

SNBL	<b>Experiment title: In-situ X-ray diffraction study of growth of Fe- and Co- containing nanowires in mesoporous silica.</b>	<b>Experiment number: 01-02-801</b>
<b>Beamline:</b> BM-1A (SNBL)	<b>Date(s) of experiment:</b> From: 08-10-2007 To: 10-10-2007	<b>Date of report:</b> 15-02-2008
<b>Shifts:</b> 6	<b>Local contact(s):</b> Dr. Dmitry Chernyshov	
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Modern information technologies require development of novel high-density data storage devices due to colossal growth of digital information volume. High-quality nanostructures and nanocomposites with detached and strongly anisotropic magnetic nanoparticles are considered as necessary components for such devices. Controlled synthesis of such nanomaterials could be performed by solid state nanoreactors technique [1] where nanoparticles are protected from external influences and aggregation. This method provides also a high monodispersity of the particles. Mesoporous silica  $\text{SiO}_2$  (MCM-41) is commonly used as a nanoreactor due to its homogenous, regular structure of pores and high chemical stability [2]. For the experiment we did at BM1A (SNBL at ESRF), magnetic nanocomposites were prepared by introducing a hydrophobic metal compound  $\text{Co}_2(\text{CO})_8$  or  $\text{Fe}(\text{CO})_5$ , into hydrophobic part of as-prepared mesoporous silica-surfactant composite. The metal compound was then decomposed under UV-irradiation in vacuum to give elementary metal and annealed in a hydrogen flow at different temperatures in order to achieve the formation of crystalline Co or Fe anisotropic nanoparticles (nanowires). In-situ study of the annealing procedure and stability of nanowires were the main goals of our experiment.

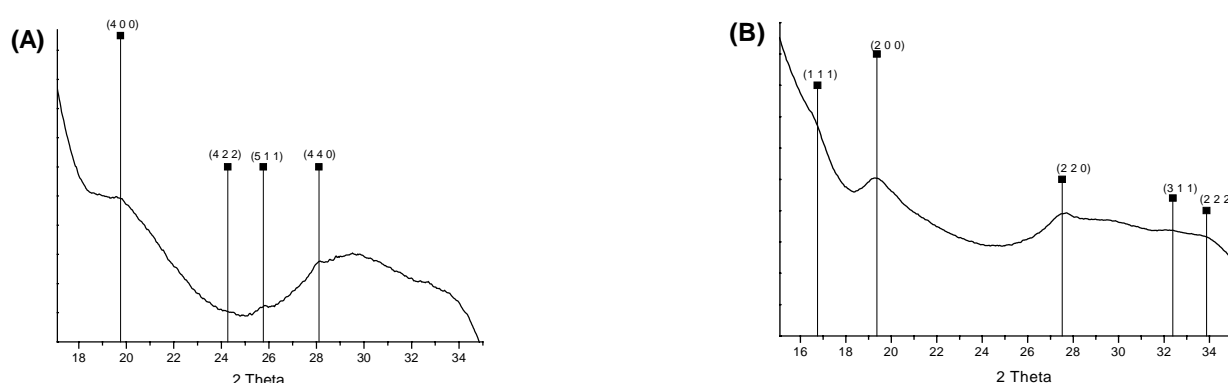


Fig. 2. X-ray diffraction patterns for (A) Fe- and (B) Co-containing nanocomposites based on mesoporous  $\text{SiO}_2$  matrix (vertical lines correspond to the position of diffraction lines for  $\gamma\text{-Fe}_2\text{O}_3$  and CoO respectively).

Fig. 1 illustrates X-ray diffraction patterns for Fe- and Co-containing nanocomposites aged for three days in air. Several weak and broad diffraction lines observed in wide-angle range agree well with  $\gamma\text{-Fe}_2\text{O}_3$  and CoO nanocrystalline phases respectively. These peaks are very broad thus indicating a small size of oxide nanoparticles forming in channels of porous matrix. Thus, porous matrix does not prevent oxidation of metal nanoparticles. The possible way of the oxide phase formation can be formulated as follows: (1) chemical reaction of elemental metal with oxygen atoms on pore walls, (2) oxidation of metal particles by  $\text{O}_2$  during

aging of the samples in air. In order to clarify real way of the nanoparticles formation the in-situ XRD experiments have been performed. XRD patterns have been collected during annealing (linear temperature sweep from 25 to 500 °C) of the samples with  $\text{Co}_2(\text{CO})_8$  and  $\text{Fe}(\text{CO})_5$  in inert atmosphere (5%  $\text{H}_2$ /95% Ar). Here we focus on the data for Co samples.

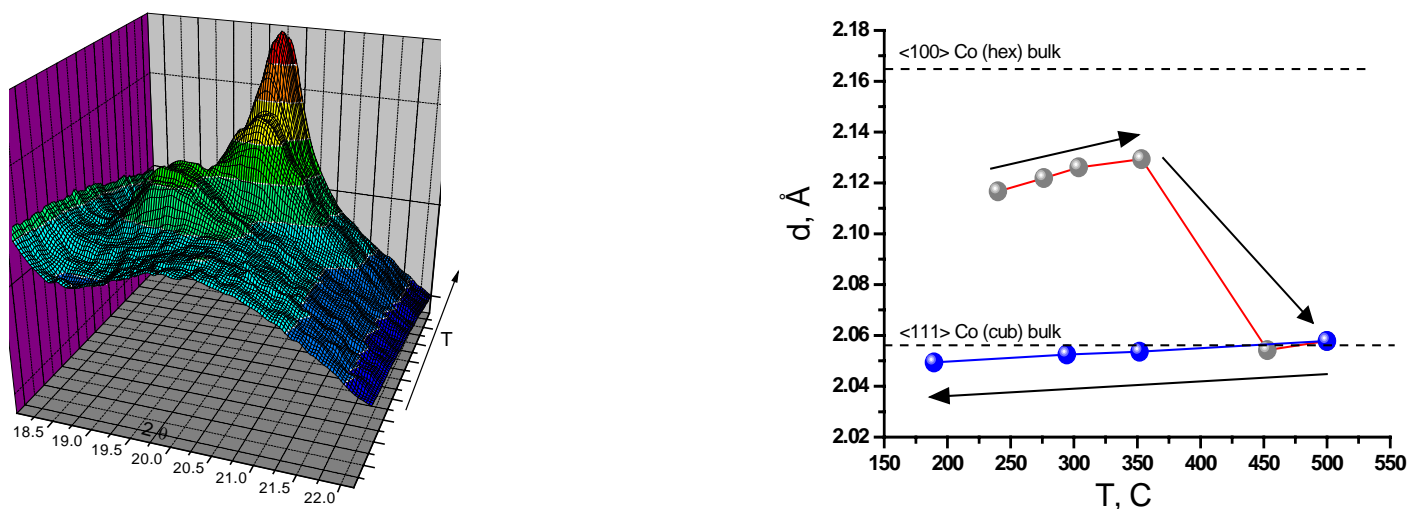


Fig. 2. Formation of Co nanoparticles inside mesoporous silica matrix. Left panel shows the development of diffraction from Co as a function of temperature, note a shift of Bragg peak indicating structural transition. Right panel illustrates the irreversible character of the hexagonal-to-cubic transformation; black arrows indicate thermal history.

The formation of the metallic Co in the sample  $\text{MS\_Co}_2(\text{CO})_8$  is observed at relatively low temperatures (200-250 °C) that is caused by the low-temperature decomposition of the metallic carbonyl complexes (Fig. 2). Appearance of the reflections agrees very well with the hexagonal structure of Co. The width of the reflection gives the average size of the nanoparticles, which is of order of 1 nm. Increase of the annealing temperature to 395 °C leads to the phase transition from the hexagonal to the cubic structure of Co accompanied by some decrease of the line-width. (Fig.2). At variance with bulk cobalt, this change of the structure is irreversible upon cooling and therefore both structural and magnetic properties of the sample depends on the maximal annealing temperature. Furthermore, the data testify that oxidation of metal particles occurs due to an interaction with  $\text{O}_2$  during aging of the samples in air.

The obtained data also reveal several strong peaks in the small-angle range, which are attributed to the hexagonal structure of nanopores of the MCM-41 matrix. The obtained data have shown that the mesoporous structure of  $\text{SiO}_2$  matrix remains well-ordered in the whole temperature range from 25 to 500 °C. The lattice parameter  $a_0$  of the mesoporous structure decreases from 4.53 to 4.31 nm with increase of temperature. This shrinkage of the pore structure is related to the evaporation of the organic compounds (template molecules, ligands of intercalated complexes) from the pores. This shrinkage is irreversible and remains with cooling the sample down to room temperature. The similar changes were observed in the diffraction experiments with pure mesoporous  $\text{SiO}_2$ , showing that introduction of carbonyl complexes into the matrix does not affect the matrix and its changes during the annealing.

In conclusion, our experiments justify the choice of synchrotron diffraction as a tool providing unique information on both the porous matrix and nanoparticles embedded in the pores. We were able to study the in-situ growth of the nanocrystalline Co particles in mesoporous silica at growing annealing temperature. This experiment gives clear information for optimization of the synthesis and the preparation technology of nanoparticles in the pores of the mesoporous  $\text{SiO}_2$ .

## References

1. J. H. Fendler, Chem. Mater., 8, 1616 (1996).
2. J. S. Beck, J. C. Vartuli, W. J. Roth et al, J. Am. Chem. Soc., 114, 10834 (1992).