MS21-O4 Structural disorder in spinel-like nanoparticles probed by total scattering

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Nano-crystalline spinel-like oxides are today widely studied because of their application in many different fields like information technology (ferrofluids, data storage), medicine (drug delivery, medical imaging) and chemistry (catalysis) [1]. Within this class Magnetite (Fe_3O_4) has a prominent role, however, a detailed understanding of some of its structural and micro-structural aspects – especially at the nanoscale – is still missing and the currently proposed structural models are not yet exhaustive of its magnetic properties. As is well-known the Fe^{2+} occupying the tetrahedral site is unstable under normal conditions, thus Magnetite is most often observed in a partially oxidised state. We studied the oxidation process of magnetite nano-particles (NP) revealing a partial ordering of the iron vacancies created during the oxidation process, leading to a partial phase transition of the NPs volume. As a second example we studied the cation disorder in the direct spinel Gahnite ($ZnAl_2O_4$) at very small NPs sizes, and we observed an important Zn-Al inversion disorder, with an inversion parameter x=0.34, higher than previously reported [3]. Our studies were performed by means of total scattering X-ray powder diffraction data (collected at the MS-Powder X04SA beamline [4] of the SLS synchrotron at PSI, Villigen, CH) and Debye scattering equation analysis [5]. In addition, for the cation disorder in $ZnAl_2O_4$ we performed for the first time using Total Scattering Anomalous Modulation Enhanced Diffraction [6] measurements at the Zn K-edge.

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MS21-O5 Local order in cadmium cyanide.

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Local order in cadmium cyanide.Cadmium cyanide $Cd(CN)_2$ is a material with exceptionally strong isotropic negative thermal expansion coefficient. This unusual property is currently not well understood, despite a related compound $Zn(CN)_2$ was very extensively studied. On the one hand, the negative thermal expansion can be attributed to the effects of vibration modes which include cadmium off-centering. Such modes have negative Grüneisen parameter and thus cause unit cell shrinkage as their amplitude increases. On the other hand, cadmium off-centering can also be caused by crystal disorder. In the average structure of $Cd(CN)_2$ cyano groups are disordered by a mirror plane, so each atomic position contain 1:1 mixture of carbon and nitrogen. In the real structure, position of cadmium atoms will be determined by the local orientation of neighboring cyano groups. Thus the volume of the $Cd(CN)_2$ crystal is influenced both by short range order and atomic vibrations.

In the current contribution we analyse single crystal diffuse scattering from $Cd(CN)_2$. The crystal shows very strong diffuse scattering in the form of very broad rods along 〈111〉 type directions and wide planes perpendicular to 〈110〉 (see figure below). The diffuse scattering is analyzed using three dimensional pair distribution function (3D-ΔPDF) in the program Yell. The 3D-ΔPDF method is advantageous in the current case because it allows to investigate both static and dynamic short range order in a unified fashion.

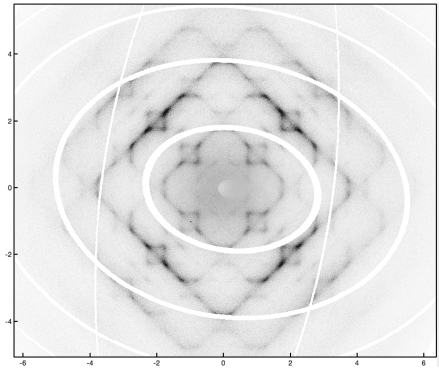

Figure 1. Diffuse scattering from $Cd(CN)_2$, hk¼ section.

Keywords: diffuse scattering, 3D-ΔPDF, disorder, local order