



International Union of Crystallography

**Commission on Mathematical and
Theoretical Crystallography**

Summer School on Mathematical and Theoretical Crystallography

Palazzo Feltrinelli, Gargnano, Garda Lake (Italy), 27 April - 2 May 2008

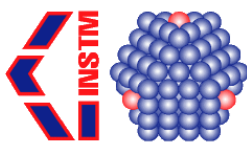
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Program and Abstracts

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Program

Sunday April 27. Registration and accommodation.

Monday April 28, morning. *Introduction to crystallographic symmetry I.* Massimo Nespolo, Université Henri Poincaré Nancy I, France

Basics of group theory. Space groups and space group types. Hermann-Mauguin symbols. Wyckoff positions, site symmetry. Unconventional settings of space groups. Extracting information from Volume A of the International Tables for Crystallography

Monday April 28, afternoon. *Introduction to crystallographic symmetry II.* Mois I. Aroyo, Universidad del Pais Vasco, Bilbao, Spain

Mappings, symmetry operations, 4x4 matrices. Basis and coordinate transformations, origin shifts. Subgroups and splitting of Wyckoff positions.

Tuesday April 29. *Group theory applied to crystallography.* Bernd Souvignier, Radboud University Nijmegen, The Netherlands

Dimension-independent fundamental notions of crystallographic groups (lattices, point groups, vector systems); classification of crystallographic groups (arithmetic/geometric classes, crystal systems, lattice systems, crystal families). Equivalent descriptions for a crystal structure (use of normalizers).

Wednesday April 30, morning. *Subgroups of space groups.* Mois I. Aroyo, Universidad del Pais Vasco, Bilbao, Spain

Exercises on the Volume A1 of the International Tables for Crystallography

Wednesday April 30, afternoon. *The symmetry principle in crystal chemistry - I.* Ulrich Müller, University of Marburg, Germany

Instructions how to build trees of group-subgroup relations between space groups. Examples for translationengleiche, klassengleiche and isomorphic subgroups; space groups related by a common supergroup; large structural families. Pitfalls and possible sources of errors.

Thursday May 1, morning. *The symmetry principle in crystal chemistry - II.* Ulrich Müller, University of Marburg, Germany

Applications: Structures with close-packed atoms and occupied interstices; symmetry aspects at phase transitions and topotactic reactions, twinning, domains; wrong structure determinations due to twinning; symmetry relations among molecular structures

Thursday May 1, afternoon. *Role of symmetry and energy in structural phase transitions.* Michele Catti, University of Milano-Bicocca, Italy

Elements of Landau theory of structural phase transitions. Symmetry group-subgroup relationships. Reconstructive, displacive and order-disorder solid-solid transformations. Evaluation of the crystal energy by periodic quantum-mechanical techniques. Applications to thermodynamic and kinetic aspects of displacive and reconstructive phase transitions of inorganic crystals

Friday May 2, morning. *Computer tools in mathematical crystallography.* Mois I. Aroyo, Universidad del Pais Vasco, Bilbao, Spain

Introduction to the Bilbao Crystallographic Server

Friday May 2, afternoon. *Understanding organic crystal packing: how intermolecular energies determine crystal symmetry and intermolecular geometry.* Angelo Gavezzotti, University of Milano, Italy

Fundamentals of intermolecular potentials. Correlation-dispersion and exchange-repulsion. Close packing symmetry elements. Restrictions on space groups for organic crystals. Use of crystallographic Databases. Models for the calculation of intermolecular energies: recognition in gas-phase dimers versus pairwise molecular interactions in crystals. Quantitative ranking of approach modes: the hydrogen bond versus other bonding interactions. Quantitative ranking of lattice energies among polymorphs; crystals structure 'prediction'.

Abstracts of the poster presentations

Coincidences of Colorings and Sublattices

Manuel Joseph Loquias and Peter Zeiner
Faculty of Mathematics, University of Bielefeld, Germany

April 10, 2008

Abstract

Let Γ_2 be a sublattice of Γ_1 . We give relations between the coincidence indices of Γ_1 and Γ_2 by looking at the coloring of Γ_1 obtained by assigning a unique color to each coset of Γ_2 in Γ_1 . In addition, the effect of coincidence rotations on the colors of the coloring of Γ_1 and its consequences are considered.

CRYSTAL STRUCTURES OF SOME PHOSPHAZENE DERIVATIVES

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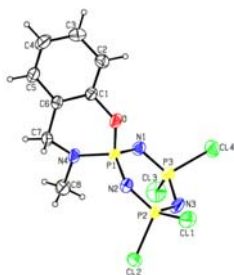
² Department of Chemistry, Ankara University, 06100 Ankara

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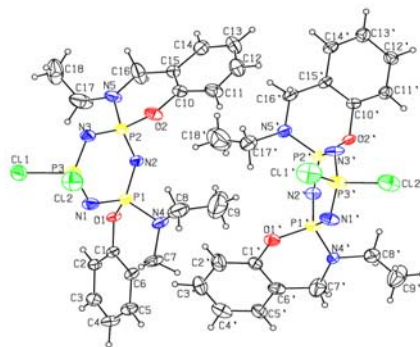
In this study, the crystal structures of $C_8H_9Cl_4N_4O_1P_3$, (I) and $C_{18}H_{22}Cl_2N_5O_2P_3$, (II) are investigated. The data were measured with Mo K_α radiation on an Enraf-Nonius CAD-4 diffractometer.

3-Methyl-4,4,6,6-tetrachloro-3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine- $2\lambda^5,4\lambda^5,6\lambda^5$][1,3,5,2,4,6] triazaphosphorine, (I), is mono *spiro* cyclic phosphazene derivative. It belongs to the space group *P-1* with cell parameters $a = 8.5545(4)$, $b = 12.1377(3)$, $c = 16.6964(4)$ Å and $\alpha = 84.618(3)^\circ$, $\beta = 77.680(4)^\circ$, $\gamma = 74.287(7)^\circ$. The asymmetric unit of (I) contains two independent molecules. The phosphazene rings are nearly planar, while the C_3NPO spirocyclic rings: A(P1/O/N4/C1/C6/C7) and A'(P1'/O'/N4'/C1'/C6'/C7') having total puckering amplitudes, Q_T , of 0.476(5) and 0.463(5) Å, respectively, and twisted-boat conformations [$\varphi = -103.8(5)^\circ$, $\theta = 78.6(5)^\circ$ and $\varphi = 71.0(5)^\circ$, $\theta = 97.5(6)^\circ$, respectively] [1]. In the phosphazene rings the P-N bond lengths are in the range 1.550(4)-1.596(4) Å have double-bond characters. However, the exocyclic P1-N4, P1'-N4' bond lengths 1.627(3) and 1.617(3) Å are at the lower limits for single bond. In the phosphazene ring, the endocyclic angles N2-P1-N1 [113.21(20)°] and N2'-P1'-N1' [113.76(21)°] are smaller than and exocyclic angles N4-P1-O [103.61(16)°] and N4'-P1'-N1' [103.59(17)°] are nearly the same as those of the 'standart' compound [endocyclic N-P-N 118.3(2)° and exocyclic Cl-P-Cl 101.2(11)°] $N_3P_3Cl_6$ [2].

6,6-Dichloro-bis{3-propyl-3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine} [$2\lambda^5,4\lambda^5,6\lambda^5$][1,3,5,2,4,6]-triazatriphosphorine(II) is di *spiro* cyclic phosphazene derivative. It belongs to the space group *Pn* with cell parameters $a = 8.297(2)$, $b = 11.849(1)$, $c = 23.838(8)$ Å and $\beta = 90.12(3)^\circ$. The asymmetric unit of (II) contains two independent molecules. The phosphazene rings are nearly planar, while the C_3NPO spirocyclic rings: A(P1/O1/N4/C1/C6/C7), B(P2/O2/N5/C10/C15/C16) and A'(P1'/O1'/N4'/C1'/C6'/C7'), B'(P2'/O2'/N5'/C10'/C15'/C16') having total puckering amplitudes, Q_T , of 0.464(9), 0.297(9), 0.476(10) and 0.336(12) Å and twisted-boat conformations [$(\varphi = 157.76(1.8)^\circ$, $\theta = 127.91(1.5)^\circ$; $\varphi = 3.15(3.5)^\circ$, $\theta = 51.58(2.8)^\circ$; $\varphi = 154.38(1.8)^\circ$, $\theta = 128.71(1.5)^\circ$ and $\varphi = 61.14(2.1)^\circ$, $\theta = 79.29(2.4)^\circ$], respectively. In the phosphazene rings the P-N bond lengths are in the range 1.539(12)-1.603(10) Å have double-bond character. However, the exocyclic P1-N4 [1.632(20) Å], P1'-N4' [1.641(13) Å], P2-N5 [1.632(12) Å], P2'-N5' [1.613(10) Å] bond lengths and are at the lower limit for single bond. In the phosphazene rings, exocyclic angles N4-P1-O [102.46(49)°], N4'-P1'-O' [102.31(53)°], N5-P2-O2 [101.62(53)°] and N5'-P2'-O2' [100.38(51)°] are nearly the same while the endocyclic angles N2-P1-N1 [115.60(55)°], N2'-P1'-N1' [114.62(55)°], N3-P2-N2 [116.59(57)°] and N3'-P2'-N2' [116.90(53)°] are smaller than the corresponding ones [endocyclic N-P-N 118.3(2)° and exocyclic Cl-P-Cl 101.2(11)°] in the 'standard' compound $N_3P_3Cl_6$ [2].



$C_8H_9Cl_4N_4O_1P_3$ (I)



$C_{18}H_{22}Cl_2N_5O_2P_3$, (II)

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Metallo-organic network based on [1.1.1.1]Metacyclophane organic unit : influence of the orientation and flexibility of the coordinating part on the dimensionnality of the resulting systems.

Ehrhart Jérôme, Planeix Jean-Marc, Hosseini Mir Wais. Email : jehrhart@chimie.strasbg.fr

Recent development of research on crystalline metal-organic frameworks (MOF) stems from the great promise brought by these materials for applications such as gas storage or catalysis.¹ The design of these architectures based on the assembly of organic bridging molecules and metal centers still remains a challenge. One approach developed in our laboratory is based on molecular tectonics,² which relies on the use of molecular building blocks with recognition sites, or tectons, which, under self assembly conditions, can organize into molecular networks.

We are currently engaged in the development of ligands which could, by their intrinsic covalent backbone, bring an added porosity to the materials. In particular, functionalized [1.1.1.1]metacyclophanes⁴ (Figure 1 a)) are appealing owing to their macrocyclic and rigid nature which can host solvent molecules or gases as demonstrated.^{3,5}

Recently, we have designed and synthesized a series of three [1.1.1.1]metacyclophanes functionalized with groups possessing nitrogen donor sites. Two of these ligands are flexible, functionalized with pyrazoles (fig1 b)) or imidazoles (fig1 c)) units, separated from the metacyclophane core by a methylene bridge, allowing the free rotation of the coordinating unit. The only structural difference between them is the orientation of the nitrogen donor site. The third molecule is functionalized with a pyridine, directly bound to the metacyclophane, offering high rigidity and pseudo-tetrahedral geometry. As a consequence of the preorganised geometry of the ligands, their self-assembly with metal salts allowed to obtain materials with different dimensionality and properties.

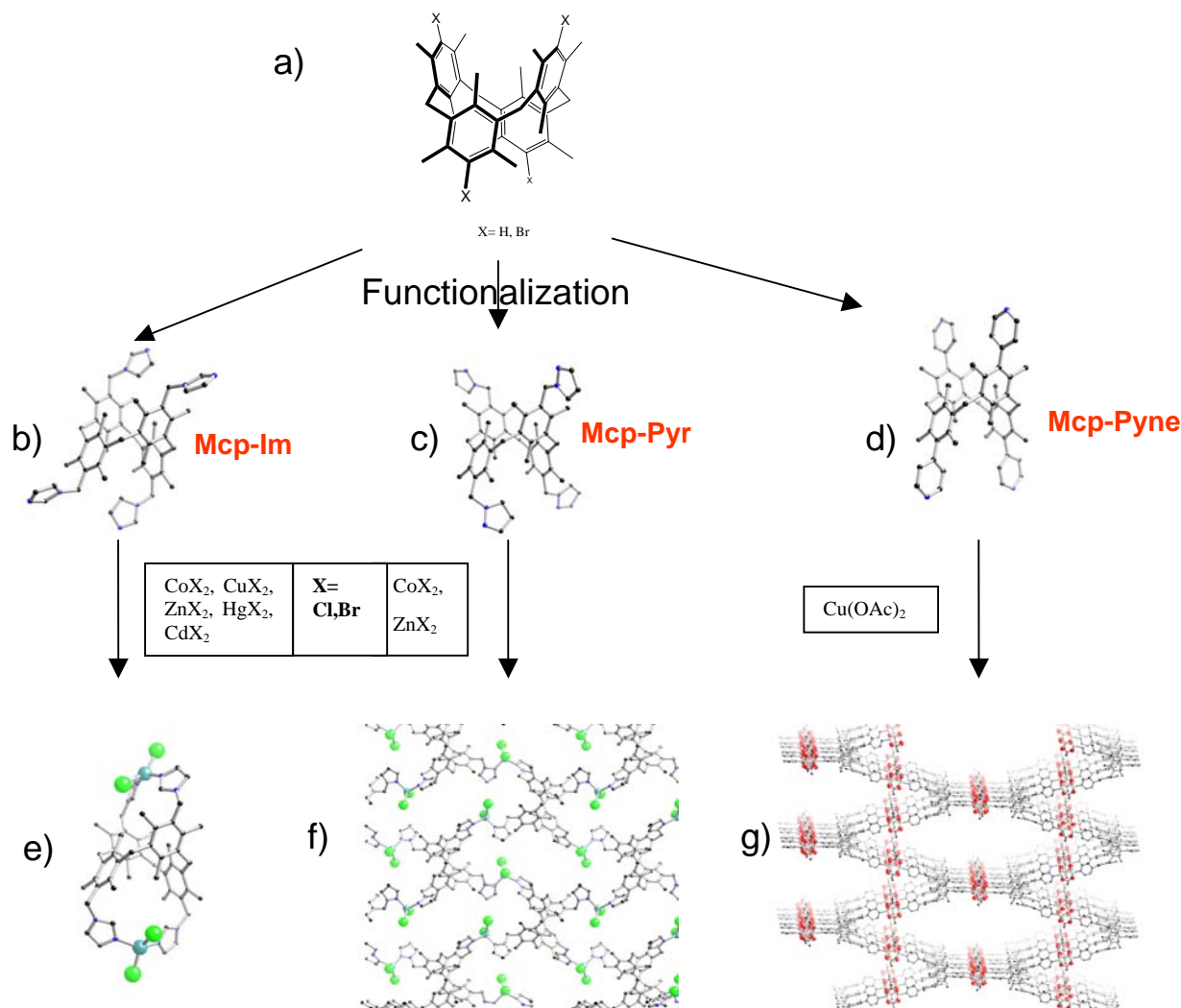


Fig 1 : a) [1.1.1.1]metacyclophane unit. b) X-ray structure of the tetramethyl(imidazole) functionalized [1.1.1.1]metacyclophane. c) X-ray structure of the tetramethyl(pyrazole) functionalized [1.1.1.1]metacyclophane. d) X-ray structure of the tetrapyridine functionalized [1.1.1.1]metacyclophane. e) X-ray structure of the discrete

entities obtained by complexation with metallic salts. f) X-ray structure of the 2D networks obtained with metallic salts g) X-ray structure of the 3D network obtained with Cu(OAc)₂.

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Setup for *in situ* x-ray diffraction study of swift heavy ion irradiated materials

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An *in situ* x-ray diffraction (XRD) setup is designed and installed in the materials science beam line of Pelletron accelerator at Inter-University Accelerator Centre (IUAC), for *in-situ* studies of phase change in swift heavy ion (SHI) irradiated materials. A high vacuum chamber with suitable windows for incident and diffracted x-ray is integrated with the goniometer and the beamline.[1] An indigenously made liquid nitrogen (LN₂) temperature sample cooling unit is due installed. The snap shots of growth of particles with fluence of 90 MeV Ag ions were recorded using *in situ* XRD experiment, illustrating the potential of this *in situ* facility. [2] Thin film of C₆₀ was used for testing of sample cooling unit. It shows that the phase of C₆₀ film transforms from cubic lattice (at RT) to fcc lattice at around T=255 °K. The insitu phase change study of the BaTiO₃ irradiated with 100MeV Ag⁺ ion at the 100K temperature is also studied using this setup. It shows that all of the peaks shifted toward the lower angle and strain is induced by ion irradiation.

References:

1. Setup for *in situ* x-ray diffraction study of swift heavy ion irradiated materials, P K Kulriya et al, Review of Scientific instrument, 78(2007)113901
2. Controlled growth of the Au nanoparticles induced by ion irradiation: insitu X-ray diffraction study, Y K Mishra, Applied Physics letter, 90(2007)073110

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Electron diffraction on organic molecules with high NLO activity

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Electron crystallography is often the only path to analyse the crystal structure of nanocrystalline small organic molecules or polymeric compounds where x-ray powder diffractograms deliver no or only poor data. Data for structural analysis is normally taken via several tilts of an appropriate crystal around selected axes [1]. Dependent on the habit of the crystals sample holders with different flexibility (rotation-tilt or double-tilt rotation) can be used. Because of the high sensitivity of the material to electron irradiation the electron dose must be kept as small as possible. In the case of nanocrystalline organic samples nanodiffraction (NED), with a parallel beam of approximately 50nm diameter, turned out to be a gentle way to sample the reciprocal space.

In order to obtain a high quality data set for crystal structure determination analysis and to reduce the electron dose on the sample further the reciprocal space should be sampled as accurately as possible in an automated way. An experimental software module [2], based on recent advances in tomography acquisition and combining STEM imaging with diffraction pattern acquisition in nano diffraction mode, has been developed for Tecnai microscope for automated diffraction pattern collection. This module and subsequent data processing allows an automated cell parameter determination and the observation of the reconstructed 3D reciprocal space for detection of special structural features like disorder [3]. It accelerates data collection and therefore allows investigation of multiphase systems in a reasonable time. Here we present structural investigation of a small organic molecule with non linear optical activity (FAPPOBE) as given in Figure 1. Both manual and automated diffraction acquisition paths have been used on this beam sensitive organic material.

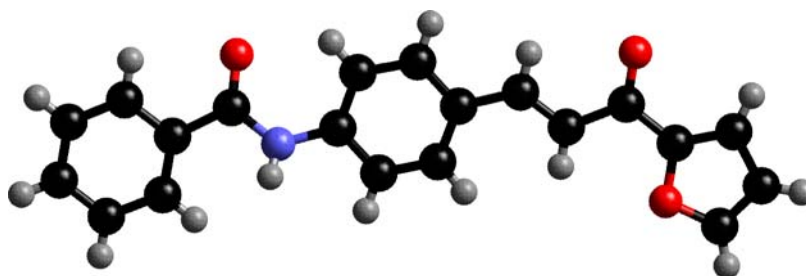


Figure 1: Scheme of FAPPOBE.

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Synthesis and Structural Characterisation of the Fullerenium Salt $C_{60}(AsF_6)_2$

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We present our recent achievement in the preparation of the first fullerenium salt in the solid state, whose chemical formula is $C_{60}(AsF_6)_2$ [1]. In this system, C_{60} molecule is oxidized by the conjugated base of the superacid $HAsF_6$.

The interest in such class of compounds is due to the fact that, based on BCS theory prediction, in an hypothetical hole-doped fullerene superconductor, the expected T_c should be even greater than in “conventional” well known electron-doped superconducting fullerenes [2,3]. However, due to the difficulties in oxidising C_{60} , this scenario has been precluded for a long time.

Synchrotron X-ray powder diffraction (beamline ID31 - ESRF, Grenoble) was performed on $C_{60}(AsF_6)_2$, in order to obtain a detailed structural characterisation. The Rietveld refinement of the data clearly indicated that in the as-prepared compound fullerenes polymerize along *1D chains* with an unusual *zigzag* arrangement (see Fig. 1), to our knowledge never observed before in other fullerene based compounds. Solid state NMR substantially confirmed these result, by showing the presence of sp^3 hybridised carbons contribution in the ^{13}C NMR spectrum.

Preliminary laboratory X-ray diffraction performed during a moderate thermal annealing of the sample allowed us to find out an irreversible polymer-to-monomer phase transition above $\sim 475K$, accompanied also by a change of stoichiometry. SQUID magnetic measurements seem to rule out the presence of superconducting transitions down to 2K in both the phases.

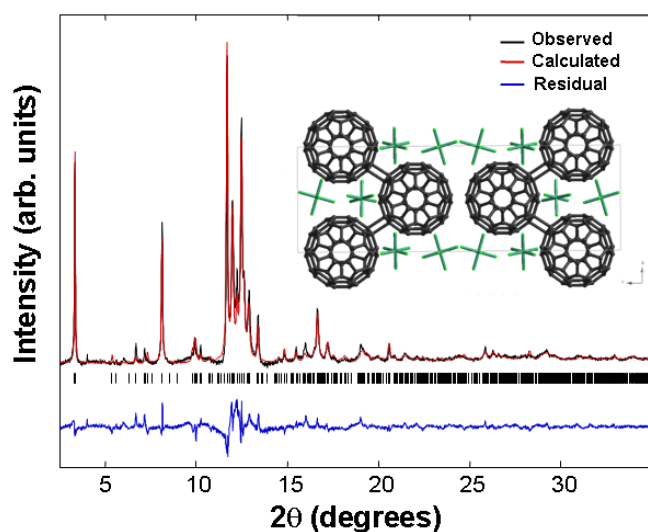


Figure 1 Calculated and observed synchrotron powder-diffraction profile of as prepared $C_{60}(AsF_6)_2$ at 300K ($\lambda=0.93370(2)$ Å, $R_{wp}=4.33\%$, $R_{exp}=1.16\%$). *Inset*: crystal structure of $C_{60}(AsF_6)_2$ polymer.

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'Crystallographic interlocking' of nano-sized domains as an origin of superhardness of c-BN/w-BN/h-BN nanocomposites and its observation via their partial coherence to X-ray scattering

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Ultrahard boron nitride compacts containing nanosized domains of the cubic (c-BN), wurtzitic (w-BN), and hexagonal (h-BN) phase were synthesized at high-pressure/ high-temperature (HP/HT) conditions. Hot-pressed and pyrolytic BN, both containing h-BN as a main component, were used as starting materials. The HP/HT products were investigated by x-ray diffraction via Rietveld and line-profile analysis, as well as high-resolution transmission electron microscopy. In particular samples, partial crystallographic coherence of adjacent domains to x-rays was observed, which has been previously found in superhard transition metalnitride-based nanocomposite coatings. This partial crystallographic coherence manifests itself by an apparent narrowing of the line widths of the low index reflections, followed by an abrupt increase of FWHM in a Williamson-Hall-Plot (FWHM-versus-sin(theta) plot). It has been shown [1] that a strong local preferred orientation for crystallites that have the same crystal structure and are smaller than approximately 15 nm causes an overlap of their reciprocal lattice points. Thus, within an area limited by the coherence length of the radiation, XRD cannot distinguish these crystallites from each other, and it "sees" them as one single coherent scattering domain, which leads to the apparent "narrowing" of the diffraction lines.

In the BN nanocomposites, the partial crystallographic coherence of nanocrystallites to x-rays was improved by their strong local preferred orientation: Due to well-known orientation relationships among h-BN, w-BN, and c-BN phases, neighboring domains "remembered" the macroscopic orientation of their larger parent h-BN grains. Moreover, because of the same reason, there were partially coherent interfaces between neighboring domains, giving rise to a high coherence and resistance to shear between them. This 'crystallographical interlocking' manifested itself in the observation that the Knoop and Vickers hardness of our specimen having crystallite sizes ranging from 6 to 50 nm was found to be significantly higher than that of c-BN single crystals, despite the presence of residual (soft) h-BN phase.

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