MS24- Defects and disorder quantification at the nanoscale

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MS24-P01

Diffraction effects of powder nano-scale materials

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Properties of nanomaterials are defined by features of the atomic structure and morphology. Investigation of crystal structure and nanostructure of such small objects is an actual problem. X-ray diffraction method can be used for this purpose. Anisotropic broadening of the diffraction peaks, redistribution of the intensities or appearance of diffuse scattering can appear for nanomaterials. Standard X-ray diffraction techniques used for bulk materials with periodic structures are often not applicable in this case.

These tasks can be solved by the Debye Function Analysis (DFA) method [1], based on Debye scattering equation (DSE) [2]. It is full-profile method which is applicable for any an arbitrary atoms collection, and therefore can be used for crystalline objects, non-crystalline materials or nanostructures.

Possibilities of modelling diffraction patterns by the DFA by our software [3] will be shown for specific examples of various nanocrystalline materials: hydroxides of magnesium and tungsten, layered structures, metastable forms of aluminum oxide, ultradispersed iron oxides et al. [4]. It is public-domain software available on the website: www.sourceforge.net/projects/dianna.

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MS24-P02

Analysis of chemical short range order using single crystal diffuse scattering

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In the average structure refinement of molecular materials, split positions are often encountered. As a consequence a molecule on one site can be present in more than one orientation. The typical structure refinement stops there and does not consider diffuse scattering, which allows statements about short range order interactions. Building and refining a short range order model to analyze the diffuse scattering takes the structure refinement to the next level.

A complex molecular crystal will usually consist of several components on several sites within the unit cell. Furthermore, a single site may be occupied by molecules in different orientations e.g. a first molecule in orientations A and B on site 1 and a second molecule in orientations C and D on site 2, see Fig. 1. In such systems short range order is common: On a local scale, the molecules tend to show preferred pair-wise arrangements. Characterizing this local order enables profound statements about molecular interactions [1].

With the help of molecular form factors [1] and the theory of diffuse scattering (e.g. Warren [2]), we developed a method that characterizes correlated chemical short range occupational disorder directly in reciprocal space. The diffuse scattering IDiff can be expressed as a function of the indices h,k,l in reciprocal space:

$$I_{Diff}(h,k,l)=I_{Laue}(h,k,l)+I_{SRO}(h,k,l)$$

Where I_{Laue} is the Laue scattering

$$\left(I_{Laue}(h,k,l)\propto\sum_{i=1}^{n_s}\sum_{A=1}^{k_i}\sum_{B>A}^{k_i}|F_{A_i}-F_{B_i}|^2 \right)$$

and I_{SRO} is the short range order scattering:

$$I_{SRO}(h,k,l)\propto\sum_{(u,v,w)}\sum_{i=1}^{n_s}\sum_{i=1}^{n_s}\sum_{A_i=1}^{k_i}\sum_{B_i=1}^{k_i} m_{A_i} m_{B_i} F_{A_i} F_{B_i}^{*} \alpha_{uvw}^{A_iB_i} \exp\left(2\pi i(h\cdot u+k\cdot v+l\cdot w)\right)$$

Here (u,v,w) are vectors in direct space, n_s is the number of different sites and k_i is the number of possible components on site i. m_{Ai} is the concentration of component A on site i, F_{Ai} is the molecular form factor of the molecule type A on site i. $\alpha_{uvw}^{A_iB_i}$ are the Warren-Cowley short range order parameters, that encode the probability to find an AB pair separated by vector (u,v,w). All parameters, except the $\alpha_{uvw}^{A_iB_i}$ can directly be determined from the average structure refinement.

We apply this formula for the analysis of the diffuse scattering of 9-Bromo-10-Methylanthracene [3]. The model for the short range order can be developed directly in reciprocal space and the formula can be used to perform a least squares regression analysis to fit the short range order parameters quantitatively.

Our method to characterize complex molecular disorder using single crystal diffuse scattering is a powerful tool to understand and model molecular interactions in disordered crystals. As the method treats data directly in reciprocal space and enables least squares fitting of disorder models, calculations can be performed on desktop computers without the excessive use of computation time.