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Non-ambient crystallography – is extreme becoming common?

One century of modern crystallography, celebrated in this year, 2014, has brought about many developments, some of which have involved the use of ‘non-ambient conditions’, which in their most severe form can be described as ‘extreme-conditions’ crystallography. In addition to recognizing this increasingly vibrant research field, this special edition also represents a refocusing of *Acta Crystallographica Section B* to become the journal of choice when it comes to publishing high-quality results from non-ambient crystallographic studies.

The first low- and high-temperature structural determinations were performed soon after the inception of X-ray diffraction structural analysis. One of the first low-temperature determinations was the structure of benzene by Cox (1932). About the same time the first reports on high-pressure powder diffraction experiments were published by Cohen (1933). The high-pressure studies required strong elaborate equipment, and high-pressure diffraction on single-crystal diffraction was carried out over 20 years later by Vereshchagin *et al.* (1958). Those high-pressure experiments yielded results of low precision due to the thick walls of the pressure vessels. In fact, the inception of X-ray diffraction methods coincided with considerable progress in high-pressure techniques developed by Percy W. Bridgman. At that time mainly piston and cylinder pressure chambers were used, or chambers pressurized by gas pumped through a capillary from an external pressure generator, as well as opposed-anvils (still called Bridgman anvils), belt or multi-anvil presses of various designs, all of considerable dimensions and weight and not suited for diffraction experiments. About that time, the first synthetic diamonds were made. Also in 1959, Jamieson *et al.* (1959) and independently Weir *et al.* (1959) invented the main device for high-pressure crystallography – the diamond–anvil cell (DAC). This simple but ingenious apparatus still continues today to break all records of pressure, exceeding that at the centre of the Earth (364 GPa). The DAC is relatively simple yet it allows precise high-pressure diffraction measurements under laboratory conditions. Soon after the DAC was later developed by the introduction of a metal gasket between the opposed anvils and by the invention of ruby-fluorescence and other spectroscopic methods for precisely calibrating pressure inside the tiny volume of the DAC chamber. The miniature DAC can now be mounted on any single-crystal diffractometer in a home laboratory, and thanks to area detectors high-pressure diffraction measurements can be run relatively easily. One of the first high-pressure structural determinations were those on chloroform by Fourme (1968) and on the high-pressure phase of benzene by Piermarini *et al.* (1969). High-pressure techniques are constantly being developed and presently laboratory X-ray diffraction studies can be complemented by spectroscopy, also on the same sample in the DAC, as well as by experiments in specialized large-facility stations at synchrotrons, and at neutron spallation and nuclear reactor sources (Katrusiak, 2008). Internally and externally heated DACs are available, as well as laser heating allowing temperatures well over 1000°C. Other types of high-pressure devices have also been developed for various specific purposes, including physical, chemical, biological and most of all materials studies. There the samples can be cooled (either in cryostats or in the stream of cold gas) or heated, and various types of measurements can be performed for the same specimen. But most importantly, high pressure can now be used in laboratories and is now routinely applied to freezing protein crystals before diffraction studies.

Variable-temperature studies have benefitted for some decades now from the commercial availability of a number of sample chambers or environments. In many cases, particularly for powder diffraction studies, these utilize a metallic heating strip on which the sample is placed and is then heated electrically, or some kind of heated chamber in which the sample is contained. In reality, the gas cryostats now routinely used in single-

crystal structure determination, to improve the quality of the structure obtained, are often all that is needed, even for powder diffraction studies, where the sample is placed in a capillary. The diffraction analysis aims at a deeper understanding of structure–property relations, such as the lowest melting point of all organic compounds (Podsiadlo *et al.*, 2013).

Of course, endeavours in non-ambient crystallography have not been limited to structural characterizations at temperatures and pressures other than ambient. There are also studies of materials exposed to different gaseous environments or where the sample is subjected to various electrical or magnetic fields. Capillary-based sample cells have been particularly popular with these kinds of studies and a number of designs for the investigation of gas–solid interactions have been presented in the literature. For powder diffraction studies, the most elegant and versatile is possibly the one by Chupas *et al.* (2008). Extending the idea further is the design of a capillary-based micro-battery cell used to study the intercalation and deintercalation of lithium into graphite (Johnsen & Norby, 2013). Literature examples of gas-sorption studies include the determination of the structure of an acetylene sorption complex of zeolite A (Amaro & Seff, 1973) and, more recently, investigations into the absorption of hydrogen into Mg(BH₄)₂ (Filinchuk *et al.*, 2011) or in the Li–N–H system (Makepeace *et al.*, 2014).

Many studies have been called *in situ* or *in operando*, particularly in the latter case when the conditions under which the X-ray diffraction (XRD) measurements are obtained are in some way similar to those of some industrially or economically important process. Hargreaves (2005) in particular espoused the insights to be gained in the field of heterogeneous catalysis by the use of *in situ* powder X-ray diffraction (PXRD). On occasion, as with the study of the methanol-to-olefin catalysts under working conditions (Wragg *et al.*, 2009), a number of characterization techniques are employed simultaneously. In some instances the term extreme crystallography might seem even more appropriate. Consider studying the pressure acid leaching of nickel laterite ores (Madsen *et al.*, 2005), or more recently the quantification of passivation layer growth in inert anodes in operational titanium electro-winning cells (Rowles *et al.*, 2012).

Non-ambient powder diffraction studies frequently can result in a set of closely related diffraction patterns, essentially the PXRD data is measured as a function of temperature, pressure, chemical environment or even time. This can afford a remarkable amount of chemically and physically meaningful data concerning the properties and behaviour of the sample under investigation. The amount of detail extractable *via* these studies can even be extended to parametric refinement (Stinton & Evans, 2007), in which a single evolving structural model is fitted to the entire dataset. Recently we have also been introduced to the possibilities associated with total scattering or pair distribution function studies carried out under non-ambient conditions. This is most strikingly illustrated in the *in situ* study of nanoparticle formation of yttria-

stabilized zirconia (YSC) all the way from ionic constituents in solution to final crystals (Tyrsted *et al.*, 2014).

Clearly non-ambient crystallography is a far broader field than can be done justice in a single Special Issue. The contents of this issue merely represent a small sampling of what is possible. Indeed, the number of non-ambient structure determinations, phase transformation and other non-ambient studies reported in the literature steadily increases annually. It indicates that researchers reach out for non-ambient conditions not only in their search for new materials but also to improve their understanding of the properties of matter not only under normal conditions, but also under various conditions, even at extreme depths inside the Earth or other planets and conceivably even stars.

It is our hope that the publication of this Special Issue on Non-ambient Crystallography will not only stimulate new research in all areas of non-ambient crystallography, but also that it would encourage publication of these results within *Section B*. We thank all the authors who have contributed directly to this issue and we encourage all researchers active in the field of non-ambient crystallography to consider *Section B* for the publication of their next research paper.

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