EXAFS analysis using the method of separating functionals

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EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy is a powerful method for the determination of the local atomic structure in amorphous materials, solid solutions, and liquids. Except for the treatment of the raw data, one of the most complicated steps in the structure determination is to solve the EXAFS equation (Fredholm integral equation of the first kind). The partial radial atomic distribution functions (RDF's or g(r)) are the solution of this equation. The calculation of RDF's from experimental data is a typical example of an inverse ill-posed problem.

The application of regularization algorithms to solve the system of equations that occur in the structural analysis was developed by several groups [1,2]. In case of multielement complexes, it is necessary to determine several RDF's and to solve the system of Fredholm integral equations. The number of measurements (number of equations) is often less than the number of desired RDF's. This leads to the nonuniqueness in the determination of the RDF's. Thus, the application of the regularization method can lead to a solution (RDF) that may not have full physical meaning.

This situation can be improved when *a priori* physical and chemical information is included in the analysis. Some compounds have RDF's consisting of a small number of narrow peaks that are separated in distance. Each peak corresponds to a coordination sphere. We suggest using this additional information for the determination of the RDF's [3]. Our EXAFS analysis consists of three steps:

1) The narrow peaks are approximated by δ-functions. The method of separating functionals is used to identify the true coordination spheres (peaks) in each RDF and to determine their approximate distances;

2) This information is used to restore the RDF's by a modified Tikhonov regularization method;

3) The characteristics of each coordination sphere, i.e., interatomic distance (r, Å), coordination number (N), and Debye-Waller factor (σ^2, Å^2), are determined directly from the calculated RDF's.

To test the method of separating functionals, EXAFS spectra [4] of a uranium compound with know structure, $UO_2(HAsO_4)$ x $4H_2O$, were analyzed. The RDF's U-U, U-As, U-O were determined from the U L3-edge and the RDF's As-As, As-U, As-O from the As K-edge spectra.

As an example, the partial radial atomic distribution function U-O of $UO_2(HAsO_4)$ x $4H_2O$ is presented in Fig.1. As can be seen from Table1, the interatomic distances agree with the crystallographic data. The method of separating functionals is a powerful alternative to the conventional EXAFS analysis methods.

Fig.1: Partial RDF U-O of $UO_2(HAsO_4)$ x $4H_2O$

- · Reconstructed RDF without *a priori* information

- · Reconstructed RDF with *a priori* information

— Theoretical model function (σ^2 = 0.003 Å^2)
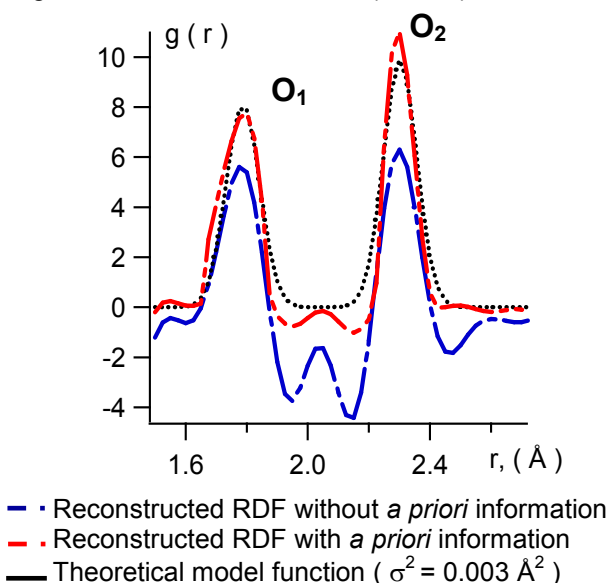
Table1: Comparison of the structural parameters for the uranium coordination spheres obtained from the RDF's with the crystallographic data [5]:

		N	r, Å	σ^2, Å^2
U-U	RDF	2.5	5.38	0.0027
	[5] Neutron Diffraction	4	5.39	-
U-As	RDF	2.5	3.70	0.0011
	[5] ND	4	3.70	-
U-O$_1$	RDF	2.1	1.78	0.0033
	[5] ND	2	1.78 1.80	-
U-O$_2$	RDF	3.6	2.30	0.0017
	[5] ND	4	2.30	-

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