Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Budker Institute of Nuclear Physics SB RAS, Novosibirsk, Russia
Baykov Institute of Metallurgy and Materials Science RAS, Moscow, Russia

XAFS study of zirconium oxides modified by yttrium and magnesium

V.V. Kriventsov, E.M. Moroz, I.S. Saenko, A.L. Udovsky

The International Conference “Synchrotron and Free electron laser Radiation”: generation and application”, July 13 – 16, 2020

- **Today mixed oxides with a fluorite structure of the composition (Zr, Y) O2-x are widely used to harden ferritic steels used as Fuel element cladding materials for new generation fast neutron reactors operating under irradiation and high temperatures. This work is devoted to study of the state and local structure of samples of zirconium oxides modified by yttrium and magnesium, prepared by coprecipitation and calcined at a temperature of 1250 °C. XAFS (XANES/EXAFS) spectra (Y-K, Zr-K edges) of studied samples were recorded at SSTRC, Novosibirsk.**
- **It was shown that from the yttrium side, the XANES spectra of both samples were almost identical. On the zirconium side, the XANES spectra have minor differences. It can be assumed that the charge state and the nearest environment of yttrium also practically does not change depending on the composition of the samples. Whereas for zirconium, with the charge state unchanged, some changes in the nearest oxygen environment appear to occur due to the composition of the samples.**
- **It was found that the curves of the radial distribution of atoms (RDFs) obtained from the EXAFS spectra studied samples have a number of characteristic features. Only first coordination spheres of the Me-O and Me-Me types are observed, but long-range coordination spheres (more than ~0.45 nm) are absent practically, which may indicate distortions of the long-range order in the structures. The local yttrium arrangement is stable when the composition of samples changes, which may indicate the formation of clusters that include only Y and O elements.**
- **The local zirconium arrangement depends on the composition of the samples, since there are some differences in the RDFs curves. Thus, the amplitudes of the peaks assigned to the coordination spheres Zr-O and Zr-Me are significantly reduced (by more than 25%) for Y,Mg-modified sample in comparison with those for Y- modified sample, which indicates distortions of the original fluorite structure. The observed changes in the Zr-O and Zr-Me distances (more than 0.05) are greater than the changes due to differences in the cell parameters for the compared samples. It has been suggested that the presence of Y-O clusters prevents refinement of structures using the model of statistical solid solution with a fluorite structure.**

Table 1. Chemical composition of the sample studied and structural parameters

Образец	Chemical composition		Cell parameter, Å
	according to synthesis	according to mass spectrometry	
Z18Y/Y18	82% ZrO_2 + 18% Y_2O_3 $Zr_{0.695}Y_{0.305}O_{1.848}\square_{0.152}$	$Zr_{0.712}Y_{0.288}O_{1.856}\square_{0.144}$	5.159
ZYM/Y9	86.5% ZrO_2 + 9% Y_2O_3 + 4.5% MgO $Zr_{0.794}Y_{0.165}Mg_{0.041}O_{1.876}\square_{0.124}$	$Zr_{0.807}Y_{0.153}Mg_{0.0400}O_{1.884}\square_{0.116}$	5.134

XRD data

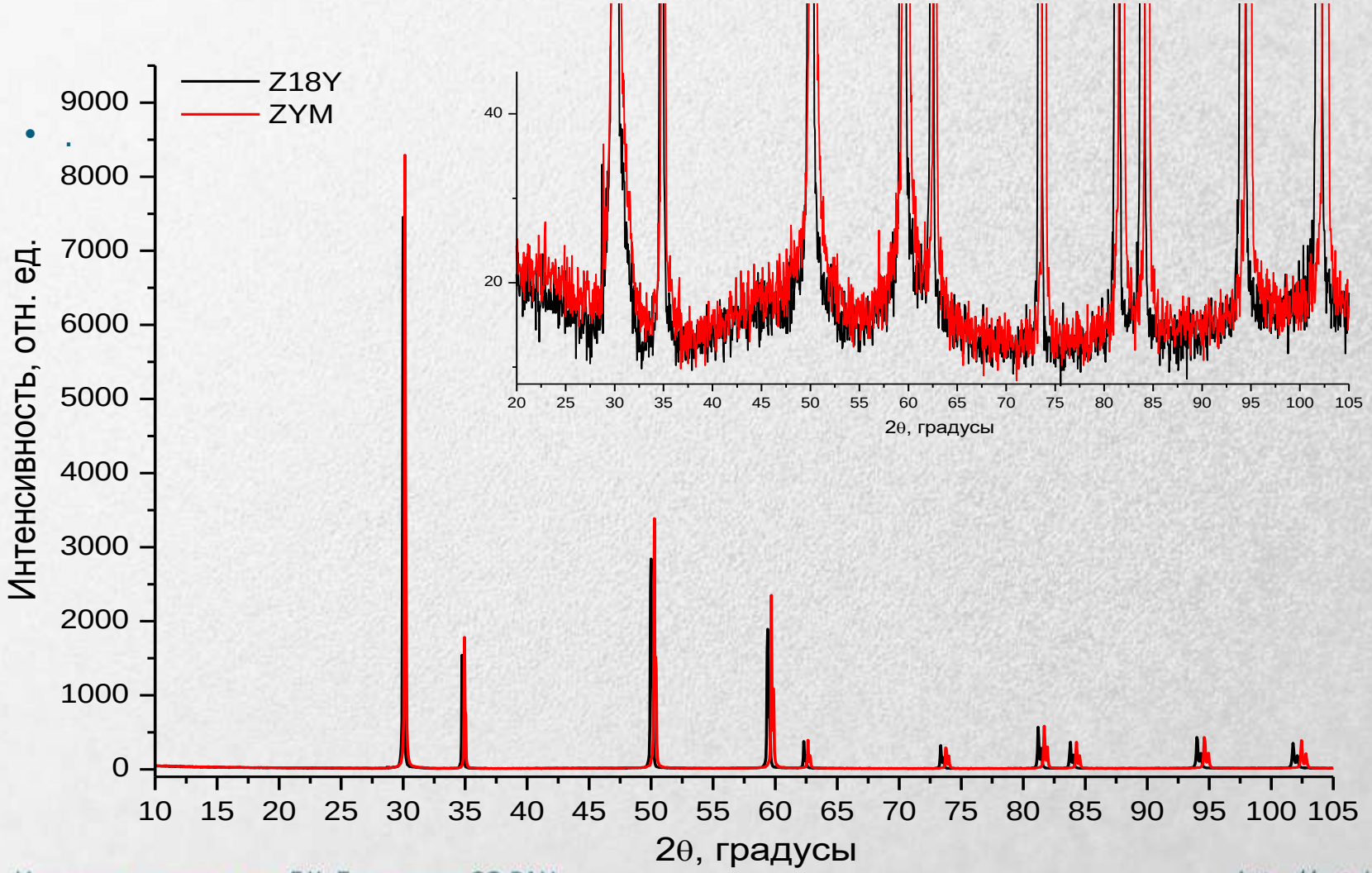


Fig.2. XANES (Y-K) spectra of studied samples: 1) **Z18Y/Y18,** 2) **ZYM/Y9**

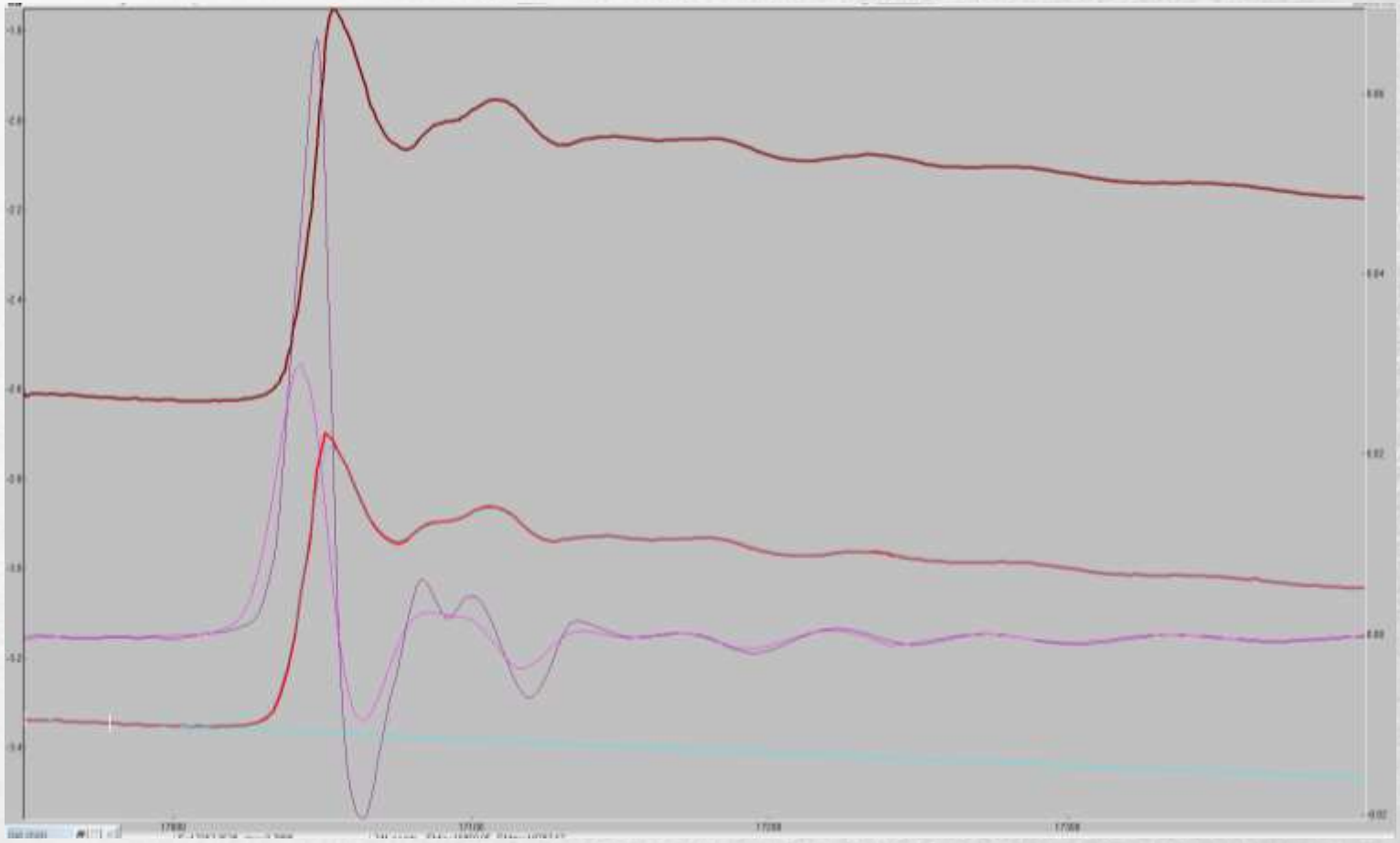


Fig.3. XANES (Zr-K) spectra of studied samples: 1) **Z18Y/Y18,** 2) **ZYM/Y9**

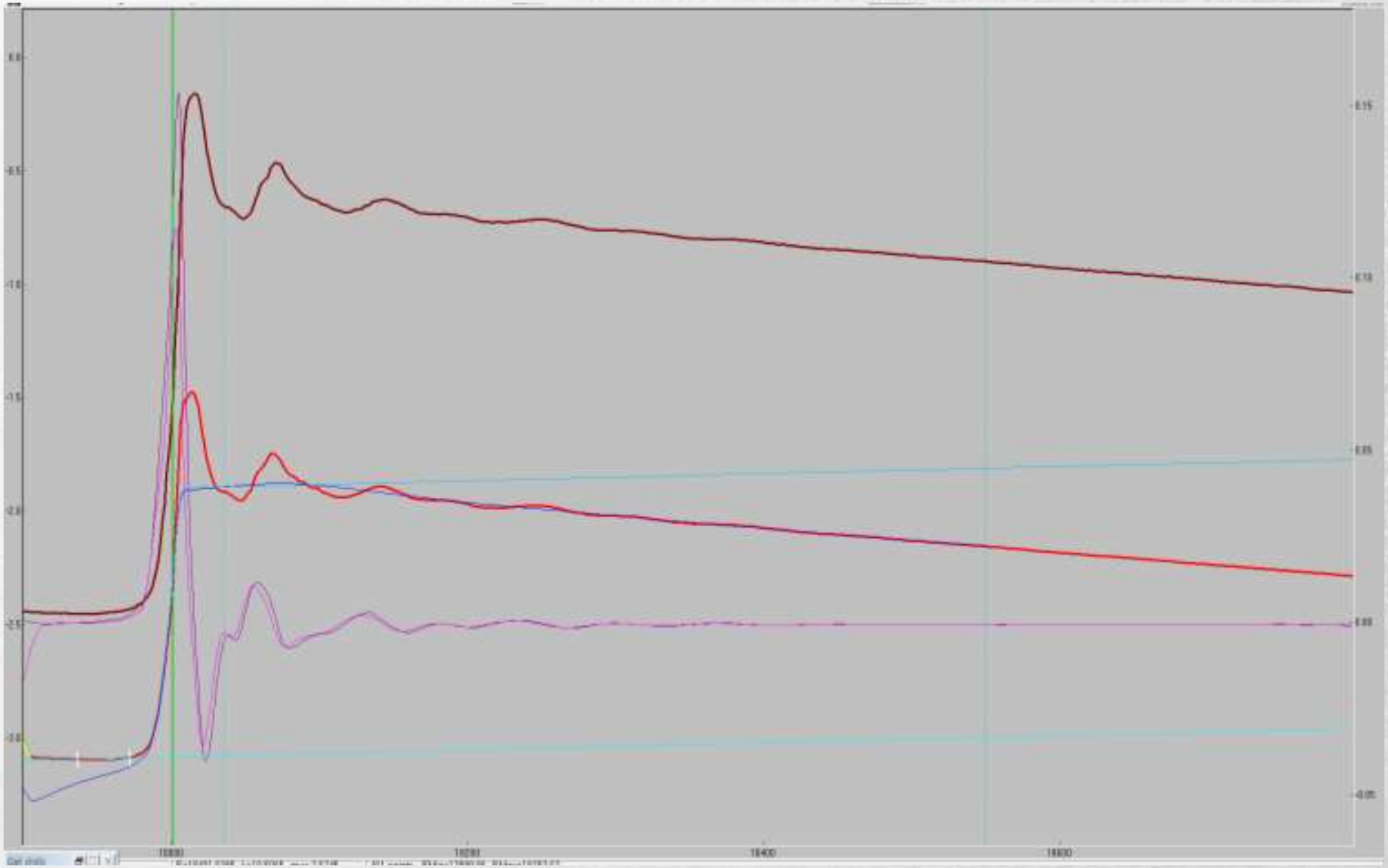


Fig.4. Curves of radial distribution function of atoms (RDFs) describing of Y local arrangement for studied samples: 1) Z18Y/Y18, 2) ZYM/Y9

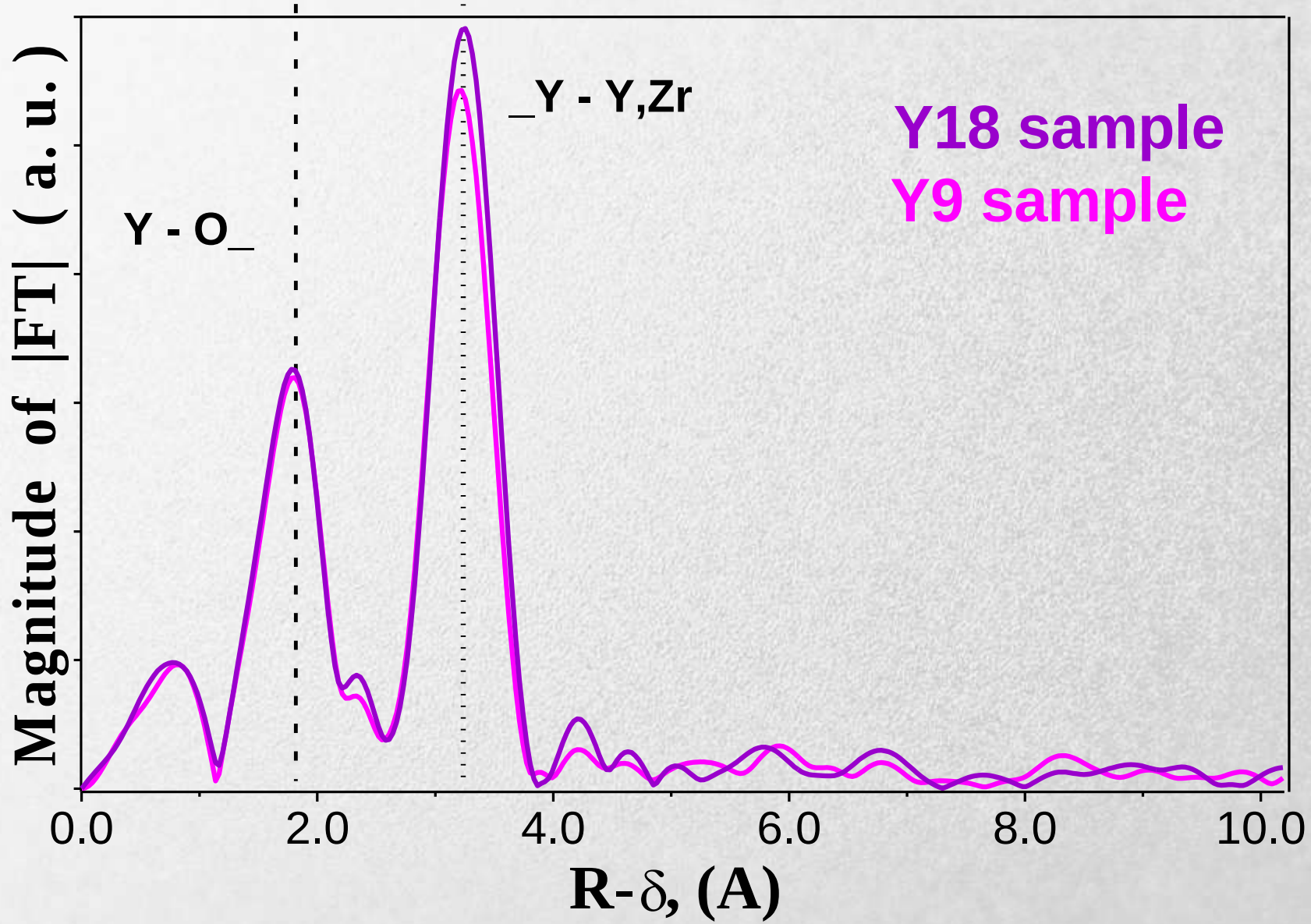
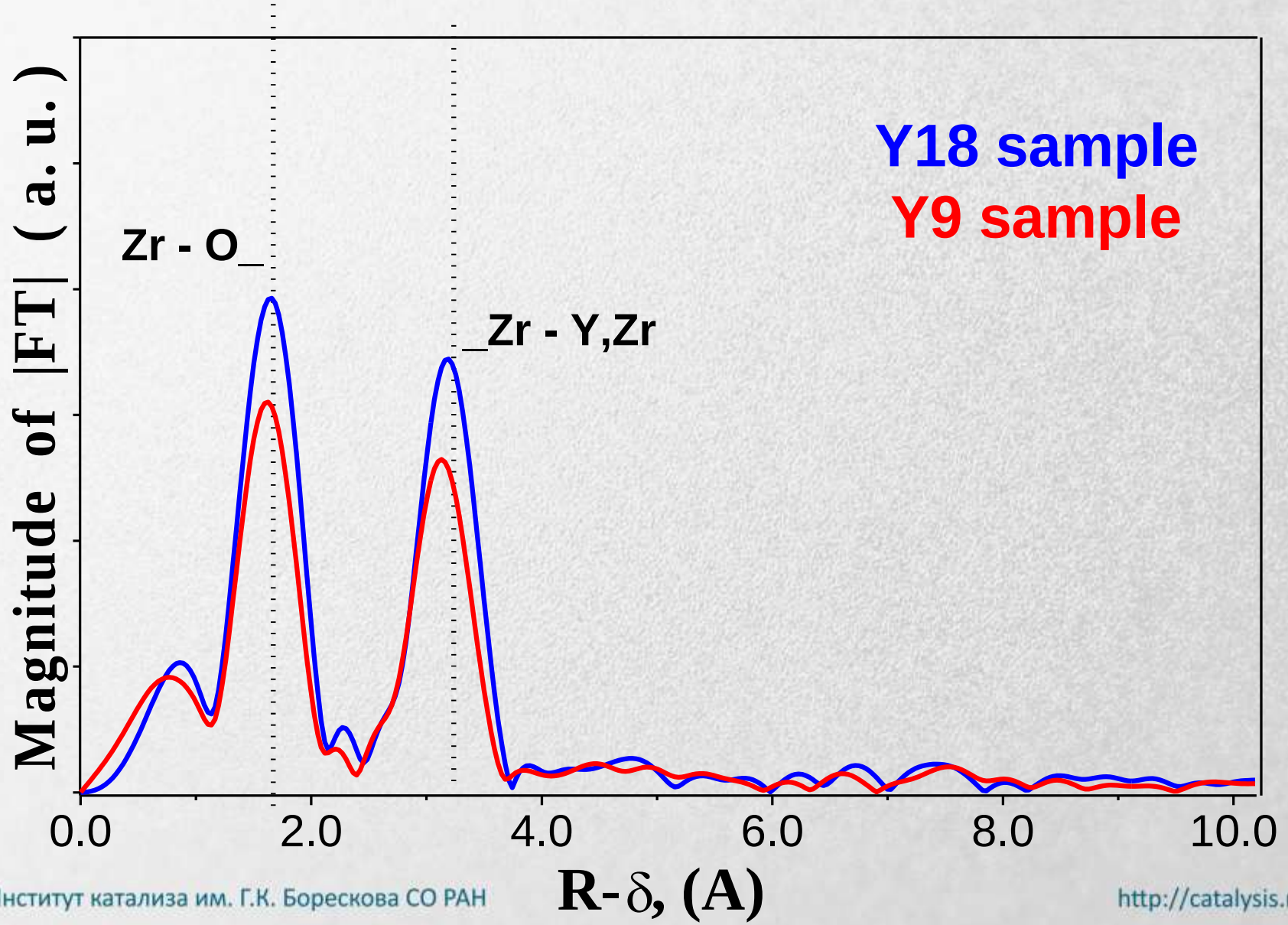


Fig.5. Curves of radial distribution function of atoms (RDFs) describing of Zr local arrangement for studied samples: 1) Z18Y/Y18, 2) ZYM/Y9



Research Methods for Nanostructured Materials

- There are many research methods for nanostructured materials. Some of them are local in nature, such as transmission electron microscopy (TEM) and scanning probe microscopy. Others are medium-volume probes that are sensitive to local structure, such as the atomic pair distribution function method (PDF) or the fine structure analysis of X-ray absorption spectra (EXAFS). The main difficulty in applying these methods to solve the nanostructure problem is that, in general, any method does not contain sufficient information to limit the unique structural solution.
- A coherent strategy is needed to combine the input of several experimental methods and theory into a self-consistent global optimization scheme: what is called "complex modeling."