Perspective

Crystallography taken to the extreme

Natalia Dubrovinskaia and Leonid Dubrovinsky

Abstract

This article is a brief autobiographical account of our life in science and the path that we took in performing the research for which we were awarded the Gregori Aminoff Prize in Crystallography 2017 by the Royal Swedish Academy of Sciences. We were invited to write it by the editor-in-chief of Physica Scripta, Suzy Lidström, who charged us with the task of contributing to a series of autobiographical articles published since 2014, the International Year of Crystallography, on the lives of the Aminoff Prize winners. As this series is intended to be of particular interest to young scientists, teachers and lecturers and those researching the history of science, we tried to adhere to this purpose while writing our story. It does not pretend to be a comprehensive review either of our own scientific results or, especially, of covering the complete history of the research field of high-pressure crystallography in which we are active.

Keywords: high-pressure crystallography, in situ single-crystal x-ray diffraction, laser heating, diamond anvil cell, crystal structure solution at extreme conditions

(Some figures may appear in colour only in the online journal)

1. Introduction

The year 2014, proclaimed by the United Nations as the International Year of Crystallography, inspired numerous publications on the subject and history of crystallography. X-ray crystallography, as a method to determine the atomic structure of crystals, certainly started from the discovery of the diffraction of x-rays by crystals by Max von Laue and his co-workers in 1912 (Friedrich et al 1913, Laue 1913) and the formulation of the diffraction law by William Lawrence Bragg (later called Bragg’s law) in the same year (Bragg 1912). However, the discovery of x-rays by Wilhelm Conrad Röntgen in 1895 (Röntgen 1895) formed the necessary foundation for the determination of crystal structures, and that was suggested to be considered as the start of modern crystallography in the book edited by Olovsson et al (2015) ‘From a Grain of Salt to the Ribosome: The History of Crystallography as Seen Through the Lens of the Nobel Prize’. At first, crystal structures were determined by the interpretation of x-ray diffraction (XRD) patterns of crystals obtained at ambient conditions.

Similarly, for high-pressure crystallography, the necessary foundation was built by Persy W Bridgman, who was awarded the Nobel Prize in Physics 1946 ‘for the invention of an apparatus to produce extremely high pressures, and for the discoveries he made therewith in the field of high pressure physics’. Although Bridgman himself did not work on crystal structure determination, dealing first with the technical matters of producing and measuring high pressure, and second with the physical phenomena which occur under high pressure (Bridgman 1946), he laid the foundation for the possibility for crystallography to be taken to the extreme. The ‘extremely high pressures’, which earned Bridgman the Nobel Prize in 1946 were of about 10 GPa. Since then, because of the invention of a diamond anvil cell (DAC), in the late 1950s (Bassett 2009) by Charles E Weir, Ellis R Lippincott and Elmer N Bunting, which is based on the same principles as Bridgman’s anvils, it took three decades of extensive research and development to...
generate pressures of one order of magnitude higher. As accepted in the community, the work of Ho-Kwang Mao with Peter M Bell (Mao and Bell 1976) became the first verified static pressure generation in excess of 1 Megabar. The first materials probed by x-rays under high pressures were powders.

Owing to further progress in the field, the DAC technique became the major tool for crystallography at extreme pressure-temperature conditions (Bassett 2009). It provided researchers with the opportunity for the in situ studying of matter at pressures extended above 300 GPa using a wide range of spectroscopic, elastic and inelastic scattering methods. The development of synchrotron x-ray sources, fast and sensitive area detectors, as well as the building of synchrotron beamlines specializing in high-pressure diffraction experiments have brought significant progress to high-pressure crystallography, enabling researchers to couple DACs with low- and high-temperature facilities (e.g. cryostats and laser-heating systems), to work with very tiny samples (as small as a few micrometers), and to investigate complex solids.

If we continue tracking the time-line of the development of high-pressure crystallography, it becomes evident that whereas powder XRD studies stepped over a megabar pressure already in the 1970s, single-crystal experiments remained much rarer, and until the late 2000s covered a very limited pressure range barely reaching 15 GPa. The reasons were mainly technical. First, a DAC is a uniaxial device (figure 1), and stresses developing in the pressure chamber tend to destroy single crystals, when a pressure-transmitting medium is solid or solidifies under pressurization (all known materials/compounds solidify below ~15 GPa at ambient temperature). Second, conventional DACs used by the mid-2000s had a rather small opening angle, allowing only restricted access to the reciprocal space. High-temperature experiments on single crystals were limited by temperatures of about 1000 K (with external electrical heating), which is too low for geosciences and solid-state chemistry applications, which are the usual driving forces in high-pressure research.

The first decade of the second millennium brought significant progress in the field. It was demonstrated that in an inert gas (He or Ne) pressure-transmitting medium, loaded under pressure of 1–2 kbar (see Kurnosov et al 2008, for example), single crystals might survive under compression in the megabar pressure range. New types of diamond anvils with a large aperture (Boehler and de Hantsetters 2004, Dubrovinskaia et al 2012) and DACs with the x-ray opening up to 90° were introduced (Yamanaka et al 2001, Boehler 2006, Kantor et al 2012). The portable double-sided laser-heating setup (Kupenko et al 2012) was developed and coupled with synchrotron radiation facilities enabling single-crystal diffraction experiments at thousands of degrees. This technological advances resulted in a revolutionary breakthrough in high-pressure crystallography.

By the beginning of the 2010s, owing to the work of our group and colleagues, it was shown that the structure solution and full refinement are possible at pressures over 100 GPa (Dubrovinsky 2010). In 2013, the special issue of the High Pressure Research journal ‘Single-crystal x-ray diffraction in the megabar pressure range’, edited by Leonid Dubrovinsky (2013), gave the first overview of the current state of the filed (for details, see seven articles of the special issue, including one review, and references therein). To date, numerous studies of single crystals of various materials, including structurally very complex, particularly incommensurate ones (Bykov et al 2015, Arakcheeva et al 2017), and those undergoing multiple pressure- (or pressure-temperature) induced phase transformations (Bykova et al 2016), have been successfully conducted.

This invited publication stands in relation to the Gregori Aminoff Prize 2017, which we were awarded ‘for having developed new methodology for in situ-experimental determination of crystal structures subjected to extreme conditions of high temperature and pressure’. Therefore, we will focus here only on high-
pressure crystallography, although our research interests are considerably broader, and the story below is about how it all began, viewed from our 30-year personal perspective.

### 2. Crystallography at Lomonosov Moscow State University: crystallography at ambient conditions

Lomonosov Moscow State University is our alma mater. We met there in 1978 and began our exciting common journey to the world of crystallography. First, we both studied geochemistry at the Geology Faculty of the University and later specialized in crystallography, with the emphasis on the structural analysis, at the Department of Crystallography and Crystal Chemistry. It was an advantage to be taught by a number of the brightest contemporary Soviet crystallographers: academician Nikolay V Belov, docents Galina N Litvinskaya, Judif G Zagalskaya and Jury K Egorov-Tismanko (figure 2). Our professors and docents were top-class professionals and enthusiasts of their own causes. Belov was among those who shaped modern crystallography and crystal-chemical science: in the Department, his famous books were referred to not by title but by color (the Blue Book by Belov (1947) and the White Book by Belov (1976)). This was exactly at the time of our undergraduate studies at Moscow University, when four volumes of Modern Crystallography (Sovremennaja kristallografiya) (Vainshtein 1981) were issued in Russian from 1979 to 1981. Translated into English, they subsequently appeared in the Springer Series in Solid-State Sciences, which published up-to-date fundamental scientific books written by leading researchers in the field. These four impressive Sovremennaja kristallografiya books, published one by one during our university time, were our appreciated annual presents to each other. Now, looking back, we realize that we came to crystallography at the right time and learnt about it at the right place.

After graduation from the University, our scientific careers started at different research institutions in Moscow. Natalia was employed at the x-ray laboratory of the Central Research Institute of Geological Prospecting for Base and Precious Metals (TsNIGRI) of the Ministry of Geology of the USSR, and Leonid—at the Institute of Geology of Ore Deposits, Petrology, Mineralogy and Geochemistry (IGEM) of the Academy of Sciences of the USSR. Nevertheless, we stayed closely connected to the University; parallel to our work at these institutions, we were

![Figure 1. Principle of a DAC: two jewelry quality diamonds are forced together (the body of the DAC is not shown in this figure) and squeeze a sample placed into the hole drilled in the metallic gasket (shown as a disc with a segment cut off to make the bottom diamond visible). This is a fragment of a film clip made by L Dubrovinsky in the early 1990s.](image-url)
each working on a PhD thesis under the supervision of Professor Vadim S Urusov (figures 2, 3) (later Academician of the Russian Academy of Sciences), the head of the Department of Crystallography and Crystal Chemistry after N V Belov. Urusov was a scientist with encyclopedic knowledge; the intellectual who inspired us in the modeling of crystal structures, and we both defended our doctoral theses on theoretical topics, Leonid in 1986 and Natalia in 1989.

The theoretical topics of our dissertations were imposed not only by our interest in the subject, but a critical situation in science at the end of Gorbachev’s era marked by the dissolution of the Soviet Union in 1991. The crumbling of Russia’s economic and political structures led to the lack of modern scientific equipment in the laboratories, which is crucial for experimental research, and to the collapse of many scientific institutes that resulted in a brain drain from Russia. In 1994, we moved to Sweden.

3. Uppsala University: crystallography at extreme conditions

At the Geocentrum of Uppsala University in Sweden, we joined the Theoretical Geochemistry Group under the leadership of Prof. Surendra K Saxena. On arriving in Uppsala, we were first involved in the computational activities of the group—thermodynamic modeling (led by S K Saxena) (Dubrovinskaya et al 1997) and atomistic simulations (together with A Belonoshko) (Belonoshko and Dubrovinsky 1995). Parallel to the theoretical work, Saxena built one of the first facilities for experiments in laser-heated DACs in Europe (Lazor et al 1993). He also decided to use both in-house and synchrotron XRD for the characterization of samples in situ in DACs under pressure, or those samples recovered after high-pressure experiments. Saxena introduced us to the high-pressure DAC technique and suggested that Leonid be in charge of the in-house x-ray diffractometer in the Uppsala laboratory. For Leonid, it was an interesting and challenging project to build and bring into operation the
in-house XRD rotating anode-based system equipped with one of the first industrially produced CCD detectors to be used for studies at extreme conditions (figure 4).

High-pressure high-temperature studies make a significant contribution to fundamental physics, chemistry, materials science and Earth and planetary sciences. In Saxena’s group, both geoscience and materials science research fields were equally encouraged. Saxena was among the pioneers in the application of synchrotron radiation for investigations in DACs and actively involved us in the field.

Leonid gained his synchrotron experience first at the Brookhaven National Laboratory and at the Advanced Photon Source (APS) of the Argonne National Laboratory (figure 5) in the USA. Then, in 1996, we were among the first users of the brand new, third-generation synchrotron in Grenoble (France)—the European Synchrotron Radiation Facility (ESRF). At that time, the methodology of experiments for obtaining scientifically meaningful results in a DAC was quite limited, and we enthusiastically engaged in the methodological development of synchrotron experiments concerning both their design and data processing.

Figure 3. Academician Prof. V Urusov in his office at Moscow State University on Leninskie Gory with N Dubrovinskaia, Moscow, 2007. Photo courtesy of L Dubrovinsky.

Figure 4. In-house x-ray diffractometer of which Leonid Dubrovinsky was in charge at the Geocentrum in Uppsala. (a) Mao–Bell massive DAC mounted on the goniometer stage. (b) N Dubrovinskaia and L Dubrovinsky at the diffractometer; photo courtesy of Johannes Borgegård, published in Uppsala University Annual Magazine Horizon Uppsala 2002.
At that time, we were particularly interested in building and testing electrically heated DACs—this was especially topical, because laser-heating options were not yet accessible in those times at the ESRF. We introduced graphite heaters, DAC bodies made from special alloys stable at temperatures up to 700°C in air, and the ‘whole cell’ electrical heating assembly for DACs (Dubrovinskaia and Dubrovinsky 2003), which allows the regulation of pressure during heating, achieves temperatures of over 1200 K and provides sufficient cell opening for powder XRD studies at synchrotron beamlines (figure 6). One of the most important results obtained in those times with the help of the electrically heated DAC was the study of the thermal equation of the state of hcp iron up to 300 GPa (Dubrovinsky et al 2000).

In the second half of the 1990s, we were one of the first groups that started actively applying the full-profile refinement for processing high-pressure (and high-temperature) powder XRD data. This was especially productive in the field of high-pressure high-temperature synthesis of novel materials, where we also actively collaborated with theoreticians (figure 7). Our combined theoretical and experimental investigations led, for example, to the discovery of new high-pressure polymorphs of titanium dioxide. We synthesized them at pressures over 60 GPa and 1000 K (Dubrovinskaia et al 2001, Dubrovinsky et al 2001). In situ powder diffraction studies in DACs allow measuring physical properties of materials at extreme conditions, and we determined the bulk moduli of the new phases. The high bulk modulus of one of them, a cotunnite-type structure, correlated well with very high hardness, we measured at low temperature, making this...
oxide the hardest one known. Our results on TiO₂ and the analysis of other available experimental data allowed us to establish that the group IVa dioxides (TiO₂, ZrO₂, HfO₂) on compression at ambient temperature all follow a common path: rutile $\rightarrow$ a-PbO₂-type $\rightarrow$ baddeleyite-type (MI) $\rightarrow$ orthorhombic OI (Pbca) structure $\rightarrow$ cotunnite-type (OII). This contributes to our fundamental understanding of the behavior of materials at extreme conditions.

4. University of Bayreuth: our life under pressure

In 2001, the development of our careers led us to Germany, where both of us joined the Bavarian Research Institute of Experimental Geochemistry and Geophysics (BGI) at the University of Bayreuth, Natalia as guest scientist, and Leonid as a member of the research staff. At first, Leonid built a new in-house x-ray system consisting of three major components: Rigaku FR-D high-brilliance source (x-ray Mo rotating anode), Osmic’s Confocal Max-Flux optics, and SMART APEX 4K CCD area detector (figure 8). At that time, it was probably the most powerful industrially available in-house x-ray source, and the first Mo rotating anode built by Rigaku for Europe (Dubrovinsky et al 2006). The setup was mainly aimed at being used for performing in-house high-pressure experiments in a limited pressure range of up to $\sim$50 GPa and for preparing samples for synchrotron experiments. Although the high-brilliance x-ray setup was not specially designed for single-crystal structural studies, it appeared to be capable of collecting the data from single crystals, and eventually played a significant role in the development of the methodology of single-crystal diffraction studies at very high pressures. Small single crystals with linear dimensions of 7–10 μm were (and still are) tested and selected using this system.

In 2007, Natalia completed her habilitation in crystallography at the Physics Department, obtained the venia legendi, and became Privatdozent at the University of Bayreuth and later at the University of Heidelberg, where she concluded an ‘Umhabilitation’ and worked as a member of the research staff from 2007 to 2011. (It was quite high-pressure commuting twice a week 300 km between
In 2011, after more than four fruitful years of work in Heidelberg, Natalia returned to the University of Bayreuth as Heisenberg Professor for Material Physics and Technology at Extreme Conditions in the Excellence Program of the German Research Foundation (DFG) and Full Professor at the Laboratory of Crystallography. Nevertheless, even during the Heidelberg time, we continued working as a scientific couple and our collaboration was never interrupted: synchrotrons, the APS and ESRF, were our frequent common destinations.

Over years of experiments with DACs at high pressures, we fully realized that in many cases to unambiguously solve structures of new phases, which appear at extreme conditions, one needs single-crystal XRD data, as the capability of powder XRD is limited. Whereas in powder diffraction experiments only the length of the reciprocal space vectors may be determined, single-crystal diffraction also provides information about their orientation, thus making indexing of the diffraction pattern and determination of the space group of the crystal unequivocal.

The first step on the way to extend the pressure range accessible for single-crystal diffraction is to preserve the quality of the single crystals upon compression. In the BGI, our team assembled a gas-loading system (figure 9) able to perform experiments in DACs in quasi-hydrostatic media—solidified, but still soft helium He and neon Ne (Kurnosov et al 2008). By 2010, we had shown that single crystals can survive at megabar pressures and acquiring accurate single-crystal XRD data at such pressures is possible (Dubrovinsky et al 2010). On
synchrotrons, at the end of the 2000s, a high-pressure single-crystal XRD data collection strategy was enthusiastically developed and pushed forward by Przemyslaw Dera and Vitali Prakapenka at the APS and Michael Hanfland and Marco Merlini at the ESRF.

In solid-state physics, pressure-induced phase transformations are likely among the most exciting phenomena to be observed. However, like pressure-induced chemical reactions, they are often hindered due to kinetic barriers, and one needs to heat samples, sometimes to thousands of degrees, to initiate and realize the process. Although stationary laser-heating systems were already available on synchrotrons for powder XRD experiments in DACs by the end of 2010s, they were of no use for in situ single-crystal diffraction, which requires rotation of the cell. We first came to the idea to miniaturize the laser-heating system to make it portable, and we combined all optical components in a single laser-heating device that we called a UniHead (Dubrovinsky et al 2009). Then, we mounted the UniHead and a DAC on the common platform, and the whole assembly was placed on the goniometer stage of a one-axis diffractometer at ID09A at the ESRF with great support and enthusiasm of Dr M Hanfland, who was responsible for the beamline. As a result, it became possible to simultaneously rotate the cell with a crystal and heat the latter, while the single-crystal XRD data were collected (Dubrovinsky et al 2010) (figure 10). In order to make the heating homogeneous, we eventually applied a combination of two UniHeads for double-sided laser heating (figure 11) (Kupenko et al 2012). Thus, we could demonstrate that single-crystal XRD is technically possible at megabar pressures and temperatures of thousands of degrees (Dubrovinsky et al 2010, Kupenko et al 2012).

Now, we have introduced portable laser-heating setups at various beamlines (ID24, ID18, ID15) at the ESRF and the Extreme Conditions beamline at PETRA III, DESY, Hamburg (figures 11, 12). This development meets the demand of rapidly growing areas of DAC applications—not only single-crystal and powder XRD, but in-house and synchrotron-based spectroscopic techniques (Mössbauer and Brillouin spectroscopies, inelastic x-ray scattering, nuclear inelastic scattering, etc).

Figure 10. Portable single-sided laser-heating system. (a) Universal laser-heating head (UniHead) (1) with a π-shaper (2) mounted for single-crystal XRD experiments in a DAC at the ID09a beamline at ESRF (Grenoble). Optical fiber (3) is connected to the 100 W laser light source; the silver-coated carbon mirror (4) and the DAC (5) are shown in the inset (green arrow in the inset shows the direction of the laser beam) (reproduced with permission of the International Union of Crystallography (https://journals.iucr.org/) Dubrovinsky et al 2009). (b) L Dubrovinsky runs an experiment at ID09a. Photo courtesy of N Dubrovinskaia.
As part of the methodology of laser heating during single-crystal data collection, two further important problems had to be worked out—the development of optimal DAC and anvil designs. The BX90 cell, which I Kantor and our team constructed and first produced at the BGI (Kantor et al 2012), became a new universal DAC design for XRD and optical measurements, suitable for different kinds of experimental studies under high pressures (figure 13(a)). The main features of the cell are an ultimate 90-degree symmetrical axial opening and high stability, making this cell design suitable for a whole range of techniques from optical absorption to single-crystal XRD studies, also in combination with external resistive or double-sided laser heating. To increase the stability of the diamond
anvils, which are obviously the most important components of a DAC, we suggested a new anvil design—diamond anvils (figure 13(b)) with a spherical support (Dubrovinskaia et al 2012).

We had all these novel devices at hand and instrumental setups installed at synchrotron facilities, yet we had to work out the XRD data collection strategy and data processing protocols. There are many peculiarities to be taken into account in high-pressure experiments. Even the size of the crystals plays a significant role. For example, the thickness of the crystal should be less than the depth of the pressure chamber at the highest expected pressure, as this prevents the crystal from being bridged between the diamonds and thus from being destroyed in the course of the experiment. This means that in DACs designed to achieve pressure of \( \sim 75 \) GPa with standard 250 \( \mu m \) culet diamonds (a typical pressure chamber diameter is about 120 \( \mu m \) and the initial thickness of a Re gasket is about 25 \( \mu m \)), the crystal should be \( \sim 10–12 \mu m \) thick. The use of 120 \( \mu m \) culet beveled diamonds (in order to perform experiments up to \( \sim 150 \) GPa) requires smaller crystals, with a thickness of \( \sim 5–7 \mu m \). The gasket hole shrinks almost twice in diameter upon noble gas loading and compression; therefore, the diameter of the sample should not exceed 30 \( \mu m \) for 250 \( \mu m \) culet diamonds and 10–15 \( \mu m \) for 120 \( \mu m \) ones. An additional constraint is the x-ray beam size—the diffracting volume should be constant or vary predictably during the measurement to provide correct intensities for symmetry-equivalent reflections. Therefore, situations in which the crystal is comparable with the beam size should be avoided—crystals should be either significantly larger or smaller than the beam. The screening of dozens, sometimes hundreds, of crystals is needed to select one with the quality satisfactory for a high-pressure single-crystal XRD experiment (figure 14).

Single-crystal XRD data collection in DACs under pressure is not routine. It requires a special procedure, as the diffraction pattern one can obtain in a DAC is much more complex compared to the one from a crystal free-staying at an ambient pressure. Diamonds, a solidified pressure-transmitting medium, and sometimes a gasket exposed to x-rays give rise to the diffraction spots and lines, which may overlap with the diffraction spots of the sample. A metallic body of the DAC causes a significant part of the reciprocal space to be shadowed, whereas the observable part of the reciprocal space is limited by the opening angle of the DAC which, in practice, does not exceed 80°. The resultant data completeness (i.e. the number of the collected reflections out of the total number of the reflections...
referred to a certain \(d\)-spacing shell) is often twice as low as the 99.5% suggested by the International Union of Crystallography at the 0.8 Å \(d\)-shell. The limited number of available reflections creates problems for the solution of low-symmetry structures and the refinement of anisotropic parameters. Therefore, we worked out a special data collection strategy described in detail in our publications and theses of our PhD students (see, e.g. Bykova2015). For example, to maximize the number of reflections with reliable intensities, one can pressurize several differently orientated crystals of the same kind in one DAC and merge those reflection intensities in specialized software, such as XPREP (implemented in SHELXTL package (Sheldrick 2008) or Jana2006 (Petříček et al 2014). The rectangular flat-panel MAR555 detector installed at ID15B (formerly ID09A) beamline at the ESRF may require the collection of two data sets at different DAC orientations (0° and 90°). To complete Friedel pairs (the reflections with indices \(hkl\) and \(-h-k-l\)), one can collect an additional \(\omega\)-scan from the opposite side of the DAC. The other choice is to collect the data in a fine slice (0.25°–0.5°) scanning mode in which a 3D profile of the reflection can be obtained. If the saturation happens, it affects only one frame out of several in which the reflection occurs; then the overexposed intensity may be ignored, while the true intensity is reconstructed using CrysAlisPro (2013) software from the calculated 3D reflection profile. Both approaches, however, drastically increase the measurement duration, which becomes an important factor during the limited synchrotron beam time.

Naturally, not only the high-pressure single-crystal XRD data collection, but also the data processing is not straightforward. Some challenges of the data processing, especially at the stages of ‘peak hunting’ and indexing of the reflections, are illustrated in a series of figures below (figures 15–19). They show the reciprocal space view for different crystals in various experiments before and after indexing of the reflections.

Figure 15 exemplifies a data set of perfect quality for the indexing of reflections collected from an enstatite calibration crystal used for the refinement of an instrument model for the particular diffractometer before an HP or HPHT experiment. The reflections, which belong to the sample, are clearly visible.
Although diamond reflections (arcs of red dots) are rather strong, automatic indexing using crystallographic software finds the correct unit cell without any problem. Even at quite high pressure of $\sim 48$ GPa, as in figure 16, if a crystal only contracts under pressure in a quasi-hydrostatic pressure medium (Ne), a perfect quality data set can be obtained. Although Ne and diamond reflections are present in the diffraction pattern of compressed Fe$_2$O$_3$, they do not prevent the automatic indexing, which provides the correct unit cell (figure 16). The increase of pressure to 54 GPa on an Fe$_2$O$_3$ crystal leads to a phase transition (figure 17). As soon as the structure modifies, the reciprocal space changes drastically. This is exactly the point where any ‘conventional’ crystallographer would have stopped with the data interpretation, considering them as of unacceptable quality. But high-pressure crystallographers take up the challenge, as for them it is exactly the point where the story just begins (figure 17). Although reflections belonging to a targeted unit cell are hardly recognizable and Ne diffraction lines and diamond reflections are so strong that they have to be ‘cleaned up’ as much as possible prior indexing, the reflections can be indexed manually (figure 17, lower panel, right). The automatic indexing leads to a unit cell with a larger volume (figure 17, lower panel, left), which is not true. After the phase transition, a diffraction pattern of the high-pressure iron oxide HP-Fe$_2$O$_3$ is formed.
due to contributions of the two twin domains related by a symmetry law that is evident from a close inspection of the reciprocal space.

The problem of recognizing individual single-crystal domains becomes a central one after laser heating of a sample. Upon single (figure 18) or multiple laser heating (figure 19) of pressurized materials, high-pressure physics (manifested in solid-state phase transitions) meets high-pressure chemistry (manifested in pressure-/temperature-induced chemical reactions), so that laser-heated samples, as a rule, contain a huge number of crystallites, which create problems in the unit cell search. The automatic indexing has very little (in practice—no) chance to

\[ \text{Figure 17. Reciprocal space view before and after the indexing of reflections of the high-pressure phase of iron oxide, HP-Fe}_2\text{O}_3, \text{ that resulted from a phase transformation of a single-crystal of Fe}_2\text{O}_3 \text{ pressurized in a DAC to 54 GPa. Reflections of the targeted unit cell should be selected manually. No diffraction lines and diamond reflections are so strong that they have to be ‘cleaned up’ prior to indexing. Results of automatic and manual indexing are shown in the lower panel. Reproduced from Bykova 2015. CC BY 3.0.} \]

\[ \text{Figure 18. Reciprocal space view of the high-pressure phase of iron oxide, HP-Fe}_3\text{O}_4, \text{ after laser heating in a DAC at 50 GPa. After heating, the sample recrystallized and a huge number of crystallites appeared. Many domains are rather intense. For successful indexing, reflections from individual domains have to be selected manually. Reproduced from Bykova 2015. CC BY 3.0.} \]
give a meaningful result. The proper unit cell can be found only if one selects peaks manually in the reciprocal space viewer or harvests peaks, also manually, from the reflection images, which requires certain skills and patience. Multifaceted physical and chemical phenomena complicate the diffraction pattern to such an extent that untangling the reciprocal space (figures 18, 19) becomes an art supported by a deep knowledge of physics, chemistry and crystallography, as well as long-term experience and scientific intuition.

Complete data processing results in the structure solution and refinement. It is important to underline that in situ HPHT single-crystal XRD is capable of solving problems, which cannot be solved by powder XRD despite all the achievements of the Rietveld method (Rietveld 2014). In particular, only single-crystal data enable determining both the phase and chemical composition of samples under extreme conditions, to solve and refine the structure unambiguously, and provide definite information regarding bond lengths, which is crucial for determining the structure type and oxidation state of the atoms. The alteration of atomic bond lengths and angles, breaking of chemical bonds and changes in the crystal symmetry generally lead to drastic changes in the electronic and magnetic properties of solids experiencing extreme high-pressure high-temperature conditions. High-pressure crystallography thus contributes to the fundamental understanding of the behavior of materials at extreme conditions, which has important implications for various fields of science and technology. It helps to answer many questions, some of which have been addressed very recently and are depicted below in a very popular form.

4.1. What about crystal chemistry at HP and HT?

Isn’t it fascinating to learn that the world is much richer than previously thought? Indeed, at ambient conditions only three iron oxides are known (FeO, Fe₂O₃ and Fe₃O₄, figure 20), but high pressure and high temperature initiate a series of enigmatic structural, electronic and magnetic transformations in these chemically very simple materials (figure 21). Single-crystal XRD and synchrotron Mössbauer source spectroscopy at pressures over 100 GPa and temperatures above 2500 K provided us with the structural data necessary to correctly describe and understand these transformations (Bykova et al 2016). Crystal-chemical analysis of structures of mixed-valence Fe(II, III) oxides showed their fundamental relationships and
demonstrated that they can be described by the homologous series $nFeO \cdot mFe_2O_3$ (figure 21).

4.2. What is happening in the Earth’s interior?

Isn’t it necessary to take into account all possible factors while interpreting what is going on in the Earth? Indeed, high-pressure high-temperature experiments allow us to reconstruct the behavior of the iron oxides inside the Earth’s mantle and suggest that mixed-valence iron oxides may play a significant role in oxygen cycling between earth reservoirs. $Fe_2O_3$ (hematite) and $Fe_3O_4$ (magnetite) are the major components of banded iron formations (BIFs) and ironstones—huge sedimentary rock formations occurring on all continents. Deposited in the world’s oceans, BIFs as part of the ocean floor are recycled into the Earth’s interior by subduction to depths extending possibly to the core–mantle boundary region. Decomposition of $Fe_2O_3$ and $Fe_3O_4$ observed in our experiments at pressures above 60 GPa and temperatures of 2000 K (Bykova et al 2016), which correspond to 1500 km below the surface of the Earth, leads to crystallization of unusual $Fe_7O_{17}$ and $Fe_{25}O_{32}$ phases (figure 20) with release of oxygen. The quantities of oxygen involved are tremendous. Based on the estimated rate at which BIFs are subducted, the decomposition of hematite alone could have produced $8–10$ times the mass of oxygen in the modern atmosphere over about two billion years. Under the conditions found in the Earth’s lower mantle, we believe that this oxygen would
exist in liquid state. Over time, this might have formed an enormous—and previously unimagined—reservoir of oxygen-rich fluid deep in the Earth’s interior. This is in itself a fascinating idea, but it also means that ideas about the geochemical processes in the Earth’s interior will need substantial rethinking. In the presence of so much oxygen, the oxidation states of the elements in the lower mantle—and thus the chemical reactions between them—will be very different to what scientists have imagined. Furthermore, as it moves, the oxygen-rich fluid will transport with it other compounds, including the many trace elements present in the Earth’s interior, giving a very different chemical distribution to what has previously been assumed. Any global models of the past and future of the Earth, including models of climatic evolution, should take the new findings into account (Capellas 2016). For example, problems of CO$_2$, other greenhouse gases, water, etc, in the atmosphere are widely discussed, but these discussions insufﬁciently cover deep geochemical processes, which contribute to atmospheric composition. Thus, the inﬂuence of humans on global planetary processes may be considerably overestimated.

4.3. Is the physics theory right?

Isn’t it important to learn whether we comprehend the world and its laws correctly? Indeed, experimental validation of theoretical predictions reveals the degree of our up-to-date comprehension of condensed matter and further promotes the development of solid-state physics and chemistry. Theoretical predictions of pressure-induced phase transformations often become long-standing enigmas because of the limitations of experimental possibilities currently available. The existence of a nonicosahedral boron allotrope has been one of them. A nonicosahedral boron allotrope, $\zeta$-B, with the orthorhombic $\alpha$-Ga-type structure (space group $Cmce$), as predicted, was recently synthesized in a DAC at extreme high-pressure high-temperature conditions (115 GPa and 2100 K) (Chuvashova et al 2017a). The structure of $\zeta$-B was solved using in situ single-crystal synchrotron XRD (figure 22).

4.4. Does it contract or expand?

Isn’t it important to know how things work and why? Indeed, mechanisms of the compression of materials and the limits of their stability are studied to learn how they will behave at variable PT conditions. This is especially important for industrially used materials, such as, e.g. boron carbide. The mechanism of its compression could not be fully clarified until recently, when in situ single-crystal
high-pressure synchrotron diffraction measurements were realized. Our analysis has shown that, in agreement with the modern understanding of bonding in α-B, γ-B and B13C2 (figure 23) based on the experimental electron-density studies (Mondal et al. 2011, Mondal et al. 2016), the compressional behavior of these boron allotropes and boron carbide depends on the types of bonding involved in the course of compression, so that the ‘effective compressibility’ of B12 icosahedra may vary in a broad range, from ca. 14% in α-B to ca. 18% in B13C2, compared to ca. 18% compression of the corresponding crystals (Chuvashova et al. 2017).

4.5. Should we pressurize... aminoffite?

Isn’t it great that high-pressure crystallography is capable of handling the structures of such complexity as aminoffite? Indeed, on the reverse side of the Gregory Aminoff medal (figure 24(a)), a crystal of the mineral named after Aminoff, aminoffite, is shown. This very rare mineral (Ca3Be2Si3O10( OH)2) was detected in the mineral deposit in Långban in Värmland, Sweden. It contains beryllium and serves as a symbol for Aminoff’s achievement in pointing out the great importance of beryllium minerals for the distinctive mineralogy of Långban (Olovsson 2014). As a matter of curiosity, we pressurized aminoffite in a DAC. The sample used in this work (figure 24(b)) was from the same location (Långban, Sweden) as in previous structural studies at ambient conditions (Huminicki and Hawthorne 2002). We took two fragments with approximate sizes of 0.01 × 0.01 × 0.07 mm³ of the rather large (~0.5 mm in the largest dimension), transparent, pale yellow, subhedral aminoffite crystal (figure 24b). Both of these small crystals were tested in-house at BGI at the three-circle Bruker diffractometer, described above, equipped with a SMART APEX CCD detector and a high-brilliance Rigaku rotating anode (Rotor Flex FR-D...
Mo-Kα radiation) with Osmic focusing x-ray optics. The lattice parameters, \(a = 9.8091\) (9) Å and \(c = 9.8438(8)\) Å, are in good agreement with the previous report (Huminicki and Hawthorne 2002). The selected crystals together with small ruby chips (for pressure estimation) were loaded into a BX90-type DAC equipped with Bohler–Almax-type anvils with culets 250 μm in diameter. A hole ∼110 μm in diameter was drilled in a Re gasket, pre-indented to the thickness of ∼25 μm, and served as a pressure chamber. Neon loaded at 1.1 kbar was used as a pressure-transmitting medium. The single-crystal high-pressure XRD experiments were conducted on the ID15b beamline at the ESRF in Grenoble (the MAR555 detector and \(\lambda = 0.4108\) Å). XRD images were collected during rotation of the DAC from −38° to +38° on \(\omega\)-axis with a step of 0.5°. Integration of the reflection intensities and absorption corrections were performed using CrysAlisPro software (2014). The structures were solved by the direct method and refined in the anisotropic approximation by full matrix least squares refinements using SHELXS and SHELXL software (Sheldrick 2008), respectively. Tables 1–3 summarize the experimental results for two pressure points—at 1.6(1) GPa (the first pressure point), and at 24.3(4) GPa (the 9th data point in the row and the last one before the quality of the crystals significantly decreased in the course of a phase transition, which will be described elsewhere). The total number of accumulated reflections was above 2300 even at 24 GPa, and about 1000 reflections were used for structural refinement. The \(R_1\) factors converged rapidly to 4.7% at 1.6 GPa, and to 8.0% at 24 GPa for a model including anisotropic-displacement parameters for all non-hydrogen atoms. The number of refinable parameters is 93 (in anisotropic approximation), and this means that on one determined parameter there are more than ten observables. The good quality of the data resulted in meaningful thermal vibration parameters (tables 2, 3).

The structure of aminoffite at 1.6 GPa is almost the same as at ambient conditions (figure 25), taking into account just a small (by about 0.5%) unit cell parameter contraction. There are two Ca positions, Ca1 and Ca2, on which calcium atoms are 7- and 8-coordinated, respectively. For Ca1 coordinating atoms there are six O atoms and one (OH) group, for Ca2—there are six O atoms and two (OH) groups. The average \(\text{(Ca–O)}\) distances are 2.455 and 2.428 Å for Ca1O7.
Table 2. Atomic coordinates and displacement parameters for aminof at 1.6 GPa.

| Site | x      | y      | z      | U_{eq} | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} | U_{33} | U_{12} |
|------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Ca1  | 0.06214(5) | 0.04275(5) | 0.25862(6) | 0.00746(15) | 0.0093(3) | 0.0065(3) | 0.0066(3) | −0.00096(14) | −0.00088(13) | 0.00221(15) |
| Ca2  | 0.2500 | 0.7500 | 0.25921(8) | 0.00592(17) | 0.0058(3) | 0.0058(3) | 0.0061(4) | 0.0000 | 0.0000 | 0.000060(19) |
| Si1  | 0.03734(7) | 0.76342(7) | 0.02955(8) | 0.00489(17) | 0.0050(3) | 0.0050(3) | 0.0046(4) | 0.0002(2) | −0.00079(19) | −0.00002(2) |
| Si2  | 0.2500 | 0.2500 | 0.00927(11) | 0.0053(2) | 0.0054(5) | 0.0042(4) | 0.0063(6) | 0.0000 | 0.0000 | −0.00004(3) |
| Be   | 0.03683(3) | 0.76853(3) | 0.5253(4) | 0.0065(6) | 0.0049(14) | 0.0062(14) | 0.0085(19) | 0.0013(9) | −0.0002(9) | −0.00004(9) |
| O1   | 0.37253(19) | 0.60949(19) | 0.0865(2) | 0.0074(3) | 0.0073(9) | 0.0075(9) | 0.0073(10) | 0.0015(6) | −0.0002(6) | −0.00020(5) |
| O2   | 0.10405(19) | 0.62423(18) | 0.0929(2) | 0.0068(3) | 0.0079(8) | 0.0046(8) | 0.0079(10) | 0.0005(5) | 0.0004(6) | 0.0014(5) |
| O3   | 0.23166(19) | 0.38653(18) | 0.1008(2) | 0.0070(3) | 0.0086(9) | 0.0057(8) | 0.0068(10) | 0.0003(5) | 0.0011(6) | 0.0010(6) |
| O4   | 0.61826(19) | 0.72563(19) | 0.0920(2) | 0.0081(3) | 0.0049(9) | 0.0117(9) | 0.0076(10) | 0.0007(6) | −0.0009(5) | 0.0004(6) |
| O5   | 0.79092(2) | 0.4662(2) | 0.1380(2) | 0.0108(4) | 0.0162(10) | 0.0091(9) | 0.0069(11) | −0.0010(6) | −0.0002(6) | 0.0010(6) |
| O6   | 0.96697(18) | 0.23285(18) | 0.1348(2) | 0.0067(3) | 0.0072(8) | 0.0073(8) | 0.0056(10) | 0.0005(5) | −0.0007(5) | −0.0004(6) |
| H    | 0.750(5) | 0.535(6) | 0.185(8) | 0.048(16) |
Table 3. Atomic coordinates and displacement parameters for aminofite at 24 GPa.

| Site | x     | y     | z     | \(U_{eq}\) | \(U_{11}\) | \(U_{22}\) | \(U_{33}\) | \(U_{23}\) | \(U_{13}\) | \(U_{12}\) |
|------|-------|-------|-------|------------|------------|------------|------------|------------|------------|------------|
| Ca1  | 0.0580| 0.0355| 0.2548| 0.0084(3) | 0.0102(5)  | 0.0054(5)  | 0.0097(6)  | 0.0004(2)  | −0.0006(2) | 0.0027(2)  |
| Ca2  | 0.2500| 0.7500| 0.2603| 0.0069(3) | 0.0072(6)  | 0.0030(6)  | 0.0103(8)  | 0.00000    | 0.00000    | 0.0010(3)  |
| Si1  | 0.0338| 0.7664| 0.0289| 0.0070(4) | 0.0061(6)  | 0.0054(6)  | 0.0096(8)  | −0.0003(3) | −0.0002(3) | −0.0002(3) |
| Si2  | 0.2500| 0.2500| 0.0046| 0.0087(4) | 0.0082(8)  | 0.0057(8)  | 0.0122(12) | 0.00000    | 0.00000    | 0.00000    |
| Be   | 0.0319| 0.7763| 0.5208| 0.0073(10)| 0.002(2)   | 0.011(2)   | 0.010(3)   | −0.0023(15)| −0.0004(14)| 0.0002(13)|
| O1   | 0.3648| 0.6081| 0.0788| 0.0092(6) | 0.0082(13) | 0.0087(14) | 0.0108(17) | 0.0016(9)  | −0.0004(9) | −0.0043(8) |
| O2   | 0.0937| 0.6207| 0.0925| 0.0097(6) | 0.0101(14) | 0.0074(13) | 0.0116(17) | 0.0019(9)  | −0.0002(9) | 0.0035(8)  |
| O3   | 0.2236| 0.3852| 0.1035| 0.0077(6) | 0.0106(14) | 0.0050(13) | 0.0076(16) | 0.0022(8)  | 0.0011(9)  | −0.0005(8) |
| O4   | 0.6199| 0.7105| 0.1072| 0.0100(6) | 0.0060(13) | 0.0123(15) | 0.0117(17) | 0.0023(10) | 0.0021(9)  | −0.0010(9) |
| O5   | 0.7966| 0.4729| 0.1490| 0.0094(6) | 0.0126(14) | 0.0073(13) | 0.0083(17) | −0.0024(9) | −0.0003(9) | 0.0034(8)  |
| O6   | 0.9724| 0.2306| 0.1429| 0.0089(6) | 0.0043(12) | 0.0078(13) | 0.0145(19) | −0.0009(9) | −0.0023(9) | −0.0006(8) |
| H    | 0.7755| 0.5276| 0.2108| 0.005(12) |
and Ca\textsubscript{2}O\textsubscript{8} polyhedra, respectively. Both of these values are by about 0.5% smaller than those at ambient conditions, and $\langle \text{Ca}_1\text{-O} \rangle$ is bigger than $\langle \text{Ca}_2\text{-O} \rangle$, despite the fact that the coordination number of Ca\textsubscript{2} is larger. Notably, the atomic displacement parameter for Ca\textsubscript{1} is larger than that for Ca\textsubscript{2}. Huminicki and Hawthorne (2002) suggested that at ambient conditions oxygen polyhedra are slightly ‘too large’ for Ca and the cation is ‘rattling’ in them. The same is probably true for the structure at 1.6 GPa. Notably, average cation-anion distances for two crystallographically different silicone atoms, Si\textsubscript{1} (1.626 Å) and Si\textsubscript{2} (1.629 Å), and for Be (1.642 Å), which are tetrahedrally coordinated by O atoms (or O and OH groups in the case of Be), change very little on compression to 1.6 GPa—just by about 0.25%.

On compression to 24 GPa the structure of aminofite alters considerably (tables 1–3; figure 25). The lattice parameter ratio $c/a$ decreases from 1.004 to 0.975, indicating an anisotropic compression of the mineral’s structure. As expected, longer interatomic distances shrink easily. The average $\langle \text{Ca}-\text{O} \rangle$ lengths are 2.134 Å (decrease by 13.5%) and 2.341 Å (decrease by 3.9%) for Ca\textsubscript{1}O\textsubscript{7} and Ca\textsubscript{2}O\textsubscript{8}, respectively; the ADPs of Ca\textsubscript{1} and Ca\textsubscript{2} become similar within the measurement uncertainties. Tetrahedra with high-charged silicon cations are compressed notably less than BeO\textsubscript{4} tetrahedra—at 24 GPa, the average $\langle \text{Si}_1\text{-O} \rangle$ is equal to 1.586 Å and $\langle \text{Si}_2\text{-O} \rangle$ to 1.600 Å (decrease by about 2.5%), while the average $\langle \text{Be}-\text{O} \rangle$ is equal to 1.582 Å (decrease by $\sim$3.8%). As a result of the different degree of contraction of BeO\textsubscript{4} and SiO\textsubscript{4} polyhedra, flat sheets of tetrahedra in aminofite at ambient conditions become ‘wavy’ at 24 GPa (figure 25).

![Figure 25. Structure of aminofite at 1.6 GPa (a), (b) and at 24 GPa (c), (d) projected onto (001) (a), (c) and (010) (b), (d) planes. SiO\textsubscript{4} tetrahedra are colored olive, BeO\textsubscript{3}(OH) tetrahedra are turquoise, oxygen atoms are red, calcium are magenta and hydrogen atoms are green.](image-url)
The assignment of OH to O5 anion in aminofite was first made on the basis of calculation of the bond-strength sum around O5 (Coda et al 1967). Bonding to 7- and 8-coordinated Ca atoms and a 4-coordinated Be atom gives \( \frac{2}{7} + \frac{2}{8} + \frac{2}{4} = 1.04 \text{ vu} \) (valence units), thus according to the valence-sum rule, Pauling’s second rule, the O5 anion requires additional bond-valence from the H atom. In our structure refinement at 1.6 GPa, the hydrogen atom was located on a difference-Fourier map, \(~\sim 1\ \text{Å} \) from the donor atom O5, similarly to Huminicki and Hawthorne (2002). With the data collected at 24 GPa it was not possible, so we used the H coordinates obtained at 1.6 GPa as starting ones for the high-pressure point. We refined the location of hydrogen atoms at 1.6 and 24 GPa without imposing any additional constraints (tables 2, 3; figure 25). This resulted in the decrease of \( R_1 \) factors by about 0.1% for both of the pressure points. At low pressure, the H position is in agreement with that reported by Huminicki and Hawthorne (2002). There is an indication that the O5-H bond slightly shortens upon compression (from about 0.98(3) Å at 1.6 GPa to 0.78(7) Å at 24 GPa). At ambient conditions, the hydrogen-bond acceptor atom was determined to be the O4 atom (Huminicki and Hawthorne 2002), and the hydrogen bond to be bifurcated between two symmetrically equivalent O4 atoms at the distances of 2.36 and 2.39 Å. The same scheme is true for the structure at 1.6 GPa, but at 24 GPa the two O4–H distances are quite different, 1.88 and 2.43 Å. Thus, only one
of the O4 atoms, at the closer distance of 1.88 Å, is involved as the hydrogen-bond acceptor atom in the O5-H...O4 hydrogen bond with the angle of 155° (figure 25).

Thus, the example of aminofite demonstrates that high-pressure crystallography is ready to make a new step forward and enables not only the characterization of structural motifs in compressed solids and the identification of the chemical composition of the products of reactions in laser-heated DACs in situ, but becomes an instrument capable of fully describing the geometry of atomic arrangements including light atoms. It opens perspectives for systematic studies of a large group of complex compounds at elevated pressures and temperatures with an ultimate goal of finding regularities in relations between compositions, structures, properties and thermodynamic parameters of measurements. Still, we would like to emphasize that the location of light atoms (especially hydrogen) requires experimental data of very high quality, which are difficult to get in DACs, and even the best quality data do not allow us to locate light elements as precisely as heavier ones.

High-pressure crystallography, nowadays, is the scientific field in which the pace and breadth of discovery and innovation is unprecedented. Among physical and chemical phenomena yet to be explored and addressed at extreme conditions, there are for instance the unconventional synthesis of novel materials, new chemistry and physics at ultra-high pressures and temperatures previously unachievable in static compression, metallization of dielectrics, including hydrogen, transformations of metals to dielectrics, high-temperature superconductivity, and many others, of which we have just mentioned a few. Our experience makes us feel that there are many things to come in high-pressure crystallography. The honorary prize we received (figures 26, 27) marks a milestone in our chosen line of research.

Acknowledgments

We are highly grateful to the Royal Swedish Academy of Sciences for the Award. We thank the editor-in-chief of Physica Scripta Suzy Lidström for inviting us to write this contribution. We greatly appreciate the enthusiasm and support of our research colleagues and co-authors all over the world and members of the technical staff at the University of Bayreuth. We thank our former and present PhD students for their dedication and passion; we used some material of our common publications with I Kantor, A Kantor, K Glazyrin, G Parakhonskiy, E Yu Zarcechnaya, I Kupenko, O Narygina, E Greenberg, V Potapkin, C Prescher, E Bykova, M Bykov, N Solopova, L Ismailova, A Černok, V Cerantola, I Chuvashova, G Aprilis and S Chariton. Special thanks to E Bykova for some material and drawings from her PhD thesis that we showed in this paper. We thank Ulf Hålenius of Naturhistoriska riksmuseet, Stockholm, for providing us with a sample of aminofite (catalog No. NRM19883823) for a high-pressure study. Financial support of the German Research Foundation (DFG) and the Federal Ministry of Education and Research, Germany (BMBF) is gratefully acknowledged.

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