Structure of crystallographically challenged materials by profile analysis of atomic pair distribution functions: study of $LiMoS_2$ and mesostructured $MnGe_4S_{10}$.

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Abstract

The approach of the atomic pair distribution function (*PDF*) technique to study the structure of materials with significant disorder is considered and successfully applied to $LiMoS_2$ and mesostructured $MnGe_4S_{10}$. We find that $LiMoS_2$ is built of layers of distorted MoS_6 octahedra stacked along the *c* axis of a triclinic unit cell with well-defined Mo-Mo bonding. Mesostructured $MnGe_4S_{10}$ is a three-dimensional framework of "adamantane-like" $[Ge_4S_{10}]$ units bridged by Mn atoms.

Introduction

Many materials of technological importance are not perfectly crystalline but contain significant disorder at the atomic scale. The diffraction patterns of such materials show a pronounced diffuse component and only a few Bragg peaks. This poses a real challenge to the usual techniques for structure determination. The challenge can be met by employing the so-called atomic pair distribution function (*PDF*) technique. The atomic *PDF* gives the number of atoms in a spherical shell of unit thickness at a distance *r* from a reference atom. It peaks at characteristic distances separating pairs of atoms and thus describes the structure of materials. The *PDF*, $G(r)=4\pi r[\rho(r)-\rho_o]$, is the sine Fourier transform of the so-called total scattering structure function, *S(Q)*,

$$G(r)=(2/\pi)\int_{Q=o}^{Q_{max}}Q[S(Q)-1]\sin(Qr)dQ, \qquad (1)$$

where $\rho(r)$ and ρ_o are the local and average atomic number densities, respectively, *Q* is the magnitude of the wave vector and *S(Q)* is the corrected and properly normalized total powder diffraction pattern of the material [1]. As can be seen the atomic *PDF* is simply another representation of the diffraction data; however, exploring the experimental data in real space is advantageous and helpful for several reasons, especially in the case of materials with significant structural disorder. First, as *eq. 1* implies the *total, not only the Bragg diffracted*, intensities contribute to the *PDF*. In this way both the average, *long-range* atomic structure, manifested in the well-defined Bragg peaks, and the *local structural imperfections*, manifested in the diffuse components of the diffraction pattern, are projected in the *PDF*. Note that conventional crystallographic studies take only the Bragg peaks into account. Second, the *PDF* is barely influenced by diffraction optics and experimental factors since these are accounted for in the step of normalizing the raw diffraction data and converting it to *S(Q)* data [1]. This renders the *PDF* a sensitive structure-dependent quantity giving directly the relative positions of atoms in materials. Third, by accessing high values of *Q*, experimental *PDF's* with high real-space resolution can be obtained and, hence, quite

fine structural features revealed [2]. Fourth, the *PDF* is obtained with no assumption of periodicity. Thus, materials exhibiting any degree of structural disorder, ranging from perfect crystals to glasses and liquids, can be studied with the same approach. Indeed the *PDF* technique has been the approach of choice for characterizing liquids and glasses for a long time. However, its application to study crystalline materials with significant disorder has been relatively recent [3]. Last but not the least, when a structural model is available, it is trivial to calculate the corresponding *PDF* and compare it to the experimentally determined *PDF*. This enables the convenient testing and refinement of structural models. Here we demonstrate how the *PDF* technique works by employing it to determine the structure of two significantly disordered materials: $LiMoS_2$ and mesostructured $MnGe_4S_{10}$.

MoS_2 is the key catalyst for the removal of sulfur from crude oil (hydrodesulfurization). The bulk material is perfectly crystalline and can be considered as built of layers of regular $Mo-S_6$ trigonal prisms. MoS_2 with Li inserted between the (Mo-S) layers is also technologically important. The material can be exfoliated in water to form a stable colloidal suspension of single (Mo-S) layers. These layers can be restacked, to encapsulate foreign species such as small molecules or long polymers. In this way, a variety of lamellar nanocomposites can be formed. Lithium intercalated MoS_2 is, however, a significantly disordered material and has a diffraction pattern with only a few Bragg peaks. This made it impossible to determine the three-dimensional atomic ordering in the material by conventional structure studies [4] and left unanswered the important question of what exactly happens when MoS_2 gets reduced with Li. Theoretical predictions suggest the appearance of considerable Mo-Mo bonding but no unequivocal experimental evidence has been advanced so far.

Mesostructured $MnGe_4S_{10}$ belongs to an important class of non-oxide metal chalcogenides with promising catalytical and electrical properties. The materials have open framework topologies resembling those of zeolites. The framework of $MnGe_4S_{10}$ is perforated with parallel hexagonally packed tunnels (see Fig. 4) with a diameter of the order of 20-30 Å with the framework wall thickness of ~ 10 Å [5,6]. The tunnels are filled with organic surfactant molecules. The diffraction pattern of $MnGe_4S_{10}$ shows a very strong single peak with d-spacing of 30-40 Å and a pronounced diffuse component. The peak reflects the average separation of mesoscopic features such as the tunnel-tunnel separation. The diffuse component comes from the non-periodic wall structure. Knowledge of this structure is needed to understand the stability and physico-chemical properties of these materials.

Experimental Details

To determine the structure of $LiMoS_2$ and mesostructured $MnGe_4S_{10}$ we carried out powder diffraction experiments and considered both the Bragg and the diffuse component of the diffraction data in terms of the corresponding atomic *PDF's*. Since high-quality diffraction data extended to high wave vectors is necessary to apply the *PDF* technique successfully [2] we employed a synchrotron radiation source. The measurements were done at the beamline X7A of the National Synchrotron Light Source, Brookhaven National Laboratory in symmetric transmission geometry. Three samples were measured: pristine MoS_2 purchased from CERAC, $LiMoS_2$ and mesostructured $MnGe_4S_{10}$. $LiMoS_2$ was obtained by reacting pristine MoS_2 with excess $LiBH_4$; the synthesis of mesoporous

MnGe$_4$S$_{10}$ was described in [6]. The powder samples were carefully packed between Kapton foils to avoid texture formation and subjected to diffraction experiments using x-rays of energy 30 keV (λ=0.4257 Å). Scattered radiation was collected with an intrinsic germanium detector connected to a multichannel analyzer. The raw diffraction data were corrected for the decay of the incoming synchrotron radiation beam, for background and Compton scattering, for sample absorption, normalized, i.e. converted into electron units, and then reduced to the corresponding structure functions *S(Q)* [1]. All data processing was done using the program RAD [7].

Results and Discussion

The experimental structure functions for MoS$_2$ and LiMoS$_2$ are shown in Fig. 1 and the corresponding *PDF's* in Fig. 2. Sharp Bragg peaks are present in the *S(Q)* of MoS$_2$ up to the maximal *Q* value of 24 Å^{-1} reached. The corresponding *G(r)*, too, features sharp peaks reflecting the presence of well-defined coordination spheres in this "perfectly" crystalline material. The well-known 6-atom hexagonal unit cell of MoS$_2$ [8] was fit to the experimental *PDF* and the structural parameters refined so as to obtain the best possible agreement between the calculated and experimental data. The fit was done with the program PDFFIT [9] and it was constrained to have the symmetry of the *P6$_3$/mmc* space group. In comparing with experiment, the model *PDF* was convoluted with a *sinc* function to account for the finite *Q$_{max}$*. The best fit achieved is shown in Fig. 2. The value of the corresponding agreement factor $R_w = \{\Sigma w(G_{exp.} - G_{mod.})^2/\Sigma w G_{exp}^2\}^{1/2}$ is 21%; it is only 8 % if the *PDF's* $g(r) = \rho(r)/\rho_o$ and not *G(r)* are compared to each other. The significance of the *PDF G(r)* versus *g(r)* is well explained in [10]. Please note, that neither of the *PDF* functions being fit is the one fit in a Rietveld refinement and, therefore, the present agreement factors R_w may not be directly compared to the goodness-of-fit indicators used in Rietveld refinements. The *PDF* fit yielded the following structure data for pristine MoS$_2$: unit cell constants *a*=3.169(1) Å and *c*=12.324(1) Å and atomic positions of Mo (1/3,2/3,1/4) and S (1/3,2/3,*z*) with *z* = 0.623(1). The present structure data are in rather good agreement with those obtained by conventional structure studies: unit cell constants *a*= 3.1604(2) Å and *c* = 12.295(2) Å and atomic positions of Mo (1/3,2/3,1/4) and S (1/3,2/3,*z*) with *z* = 0.629(1) [8]. The good agreement obtained for MoS$_2$ documents the fact that the *PDF* is a reliable basis for structure determination.

The diffraction pattern of LiMoS$_2$ has only a few Bragg peaks positioned at low wave vectors. At high-*Q* vectors an oscillating diffuse component is present. Evidently the material is significantly disordered. A diffraction pattern so poor in Bragg peaks lacks the number of "good, statistically independent reflections" needed to successfully apply the conventional techniques for structure determination from powder data, such as the Rietveld technique [11]. The corresponding atomic *PDF* is, however, rich in well-defined, structure related features and lends itself to structure determination. It may be noted that the presence of well-defined peaks in the *PDF* of LiMoS$_2$ given the rather diffuse nature of the corresponding diffraction data is not a surprise. It is a property of the Fourier transform to convert broad, slowly oscillating features into sharp ones. Thus, when considered in terms of the corresponding *PDF*, the diffraction data clearly reveal the regular sequence of relatively well-defined coordination spheres present in the rather disordered but still
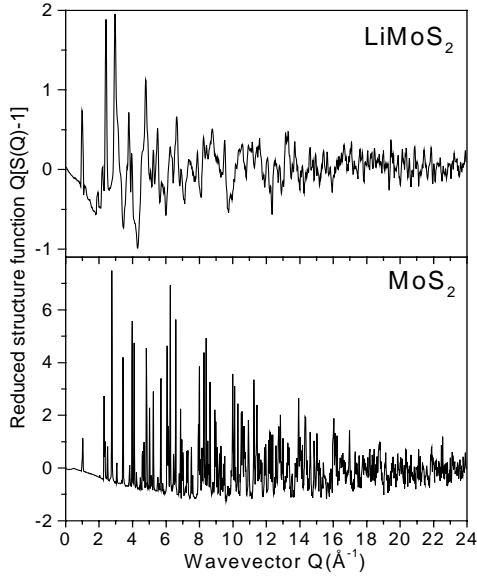
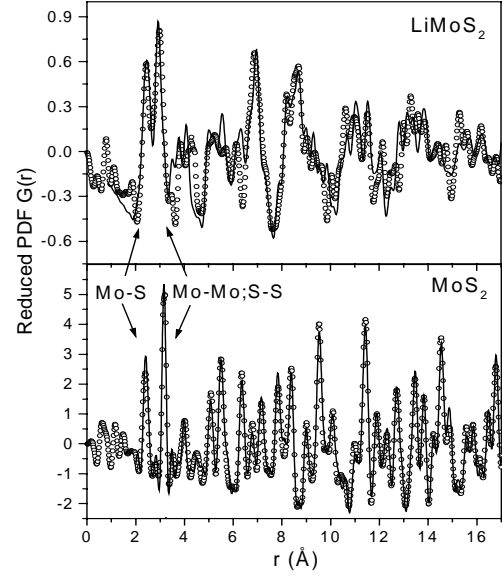Figure 1. Experimental structure functions of MoS_2 and $LiMoS_2$.

Figure 2. Experimental (dots) and fitted (solid line) PDFs for MoS_2 and $LiMoS_2$. The first two peaks in the PDFs are labeled with the corresponding atomic pairs.

crystalline $LiMoS_2$. For example, the first peak in the *PDF* reflects the Mo-S and the second the Mo-Mo and S-S coordination spheres, respectively. To determine the structure of $LiMoS_2$ we explored several structural models [12] and found that it is best described in the space group $P\bar{1}$ of the triclinic system with 4 formula units in the cell, and lattice parameters a=6.963(1) Å, b=6.386(1) Å, c= 6.250(1) Å, α =88.60°, β = 89.07° and γ = 120.06°. The structural model fits all important details in the experimental *PDF* as can be seen in Fig. 2. The corresponding agreement factor R_w is 29 %; it is only 10 % when the experimental and model *PDF's* $g(r)=\rho(r)/\rho_o$ and not $G(r)$ are compared to each other. The refined structural parameters are summarized in ref. [12]. The structure features Mo-Mo bonding forming "diamond-type" chains within (Mo-S) layers stacked along the c axis of the unit cell with Li atoms residing between the layers. The Mo-Mo bonding distances within and between the "diamonds" are 2.90 Å and 3.09 Å, respectively. The structural data obtained enabled us to calculate the electronic structure of $LiMoS_2$ and, hence, predict the properties of the material. A band gap of about 0.2 eV was found suggesting that the material should exhibit semiconductor properties [12]. By comparison, in pristine MoS_2 the band gap is 1.4 eV. Interestingly, recent first-principle calculations predict that $LiMoS_2$ should have a triclinic (S.G. $P\bar{1}$) unit cell with Mo atoms arranged in a "diamond-chain" scheme and that such an atomic arrangement would lead to the opening of a gap of about 1 eV in the electronic structure [13]. The good agreement between these theoretical predictions and the results of the present experimental *PDF* study is strong evidence in support to the reliability of the latter.

The experimental structure function for $MnGe_4S_{10}$ and its Fourier associate, *G(r)*, are shown in Fig. 3. The structure function lacks sharp, Bragg-like features which shows that the material lacks three-dimensional long-range order. Instead, the structure function
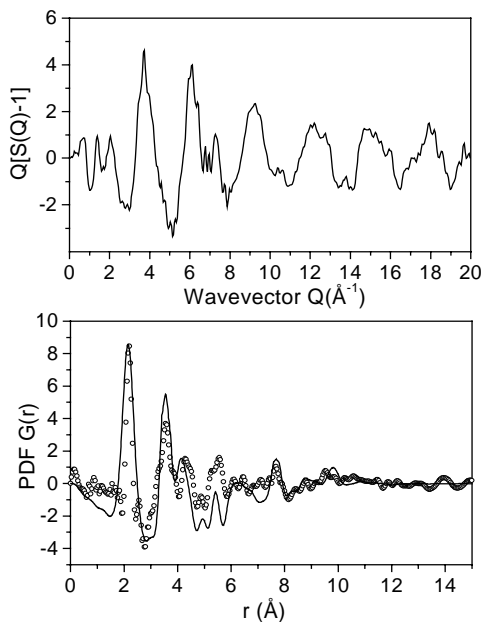
Figure 3. Experimental reduced structure function Q[S(Q)-1] (upper part) and the corresponding PDF G(r) (lower part; symbols) for $MnGe_4S_{10}$. A model PDF based on a distorted adamantane-type lattice is shown for comparison as a solid line.
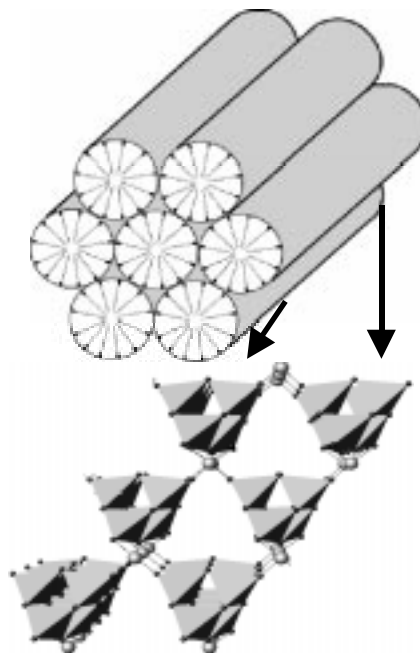

Figure 4. Schematic depiction of mesoporous $MnGe_4S_{10}$. Framework walls are built of adamantane-like $[Ge_4S_{10}]$ units linked by Mn atoms (large spheres)

exhibits prominent low-frequency oscillations up to the maximum Q value reached. These oscillations may only come from the presence of well-defined structural units building the material. The units are seen as a well-defined first peak in the experimental *PDF*. The peak is positioned at 2.2 Å which corresponds to the Ge-S distance occurring in the "adamantane" $[Ge_4S_{10}]$ unit being a closed loop of four corner-linked GeS_4 tetrahedra [8]. This finding suggests that "adamantane-like" units are the basic building blocks of the non-periodic framework in mesostructured $MnGe_4S_{10}$. A model PDF for a fully connected "adamantane-like" lattice of the type occurring in crystalline $MnGe_4S_{10}$ [14] is shown in Fig. 3. The model *PDF* reproduces well the basic features of the experimental data consistent with the walls in mesostructured $MnGe_4S_{10}$ being a three-dimensional framework of "adamantane" $[Ge_4S_{10}]$ units bridged by Mn atoms as shown in Fig. 4. However, the framework structural coherence is lost at distances as short as 10 Å as the experimental *PDF* shows. This is most probably due to the lack of well-defined orientational relationship between the neighbouring "adamantane" units. We estimate that between six to ten such units are able to enclose a tunnel with a diameter of 20-30 Å by only changing their positions relative to each other, but not the connectivities. Extensive modeling of the framework including the perforating tunnels is in progress; details will be reported elsewhere [15].

Conclusions

The results presented demonstrate that the PDF approach can be confidently employed in structural studies of "crystalographically challenged" materials. The approach requires that the diffraction data is carefully collected over a wide range of wave vectors and converted into the corresponding atomic PDF. Then, like all powder diffraction techniques, the 3-D structure is inferred through modeling. This is a major advantage since testing and refining of structural models can be accomplished even when the diffraction patterns of materials are very poor in Bragg peaks due to the presence of significant structural disorder.

Acknowledgements

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