P-04

EXAFS STUDIES OF BIMETALLIC PALLADIUM-COBALT NANOCLUSTERS USING MOLECULAR DYNAMICS SIMULATIONS

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Properties of highly dispersed bimetallic clusters are in the focus of research since the beginnings of the EXAFS technique development [1-4]. In the present studies we deal with determination of structural features of bimetallic palladium-cobalt nanoclusters with average diameter smaller than 3 nm.

In the ideal lattice the same type of atoms have the same local environment, while in the case of bimetallic nanoclusters they usually have a different local neighborhood. Moreover, their atomic structure depends on the chemical environment. For example changes in concentration profile depending on the nature of the gas for Pd-Au alloy nanosystem is reported by Kaszkur [5].

Between many experimental techniques used for characterization of nanoclusters there are two x-ray structural methods: XRD and EXAFS. Former one, X-ray Diffraction technique, seems surprisingly to be a very sensitive tool for monitoring fine surface changes of metallic nanoclusters [5-7]. The latter one, commonly used for nanocrystals (nanoclusters) structural studies, is based on the interpretation of the extended x-ray absorption fine structure (EXAFS). It is a very unique tool because it gives information about a local structure in the vicinity of the absorbing atom. It has already been applied in many fields for qualitative and quantitative analyses of almost any kind of matter and among them it is widely used for characterization of supported metal catalysts [8, 9]. Analysis of EXAFS spectra gives average values of structural parameters: coordination shell radii, coordination numbers and EXAFS Debye-Waller coefficients [8, 10]. In a typical experiment the best accuracy in determining interatomic distances is of 0.01 Å and of 20% in value of the coordination number. The significant error of the latter parameter is caused by its strong correlation with other parameters in the equation describing amplitude of the EXAFS function oscillations.

Because the environment of every atom of the nanocluster may differ and the EXAFS method brings about average values of structural parameters, the differences of local atomic arrangement inside the cluster are reflected mainly in EXAFS Debye-Waller parameter. Thus a very important questions arise: in what way do the EXAFS spectra reflect structural disorder of such objects and what is a true physical meaning of the measured EXAFS structural parameters?

Tools for modeling spatial arrangement of atoms in bimetallic nanoclusters and simulation of both: XRD patterns and EXAFS spectra have been developed and applied to explain observed features of XRD patterns measured for Pd and Pd-Co supported on silica [11] and EXAFS spectra of Pd-Co supported on silica [12]. This program package containing programs CLUSTER and MD_EXAFS was described in details previously [13]. The segregation effects in a model nanocluster obtained by simulation using Monte-Carlo and Molecular Dynamics were discussed and the obtained results were compared with experimental XRD studies [11]. The applicability of the partial segregation profile resulting from these simulations has been shown.

Experimental EXAFS data of Pd-Co/SiO_2 were collected on LURE synchrotron. The results of the standard analysis [10] of the first shell of these EXAFS spectra have been reported in Ref. [12]. These results have confirmed the segregation model proposed in the previous paper [11].

The effect of various segregation “onion” models on simulated EXAFS functions has also been tested in [14]. Several models of PdCo spatially relaxed nanoclusters with various diameters and monometalic Co and Pd clusters of two types of ordering icosahedral and cubooctahedral have been considered. The EXAFS spectra for all of them were calculated and analyzed using standard procedure. Having full information about the atom arrangement in the model clusters we also calculated their structural parameters directly. An influence of different distributions of atoms of both metals and difficulty of distinguishing cubooctahedra and icosahedra were illustrated and discussed.

But to compare the real, experimental and simulated data one needs to add the dynamic dimension *e.g.* via molecular dynamics method to the calculated data. Therefore nanoclusters with different composition have been built and relaxed with Monte Carlo algorithm using program CLUSTER. All of them have been then subjected to Molecular Dynamics procedure (MD) at room temperature. And the radial distribution functions calculated directly.

For the obtained model cluster the MD_EXAFS program calculates EXAFS spectrum, averaging its over MD runs. Calculated this way spectra for 50%Pd-50%Co clusters have been compared with experimental ones for both: Pd and Co K absorption edges showing qualitative agreement (Fig. 1).

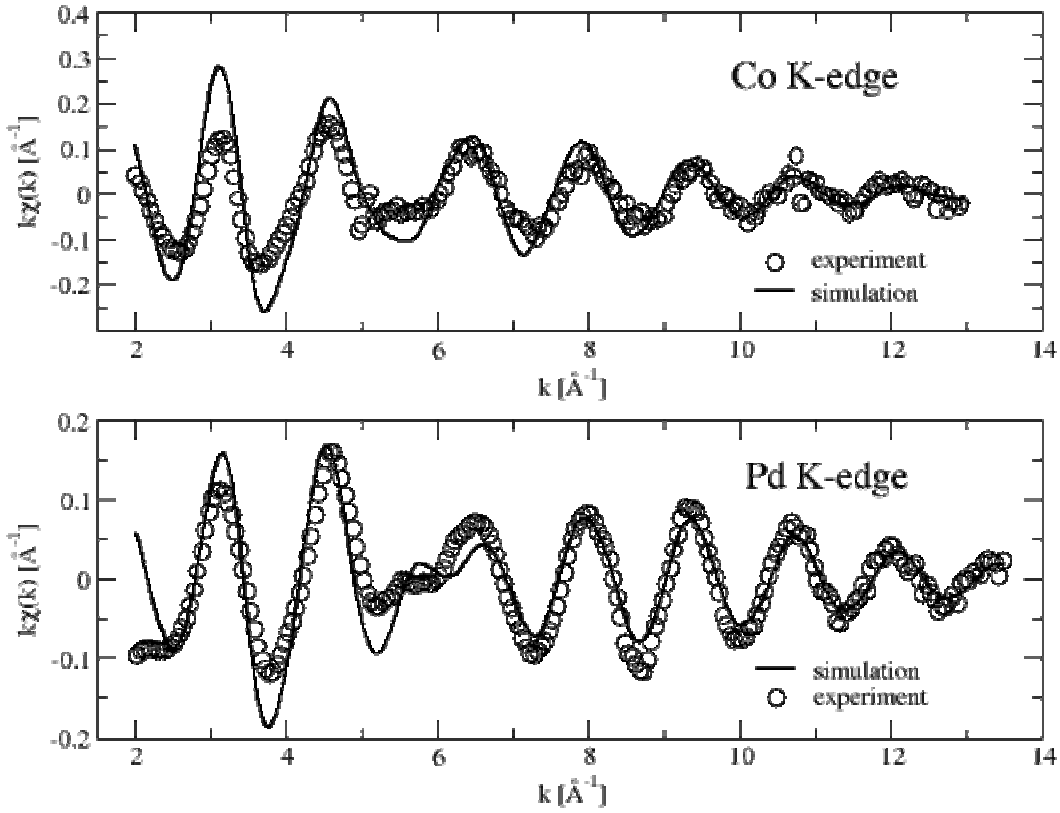

Figure 1. Comparison of experimental and simulated EXAFS spectra of PDCo clusters.

It is shown that the MD procedure adds naturally dynamical features (Debye-Waller factor) to the simulated distribution of interatomic distances. Presented is also a comparison of the model data with the description of anharmonicity of interatomic distances offered by the cumulant expansion method.

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