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THE STRUCTURAL COMPLEXITY OF A POLAR, MOLECULAR MATERIAL BROUGHT TO LIGHT BY SYNCHROTRON RADIATION

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Diffuse scattering in the polar host-guest material (Perhydrotriphenylene)$_5$ · Nitrophenylpiperazine has been investigated at the mesoscopic length scale with synchrotron radiation and a model of the disordered structure developed with the help of a genetic algorithm.

Keywords: diffuse scattering; host-guest compound; disorder; mesoscopic structure determination; perhydrotriphenylene

Intermediate stages in solid state reactions as well as certain crystalline materials are highly disordered. Different unit cells differ in molecular occupation, orientation or position. If such materials happen to have interesting properties, one would like to know the nature of the disorder and whether or not it is related to these properties. Molecular inclusion compounds of the hydrocarbon host molecule perhydrotriphenylene (PHTP) with polar guest molecules, e.g. nitrophenylpiperazine (NPP), provide an example [1]. Stacks of host molecules form a honeycomb architecture whose tunnels are filled with chains of guest molecules, see Figure 1. Right- and left-handed host molecules occupy the stacks in a not quite random fashion. The chains of guest molecules register at different height in different channels. Remarkably, they are all parallel, even though the channels are ∼15 A apart. The crystals are macroscopically polar and show second harmonic generation.

The material produces an extraordinarily rich diffraction pattern including 1D, 2D and 3D diffuse features, incommensurate satellites and Bragg peaks. Nearly complete patterns have been measured at 298 and 120 K on beam line BM1A (Swiss Norwegian Beam Lines at the European Synchrotron Research Facility, Grenoble) in the center and at one tip of a prismatic crystal in 16-bunch mode with an area detector. Five Gbytes of

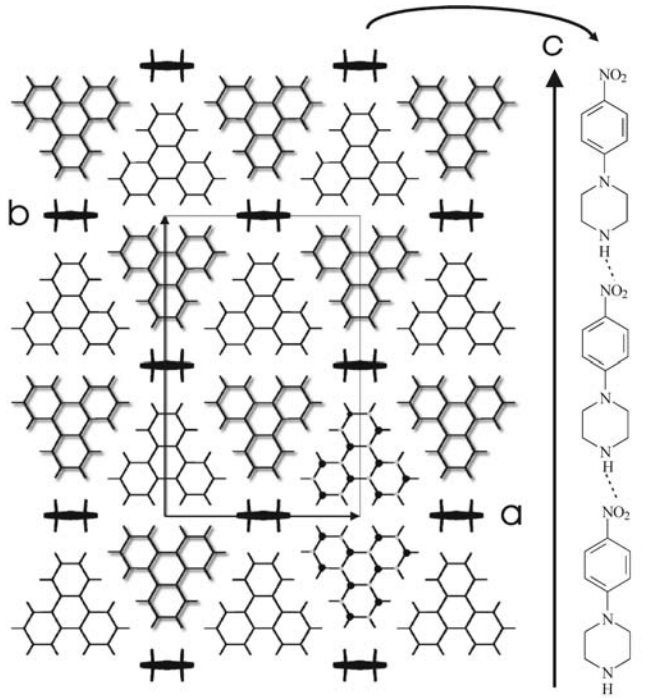

FIGURE 1 Projection of $PHTP_5 \cdot NPP$ along **c** onto the **a**, **b** plane (left). Shadowed and unshadowed PHTP-molecules differ in z by 0.5 **c**. Note that the PHTP-molecules are chiral (molecular symmetry D_3). Polar NPP-chains extend along **c** (right) and are all parallel. Projected along their long axis they ressemble a wide letter 'H' (left).

accurate, raw data have been processed into 400 layers in reciprocal space, see Figure 2, bottom [2].

Most of the diffuse and satellite scattering can be assigned to occupational disorder of the host, positional disorder of the guest, or local distortions of the average structure [3], see Figure 2 for an example.

The disorder of the host structure is simulated with a Markov growth model. Its parameters are optimized with an evolutionary algorithm. Structure simulations, Fourier transformations and an R-value based fitness criterion are calculated for 40 individuals/generation through a scheme of distributed computing. Up to ten processes were run simultaneously on PC's, SUN and SGI workstations. The computations progressed at a rate of $\sim$8 generations/day and took $\sim$30 days in all. The

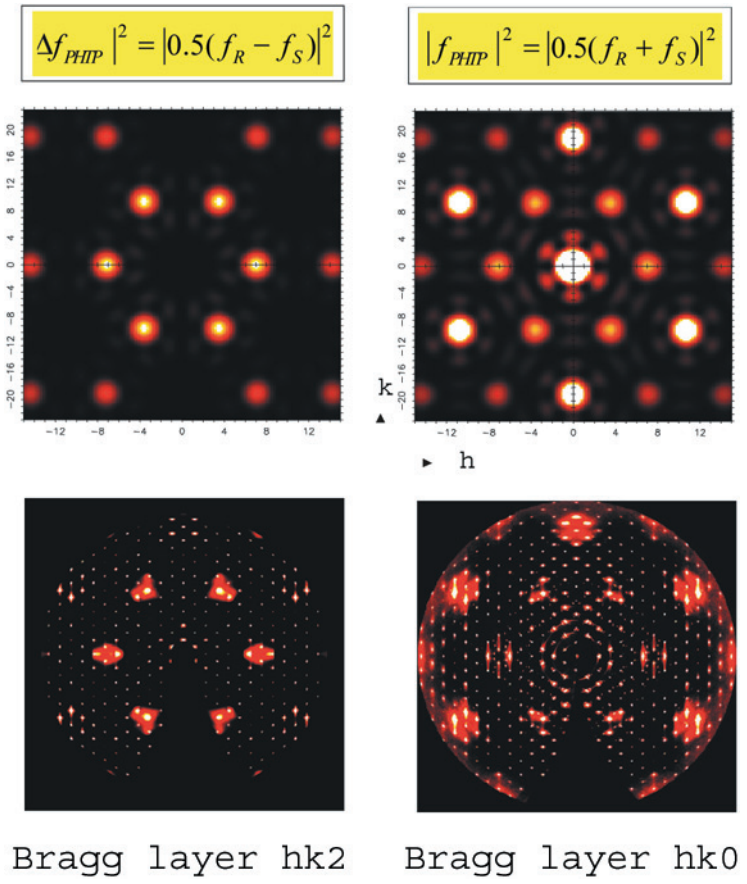

FIGURE 2 Examples of qualitative assignments of diffuse scattering: f_R and f_S are the molecular scattering factors of R- and S-PHTP molecules. Diffuse scattering resembling Δf_{PHTP} (top left) provides information on the R/S distribution along PHTP-stacks; for an example see the Bragg layer hk2 (bottom left); f_{PHTP} (top right) provides information on disorder affecting R- and S-molecules equally; for an example see the Bragg layer hk0 (bottom right).

structural model shows homochiral stacks $\sim$15 molecules long and a small preference for heterochiral contacts between stacks.

The diffuse scattering from 100 μ-slabs in the center and at one tip of the prismatic crystal is different. In the center diffraction symmetry is nearly orthorhombic, at the tip it is monoclinic implying that the crystal is not homogeneous along the stacking direction of the host and guest molecules.

Results and conclusions following from this study include: (1) accurate and complete 3D diffuse diffraction data of a complex disordered material were recorded in ~1 day. (2) A 3D model of the R/S disorder of PHTP was derived in ~30 days. (3) The scope of such studies becomes significantly broader if distributed computing on work stations is replaced by parallel computing on more powerful machines. (4) Diffuse scattering and thus the structural disorder changes along the growth direction. (5) The present spatial resolution can be improved by at least an order of magnitude thereby providing more detailed records of the crystallization history of disordered materials.

In summary this work shows that interpreting diffuse scattering is becoming a practical tool for studying the structure of disordered materials at the mesoscopic length scale.

REFERENCES

[1] König, O., Bürgi, H. B., Armbruster, Th., Hulliger, J., & Weber, Th. (1997). *J. Am. Chem. Soc.*, *119*, 10632.
[2] Estermann, M. A. & Steurer, W. (1998). *Phase Trans.*, *67*, 165.
[3] Weber, Th., Estermann, M. A., & Bürgi, H. B. (2001). *Acta Cryst.*, *B51*, 559.