Session V, May 27, Wednesday

L15

LATEST DEVELOPMENTS IN STRUCTURE ANALYSIS BY 3D ELECTRON DIFFRACTION

L. Palatinus

Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, Prague 8
palat@fzu.cz

In the roughly two decades since its introduction, 3D electron diffraction (3D ED) has evolved from a niche technique to a widely used, established structure determination method. It has undergone rapid development in all stages of the analysis, from data collection techniques and instrumentation to improvements in data processing and structure-refinement techniques, which now enable the application of the dynamical theory of diffraction in the calculation of model intensities.

At present, the fundamentals of 3D ED are well established, and the technique is routinely used to determine crystal structures of micro- and nanocrystals. The focus of the development is shifting towards specific applications and remaining problems. The presentation will focus on these developments.

One direction is the continuous improvement of the attainable accuracy of the resulting structure models. The refinement R-factors can reach values as low as 3% in exceptionally good cases, and values below 6% are not uncommon. At this level of accuracy, it becomes possible to go beyond simple structure determination, and charge density studies become feasible. Indeed, a few recent publications [1-3] have demonstrated that charge-density studies are feasible with 3D ED. Interestingly, charge-density analysis of structures containing heavy atoms is easier with electron diffraction than with X-ray diffraction, due to the different sensitivity of electron diffraction to charge density effects.

Another direction of development focuses on improving the refinement procedure itself. In particular, the above-mentioned high-quality refinements are possible only on perfect crystals. When the crystal contains imperfections, the quality of the dynamical refinement can quickly deteriorate. To address this problem, models have been developed to account for crystal mosaicity, and models that handle the presence of crystal defects are under development – some of these efforts will be discussed in the contribution by prof Holý at this meeting.

Other efforts are aiming at high-throughput data collection and processing. Systems like AutoLEI [4] aim to automatically collect and process many datasets, with the idea that averaging across datasets can at least partially remove dynamical diffraction effects, and that a high-quality refinement can then be obtained with a simple kinematical theory. A specific application of a high-throughput data collection is the determination of the enantiomeric excess of a chiral, but not enantiomorphically pure material. Such determination requires combining measurements from many crystals with the absolute-structure determination for each by dynamical refinement [5]. It is a challenging method, but the benefit is that it is the only available technique for determining the enantiomeric excess of a material that does not contain chiral constituents, such as some chiral MOFs or zeolites.

Finally, a significant amount of effort is invested in a technique called SerialED. In this technique, analogous to serial X-ray crystallography, a single diffraction pattern is collected from each crystal, and a complete dataset is obtained by combining diffraction patterns from many crystals. Recent work [6] has demonstrated that using precession electron diffraction – a technique many considered out of fashion in recent years – can significantly boost the power of SerialED and yield structure models of comparable quality to those obtained from single crystals.

All these efforts aim to make 3D ED an even more versatile, broadly applicable, and accurate technique than it already is.

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L16

POLYMORPHISM AND COOPERATIVE PHASE TRANSITIONS IN C6-BTBT (X=4,6,8) MOLECULAR CRYSTALS

P. Brázda, K. Gurung. J Rohlíček

Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 18200 Prague 8, Czechia
brazda@fzu.cz

Cooperative phase transitions are diffusionless and reversible phase transitions caused by a concerted displacement of molecules, atoms, and ions in crystals. They are generally associated with interesting macroscopic phenomena, such as the tuning of the mechanical properties of the materials undergoing the transition and shape-shifting effects, and they have been extensively studied in metals, inorganic alloys and ceramics [1]. Reports on cooperative polymorphic transitions of molecular crystals are still rare and the molecular mechanisms underlying these peculiar transformations are still largely unknown [1-3]. Understanding these processes can lead to an unprecedented control of molecular polymorphism that might be exploited in a wide range of fields, e.g., drugs development, high-energy materials, next-generation electronic and optoelectronic materials, or soft actuators.

One class of molecules potentially exhibiting cooperative phase transitions is BTBT with symmetrical long aliphatic hydrocarbon side chains (Figure 1).

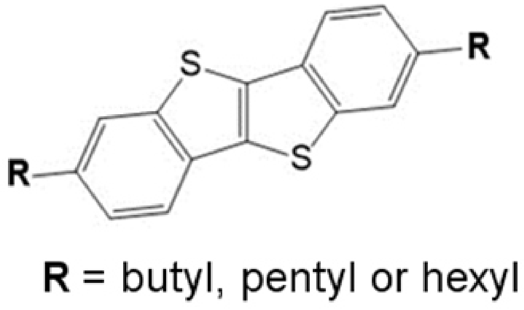

Figure 1. BTBT with butyl, pentyl and hexyl side chains.

So far, reported structures of these compounds at room or low temperatures showed nearly only so-called herringbone packing of the molecules, alternatively, -stacking was also observed in a few cases (Figure 2). The known structures for each molecule were only up to two polymorphs and no transitions between herringbone and -stacking was reported.

We prepared the starting materials both by crystallization from solvent and by sublimation, including direct sublimation on TEM grids. Further, we combined powder X-ray diffraction, which provided a quick identification of phase transition temperatures and 3D electron diffraction to solve crystal structures. Imaging in TEM was also used to study shape-shifting of the crystals during phase transitions.

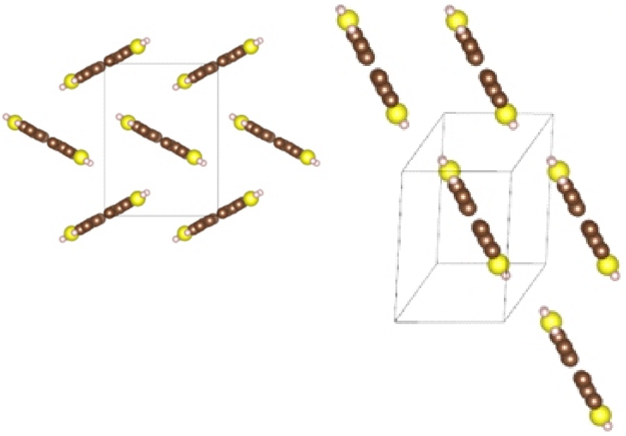

Figure 2. Example of herringbone (left) and -stacking (right) packing of the aromatic cores of Cx-BTBT.

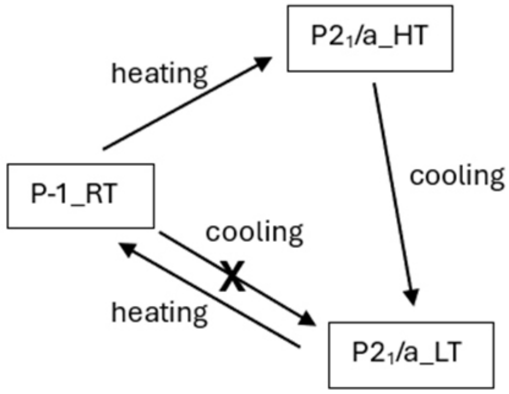

Figure 3. Phase transitions of C4-BTBT.

Study of C4-BTBT revealed two new polymorphs apart from the known room temperature one crystallizing in P-1 space group (Figure 3) which adopts -stacking packing. Transition to P2$_1$/a_HT polymorph occurs above 350K and the packing of this polymorph is herringbone. Cooling below 220K leads to transition to P2$_1$/a_LT polymorph, which has -stacking packing of the cores. Substantial shape-shifting was observed for P2$_1$/a_LT to P-1_RT phase transition (Figure 4).

We identified five different polymorphs of C6-BTBT. Two room- and three low-temperature polymorphs. The room temperature polymorphs show both herringbone packing. They are polytypes, one with primitive unit cell and the other with I-centered cell. The nearly pure polymorph with centered cell was prepared only by sublimation on TEM grids. The crystals prepared by crystalliza-

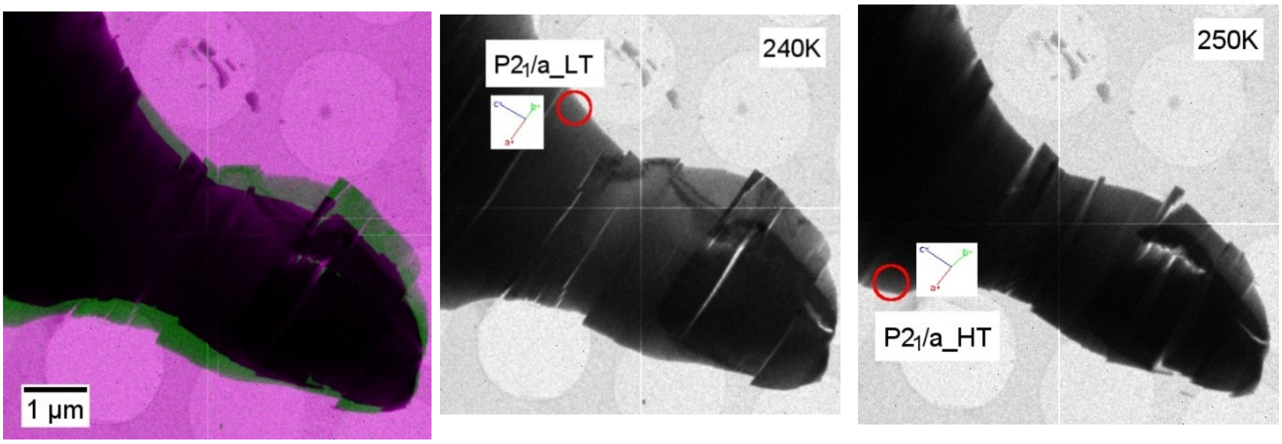

Figure 4. Transformation of C4-BTBT P2$_1$/a_LT to high temperature phase, presumably P-1_RT according to XRPD.

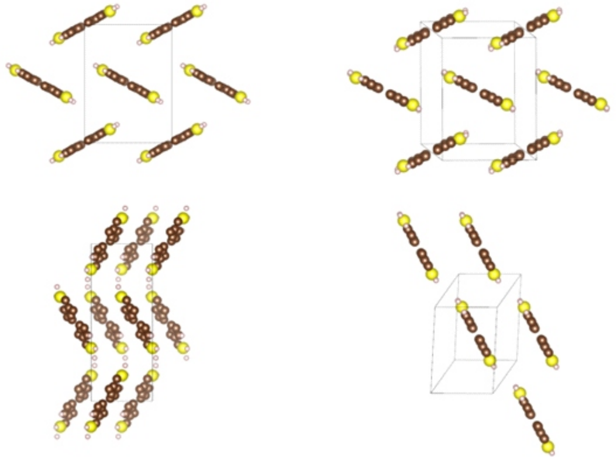

Figure 5. Left to right, top to bottom structures of C6-BTBT (only aromatic cores shown) P2$_1$/a (herringbone), P-1_HT (herringbone), C2/c (-stacking) and P-1_LT (-stacking).

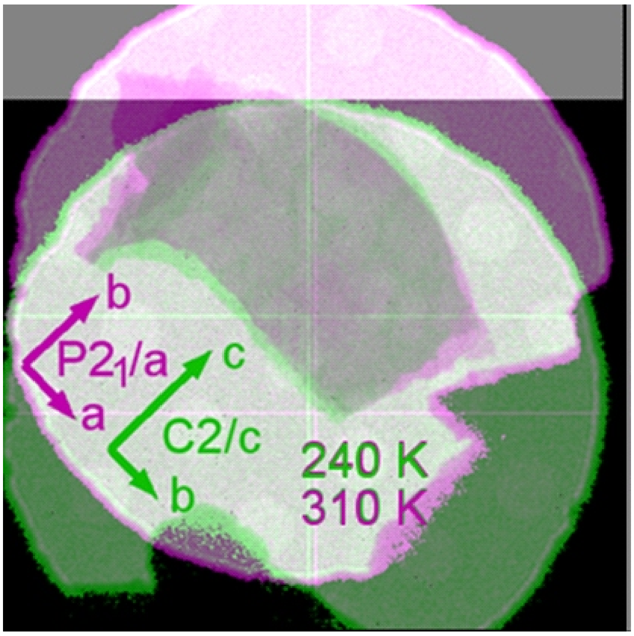

Figure 6. C6-BTBT transition from C2/c to P2$_1$/a.

tion from solvent had primitive unit cell and often showed competition between these two polytypes resulting in specific diffuse scattering. Below 250K, the room temperature P2$_1$/a phase transforms to P-1_HT phase, which still adopts the herringbone packing. Cooling below 230K leads to transition to C2/c structure with -stacking packing and further cooling below 90K leads to transition to P-1_LT with a different -stacking packing (Figure 5). Figure 6 shows significant shape-shifting in transition from C2/c to P2$_1$/a.

C8-BTBT showed four different polymorphs. One room-temperature and three low-temperature. The room-temperature one is analogous to C6-BTBT structure. Also the phases at the lowest temperature are analogous (P-1_LT). The difference occurs upon transition to room-temperature P2$_1$/a, where C8-BTBT material transforms via a transition phase stable only in a narrow (about 20K) temperature range, which is incommensurately modulated. The modulation is very strong and affect mainly the distance between the -stacked aromatic cores. The last observed phase was affected by a very strong disorder, so its structure could not be solved. The structure is very probably similar to C6-BTBT C2/c, but the layer stacking is virtually random and oscillates between primitive and C-centered polytypes. A situation similar to room-temperature polytypes of C6-BTBT.

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L17

Mg/Fe DISTRIBUTION IN CLINOFERROSILITE FROM 3D ED DATA

M. Klementová[1], L. Palatinus[1], R. Skála[2]

[1]FZU-Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, 182 00 Prague, Czechia
[2]Institute of Geology of the Czech Academy of Sciences, Rozvojová 269, 165 00 Prague, Czechia
klemari@fzu.cz

Site occupancy in minerals is an important parameter in earth and planetary science, as it may reveal the geological history of the involved phases. In particular, the studies of intracrystalline exchange reflect temperatures and/or pressures of crystallization or system closure, or they may indicate cooling rates for a rock hosting a given mineral. Procedures have been developed and calibrated for common simple silicates like olivine, garnet or pyroxene mostly because they represent important rock-forming minerals. The thermodynamic basis of intracrystalline geothermometry in monoclinic pyroxenes ($M2M1T_2O_6$) is governed by the Fe^{2+}–Mg exchange equilibrium between the two crystallographically distinct octahedral sites (M1 and M2) within the pyroxene structure.

We have studied clinoferrosilite from an inclusion in the Muong Nong-type tektite (indochinite) from Laos. The studied inclusion is round about 8 micrometers in diameter. It is mostly composed of sulfides – Ni-rich pentlandite and Fe-rich pyrrhotite. However, the most enigmatic phase is its magnesium rich rim formed by clinoferrosilite. Clinoferrosilite was studied by the 3D electron diffraction technique and the structure its structure was refined using the dynamical approach. The results were compared with the clinoferrosilite data available in the ICSD database.

Our data of Fe occupancy closely follow the trendlines (Figure 1), which means that the dynamical refinement of 3D ED data gives results comparable to the established techniques of X-ray diffraction and Mössbauer spectroscopy. And therefore, the method can be used for full geological interpretation and comparison with XRD data.

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Session V, May 27, Wednesday

L18

ELEKTRONOVÁ DIFRAKCE V NÁHODNĚ PORUŠENÝCH KRYSTALECH

Václav Holý[1], Lukáš Palatinus[2]

[1]Faculty of Mathematics and Physics, Charles University, Prague
[2]Institute of Physics, Czech Academy of Sciences, Prague

Dynamická teorie elektronové difrakce je důležitý nástroj pro analýzu elektronových difrakčních dat. Na rozdíl od běžně užívané dynamické rtg difrakce, vyžaduje dynamická elektronová difrakce použití mnoha (několik set) rovinných komponent elektronové Blochovy vlnové funkce, což komplikuje teoretický popis. Elektronová vlna difraktovaná krystalem s náhodně rozloženými defekty je superpozici koherentní a difuzní komponenty; koherentní vlna (pokud je přítomna) vytváří ostrá difrakční maxima a difuzní složka přispívá do pomalu se měnícího pozadí. Elektronová strukturní analýza používá většinou jen koherentní složku a je proto důležité korektně dynamicky počítat koherentní difraktovanou vlnu na základě strukturního modelu defektů.

Příspěvek obsahuje poslední výsledky našich výpočtů pro jednoduchý strukturní model defektů. Metoda je odvozena ze statistické dynamické teorie rtg difrakce publikované jedním z nás (V.H.) před asi 45 lety a používá formalismus analogický Dysonově rovnici používané v teorii pevných látek.

L19

ELECTRON DIFFRACTION OF SmNuc1 NUCLEASE

T. Skálová[1], P. Brázda[2], D. G. Waterman[3,4], K. Adámková[1], J. Dohnálek[1]

[1]Institute of Biotechnology of the Czech Academy of Sciences, v.v.i., Průmyslová 595, 252 50, Vestec, Czech Republic
[2]Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic
[3]STFC Rutherford Appleton Laboratory, Didcot, UK
[4]CCP4, Research Complex at Harwell, Rutherford Appleton Laboratory, Didcot, UK
t.skalova@gmail.com

Stenotrophomonas maltophilia is a gram-negative bacterium from the class Gammaproteobacteria, recognized as a cause of hospital-acquired infections and notable for its multidrug resistance. One of its nucleases, SmNuc1, belongs to the S1-P1 family of enzymes that cleave nucleic acids. While S1-P1 nucleases are found in several multidrug-resistant bacteria, their biological roles remain poorly understood.

SmNuc1 is a zinc-dependent enzyme with a predominantly -helical fold. Its active site is a surface cleft containing a trinuclear zinc cluster coordinated by nine residues. Previous studies have described the expression, purification, and characterization of SmNuc1 [1], and recently, seven X-ray crystal structures the free enzyme and complexes with RNA, cleavage products have been reported [2].

Small needles of SmNuc1 were crystallized, pipetted to golden grids and vitrified using a Vitrobot. Electron diffraction data were collected in the Institute of Physics AS CR (a 200 kV transmission electron microscope FEI Tecnai G2 20 equipped with a CheeTah M3 hybrid pixel detector). The collected diffraction data were visually checked using PETS2 [3] and finally processed in DIALS [4]. The data merged from five crystals were processed to 2.86Å resolution with overall completeness 83.4 %. The phase problem was solved by molecular replacement in Phaser [5] using one chain of a SmNuc1 X-ray crystal structure with PDB code 8QJO. The structure is under refinement in Phenix [6] with current R-factor 30.9 % and R_{free} 35.6 %.

The presentation will describe our first protein structure solved using electron diffraction and overcoming difficulties in individual steps of solving the structure.

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L20

ION BEAM METHODS AND ION MICROPROBE AT LABORATORY OF TANDETRON AT NPI ŘEŽ

Vladimír Havránek

Nuclear Physics Institute of the CAS, Řež 292, 250 68 Husinec
havranek@ujf.cas.cz

The Nuclear Physics Institute (NPI) has a long tradition in the use of nuclear analytical techniques. A significant milestone was achieved in 2006 with the installation of a 3 MV Tandetron accelerator. Since then we have constructed several ion beam lines and target chambers for specialized ion beam techniques including MeV ion microprobe, TOF ERDA (time of flight energy recoil detection analysis), high energy ion implantation, RBS (Rutherford backscattering) channelling, general purpose chamber for simultaneous analysis with PIXE (proton induced X-ray emission), RBS or NRA (nuclear reaction analysis), PIGE (proton induced gamma-ray emission) and PESA (proton elastic scattering analysis) or ERDA. A general-purpose analysis chamber has been developed to enable simultaneous application of multiple techniques, such as PIXE (proton-induced X-ray emission), RBS, NRA (nuclear reaction analysis), PIGE (proton-induced gamma-ray emission), PESA (proton elastic scattering analysis), and ERDA. This chamber is designed to accommodate large samples, provides a variable beam spot size, supports automated measurements of large sample series, and allows testing of particle detectors as well as the integration of additional methods, including IBI (ion beam–induced luminescence) and track detector studies.

The large volume of the chamber and its inner arrangement allow us easily change the experimental design and add detectors of our choice. More recently, a dedicated stage for external beam applications has also been constructed. The overall arrangement of the ion beam lines is shown in Figure 1.

The Tandetron accelerator can provide ion beams of almost all elements, with the exception of noble gases heavier than helium. Typical beam energies range from 400 keV up to several MeV for protons and helium ions, and from 10 to 30 MeV for heavier ions.

The ion beams are used for materials analysis, ion-beam modification of materials, radiation hardness testing, dosimetry, and particle detector testing. These applications cover a broad spectrum of scientific and technological fields. Typical examples of experiments performed at the Tandetron accelerator and description of used IBA methods will be presented.

The research has been carried out at the CANAM (Centre of Accelerators and Nuclear Analytical Methods) infrastructure LM 2015056. The authors acknowledge the assistance provided by the Advanced Multiscale Materials for Key Enabling Technologies project, supported by the Ministry of Education, Youth, and Sports of the Czech Republic. Project No. CZ.02.01.01/00/22_008/0004558, Co-funded by the European Union." – AMULET project.

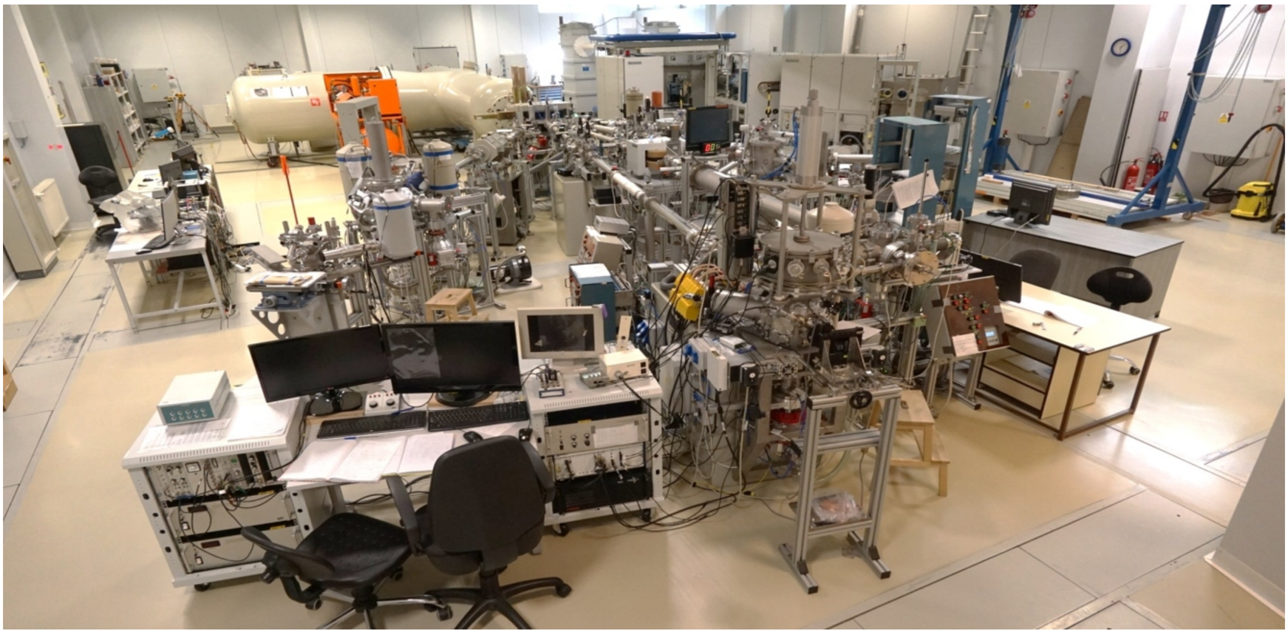

Figure 1. TANDETRON accelerator and beam lines at NPI. From left, general purpose IBM line with external beam stage, ion micro-beam line, high energy implantation line, TOF-ERDA and RBS channelling line.

L21

MODERN METHODS FOR THE ANALYSIS OF STRUCTURE AND PHASES OF MATERIALS: XRD SOLUTIONS OFFERED BY SCANMAT AND LANSCIENTIFIC

P. Wróbel

SCANMAT, Warsaw, Poland

X-ray diffraction (XRD) remains one of the key methods used in the analysis of crystal structure and phase identification of solid materials. With the development of instrumentation technology, XRD systems are becoming increasingly efficient, compact, and adapted to a variety of applications, from basic research to industrial quality control. The presentation will introduce selected XRD solutions and other techniques offered by Scanmat in cooperation with LANScientific.