due to the multiple scattering in the direction of the longer bond in the Cu sites has in fact been observed in the XANES spectra of

Cu^{2+} solution and consequently an average distortion $\Delta = 0.3 \text{ \AA}$ has been deduced. Finally the EXAFS signal has been analysed using the new spherical wave approximation⁽¹⁸⁾ which allows the EXAFS analysis to be performed also at low wave vector (k) values. Our analysis shows that it is impossible to distinguish between the distorted and undistorted cluster by using only the EXAFS signal. This fact points to an inherent limitation of the EXAFS analysis for detecting small distortions in the coordination shell of a metal ion in solution.

Experimental

The solutions were prepared by dissolving weighted quantities of hydrated $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in bidistilled water. Solutions of approximately 50 mM, 0.3 M, and 1M were used. The experiments were carried out at the ADONE storage ring of the Frascati synchrotron radiation facility, working at 1.5 GeV and with a beam current in the range 30-100 mA. The Cu K-edge spectrum was recorded in the transmission mode using a double crystal monochromator Si(111). For recording the XANES spectra we used an entrance slit of 0.1 mm giving a spectral resolution of $\approx 1 \text{ eV}$. In the EXAFS experiments a entrance slit of 1mm was used. Samples were measured in mylar cells with thickness ranging between 0.1 mm to 1mm in order to optimize the sample thickness. The crystalline CuO sample was prepared by powder spread on a kapton tape.

Results

The XANES spectra for these three solutions are identical and we have not found any difference between them and/or in their derivative. This means that the same coordination symmetry is present in the three concentrations. In Fig. 1. the spectra and their derivatives for Cu^{2+} water solution, CuO crystalline and Ni^{2+} solutions⁽¹⁶⁾ after background removal and normalization at the high energy region (EXAFS) are plotted. The $\text{Ni}^{2+}(\text{H}_2\text{O})_6$ spectrum shows, similar to other octahedral complexes,⁽¹⁶⁾ a main resonance at the rising edge and a shoulder B, the $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ spectrum is similar to the $\text{Ni}^{2+}(\text{H}_2\text{O})_6$ one, but a new structure appears at the rising edge (structure C) which is clearly evident in the derivative spectrum. This structure can be undetectable if a poor resolution is used in the experiment. We have indeed verified that if a 1 mm slit is used this slope change becomes undetectable. This feature C, not present in other regular octahedra proves to be characteristic of a tetragonal distortion. In fact published results on local J.T. distorted Cu^{2+} crystalline compounds show the same feature in the spectrum.^(14,15) Similarly to the XANES spectra, the EXAFS signals do not show any difference between the three studied concentrations. The EXAFS spectrum of the 0.3 M CuCl_2 concentration is plotted in the upper part of Fig. 2. We have taken the E_0 value 15 eV lower than the inflexion point of the rising edge, and the Fourier Transform (F.T.) has been carried out in the range $3 - 9.6 \text{ \AA}^{-1}$ using a Gaussian window.

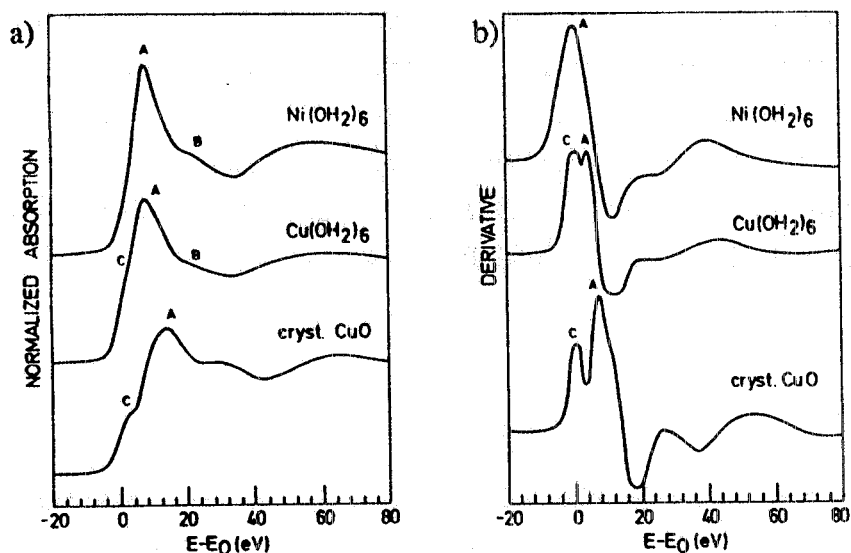
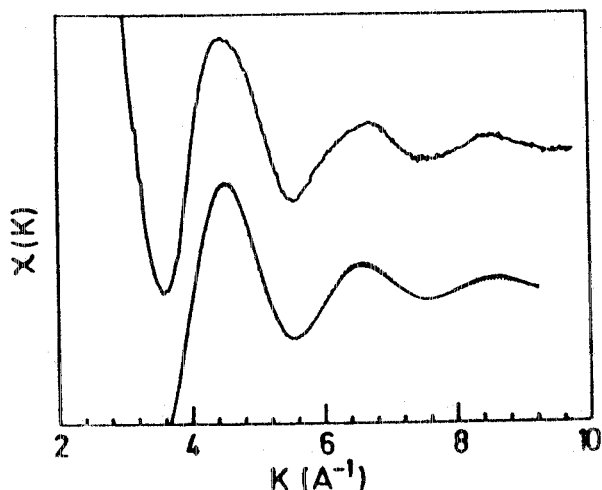


FIG. 1 - Normalized experimental XANES spectra (panel a) and their derivatives (panel b) of water solutions of NiCl₂, CuCl₂ and crystalline CuO at the transition metal K edge.

FIG. 2. EXAFS spectrum of Cu²⁺ water solution (upper curve). In the lower part are plotted the Fourier filtered EXAFS signal (continuous line) and the best fit for one coordination distance (dotted line). The parameters obtained are: $N=6$, $\sigma^2=0.01 \text{ \AA}^2$ and $R=1.95 \text{ \AA}$.



The main oscillation has been extracted by backfourier transforming the F.T. between 0.5 and 2.4 \AA . The total phase of the extracted signal does not show any inflection point characteristic of the presence of two different coordination distances; this fact is also supported by the symmetry of the radial distribution function. This filtered oscillation has been analyzed with a minimum criterium fitting procedure using as a model the EXAFS signal obtained from a multiple scattering calculation in the H.L. approximation for the interstitial potential.⁽¹⁹⁾ In this calculation we have used a symmetrical octahedral cluster of oxygen atoms at a distance of 1.95 \AA . The fitting procedure to analyze EXAFS spectra is highly dependent of the initial fixed parameters and their variation limits because of the high correlation within the free parameters, i.e. coordination number with Debye-Waller factors and mean free path or E_0 with interatomic distance. Our results show different best fits depending on the initial fixed parameters, so that, in principle we could discriminate on the basis of a best fitting procedure between a symmetrical configuration of six

oxygen atoms surrounding the Cu atom or a distorted configuration. In Table I are given different fits in which the R parameters are comparable. In fact the values obtained by Sham et al ⁽⁷⁾ are similar to one of our fits. But this fit is not better than that obtained with only one coordination distance. We conclude that from EXAFS analysis only, it is not possible to discriminate if this system is distorted, principally due to effects associated to large Debye Waller factors. In Fig. 2 are plotted the filtered signal and the best fit curve for one coordination distance.

TABLE I - Parameters obtained from the minimum criterium fitting procedure of the filtered EXAFS signal of CuCl₂ water solution using two Cu-O distances and one distance respectively. The meaning of symbols is as following: N₁, N₂ are coordination numbers, R₁ and R₂ are oxygen copper distances, σ^2 are square Debye Waller factors, ΔE is the energy threshold shift from E₀=-15 eV and λ the photoelectron mean free path. The numbers underlined are fixed parameters in the minimum fit procedure. The fit procedure minimizes the R value defined as $R = \sum_i (X_i^{fit} - X_i^{exp})^2 / \sum_i (X_i^{exp})^2$

N ₁ /N ₂	R ₁	σ_1^2	ΔE	λ	N ₁ +N ₂	R ₂	σ_2^2	R*10 ²
0.41	2.57	0.0276	-2.03	1.9*k	<u>6</u>	1.93	0.0711	0.34
0.45	2.57	0.0291	-1.94	<u>2.0*k</u>	<u>6</u>	1.93	0.0070	0.34
0.14	2.35	0.0201	0.86	<u>2.0*k</u>	<u>6</u>	1.92	0.0097	0.23
N ₁	R ₁	σ_1^2	ΔE	λ				R*10 ²
4.88	1.95	0.010	-2.88	2.0*k	-	-	-	0.96
<u>6</u>	1.95	0.010	-3.00	1.7*k	-	-	-	0.55

Discussion

In order to obtain qualitatively the distortion we have performed theoretical calculations of the total cross section in the framework of the multiple scattering theory. This theory is an extension of the bound state molecular scattered wave method of Johnson⁽²⁰⁾ to calculate continuous wave functions. In this scheme the total potential is represented by a cluster of non-overlapping potential spheres centred at the atomic sites. The molecular potential is approximated by a potential of the muffin-tin type with a constant interstitial value given by the potential average in the interstitial region. The Coulomb and the exchange parts are calculated on the basis of the total charge density, obtained by superposing the charge densities of the individual atoms constituting the cluster as given by the Clementi and Roetti tables⁽²¹⁾. In this theory, the total wave function in the interstitial region can be interpreted as a sum of the exciting wave plus all the scattered waves coming from each sphere in the cluster. The model is therefore a multiple scattering model for several centres with free propagation in the interstitial region.

In our calculations, we have used a 10% overlapping between muffin-tin spheres and the exchange potential has been treated in the X- α approximation which in the XANES region gives results similar to those given by the H.L. exchange and correlation potential. Our program gives

also the expansion of the total cross section in terms of the different multiple scattering events⁽¹⁶⁾. This expansion permits us to understand the origin of the different spectral features in the XANES spectra. We have not used any convolution of the theoretical spectrum to take account of the core hole life-time and of the experimental resolution. Also dynamic effects due to thermal vibrations have not been considered. Several calculations with different magnitudes of tetragonal distortion have been performed and the resulting spectra are shown in Fig. 3a together with their derivatives (Fig. 3b). They are ordered from top to bottom in order of increasing amount of distortion. As a reference the uppermost spectrum corresponds to an undistorted octahedral cluster of a Cu atom surrounded by six oxygens at a distance of 1.95 Å. This spectrum shows the typical shape of an octahedral coordination with a main line at the rising edge originated by a multiple scattering resonance in which all the multiple scattering contributions are in phase and a shoulder "B" which comes from the incoherent interference between successive multiple scattering oscillation. The last part of the spectrum is the EXAFS region in which the important contribution arises only from single scattering processes.⁽²²⁾

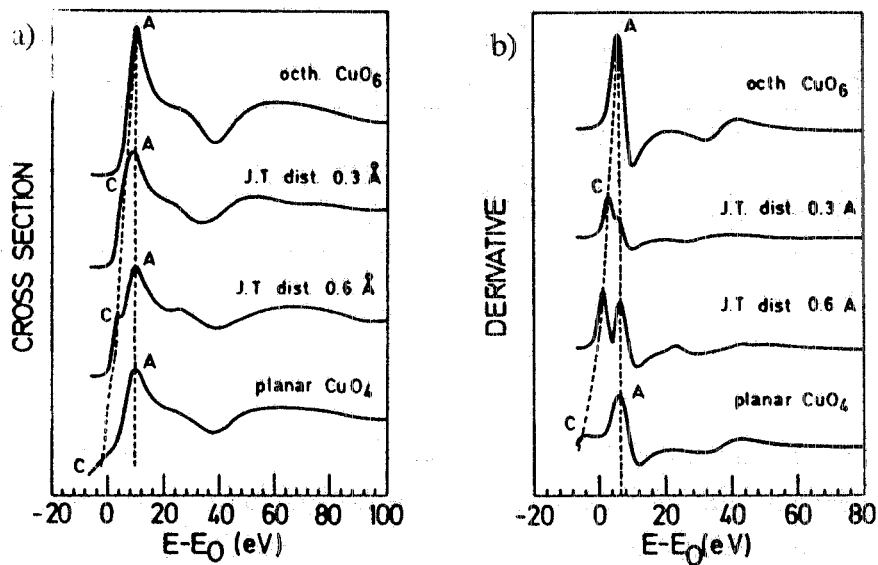


FIG. 3 - Theoretical XANES spectra of CuO_6 cluster. a) octahedral cluster, interatomic distance $R=1.96$ Å. b) Tetragonal distorted, $R_{\text{eq}}=1.96$ Å, $R_{\text{ax}}=2.25$ Å. c) Tetragonal distorted, $R_{\text{eq}}=1.96$ Å, $R_{\text{ax}}=2.6$ Å. d) Planar CuO_4 cluster.

The second spectrum correspond to a model in which the two axial oxygen atoms are elongated by 0.3 Å. Small changes are observed in the spectrum when compared with the spectrum of the symmetrical cluster. The differing features are: a decrease of the main line intensity, an interference in the EXAFS region and the appearance of a slope change in the rising edge which is clearly put in evidence in the derivative spectrum (peak C in Fig. 3b). The third spectrum which corresponds to a distorted octahedron $\Delta = 0.64$ Å shows a spike called "C" which characterizes large distortions. Notice however in this case the absence in the EXAFS region of a significant interference effect. In

the bottom of Fig. 3 the calculation for a planar CuO_4 cluster shows that the C structure persist in this limit geometry.

In order to understand the appearance of the spectral structure C we have decomposed in Fig. 4 the unpolarized spectrum of CuO_6 , tetragonally distorted by a positive elongation of $\Delta = 0.3 \text{ \AA}$ into the two contributions with electric field polarization \mathbf{e} vector parallel to the axis of distortion ($\mathbf{e} \parallel \mathbf{z}$) and perpendicular to it ($\mathbf{e} \perp \mathbf{z}$). As seen from the figure, the two polarized spectra peak at different energies so that the total unpolarized spectrum (equal to one third of their sum) shows a shoulder C before the main maximum A. Their energy separation is a clearly a function of the distortion. Notice that the spectral shape of the two contributions is similar, seemingly indicating that the multiple scattering paths most important in determining such a shape are the collinear paths involving only the central copper atom and two diametrically opposed oxygen atoms at a time.

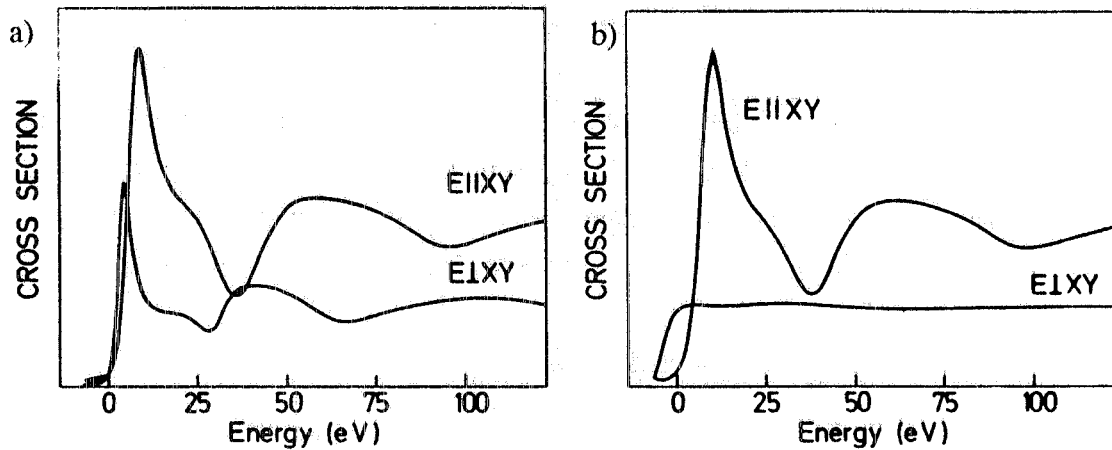


FIG. 4. - Theoretical polarization resolved multiple scattering calculations for the CuO_6 tetragonal distorted cluster (panel a) and for square planar configuration (panel b). The curves are labelled by $\mathbf{E} \perp \mathbf{xy}$ or $\mathbf{E} \parallel \mathbf{xy}$ meaning that the electric field \mathbf{E} is either perpendicular or parallel to the equatorial plane.

This fact would then imply the validity of the rule $k_r \cdot R = [E_r - E_0]^{1/2} \cdot R = \text{const}$, where E_r is the resonance energy (peak energy), E_0 is the constant interstitial potential and R is the length of the bond ⁽²³⁾. Since $E_0 = -12.2 \text{ eV}$, relative to the zero of the energy scale of the figure (which is also the theoretical ionization threshold), we find by inspection:

$$k_A R_A = [E_A - E_0]^{1/2} R_A = (20.5)^{1/2} \cdot 1.95 = 8.8 \text{ (eV)}^{1/2} \text{ \AA}$$

$$k_C R_C = [E_C - E_0]^{1/2} R_C = (16.6)^{1/2} \cdot 2.25 = 9.2 \text{ (eV)}^{1/2} \text{ \AA}$$

where E_A and E_C are the energy positions, relative to the same zero, of the resonance maxima for the two polarization. We then see that the relation is not exactly obeyed, pointing to the fact that other paths contribute in determining the position of the resonance maxima. This was to be expected,

since for spherical waves very near threshold the rule that the contribution of the multiple scattering paths is proportional to the cosine of the angle between the first outgoing path vector and the last incoming path vector is not exactly true, as it would be for plane waves at all energies and for spherical waves at energies beyond about three Rydbergs (≈ 40 eV) above threshold. For higher distortions the discrepancy between the two constants is still bigger. For example for $\Delta = 0.64$ we find

$$k'_A R'_A = [E'_A - E'_0]^{1/2} R_A = (21.4)^{1/2} \cdot 1.95 = 9.02 \text{ (eV)}^{1/2} \text{ \AA}$$

$$k'_C R'_C = [E'_C - E'_0]^{1/2} R_C = (15.0)^{1/2} \cdot 2.60 = 10.0 \text{ (eV)}^{1/2} \text{ \AA}$$

and fails completely for the planar CuO_4 cluster ($\Delta = \infty$). This is not a surprise, since one expects the relation to be valid only for "small distortions": $\Delta R/R \leq 20\%$. As a consequence one cannot use the relation $K'_r \cdot R = \text{const}$ for determining the amount of the distortion from the energy separation of the two features A and C. A complete XANES calculation has to be performed with such a distortion as to reproduce the observed energy splitting. In this way we have obtained a Jahn-Teller distortion of $\Delta = 0.3 \text{ \AA}$ for our $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex.

As an empirical fact we notice however that if we take as the reference energy E_0 the transition energy to a 3d state, following the argument put forward in ref. 23, then we find for $\Delta = 0.3 \text{ \AA}$

$$\Delta E_A R_A^2 = 15.4 \cdot (1.95)^2 = 58.5 \text{ eV \AA}^2$$

$$\Delta E_C R_C^2 = 11.5 \cdot (2.25)^2 = 58.2 \text{ eV \AA}^2$$

In other words we can empirically use this relation to derive the amount of distortion from the energy separation of the features A and C from the 3d pre-edge feature.

Conclusions

In this study we have identified the shoulder half-way up the edge as being characteristic of a tetragonal distortion of the regular Cu octahedron and have established that the energy separation of this feature to the main peak gives a measure of the degree of tetragonal distortion. This relation is non linear and the separation limit tends asymptotically to that obtained for the planar configuration. This feature is also present in Cu^{2+} crystalline compounds in which the Cu^{2+} has a distorted octahedral oxygen coordination and in quasi planar complexes^(14,15). However, the correlation between the degree of distortion and the energy position of the feature C is difficult to establish in the general case both from an experimental and a theoretical point of view, due to the possible presence of other structures or small changes in energy position of the reference feature coming

from scattering of further shells or multiple scattering paths involving all ligand atoms at a time.

Similar conclusions have been drawn in the interpretation of the XANES spectra of copper imidazole complexes, in which the copper has a planar configuration of nitrogen atoms⁽²⁴⁾, and in liquid solutions with varying pH.⁽²⁵⁾

In our case we obtain that Cu^{2+} complex in solution is Jahn-Teller distorted with an elongation of about $\Delta = 0.3 \text{ \AA}$ as derived from the energy distance between the C structure and the main resonance line A, in agreement with previous results obtained from the study of the radial distribution function⁽¹⁰⁻¹²⁾. Moreover, our results show that limitations in the resolution of the EXAFS spectra can be overcome through an analysis of the XANES spectra.

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