Structure on different length-scales from powder diffraction: the real-space pair distribution function (PDF) technique

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Modern functional materials often contain defects and are quite disordered. In fact, it is often the defects that give them their interesting properties [1]. It is obviously of the greatest importance to have techniques that can characterize crystalline materials which are significantly disordered at the atomic scale. Powder diffraction data contains a great deal of information, in the form of diffuse scattering, about defects and disorder. When the (properly normalized) powder diffraction data are Fourier transformed into real-space coordinates we obtain the atomic pair distribution function (PDF). This is simply another representation of the powder diffraction data; however, it can often be revealing and helpful to study the data in real-space. The PDF has peaks at characteristic distances separating pairs of atoms and by calculating the PDF from model structures and comparing them to the measured PDF we can extract information about the local structure [2].

By studying the same PDF on different lenth-scales we can get information about microstructured materials. For example, consider the PDF from a sample that has some kind of domain structure with a characteristic domain size of ξ. If you look in the PDF on a length-scale $<< \xi$ the pairs of atoms that you probe will predominantly lie within the same domain as each other and the resulting structure will be the intra-domain structure. If you look in the same PDF at a distance $r > \xi/2$ then most of the pairs of atoms giving rise to features in the PDF lie in different domains and the result is a coherent average of the different local structures. This is nowhere better illustrated than if we think of solid C_{60} as a microstructured material where each bucky ball is a single domain. The bucky ball, its scattering and PDF, are shown in Fig. 1. The diameter of the ball is 7.1 Å. Sharp peaks are observed in the PDF coming from the characteristic C-C pairs on the ball up to 7.1 Å. Thereafter only broad featureless structure exists. The sharp peaks are the intra-molecular structure and the broad features in the data are the inter-molecular structure, or ball-ball correlations. This separation of the intra- and inter-domain structure occurs as a natural consequence of the Fourier transform.

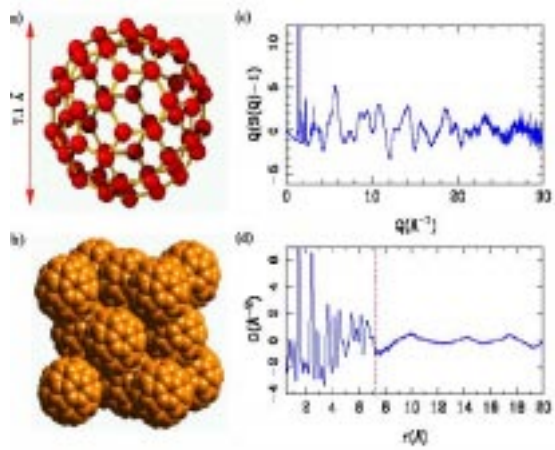

Figure 1. C_{60} (a and b), its normalized neutron diffraction pattern (c) and the corresponding PDF (d). The vertical dotted line in (d) is at 7.1 Å, the diameter of the ball.

Inhomogeneous and microcrystalline materials can have very well defined local structures. An excellent example of this is the metastable structure of exfoliated-restacked WS_2 [3]. The material is made up of covalently bonded S-W-S layers which stack into a three dimensionally ordered crystal structure. The diffraction pattern is shown in Fig. 2(a). After intercalating Li between the layers, they can be stripped apart and form a colloidal suspension of single layers, the exfoliated state. On further changing the chemistry in the beaker the layers can be restacked and the Li removed. We are back to the starting state of a precipitate of pure WS_2; however, the exfoliated-restacked compound has undergone a dramatic structural modification as evidenced by the diffraction pattern in Fig. 2(b). Bragg peaks are broad and sparse and traditional structure solution methods are powerless. The broad Bragg/diffuse scattering peaks indicate that the sample has become microcrystalline with very limited structural coherence. However, when the data are Fourier transformed to obtain the PDF we see two remarkable things. First, the peaks in the PDF are just as sharp in both the

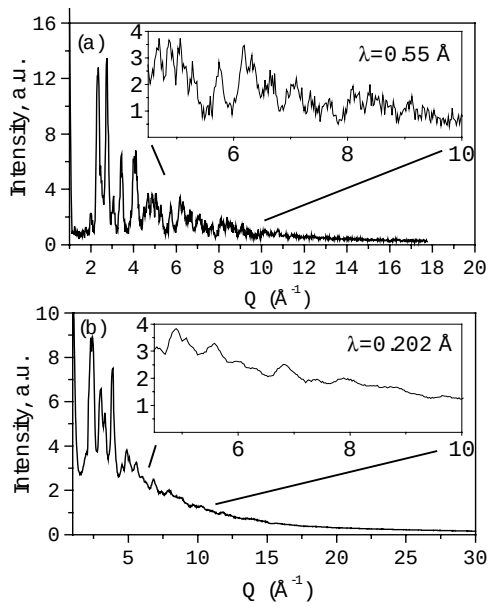

Figure 2. Powder diffraction patterns of pure (a) and restacked (b) WS_2.

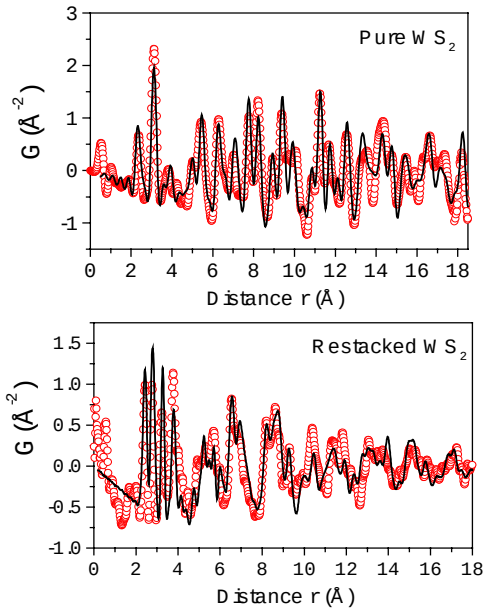

Figure 3. Experimental (symbols in red) and fitted (solid line) PDF's of pure and restacked WS_2.

pure and restacked samples (Fig. 3). Both have a very well defined local structure. Second, we see that the first two peaks in the PDF of pure WS_2 have split into 4 peaks. This shows clearly that the symmetry of the local environment of W has fallen. Modeling, shown by the solid lines in Fig. 3, indicates that the environment has changed from octahedral to prismatic and short W-W distances have appeared in a chain-like fashion. The microcrystalline nature of the metastable product is evident by the fall-off in amplitude of the features in its PDF and from this we can estimate the range of the structural coherence to be ~20Å.

By way of illustration we have presented here just a few examples of our recent applications of the PDF technique to study inhomogeneous and microcrystalline materials. Other examples we are studying where the microstructure has a profound bearing on the material properties are high temperature superconductors [4,5], colossal magneto-resistant manganites [6,7], semi-conductor alloys [8] and nanophase carbons [9]. To learn more about our work, or how to apply the PDF technique, please contact the authors (billinge@pa.msu.edu, proffen@pa.msu.edu, petkov@pa.msu.edu) or visit our web-page at: http://www.totalscattering.org.

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