Ultracold Atoms in Crystals of Light - Novel Opportunities for Exploring Quantum Many-Body Systems

Immanuel Bloch
Max-Planck Institut für Quantenoptik & Ludwig-Maximilians Universität
(Hans Kopfermann Str. 1, 85748 Garching, Germany & Ludwig-Maximilians Universität, Schellingstr. 4, 80799 München, Germany)

More than 30 years ago, Richard Feynman outlined the visionary concept of a quantum simulator for carrying out complex physics calculations. Today, his dream has become a reality in laboratories around the world. In my talk I will focus on the remarkable opportunities offered by ultracold quantum gases trapped in artificial crystals of light, so called optical lattices, to address fundamental physics questions ranging from condensed matter physics over statistical physics to high-energy physics with table-top experiment.

Starting with atomic or molecular quantum gases at nano Kelvin temperatures, such ultracold quantum ensembles can be loaded into an array of microscopic light traps formed by optical interference of laser beams. These artificial light crystals are widely tunable both in their depth, geometry and dimensionality and enable one to realize perfect defect free crystal structures. They can even be engineered to generate artificial electromagnetism, such that neutral particles can exhibit a behaviour close to the one of charged particles in strong magnetic fields. Very recently, the introduction of high-resolution optical imaging has enabled one to record photographic snapshots of individual atoms in optical lattices and to control the particles with single-site resolution and single-atom sensitivity. The remarkable opportunities offered by these systems has allowed us to enter a new era of probing and controlling many-body quantum systems.

Protein structure and dynamics using X-ray free-electron laser pulses

Henry N. Chapman
Centre for Free-Electron Laser Science (CFEL), DESY, Hamburg, Germany

Xray free-electron lasers provide a new disruptive technology for protein structure determination. The pulses from these sources are a billion times brighter than the brightest synchrotron beams available today. When focused to micron dimensions, such a pulse destroys any material, but the femtosecond-duration pulse terminates before significant atomic motion can take place. Therefore we can actually use the short pulses to overcome a long-standing problem in protein structure determination by X-ray crystallography, which is that with synchrotron beams exposures are limited by the onset of radiation damage. This has required protein crystals to be grown of sufficient size and quality to give high-quality diffraction patterns with that very limited exposure. Large protein crystals are often difficult to produce and this requirement imposes a severe bottleneck on structure determination. With FEL pulses we can carry out room temperature measurements at high resolution with a dose thousands of times higher than tolerable with synchrotron radiation sources, from crystals that can be smaller than 10 unit cells across. These "nanocrystals" may be more ubiquitous and easier to obtain than large ones. Combined with high frame-rate detectors and novel sample delivery methods we have a new paradigm of serial crystallography in which snapshot diffraction patterns are collected from single grains in a flowing suspension and then combined to give a set of structure factors. Irreversible reactions can be studied, synchronised with the short pulses, with new sample being constantly replenished. We have yet to reach the limit of the smallest samples that can be studied this way, and many innovations indicate the feasibility of single molecule diffractive imaging.

References:

P. Emma et al, "First lasing and operation of an Ångstrom-wavelength free-electron laser" Nature Photonics 4, 641–647 (2010).

H.N. Chapman et al, "Femtosecond x-ray protein nanocrystallography" Nature 470, 73–77 (2011).

M.M. Seibert et al, "Single mimivirus particles intercepted and imaged with an x-ray laser" Nature 470, 78–81 (2011).

S. Boutet et al, "High-resolution protein structure determination by serial femtosecond crystallography," Science 337, 362–364 (2012).

L. Redecke et al, "Natively inhibited Trypanosoma brucei cathepsin B structure determined by using an X-ray laser," Science 339, 227–230 (2013).

Interaction of art and symmetry in cultures and history

Emil Makovicky
Københavns Universitet

Symmetry was one of the human inventions which helped people to orient themselves in their environment and in their own activities. Explosion of abstract periodic patterns in societies which started settlements and agriculture shows that it was discovered and refined in connection with brick-building, weaving and basket-making. The practical symmetry was soon crowned with an abstract superstructure, which then actively helped its further development. Copying and borrowing across cultures has been a universal phenomenon, as also was a constant development of symmetry designs. In the never-ending competition between geometric abstract art and pictorial art, relative importance of these two aspects of human culture varies widely between different cultures and periods.

According to the dimensionality of a periodic pattern, we have 0D, 1D, 2D, and 3D patterns. The matter is complicated by their embedding in the space with at least the same or higher dimensionality. Thus, for the art symmetry it is important whether the 1D pattern is a frieze pattern in 2D space, or a rod pattern in 3D space; and whether a 2D pattern is a plane-group pattern in 2D space or a two-sided layer-group pattern in 3D space; even the 0D point-group patterns do not escape this problem. Black-and-white colouring of ceramic ornamentation led soon to dichroic groups of symmetry, and further development opened the realm of polychromatic groups, with certain symmetry operations connected with colour change. This development continued up to the modern times. Practical problems led to plane patterns based on similarity operations combined with other symmetries, as well as to cylindrical patterns, and to inversion on a circle. Affinity and hyperbolic symmetry belong to more modern applications, fractals had limited appearance already in the Romanesque times and quasiperiodicity was developed and used already in 12th-14th century. Profusion of concepts has been accompanied by a profusion of materials and techniques.

Frieze and rod patterns have been perfected by cultures as diverse as Maori of New Zealand, ancient Greeks, and the Cosmatic masters of Romanesque Italy. A blossom time of plane-group patterns constructed as ornamental brick courses was the pre-glaze building period in the arid Middle East, with rich examples from Seljuk Iran. Development of glaze techniques led on the one hand to richer, sometimes dichroic patterns (examples from Islamic Turkey) and on the other hand to a variety of multicoloured schemes, in which the painted (symmetric or less symmetric) motif became independent of the brick/tile pattern (Safavid Iran). The flowery Iznik tiles from Turkey have colouring schemes of their own. In the Pueblo pottery of North American South-West we often have a problem of interpretation –friezes, 2D patterns or a cylinder surface? Romanesque period in Italy offers beautiful examples of complex floor and wall mosaics.

There are differences between the understanding of polychromatic symmetry by old cultures and by the modern science and art, the modern interpretation was introduced by two constructivist painters, Escher and Hinterreiter. The pinnacles of ornamental art are the Islamic constructions of decagonal and octagonal quasiperiodic patterns in 12th century Iran and 14th century Islamic Spain and Morocco. Both these occurrences were followed by a long chain of ‘epigons’ who more and more modified these patterns, giving them more ornamental character and reducing their ‘mathematical’ character.

The modern world is not very fond of periodic patterns, trying to modify them if possible (Hinterreiter, Castera). A delightful fight of symmetry and asymmetry can be seen in Art Nouveau, sometimes with subtle examples of symmetry breaking, which are also seen in the Islamic calligraphy panels in Turkish Basra. A competition of colour (sometimes also shape) symmetries and antisymmetries via more than one inversion point in the panel is the hidden factor which gives internal tension to the best modern pictures (starting with Rembrandt).

This talk is not going to explain and analyze actions and anatomy of different types of symmetry groups – it will use them. I hope that you will enjoy a small selection of the infinitely large beautiful world of geometric art.

Single nano crystal analysis using electron diffraction tomography

Enrico Mugnaioli
Johannes Gutenberg Universität, Mainz, and Università di Siena

In the last century, X-ray crystallography allowed the determination of the atomic structure of hundreds of thousands of materials, either organic and inorganic. Still, single-crystal X-ray diffraction can be performed only on coherent domains of some cubic microns, while many new synthetic phases do not grow in crystals of such dimensions. For finer materials, diffraction data can be achieved only by X-ray powder diffraction (XRPD). XRPD has witnessed a fast growth in the last decades, boosted by synchrotron sources, Rietveld method for full plot refinement, development of global optimization algorithms and considerable hardware and software empowering. Despite its widespread use, XRPD has two important limitations: 1) diffraction comes from the whole sample and not from a specific single crystallite; 2) the crystallographic information is projected in one dimension. These limitations are critical when the sample is polyphasic or polytypic and when structures are characterized by large cell parameters or pseudo-symmetry, triggering accidental or systematical overlap of unrelated reflections at medium-high resolution.

Crystallographic methods based on the scattering of accelerated electrons are able to collect three-dimensional structural data on single crystallites 10-1000 times smaller than the ones typically feasible for X-ray single-crystal techniques. This is due to the high cross section between electrons and matter and the possibility to focus an electron beam into a nanometric probe. High-resolution transmission electron microscopy (HRTEM) is extensively used for structure investigation of nanocrystalline materials. Though, its use for quantitative structure characterization is limited by the difficulty in obtaining a comprehensive three-dimensional information with atomic resolution and by the strong illumination required, that quickly degrades and destroys beam sensitive materials like porous, water-containing and organic phases.

Electron diffraction data provide a better resolution and can be acquired with a far milder illumination than HRTEM. Pioneering structure investigations using electron diffraction data collected by TEM from single nanocrystals date to late 1970' [1]. In the following years the interest for electron diffraction increased, leading to several promising results (see for example [2-6]). Nevertheless, experimental and theoretical investigations pointed out the limits posed by dynamical effects and low data completeness [7-8]. Both these problems are emphasized by the classical way of acquiring electron diffraction patterns along prominent crystallographic zones. The introduction of precession electron diffraction (PED) [9] allowed to reduce dynamical effects and thus the dependency of reflection intensities from thickness and misalignment [8,10], but did not turn this electron diffraction into a routine for structure determination of nanocrystalline materials.

The need for less dynamical and more complete electron diffraction data led to the development of electron diffraction tomography (EDT) methods. Automated diffraction tomography (ADT) was the first method to be developed and used for the structure determination of different classes of nanocrystalline phases [11-14]. In ADT, electron diffraction patterns are acquired around an arbitrary tilt axis (not corresponding to a specific crystallographic orientation) and collected in sequential steps of 1° within the full tilt range of the microscope (normally about ±60°). Data completeness is generally higher, as those reflections not belonging to low-index zones are also collected. Since reflections are measured off-zone, fewer reflections are simultaneously excited at the same time, which implies a reduction of multiple scattering and hence of dynamical effects. Finally, ADT method simplifies and speeds data acquisition, making it possible to work with highly beam sensitive materials.

The success of ADT has encouraged other groups to develop their own systems for EDT data acquisition and analysis [15-17]. A major development was proposed with the rotation electron diffraction (RED) method, where mechanical sample tilt is supplemented by beam tilt [18-19]. Because beam tilt can be controlled with greater precision, RED method allows acquiring data with a finer slicing of the reciprocal space.

Diamonds: a journey into the deep Earth

Fabrizio Nestola
Dipartimento di Geoscienze, Università degli Studi di Padova, Via Gradenigo 6, 35131 Padova

Diamond is the deepest terrestrial material reaching the Earth's surface. When such high-pressure form of pure carbon contains mineral inclusions it represents real “unaltered and uncorrupted rock fragments” of our deep Planet. Thus, diamonds, beyond their high economic impact on the society, could be considered open windows to the Earth's interior and unique direct very deep rock sampling impossible to be obtained by any other approach. Based on their mineral inclusions diamonds have been dated between 1 and 3 billion of years and therefore they “tell” much about the evolution of the pristine Earth.

Based on the inclusions, diamonds were considered to crystallize mainly between 150 and 200 km depth and at temperatures between 900 and 1400°C within the so called “diamond window” ([1] for a review). Diamonds formed under such conditions are known as “lithospheric diamonds” and represent about 94% of the entire diamond production. However, the remaining 6% of diamond opened a completely different scenario on the diamond formation processes and at the same time on the Earth evolution. It is now well known that diamonds do not form only within the diamond window but recent discoveries indicate that they can form at even greater depths between 410 and 660 (the so called “Earth's transition zone [2]) and between 660 and 2900 km (that part of Earth interior called “lower mantle [3]). Diamonds formed at such depths are called “super-deep diamonds”.

The age and origin of diamonds inferred from their mineral inclusions derive from the assumption that they are “syngenetic” (e.g. diamond and its inclusions mutually growth in the same environment and at the same time from a single chemical reaction). However, the syngenetic relationship was never definitively demonstrated and recently a few works are trying to better elucidate such aspect [4]. A second issue absolutely crucial is the determination of the actual pressure of formation of diamonds. For this second aspect, like for the syngenesis/protogenesis one, we only have very rare reliable data and a general worldwide information is not available at all.

In this talk I will show how crystallography can provide crucial information both for the (i) syngenesis/protogenesis debate and for (ii) the determination of the pressure of formation of diamond. Relatively to (i), it was proposed that the occurrence of epitaxial relationships between diamond and its inclusions could be a strong argument in favor of syngenesis but no convincing evidence of epitaxial relationships had never been provided. We have recently measured the crystallographic orientations of a very high number of inclusions still trapped in their diamond hosts and casted several doubts for any recurrent orientation, at least for one of the common mineral found in diamond (olivine, Mg_2SiO_4, space group *Pbnm*). Concerning issue (ii) we applied crystallographic methods to refine the crystal structure of inclusions still kept under pressure inside their diamond hosts. This allowed us to obtain compositional information on the inclusion and, because the unit-cell volume – pressure trend is known for that type of inclusion, we could estimate the so called “internal pressure”. Finally, having derived by crystallographic methods the thermoelastic properties for diamond and inclusion (unit-cell volume thermal expansion, unit-cell volume compressibility, dependency of the compressibility and thermal expansion with temperature, shear modulus) it is now possible to retrieve the actual pressure of formation [5].

References

[1] Stachel T., Harris, J.W. (2008) Ore Geology Review, 34, 5–32.
[2] Pearson D.G., Brenker F.E., Nestola F., McNeill J., et al. (2014) Nature, 507, 221-224.
[3] Walter M.J., Kohn S.C., Araujo D., Bulanova G.P., et al. (2011) Science, 334, 54-57.
[4] Nestola F., et al. (2014) International Geology Review, submitted.
[5] Nestola F., Nimis P., Ziberna L., Longo M., et al. (2011) Earth and Planetary Science Letters, 305, 249-255.

Differently from traditional in-zone electron diffraction patterns, EDT non-oriented patterns cannot be directly indexed and measured. The collected tilt series must be transformed into a three-dimensional diffraction volume. Cell vectors, containing cell parameter and orientation matrix information, are automatically defined by clustering routines working in difference vector space [12,20] or arbitrarily defined on the basis of visual inspection. Features like diffuse scattering, twinning and polycrystallinity can also be visualized and measured in the three-dimension space, and related to cell parameters and crystal shape. After the cell has been found, it is possible to proceed with reflection indexing and intensity integration. EDT intensities can be normally used for structure determination neglecting dynamical effects and assuming the simple kinematic approximation ($I_{\mathrm{hkl}} = F_{\mathrm{hkl}}^2$) [13-14].
EDT data has been used in the last 6 years for the structure determination of tens of nanocrystalline phases that could not be characterized by standard X-ray techniques. An important application concerns porous materials, that are often nanocrystalline, beam sensitive and characterized by long cell parameters [21]. Several inorganic zeolites [22-24], metal organic frameworks (MOF) [25-26] and layered porous materials [27-28] have been characterized on the basis of EDT data.
A major advantage of electron diffraction, and of EDT in particular, is the ability to sample single nanosized grain, and even specific nanodomain inside a given crystal. It is therefore possible to collect data just from the nanovolume of interest, and the information is not influenced or spoiled by eventual other surrounding phases or polytypes [24,29]. A particularly challenging case is represented by samples where more commensurated polytypes coexist and form intergrowth sequences, as in the order-disorder mineralogical system charoite, where two polytypes are always contemporarily present in the same sample and often in the same microfiber [30-31]. The most complicate case for XRPD is the characterization of minor phases in polyphasic samples. An extreme example the natural phase $(S_2)_{1+x}[Bi_{9-x}Te_x(OH)_6O_8(SO_4)_2]_2$ [32], whose existence was first discovered through ADT data and whose structure was indeed determined before any imaging technique revealed its crystal shape and mineralogical environment.
Another main benefit of EDT is the ability to deliver three-dimensional information about local nanosized structural features, like disorder, epitaxial growth and twinning. For example, EDT was used to investigate nanotwinning in MOF CAU-7 microfibers [26], epitaxial hydratation of WO_3 nanoparticles [33] and epitaxial regrowth of Fe-oxides in high-pressure samples [34].
Tomographic ED is an emerging method that allowed the structure determination of several nanocrystalline materials that could not be characterized by standard X-ray methods or HRTEM. The implementation of electron scattering for different structure solution algorithms, like dual-space [15,35] and global optimization methods [26,36] and the availability of more sensible detectors is further expanding the EDT potentiality for the investigation of more complex phases, as demonstrated by the recent attempts of protein structure characterization [37]. In the future EDT may be a technique of reference for the structure characterization of new nanocrystalline materials belonging to any material class.

References

[1] Dorset, D. L., Hauptman, H. A. (1976). *Ultramicroscopy*, **1**, 195–201.

[2] Nicolopoulos, S., González-Calbet, J. M., Vallet-Regí, M., Corma, A., Corell, C., Guil, J. M., Pérez-Pariente J. (1995). *J. Am. Chem. Soc.* **117**, 8947–8956.

[3] Voigt-Martin, I. G., Yan, D. H., Yakimansky, A., Schollmeyer, D., Gilmore, C. J., Bricogne, G. (1995). *Acta Crystallogr. A*, **51**, 849–868.

[4] Weirich, T. E., Ramlau, R., Simon, A., Hovmöller, S., Zou, X. (1996). *Nature*, **382**, 144–146.

[5] Wagner, P., Terasaki, O., Ritsch, S., Nery, J. G., Zones, S. I., Davis, M. E., Hiraga, K. (1999). *J. Phys. Chem. B*, **103**, 8245–8250.

[6] Dorset, D. L. (2007). *Ultramicroscopy*, **107**, 453–461.

[7] Dorset, D. L., Roth, W. J., Gilmore, C. J. (2005). *Acta Crystallogr. A*, **61**, 516–527.

[8] Own, C. S., Marks L. D., Sinkler, W. (2006). *Acta Crystallogr. A*, **62**, 434–443.

[9] Vincent, R., Midgley, P. A. (1994). *Ultramicroscopy*, **53**, 271–282.

[10] Palatinus, L., Jacob, D., Cuvillier, P., Klementová, M., Sinkler, W., Marks, L. D. (2013). *Acta Crystallogr. A*, **69**, 171–188.

[11] Kolb, U., Gorelik, T., Kübel, C., Otten, M. T., Hubert, D. (2007). *Ultramicroscopy*, **107**, 507–513.
[12] Kolb, U., Gorelik, T., Otten, M. T. (2008). *Ultramicroscopy*, **108**, 763–772.
[13] Mugnaioli, E., Gorelik, T., Kolb, U. (2009). *Ultramicroscopy*, **109**, 758–765.
[14] Kolb, U., Mugnaioli, E., Gorelik, T. E. (2011). *Cryst. Res. Technol.* **46**, 542–554.
[15] Palatinus, L., Klementová, M., Dřínek, V., Jarošová, M., Petříček, V. (2011). *Inorg. Chem.* **50**, 3743–3751.
[16] Gemmi, M., Campostrini, I., Demartin, F., Gorelik, T. E., Gramaccioli, C. M. (2012). *Acta Crystallogr. B*, **68**, 15–23.
[17] Fan, J., Carrillo-Cabrera, W., Akselrud, L., Antonyshyn, I., Chen, L., Grin, Y. (2013). *Inorg. Chem.* **52**, 11067–11074.
[18] Zhang, D., Oleynikov, P., Hovmöller, S., Zou, X. (2010). *Z. Kristallogr.* **225**, 94–102.
[19] Wan, W., Sun, J. L., Su, J., Hovmöller, S. (2013). *J. Appl. Crystallogr.* **46**, 1863–1873.
[20] Schlitt, S., Gorelik, T. E., Stewart, A. A., Schömer, E., Raasch, T., Kolb, U. (2012). *Acta Crystallogr. A*, **68**, 536-546.
[21] Mugnaioli, E., Kolb, U. (2013). *Micropor. Mesopor. Mat.* **166**, 93–101.
[22] Jiang, J., Jorda, J. L., Yu, J., Baumes, L. A., Mugnaioli, E., Diaz-Cabanas, M. J., Kolb, U., Corma, A. (2011). *Science*, **333**, 1131–1134.
[23] Martínez-Franco, R., Moliner, M., Yun, Y., Sun, J., Wan, W., Zou, X., Corma, A. (2013). *P. Natl. Acad. Sci. USA*, **110**, 3749–3754
[24] Su, J., Kapaca, E., Liu, L., Georgieva, V., Wan, W., Sun, J., Valtchev, V., Hovmöller, S., Zou, X. (2014). *Micropor. Mesopor. Mat.* **189**, 115–125.
[25] Denysenko, D., Grzywa, M., Tonigold, M., Streppel, B., Krkljus, I., Hirscher, M., Mugnaioli, E., Kolb, U., Hanss, J., Volkmer, D. (2011). *Chem.-Eur. J.* **17**, 1837–1848.
[26] Feyand, M., Mugnaioli, E., Vermoortele, F., Bueken, B., Dieterich, J. M., Reimer, T., Kolb, U., de Vos, D., Stock, N. (2012). *Ang. Chem. Int. Ed.* **124**, 10519–10522.
[27] Bellussi, G., Montanari, E., Di Paola, E., Millini, R., Carati, A., Rizzo, C., Parker O'Neil, W. J., Gemmi, M., Mugnaioli E., Kolb U., Zanardi, S. (2012). *Angew. Chem. Int. Ed.* **51**, 666–669.
[28] Guo, P., Liu, L., Yun, Y., Su, J., Wan, W., Gies, H., Zhang, H., Xiao, F.-S., Zou, X. (2014). *Dalton T.* **43**, 10593–10601.
[29] Mugnaioli, E., Sedlmaier, S. J., Oeckler, O., Kolb, U., Schnick, W. (2012). *Eur. J. Inorg. Chem.* **2012**, 121–125.
[30] Rozhdestvenskaya, I., Mugnaioli, E., Czank, M., Depmeier, W., Kolb, U., Reinholdt, A., Weirich, T. (2010). *Mineral. Mag.* **74**, 159–177.
[31] Rozhdestvenskaya, I., Mugnaioli, E., Czank, M., Depmeier, W., Kolb, U., Merlino, S. (2011). *Mineral. Mag.* **75**, 2833–2846.
[32] Capitani, G. C., Mugnaioli, E., Rius, J., Gentile, P., Catelani, T., Lucotti, A., Kolb, U. (2014). *Am. Mineral.* **99**, 500-510.
[33] Hoshyargar, F., Mugnaioli, E., Branscheid, R., Kolb, U. Panthöfer, M., Tremel, W. (2014). *CrystEngComm*, **16**, 5087–5092.
[34] Koch-Müller, M., Mugnaioli, E., Rhede, D., Speziale, S., Kolb, U., Wirth, R. (2014). *Am. Mineral.*, doi:10.2138/am-2014-4944.
[35] Smeets, S., McCusker, L. B., Baerlocher, C., Mugnaioli, E., Kolb, U. (2013). *J. Appl. Crystallogr.* **46**, 1017–1023.
[36] Zhang, Y.-B., Su, J., Furukawa, H., Yun, Y., Gándara, F., Duong, A., Zou, X., Yaghi, O. M. (2013). *J. Am. Chem. Soc.* **135**, 16336–16339.
[37] Nannenga, B., Shi, D., Leslie, A. G. W., Gonen, T. (2014). *Nat. Methods*, **11**, 927–930.

Computational Materials Discovery: from Novel Chemical Phenomena to Planetary Materials

Artem R. Oganov
Stony Brook University, New York

The development of powerful structure prediction methods and codes, such as our USPEX code [1-3] enables prediction of materials with superior or unusual properties. I will discuss several thrusts of our recent work and related fundamental questions:

A. Search for superhard and ultrahard materials. Discovery of new ultrahard phases (e.g. MnB_3 [4]) in apparently well-studied systems at normal conditions. Phase diagram of the elusive C-N system [5]. Can a material harder than diamond exist? [6,7].

B. Low-dimensional systems. New techniques have been developed to deal with surfaces, 2D-crystals, polymers. Recently, we made discovered two new high-permittivity polymers [8], and predicted a 2D boron crystal, much more stable than previous proposals and having massless Dirac fermions [9].

C. Search for exotic chemistry, which produces unusual materials.

Recently, we predicted a new hydrogen hydrate H_2O*2H_2 (i.e. H_6O) to be stable at pressures above 38 GPa [10]; having 18 wt.% of easily removable hydrogen, this could be an ideal energy storage material if one can find a way of stabilizing it at normal conditions.

More intriguingly, we have discovered a class of “impossible” chemical compounds – such as Na_3Cl, Na_2Cl, Na_3Cl_2, $NaCl_3$, $NaCl_7$ [11] – to become stable under pressure. More recently, we predicted some of such compounds, e.g. KCl_3, to be stable at normal conditions [12]. KCl_3 can find industrial use as a chlorine storage material. Similar exotic compounds have been found in many other systems, including important planet-forming systems Mg-O (MgO_2, Mg_3O_2 become stable under pressure) [13] and Al-O (Al_4O_7, AlO_2 become stable) [14].

I will also discuss our recent discovery of stable compounds of helium at experimentally reachable pressures - Na_2He and Na_2HeO [15]. This indicates that helium is not as inert as previously thought and can form very stable compounds.

References

[1] Oganov A.R., Glass C.W., *J.Chem.Phys.* **124**, 244704 (2006).
[2] Oganov A.R., Lyakhov A.O., Valle M., *Acc. Chem. Res.* **44**, 227-237 (2011).
[3] Lyakhov A.O., Oganov A.R., Stokes H.T., Zhu Q., *Comp. Phys. Comm.* **184**, 1172-1182 (2013).
[4] Niu H.Y., et al., *Phys. Chem. Chem. Phys.* **16**, 15866-15873 (2014).
[5] Dong H.F., Oganov A.R., Zhu Q., Qian G.R. In prep. (2014).
[6] Lyakhov A.O., Oganov A.R., *Phys. Rev.* **B84**, 092103 (2011).
[7] Oganov A.R., et al., *In: Comprehensive Hard Materials Review* (v.3), Elsevier, 59-79 (2014).
[8] Sharma V., et al., *Nature Communications*, in press. (2014).
[9] Zhou X.-F., Oganov A.R., Qian G.R., Zhu Q., *Phys. Rev. Lett.* **109**, 245503 (2012).
[10] Qian G.R., Lyakhov A.O., Zhu Q., Oganov A.R., Dong X. *Scientific Reports* **4**, 5606 (2014).
[11] Zhang W.W., Oganov A.R., Goncharov A.F., et al., *Science* **342**, 1502-1505 (2013).
[12] Zhang W.W., et al. Submitted. (2014).
[13] Zhu Q., Oganov A.R., Lyakhov A.O. *Phys. Chem. Chem. Phys.* **15**, 7796-7700 (2013).
[14] Liu Y., et al. Submitted. (2014).
[15] Dong X., et al. Submitted (2014).

Materials and Crystallography:
a Personal Account of a Journey Into the Future

João Rocha
University of Aveiro, Department of Chemistry
(CICECO, 3810-193 Aveiro, Portugal
rocha@ua.pt, www.ciceco.ua.pt/jr)

In my personal scientific quest I have always travelled with crystallography in the sidecar, a faithful friend continuously guiding me on the road. There is another passenger in the sidecar, nuclear magnetic resonance. This talk highlights some of the stops in my personal scientific itinerary of over 25 years.

I have started out on very thin crystals of mineral kaolinite that stacked together forming beautiful 'libraries'. At that time, some of the outstanding questions, which I have addressed included the thermal decomposition of kaolinite to metakaolinite,[1] a reaction first studied by Le Chatelier. The latter is a much disordered an intriguing phase, whose structure could hardly be studied by X-ray diffraction and so it was my first NMR playground. Other issues I have investigated encompassed, among others, the reverse reaction, *i.e.*, the rehydration of metakaolinite to kaolinite, and the intercalation of small molecules (*e.g.,* DMSO) in between kaolinite sheets.[3]

Later, I became interested in zeolite-type silicates bearing transition metals, rather than aluminium, and looked into minerals in nature for inspiration. My first problem was also one of the toughest in my career: solving the structure of ETS-10, a microcrystalline and highly disordered microporous titanosilicate first made at Engelhard Corp.[4] This was only possible by bringing together X-ray diffraction, electron microscopy and solid-state NMR, and a group of excellent scientists (notably, M. W. Anderson and O. Terasaki). Dozens of microporous (and some layered) transition-metal silicates were prepared in my laboratory and, in most cases, the structures were solved from powder X-ray diffraction, often profiting from the fact that similar mineral structures had already been solved.[5] I have also studied the sorption and catalytic properties of these materials, sometimes shaped in the form of films and membranes.[6]

With the turn of the century, I wanted to explore properties not generally associated with zeotype materials, and switched from transition metals to lanthanides to generate 'light at the end of the tunnel'. Again inspiration from nature served me well and I started by mimicking minerals such as montregianite and soon many new microporous and layered lanthanide silicates were prepared.[7]

The last decade has seen a resurgence of coordination chemistry, now in the disguise of metal-organic frameworks (MOFs), solids with fascinating topologies, chemistry and promise of useful properties. MOFs are a very attractive field for crystal engineering and for those interested in structure-properties relationships. Our main interest has been in designing light-emitting MOFs bearing microporosity targeting the sensing of small molecules,[8] pH[9] and temperature.[10] Another, more fundamental, area I have engaged in is the study of the nature and status of water clusters in the intracrystalline voids of MOFs, perhaps as models for protein-active centres.[11]

In the last 6 years or so my interests began switching again, now towards the tinny nanoparticles of oxides and gold, aiming at producing new nanothermometers based on the light emission of lanthanides, sometimes coupled with nanoheaters.[12] This work poses new challenges to diffraction techniques which, nevertheless, are still central to our work. One of my visions is to blend together, effectively, NMR, diffraction and modelling into a formidable structural tool and I am contributing to the progress in this area.[13]

I thank FCT (PEst-C/CTM/LA0011/2013), QREN, FEDER, COMPETE, and the Portuguese National NMR Network.

X-ray Free-Electron Lasers – a bright future for structural biology

Ilme Schlichting
Max Planck Institute for Medical Research, Heidelberg, Germany

Protein crystallography using synchrotron radiation sources has had tremendous impact on biology, having yielded the structures of thousands of proteins and given detailed insight into their working mechanisms. However, the technique is limited by the requirement for macroscopic crystals, which can be difficult to obtain, as well as by the often severe radiation damage caused in diffraction experiments, in particular when using tiny crystals. To slow radiation damage, data collection is typically performed at cryogenic temperatures.

With the advent of free-electron lasers (FELs), capable of delivering extremely intense femtosecond X-ray pulses, this situation appears remedied. Theoretical considerations had predicted that with sufficiently short pulses useful diffraction data can be collected before the onset of significant radiation damage that ultimately results in Coulomb explosion of the sample[1, 2]. This has been shown recently at the first hard X-ray FEL, the LCLS at Stanford. High resolution data collected of a stream of microcrystals of the model system lysozyme agree well with conventional data collected of a large macroscopic crystal[3]. With the demonstration that *de-novo* phasing is feasible[4], serial femtosecond crystallography has been established as a useful tool for the analysis of tiny crystals[3, 5, 6], and thus the large group of proteins that resist yielding macroscopic crystals such as membrane proteins. In addition to ensure the required fast exchange of the microcrystals upon exposure, liquid jet delivery has the advantage of allowing data collection at room temperature[6,7, 8]. As demonstrated recently[9], this is important since structural dynamics and thus the observed conformation is often temperature dependent. Monitoring room-temperature conformational ensembles by X-ray crystallography can reveal motions crucial for catalysis, ligand binding, and allosteric regulation[9]. Recent results will be described.

1. Solem,J.C. Imaging biological specimens with high-intensity soft x rays. *J Opt. Soc. Am. B* **3**, 1551-1565 (1986).
2. Neutze,R., Wouts,R., van der Spoel,D., Weckert,E., & Hajdu,J. Potential for biomolecular imaging with femtosecond X-ray pulses. *Nature* **406**, 752-757 (2000).
3. Boutet,S. *et al.* High-Resolution Protein Structure Determination by Serial Femtosecond Crystallography. *Science* **337**, 362-364 (2012).
4. Barends,T.R. *et al.* De novo protein crystal structure determination from X-ray free-electron laser data. *Nature* **505**, 244-247 (2014).
5. Redecke,L. *et al.* Natively inhibited Trypanosoma brucei cathepsin B structure determined by using an X-ray laser. *Science* **339**, 227-230 (2013).
6. Liu,W. *et al.* Serial femtosecond crystallography of G protein-coupled receptors. *Science* **342**, 1521-1524 (2013).
7. Weierstall,U., Spence,J.C., & Doak,R.B. Injector for scattering measurements on fully solvated biospecies. *Rev. Sci. Instrum.* **83**, 035108 (2012).
8. DePonte,D.P. *et al.* Gas dynamic virtual nozzle for generation of microscopic droplet streams. *J. Phys. D: Appl. Phys.* **41**, 195505 (2008).
9. Fraser,J.S. *et al.* Accessing protein conformational ensembles using room-temperature X-ray crystallography. *Proc. Natl. Acad. Sci. U. S. A* **108**, 16247-16252 (2011).

References

[1] Rocha, J., Klinowski, J., "^{29}Si and ^{27}Al magic-angle-spinning NMR studies of the thermal transformation of kaolinite", *Phys. Chem. Min.,* **17**: 179 (1990).

[2] Rocha, J., Klinowski, J., "The rehydration of metakaolinite to kaolinite", *J. Chem. Soc., Chem. Commun.,* 582 (1991).

[3] Rocha, J., Duer, M. J., Klinowski, J., "Solid-state NMR studies of the molecular motion in the kaolinite:DMSO intercalate", *J. Am. Chem. Soc.,* **114**: 6867 (1992).

[4] Anderson, M. W., Terasaki, O., Ohsuna, Philippou, A., MacKay, S. P., Ferreira, A., Rocha, J., Lidin, S., "Structure of the microporous titanosilicate ETS-10" *Nature*, **367**: 347 (1994).

[5] Lin, Z., Rocha, J., Ferreira, A., Esculcas, A. P., Philippou, A., Anderson, M. W., "Synthesis and structural characterization of microporous penkvilksite, umbite and other titanosilicates", *J. Phys. Chem. B,* **101**: 7114 (1997).

[6] Sebastián, V., Lin, Z., Rocha, J., Téllez, C., Santamaria, J., Coronas, J., "A new titanosilicate umbite membrane for the separation of H_2", *Chem. Commun.,* 3036 (2005).

[7] Ananias, D., Ferreira, A., Rocha, J., Ferreira, P., Rainho, J. P., Morais, C., Carlos, L. D., "Novel microporous framework europium and terbium silicates", *J. Am. Chem. Soc.,* **123**, 5735 (2001).

[8] Harbuzaru, B. V., Corma, A., Rey, F., Atienzar, P., Jordá, J. L., García, H., Ananias, D., Carlos L. D., Rocha, J., "Metal-organic nanoporous structures with anisotropic photoluminescence and magnetic properties and their use as sensors", *Angew. Chem. Int. Ed.,* **47**: 1080 (2008).

[9] Harbuzaru, B. V., Corma, A., Rey, F., Jordá, J. L., Ananias, D., Carlos, L. D., Rocha, J., "A miniaturized linear pH sensor based on highly photoluminescent self-assembled Europium(III) metal–organic framework", *Angew. Chem Intl. Ed.,* **48**: 6476 (2009).

[10] Cadiau, A., Brites, C. D. S., Costa, P. M. F. J., Ferreira, R. A. S., Rocha, J., Carlos, L. D., "Rathiometric nanothermometer based on an emissive Ln^{3+}- organic framework", *ACS Nano*, **7**: 7213 (2013).

[11] Rocha, J., Shi, F. N., Almeida Raz, F. A., Mafra, L., Sardo, M., Cunha-Silva, L., Chisholm, J., Ribeiro-Claro, P., Trindade, T., "2D-2D-0D stepwise deconstruction of a water Framework templated by a nanoporous organic-inorganic hybrid host", *Chem. Eur. J.,* **16**: 7741 (2010).

[12] Debasu, M. L., Ananias, D., Pastoriza-Santos, I., Liz-Marzan, L. M., Rocha, J., Carlos L. D., "All-in-one optical heater-thermometer nanoplatform operative from room temperature to 2000 K", *Adv. Mater.,* **35**: 4868 (2013).

[13] Santos, S. M., Rocha, J., Mafra, L., "NMR Crystallography: toward chemical shift-driven crystal structure determination of β-lactam antibiotic amoxicillin trihydrate", *Cryst. Grow Design,* **13**: 2390- (2013).

The bacterial ribosome, molecular machine and antibiotic target

Maria Selmer
Department of Cell and Molecular Biology, Uppsala University

In all living cells, ribosomes translate the genetic code in the form of mRNA into amino acids building proteins. During their function, ribosomes go through a cycle where they bind and release transfer RNA molecules and translation factors and undergo a series of conformational changes. Many aspects of ribosome structure and function are conserved in all kingdoms of life, but differences between bacterial and human ribosomes can be used to specifically target the bacterial ribosomes with inhibitors that act as antibiotics.

In this talk, I will present some of the crystallographic breakthroughs that allowed crystallographic structure determination of the ribosome. Further, I will show how structures in combination with functional studies have increased our understanding of the ribosome as a molecular machine and clarified the mechanism of action of many antibiotics. I will also present examples of how crystallography together with biochemistry can explain how bacteria gain resistance to antibiotics.