Acta Cryst B
STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS
ISSN 2052-5206

Mapping high-pressure crystallography in a structural chemistry landscape

David R. Allan*

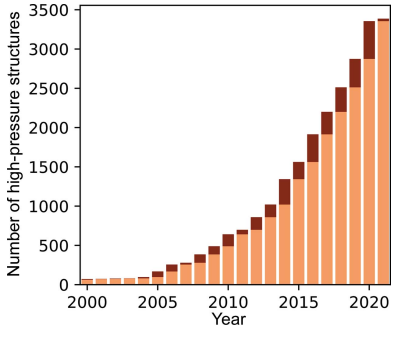
Diamond Light Source Ltd, Diamond House, Didcot, Oxfordshire OX11 0DE, United Kingdom. *Correspondence e-mail: david.allan@diamond.ac.uk

Keywords: high-pressure crystallography; Cambridge Structural Database; data mining.

In this issue of *Acta Crystallographica Section B*, Michal Kaźmierczak and Ewa Patyk-Kaźmierczak (2021) provide a comprehensive survey of high-pressure crystal structural depositions in the Cambridge Structural Database (Groom *et al.*, 2016) and offer a valuable perspective on the status of high-pressure research within the field of crystal chemistry.

For structural chemists, X-ray crystallographic techniques have been recognized as providing an extremely powerful method for the determination of the structure of matter and, specifically, the arrangement of atoms of a crystalline solid in three-dimensional space. The origin of the field comes from the theoretical work of Paul Ewald who, in collaboration with Max von Laue examined the propagation of X-rays through crystals. Encouraged by Laue, Walter Friedrich and Paul Knipping carried out an experiment where they shone a beam of X-rays at a crystal of zinc blende (ZnS) with a photographic film placed behind it to record the diffraction spots. The interpretation of the diffraction images was determined fully by Lawrence Bragg, who inferred that the diffraction events could be understood in terms of mirror-like reflections from planes within the crystal, which he formulated as the now very familiar 'Bragg's law'. For their work on translating the information recorded on diffraction images to crystal structure determination at atomic resolution Max von Laue and Lawrence Bragg (with his father William Bragg) won the Nobel Prize for Physics on consecutive years, 1914 and 1915 respectively (Woolfson, 2018). This brief period unlocked the use of X-ray crystal structure analysis for scientists working in disparate fields and by 1929 the output of the fledgling X-ray crystallography community was of sufficient volume for the founding of *Strukturberichte*, to provide a regularly published source of recent crystal structure determinations. *Strukturberichte* eventually became *Structure Reports* as an official publication of the International Union of Crystallography until the 1990s. The period also marked the evolution of X-ray crystallography and crystal structure analysis away from its origins in inorganic chemistry. Long-standing questions on the nature of chemical bonding and interactions in organic chemistry were addressed and the structures of a wide range of natural and synthesized molecules were determined. The biological and life sciences also embraced X-ray crystallography and went on to address several dauntingly complex challenges which, in turn, have revolutionized our understanding of life at the molecular level (Groom & Allen, 2014).

From 1929 to the early 1960s, crystal structure compilations and references were print based, with both *Strukturberichte* and *Structure Reports* joined by several other publications, and by the late 1940s there were growing concerns about the plethora of sources for primary scientific material, which was dubbed 'the information explosion'. In 1964, when computer-based systems became feasible, Olga Kennard was invited to create a 'Crystallographic Data Centre' with funding from the new UK Office for Scientific and Technical Information (OSTI) and by the following year she had established the Cambridge Crystallographic Data Centre (CCDC) at the University of Cambridge. The remit of CCDC was to establish a comprehensive and retrospective database of organic and metal–organic structures determined by both X-ray and neutron diffraction methods. As well as including the bibliographic, chemical and overall crystallographic information, it was, crucially, to include the three-dimensional atomic coordinate data. The resulting Cambridge Structural Database (CSD), the first fully electronic numerical data depository, was later joined by other databases in the early 1970s, such as the Inorganic Crystal



Structure Database (Karlsruhe, Germany) and the Protein Data Bank (Brookhaven National Laboratory, NY, USA) (Groom & Allen, 2014).

In the past 50 or so years the CSD has collated more than 1.1 million structures and a range of powerful software tools are available to enable systematic data mining over a broad range of search items. The 'CSD-Core' contains a suite of applications with search (*WebCSD*, *ConQuest*), visualization (*Mercury*) and analysis features (*Mogul*, *IsoStar*) that provide crystallographers a means of gaining a quantitative understanding of structural correlations and trends across a broad range of molecular systems. These surveys in themselves offer sufficient scientific insight to merit a source of original structural chemistry research and makes full use of all deposited structures derived from what could be considered, at least at first glance, unrelated research areas (Sykes *et al.*, 2011).

The foundation of the CSD coincides with the earliest use of diamond-anvil cells in high-pressure crystallography. These single-crystal X-ray diffraction studies were carried at the National Bureau of Standards using relatively bulky lever-arm cells and adapted precession cameras to record the diffraction data on photographic film (Weir *et al.*, 1969). This work led to some of the first high-pressure structure depositions recorded in the CSD (Piermarini *et al.*, 1969; Weir *et al.*, 1969). However, it was not until the development of the miniature diamond-anvil cell by Merrill & Bassett (1974), which was small enough and sufficiently light to be used on standard laboratory single-crystal diffractometers, that routine high-pressure structural studies became possible and more widely accessible. The Merrill–Bassett cell is still widely used, and elements of its design are present in the many variants of more modern diamond-anvil cell designs that were inspired by it (Moggach *et al.*, 2008). Stemming from the early work of Merrill and Bassett, significant contributions to high-pressure structural chemistry from this period were provided using the point detectors available at the time [notably by the groups of Katrusiak (Katrusiak, 2019) and Boldyreva (Boldyreva, 2018)] but perhaps the most significant contribution to the relatively recent rapid growth is the wide adoption of area detectors, particularly CCD detectors for chemical crystallography (Allan *et al.*, 2000). With the accompanying increased efficiency and speed of data collections, coupled with the incorporation of high-pressure routines in both the data acquisition and data processing software by the instrument manufacturers, the path to establishing an element of high-pressure research in chemical crystallography laboratory became greatly simplified.

Kaźmierczak & Patyk-Kaźmierczak (2021) report remarkable growth in the volume of high-pressure structural chemistry CSD depositions particularly from about 2000, when the use of area detectors became ubiquitous and modern commercial instruments made the barrier to participating in high-pressure structural chemistry less onerous for many laboratories – though many of the high-pressure CSD depositions still appear to be dominated by research groups based in Europe. The report provides an extremely valuable survey of the CSD to establish the current standing of high-pressure crystallography within the field of structural chemistry. They also, significantly, highlight the importance of recording high-pressure metadata within the CIF fields to ensure that searches of the CSD are accurate and the extracted structural details can be used to their full potential. The standardization of cif fields for metadata is the subject of increasing scrutiny not just for high-pressure crystallography but also for permanent curation of fully documented raw data at home laboratories and central facilities within the FAIR principles (Findable, Accessible, Interoperable, Reusable) – see, for example, the photon and neutron open science cloud (PaNOSC, 2021) and European Open Science Cloud Photon and Neutron Data Services (ExPaNDS, 2021).

References

Allan, D. R., Clark, S. J., Parsons, S. & Ruf, M. (2000). *J. Phys. Condens. Matter*, **12**, L613–L618.

Boldyreva, E. V. (2018). In *Understanding Intermolecular Interactions in the Solid State – Approaches and Techniques, Monographs in Supramolecular Chemistry No. 26*, edited by D. Chopra, pp. 32–97. UK: Royal Society of Chemistry.

ExPaNDS (2021). https://expands.eu/.

Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Katrusiak, A. (2019). *Acta Cryst.* B**75**, 918–926.

Kaźmierczak, M. & Patyk-Kaźmierczak, E. (2021). *Acta Cryst.* B**77**, 1012–1020.

Merrill, L. & Bassett, W. A. (1974). *Rev. Sci. Instrum.* **45**, 290–294.

Moggach, S. A., Allan, D. R., Parsons, S. & Warren, J. E. (2008). *J. Appl. Cryst.* **41**, 249–251.

PaNOSC (2021). https://www.panosc.eu/about-panosc/.

Piermarini, G. J., Mighell, A. D., Weir, C. E. & Block, S. (1969). *Science*, **165**, 1250–1255.

Sykes, R. A., McCabe, P., Allen, F. H., Battle, G. M., Bruno, I. J. & Wood, P. A. (2011). *J. Appl. Cryst.* **44**, 882–886.

Weir, C. E., Piermarini, G. & Block, S. (1969). *Rev. Sci. Instrum.* **40**, 1133–1136.

Woolfson, M. M. (2018). *Phys. Scr.* **93**, 032501.