Laboratory high-pressure single-crystal x-ray diffraction—recent improvements and examples of studies

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Abstract
Some recent improvements made to the high-pressure single-crystal x-ray diffraction (XRD) experiments in use in our laboratory are reviewed. In particular a set-up to perform high-pressure (0–3.0 GPa)–low-temperature (300–9 K) investigations as well as a protocol for high-pressure XRD data collection using a CCD detector are shown. Examples of studies are also presented.

(Some figures in this article are in colour only in the electronic version)

Abbreviations

TMTSF	tetramethyltetraselenofulvalene
TRP	tris(1-(2-azolyl)-2azabuten-4-yl)amine
TseT	tetraselenotetracene
XRD	X-ray diffraction

1. Introduction

The study of the structure–property relationship in the solid state is a preliminary step in the design of new materials with physical properties that fulfil industrial requirements. In this context, the determination by x-ray diffraction (XRD) of the structural properties of molecular materials at high pressure is a stimulating but still rare experiment. Indeed, very few crystal structures of molecular compounds at high pressure are available in the literature, despite more and more physical properties being characterized as a function of pressure.

In our group, we have developed a laboratory high-pressure single-crystal XRD experiment. Single crystals can be studied up to an *in situ* pressure of 3.0 GPa at room

Figure 1. View of the vertical Weissenberg camera (left) and the Huber diffractometer (right), each with their cryostat.

temperature. This set-up has been used in the last decade to study the pressure dependence of the structure–property relationship in molecular conductors [1] and in spin crossover complexes [2]. However, access to such an investigation is still difficult due to the perturbations induced by the pressure cell on data collection and processing. In order to increase the accessible temperature range and to increase the feasibility of such experiments, we have recently modified the set-up. In this paper, two recent improvements are presented. The first concerns the possibility of performing high-pressure–low-temperature XRD experiments and the second concerns the use of a CCD x-ray detector to collect the Bragg peaks.

2. High-pressure XRD studies at low temperature

2.1. Experimental details

In this section the experimental techniques in use in our laboratory for room-temperature high-pressure XRD studies and XRD studies at ambient pressure and very low temperature are first recapitulated. Then the improvement made to obtain coupling between both techniques is described.

2.1.1. Pre-existing x-ray set-up

X-ray apparatus. X-ray diffraction experiments under extreme conditions are performed using a commercial Huber three-circle diffractometer as well as a locally built vertical Weissenberg camera (figure 1). The latter differs from a commercial Weissenberg camera by the rotation axis, which is vertical. Very sensitive films are used and only a few minutes or a few hours exposure are necessary for a Bragg or a Weissenberg film respectively, even with weakly diffracting crystals. It is worth noting that this camera is also easily convertible into a Laue camera, which may be useful for investigating low-temperature phenomena. For both types of apparatus, an electron impact generator (30 mA $\times$ 50 kV) with Cu Kα_1 radiation
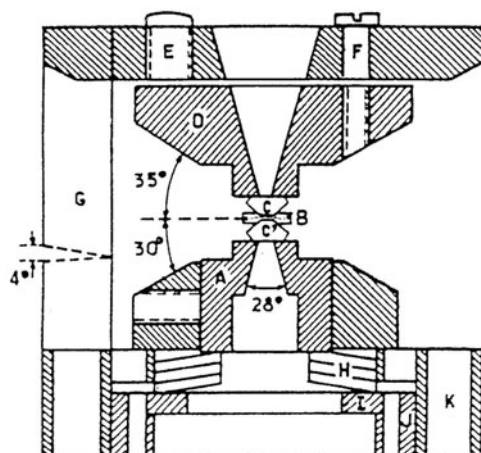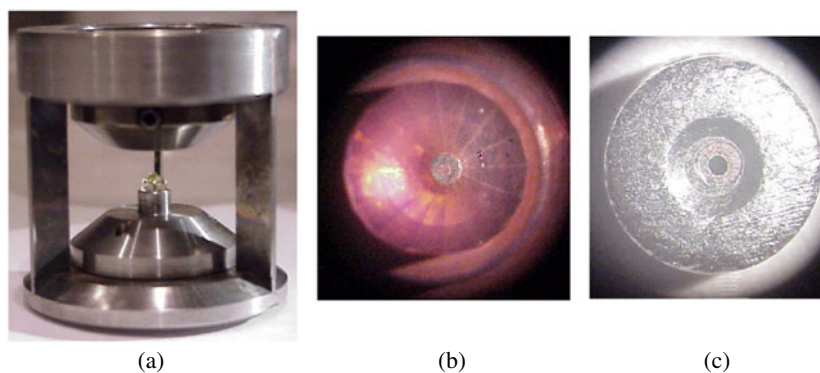
Figure 2. The high-pressure cell (4 cm high), diamond anvils (C) and beryllium gasket (B).

(1.5418 Å) is used. The closed-cycle He Displex cryostats mounted on both types of apparatus allow them to be cooled down to 7 K.

XRD low-temperature environment.   The single crystal is enclosed in a beryllium container (25 mm diameter, 0.5 mm thick) filled with He gas that is surrounded by a second Be container (40 mm diameter, 0.5 mm thick) which constitutes the vacuum chamber. Air-tightness is maintained by indium gaskets. The two Be containers are separated by a thermal screen made of Mylar. When cooling, the crystal moves upwards due to thermal contraction of the cold finger onto which it is glued (it moves up by around 0.6 mm as temperature is increased from 300 to 9 K). The x-ray collimator is mounted on a goniometer head in order to align the crystal in the beam whatever the temperature. The cryostat may also translate vertically (a few centimetres) in order to eventually correct the position of the crystal in the x-ray beam.

XRD pressure cell.   The XRD high-pressure cell (figure 2) is a Ahsbahs type cell [3] with some local modifications [4]. This cell is based on two diamond anvils which press on a beryllium gasket in which a 0.3 mm diameter cylindrical hole forms the high-pressure cavity. This kind of cell is particularly suitable for the study of materials that may diffract weakly [5], which is often the case for the molecular materials that we study. The pressure cavity is a cylindrical hole (0.5 mm high, 0.3 diameter) in a Be gasket (figure 3). This pressure hole, which contains the single crystal, is filled with a pressure-transmitting fluid; the applied pressure is thus hydrostatic. An interesting feature of this cell is that the x-ray beam goes through the gasket and not through the diamonds. Consequently, the cell geometry offers a wide diffracting angle of 342° rotation together with a relatively low absorption of the incident and diffracting x-ray beams. The dimensions of the single crystal must not exceed 80% of the volume of the high-pressure cavity at ambient pressure in order to avoid damage when the pressure cavity is closed and pressed. A classical volume for the investigated crystal is around 0.007 mm^3, even though we have already used sample volumes 10 times smaller. The maximum pressure value is around 3.0 GPa with an accuracy of 0.05 GPa. The *in situ* pressure value is obtained using a deposited thin film of nickel dimethylglyoxime known for the linear dependence of its light absorption properties as a function of pressure [6].

Figure 3. (a) The high pressure cell (4 cm high), (b) top view of a diamond anvil (4 mm diameter) and (c) top view of the pressure cavity (0.3 mm diameter) inside the Be gasket.
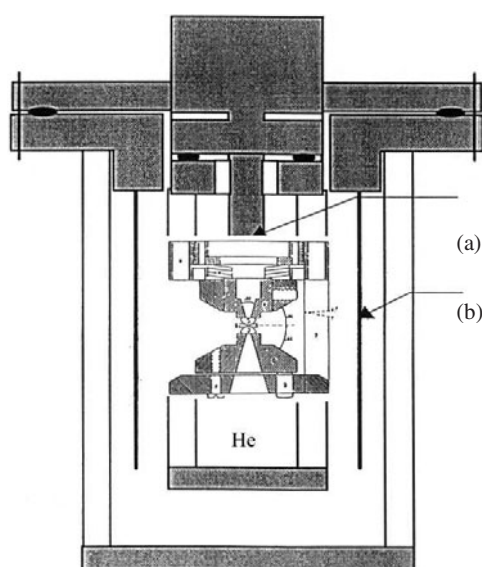
Figure 4. View of the pressure cell mounted into the low-temperature containers: (a) cold finger, (b) mylar.

2.1.2. Coupling high pressure and low temperature.   To set up high-pressure–low-temperature experiments we used the above-described x-ray apparatus and pressure cell. The latter being introduced in a low-temperature environment analogous to the previously described one but with larger dimensions (figure 4). Such a set-up allows XRD experiments in the pressure range 0–3.0 GPa coupled to the temperature range of 300–7 K. Nevertheless, the temperature is measured on the cold finger and not in the pressure cell. This point must be improved. Trials were performed to check the behaviour of the high-pressure cell at very low temperatures; neither loss nor increase in the pressure was observed during cooling to 7 K. Despite the diffracted x-ray beam going through three beryllium walls, absorption of the x-ray beam appears to be weak. Alignment of the single crystal in the x-ray beam is tricky and requires a fine adjustment. However, such a high-pressure–low-temperature environment gave satisfactory results, as proved by the following examples of our investigations.

2.2. Examples of high-pressure XRD studies at low temperature

We used the high-pressure–low-temperature XRD apparatus to complete the phase diagram of two molecular conducting salts. Only the main conclusions of these experiments are summarized here, detailed results and discussions being referenced for further information.

2.2.1. The molecular superconducting salt $(TMTSF)_2ClO_4$

Physical properties. This compound is the first Bechgaard salt to become superconducting at ambient pressure at low temperature. Indeed at 24 K and ambient pressure it undergoes a metal–superconductor transition corresponding to an ordering of the ClO_4^- anion. The latter induces a $(0, 1/2, 0)$ superstructure. The pressure dependence of the transition temperature is controversial. Indeed, measurements [7] and magnetoresistance investigations [8] showed inconsistent results concerning the possibility of anion ordering at a pressure higher than 0.5 GPa at low temperature. The determination of the crystal structure in such conditions can arbitrate in the debate.

Structural properties. The crystal structure of $(TMTSF)_2ClO_4$ was thus determined at low temperature (7 K, 1 bar) and at low temperature and high pressure (7 K, 0.5 GPa) [9]. This salt crystallizes in the triclinic space group $P\bar{1}$ whatever the conditions. At room temperature, the unit cell contains two TMTSF cations and one anion. The cations stack along the a direction in a zigzag mode. TMTSF columns make sheets separated by the anions. The latter show a statistical disorder. At (7 K, 1 bar), superstructure reflections correspond to the doubling of the b parameter. Such doubling of the unit cell coincides with the ordering of the anion. On the contrary, at (7 K, 0.5 GPa) no superstructure reflections are observed and thus the anion remains disordered. Consequently, this study showed that, at low temperature, the application of high pressure prevents ordering of the anion.

2.2.2. The metallic molecular salt $(TseT)_2Cl$

Physical properties. At ambient pressure, this compound behaves as a metal down to 26 K, then undergoes a transition to a semi-metallic state. The application of pressure induces an abrupt transition at 0.5 GPa to another metallic state [10], which suggests a structural rearrangement. We aimed to confirm and characterize this structural rearrangement.

Structural properties. The crystal structure of this compound was determined at (7 K, 1 bar), (300 K, 0.7 GPa) and (7 K, 0.7 GPa) [11] and compared with the crystal structure at ambient conditions. At (7 K, 1 bar) no evidence for a metal to semi-metal transition is noticed as the crystal structure is very similar to the room-temperature one, with even stronger intermolecular interactions. The application of pressure induces, at any temperature, a structural phase transition with a change of symmetry (from tetragonal $P4_2/n$ to orthorhombic $P2_12_12$). The structural rearrangement corresponds to the migration of half of all the chloride anions that then appear aligned at high pressure (figure 5). Such a migration is driven by the high density of the TseT packing. Interestingly, the temperature has no effect on the structural rearrangement at high pressure.
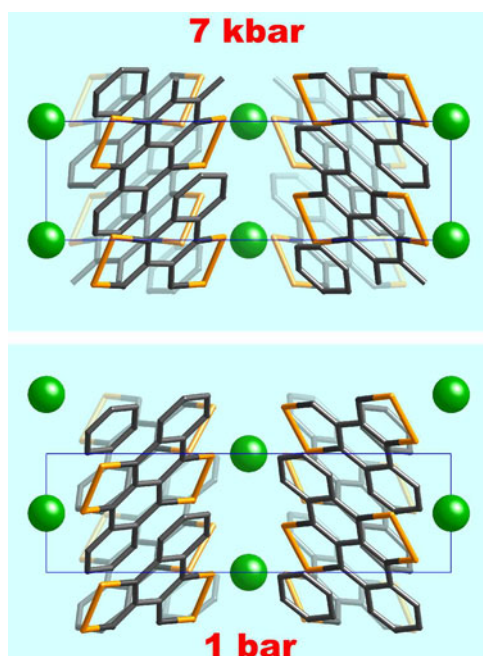
Figure 5. View along *b* of the crystal structure of (TseT)$_2$Cl at 7 K as a function of pressure.

## 3. High-pressure XRD studies using an area CCD detector

3.1. Experimental details

The high-pressure XRD cell described above is particularly easy to fit onto a commercial diffractometer as the cell can be directly mounted on a classical goniometer head (figure 6). The main difficulties in using a CCD detector appeared first in the centring of the crystal in the x-ray beam and also in the image processing. Acceptable centring of the crystal has been obtained by monitoring the intensity of crystallographically equivalent reflections using the movement of the goniometer head. The CCD images are perturbed by the pressure cell itself and the beryllium gasket (figure 7). In this context, the accuracy of the first determination of the unit cell, used later to index the images, is crucial. With this aim, Bragg peaks were first extracted manually from the images. Once the unit cell is well determined the image integration must take into account that the intensity of some reflections may be wrong due to the beryllium rings, the steel frames of the cell or some diamond diffraction peaks. A specific means of data processing was then designed. A first trial, presented below, gave satisfactory results.

3.2. Example of study: the Mn(III) spin crossover complex [Mn(TRP)]

XRD study of spin crossover complexes is very rare despite the strong pressure dependence of the magnetic features such as the temperature of transition, the hysteresis width and the abruptness of the transition [12]. Very few high-pressure crystal structures of spin crossover complexes have been determined so far and they all concern iron(II) complexes [13]. One of the main reasons for this is the weak diffraction pattern generally shown by these complexes. The use of a CCD x-ray detector may make such investigations more feasible. In order to
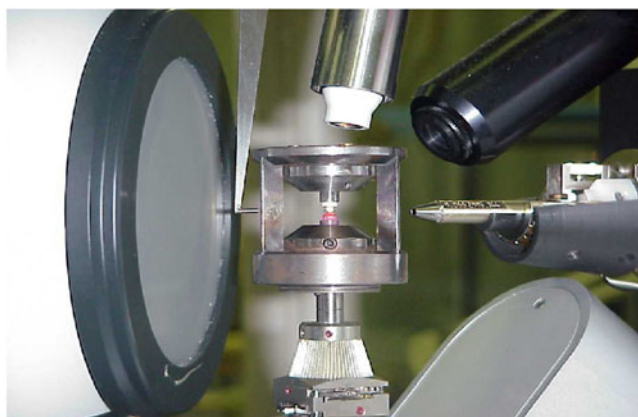
**Figure 6.** View of the high-pressure cell mounted on a Nonius k-CCD.
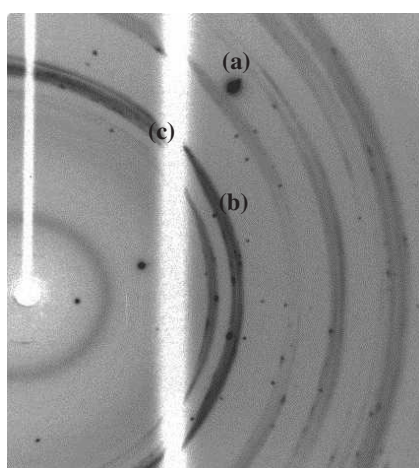
Figure 7. X-ray diffraction frame obtained with a sample in the pressure cell showing the diamond diffraction (a), beryllium ring (b) and shadow of the pressure cell (c).

test the above set-up, we decided to investigate first a spin crossover complex that shows a high crystal symmetry. The Mn(III) spin crossover complex, denoted [Mn(TRP)], shows a cubic symmetry, which is quite unusual in molecular spin crossover complexes. This complex undergoes a spin crossover at 43 K [14]. The magnetic behaviour under pressure has not been reported so far.

The crystal structure was determined at 0.16 GPa and at 1.0 GPa with a structural quality criterion ($R_{obs} = 4.6\%$ and 3.9% respectively) similar to that of the ambient pressure study ($R_{obs} = 3.2\%$). However, the number of observed independent reflections has been divided by three in the high-pressure experiment and the ratio of the number of observed reflections to the number of refined parameters decreases from 12 at ambient pressure to 4 at high pressure. The accuracy of the atomic positions is nevertheless sufficient to discuss the structures. The accuracy and reliability of the results obtained for this first XRD investigation using our pressure cell and a CCD detector are similar to those generally obtained with the same pressure cell and a point detector [1, 2, 4, 9, 11]. However, the feasibility of the experiment has increased substantially even though numerous points require improvement.
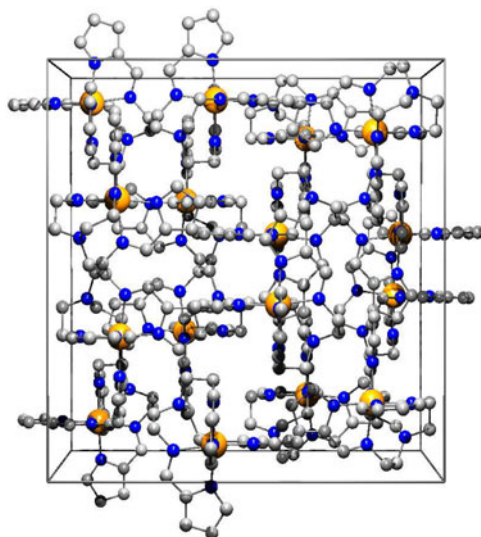
Figure 8. Crystal packing of [Mn(TRP)].

The crystal structure of [Mn(TRP)] (figure 8) is similar at ambient pressure or at 1.0 GPa. Applying pressure corresponds to a strong isotropic contraction of the crystal packing. The Mn bond lengths as well as the distortion of the metal octahedron [15, 16] show that there is no spin crossover within this pressure range. In parallel to the determination of the crystal structures, the unit cell pressure dependence was recorded. This study sheds light on some differences between applying a pressure and cooling to very low temperature in this complex. For example, when cooling at ambient pressure the spin crossover conversion occurs after a unit cell contraction of 222 Å^3 while applying a pressure of 1.0 GPa at room temperature does not induce the spin crossover despite a unit cell contraction of 600 Å^3. Such a difference could have its origin in the atomic displacement parameters that strongly decrease at low temperature but barely change under high pressure. Besides, the pressure dependence of the unit cell parameters has confirmed that in terms of unit cell volume contraction, cooling to 10 K is equivalent to applying a pressure of 0.5 GPa [17]. Detailed results should be published soon [18].

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