Finite size induced structural distortions in ferecrystals

Functional nanomaterials are increasingly relevant for information technology, medical applications, energy storage and conversion, catalysis, coatings, or phosphors [1]. An important aspect of their enhanced physical properties is related to size induced deviations of their atomic structure. Structure determination in nanomaterials is challenging and mostly addressed using local structure techniques [2], but in particular the study of surface-near structural distortions in nanomaterials is generally limited by extended size distributions. In order to overcome this limit in one dimension, we employed ferecrystals as model systems of atomically precise nanolayers for the investigation of finite-size induced structural phenomena. Ferecrystals represent a new class of misfit layer compounds of the general composition $[(MX)_{1+\delta}]_m[TX_2]_n$ (X: chalcogenide; M: Sn, Pb ; T: group IV, V, VI transition metal; δ: misfit parameter), thus consisting of rock salt (MX) and dichalcogenide (TX_2) binary constituents that are interleaved in a coherent stacking order, but with turbostratic disorder between the layers, which are thus not epitaxially aligned and strain-free.

In the framework of our ESRF experiment MA 2249, carried out at ID03 on 28. Aug – 1. Sept 2014, we have followed two distinct approaches towards the finite size induced structural distortions in ferecrystals. First, we measured the specular reflectivity of the samples in a wide range of the wave vector Q, and including the slightly off-specular scattering intensities using the Maxipix detector available at ID03. The obtained data are of very high quality (Fig. 1) and will enable us to separate the dynamic and kinematic scattering intensities in order to evaluate the data using reflectometry and Rietveld refinement approaches, respectively. Both analyses are expected to yield – within their respective spatial resolution – complementary information on the atomic structure profile of the ferecrystal.

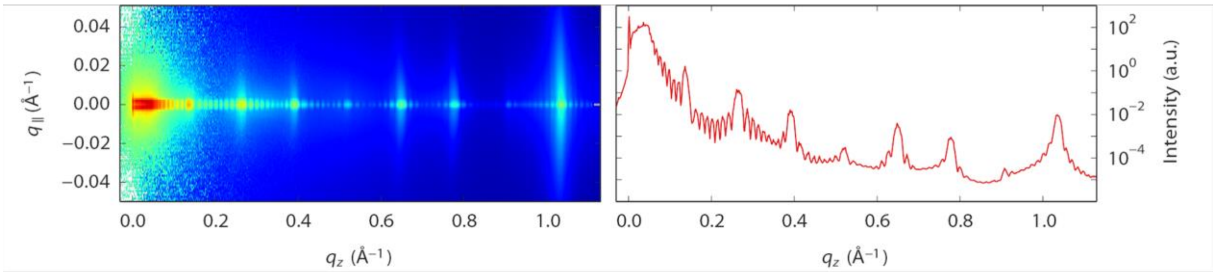

Fig. 1: specular and slightly off-specular scattering intensity of a [PbSe][$TiSe_2$] ferecrystal.

In the second part of the experiment, we rotated the detector out of the scattering plane and measured the scattering intensity in selected *l* reflection series of the binary constituents. As the 2D powder has reciprocal lattice rings instead of lattice points, adjustment of the azimuthal angle was not necessary. Due to the atomically precise finite size of the individual layers, we observe the characteristic Laue oscillations in between Bragg reflections (Fig. 2a). Detailed analysis of these features will allow for a more precise determination of the atomic structure in the individual constituents' layers, giving insight into the surface or interface-near structural distortions on the atomic size level.

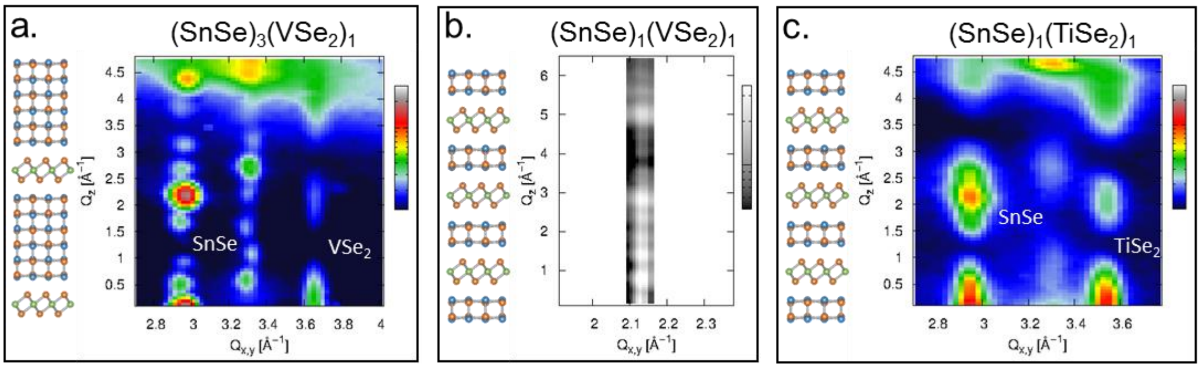

Figure 2: Reflection series measured for typical ferecrystal compounds. a) Laue oscillations are observed in SnSe reflection series with m>1 b) long range correlation peaks in a m=n=1 ferecrystal c) typical reflection series as expected for a non-correlated m=n=1 compound. Note that these data are presented as a very preliminary example. After final data reduction, the resolution and statistics will be comparable to (or even better than) the example shown in Fig. 1.

The high quality data obtained on a large amount of different ferecrystal samples during this experiment will enable us to determine the intralayer atomic structure in ferecrystals with unprecedented precision. In consequence, we will get detailed insight into the surface- or interface-near structural distortions in nominally rock salt type compounds.

Moreover, we have observed additional reflections in the crystal truncation rods of m=n=1 ferecrystals which indicate long range order beyond the individual layer thickness (Fig. 2b). As these additional reflections are observed exclusively in overlapping reflection series of both rock salt and dichalcogenide compounds, we infer a commensurate relation between the nanolayers in these directions. If this effect is proven, it will represent the first example of interlayer correlations in ferecrystals. A continuation study of these interlayer structural aspects is thus intended.