A Test of the Accuracy of High-Pressure Measurements using a Merrill–Bassett Diamond-Anvil Cell

BY ANDRZEJ KATRUSIAK* AND RICHARD J. NELMES

Department of Physics, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, Scotland

(Received 29 July 1985; accepted 14 October 1985)

Abstract

The accuracy of structural parameters obtainable from measurements carried out with a Merrill–Bassett diamond-anvil high-pressure cell has been tested in an X-ray diffraction study of cubic CaF$_2$. The measurements were performed at 0.0001, 0.70, 1.70, 2.60, 2.90, 3.66 and 4.42 GPa. It was found that a simple modification of the shape of the gasket can eliminate the problem of partly obscured reflections and yield reliable values for the Ca and F thermal parameters—the only variables in this simple structure, and hence particularly sensitive to any systematic errors in the data.

Introduction

The present study follows the high-pressure/high-temperature study of cubic calcium fluoride by Hazen & Finger (1981). These authors performed their X-ray diffraction experiments with a Merrill–Bassett (hereafter M–B) diamond-anvil cell (Merrill & Bassett, 1974; Hazen & Finger, 1982) at pressures up to 1.92 GPa and temperatures up to 573 K. Their work was primarily aimed at testing the use of CaF$_2$ crystals as an internal standard for pressure calibration in high-pressure/high-temperature cells, where there is no access for spectroscopic methods to be applied. Our work, on the other hand, is directed at testing the performance of the M–B cell itself. Since the only structural variables of cubic CaF$_2$ are the (isotropic) thermal parameters of Ca and F, the refinement of the CaF$_2$ structure affords a stringent test of the accuracy of data obtained from the cell. Hazen & Finger's (1981) study showed that the intensities of reflections from a crystal inside the M–B cell were subject to systematic errors that gave rise to refined temperature factors higher than expected. The authors suggested that this could be attributed to the sample crystal being shadowed by the gasket, especially when the high-angle reflections were measured. We have now confirmed that diagnosis and have devised a simple method to overcome the problem.

Fig. 1 shows the geometry of the high-pressure chamber in the M–B cell. The small and usually flat sample crystal is attached to one of the diamond faces inside the small circular hole in the metal gasket. The cavity of the hole is filled with the hydrostatic fluid. The recommended thickness of the gasket is 0.20–0.25 mm and the diameter of the hole ~0.30 mm. Besides decreasing its thickness, compression of the gasket by the diamond anvils initially causes contraction of the diameter of the hole. This process continues until the pressure inside the chamber reaches ~2.0 GPa (for Inconel gaskets), whereafter further compression is accompanied by widening of the hole under pressure from the hydrostatic fluid. The M–B cell allows 40° access angles for the incident and diffracted beams, as indicated in Fig. 1. Assuming that the diameter of the hole remains at 0.30 mm and the crystal is 0.10 mm across, the high-angle reflections (i.e. here the reflections for which either the primary or diffracted beam approaches an inclination of 40° to the axis of the M–B cell) will be shadowed by the edges of the gasket, even if it is compressed to the thickness of ~0.10 mm. This, however, does not happen for measurements at higher

---

*On leave of absence from Adam Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland.
pressures (i.e. more than 2.0–2.5 GPa) when the chamber diameter is significantly expanded and the gasket thickness is <0.10 mm.

**Experimental details**

Small high-quality single crystals of CaF$_2$ were selected from the fragments obtained by crushing a large crystal, obtained from Metal Crystals Ltd, Cambridge, England. The crystal used for data collection was a triangular plate of thickness 0.025 mm and edge length 0.09 mm. As in Hazen & Finger’s (1981) experiment, the sample was glued to the diamond surface with a dab of silicon vacuum grease. Inconel gaskets (Ni:Cr:Fe = 72:16:8), 0·20 mm thick with 0·30 mm holes, were used; and a 4:1 methanol–ethanol mixture was the hydrostatic fluid (Hazen & Finger, 1982). The pressure inside the cell was measured using the ruby-crystal fluorescence method (Piermarini, Block, Barnett & Formon, 1975), allowing a pressure measurement with ±0.05 GPa uncertainty. To eliminate the shadowing of the primary or diffracted beam by the edges of the gasket, the shape of the hole was modified, as illustrated in Fig. 1: the upper part of the high-pressure chamber then has a conical shape. By making $\psi$ scans of several reflections, we have confirmed that this simple modification eliminates the shadowing (in $\psi$ scans the angles between the cell axis and the primary and diffracted beams are varied). A further advantage of this gasket shape is that the initial compression causes only the conical part of the hole to reduce in diameter, the cylindrical part not changing its dimensions: this unanticipated behaviour helpfully prevents any shadowing of the sample that – despite the modification – might have been caused by reduction in the hole diameter with compression, and also tends to minimize changes in the orientation of the sample while increasing the pressure. The modified geometry of the high-pressure chamber does, however, reduce the limiting pressure that can be reached: the highest pressures obtained with these gaskets were about 3.0 GPa. Therefore, a gasket with a standard 0·30 mm cylindrical hole was used for the two measurements we made above 3.0 GPa – at which pressure, as explained above, the hole in the standard gasket is sufficiently enlarged and the gasket sufficiently thin to cause no shadowing.

The measurements were performed with a CAD4 diffractometer and graphite-monochromated Mo K$\alpha$ radiation. The $\omega$-scan method was applied with the scan speed depending on the intensity of the reflection. A high-pressure program package for data collection on a CAD4 with a M-B cell was used (King, 1981) – based on Finger & King’s method for diffractometer-angle setting for the M-B cell (Finger & King, 1978). For each pressure a hemisphere of the accessible data within the 40° $\theta$ limit was collected. But only reflections for which both the incident and diffracted beams were within 37.5° of the axis of the cell were accepted for further calculations, this angle giving a small safety margin on the limit (40°) imposed by the steel mounting of the beryllium discs (to which the diamonds are attached: Merrill & Bassett, 1974). The transmission coefficients of the cell were determined experimentally (King, 1981) and used to correct the intensities of reflections for the absorption of the diamond anvils and the beryllium discs. Corrections were also applied for the $L_p$ factor and for absorption by the sample: $\mu$(Mo K$\alpha$) varies from 32.05 up to 32.25 cm$^{-1}$ at 4.4 GPa, and transmission factors range from ~0.84 to ~0.94 at each pressure. Although this is a relatively small effect, the corrections were necessary because the shape of the crystal (a plate) and its orientation in the cell (perpendicular to the cell axis) produce absorption that is correlated with the diffraction angle for most reflections allowed by the cell. After applying the corrections the reflections were averaged – the number of independent observations varied from 20 to 23 for different pressures, this being due to small changes of the orientation of the crystal. No reflections were omitted in the course of the refinements.

The structure refinements were performed with SHELX76 (Sheldrick, 1976). An isotropic extinction correction was included in the refinements. The final results are listed in Table 1.

**Results**

The pressure dependence of the unit-cell parameter $a$ is plotted in Fig. 2. It shows that in this pressure range, to 4·5 GPa, the magnitude of $a$ decreases almost linearly with increasing pressure. The rate of change of $a$ with pressure is in good agreement with that obtained over the range up to 1·92 GPa by Hazen & Finger (1981), and is very close to that predicted by Wong & Shuele (1968) from measurements of the elastic constants. These latter authors estimated a value of 5·38 Å for $a$ at 4·5 GPa. The changes in the

---

**Table 1. The unit-cell parameter, $a$, and refined mean-square thermal amplitudes, $U$, obtained for CaF$_2$ at different pressures**

For each refinement the conventional crystallographic $R$ factors, weighted and unweighted, are given. AP denotes atmospheric pressure.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$a$ (Å)</th>
<th>$U$(Ca) (Å$^2$)</th>
<th>$U$(F) (Å$^2$)</th>
<th>$R$(%)</th>
<th>$wR$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-air</td>
<td>5·463(1)</td>
<td>0·0058(1)</td>
<td>0·0089(1)</td>
<td>1·19</td>
<td>1·10</td>
</tr>
<tr>
<td>AP-M-B cell</td>
<td>5·463(1)</td>
<td>0·0061(4)</td>
<td>0·0092(5)</td>
<td>2·15</td>
<td>1·87</td>
</tr>
<tr>
<td>0·70</td>
<td>5·452(2)</td>
<td>0·0099(4)</td>
<td>0·0094(4)</td>
<td>1·19</td>
<td>1·11</td>
</tr>
<tr>
<td>1·70</td>
<td>5·432(2)</td>
<td>0·0061(8)</td>
<td>0·0099(13)</td>
<td>3·06</td>
<td>2·61</td>
</tr>
<tr>
<td>2·60</td>
<td>5·426(2)</td>
<td>0·0060(6)</td>
<td>0·0090(8)</td>
<td>2·58</td>
<td>2·54</td>
</tr>
<tr>
<td>2·90</td>
<td>5·422(2)</td>
<td>0·0058(6)</td>
<td>0·0088(6)</td>
<td>1·54</td>
<td>1·94</td>
</tr>
<tr>
<td>3·66</td>
<td>5·410(3)</td>
<td>0·0063(3)</td>
<td>0·0083(4)</td>
<td>1·58</td>
<td>1·45</td>
</tr>
<tr>
<td>4·42</td>
<td>5·392(2)</td>
<td>0·0054(6)</td>
<td>0·0083(6)</td>
<td>2·42</td>
<td>2·42</td>
</tr>
</tbody>
</table>
isotropic thermal parameters of Ca and F with pressure are shown in Fig. 3. The systematic errors found by Hazen & Finger have clearly been eliminated: at atmospheric pressure the same values of \( U(\text{Ca}) \) and \( U(\text{F}) \) are obtained with the sample in the cell as with the bare sample, and the magnitudes of the thermal parameters indicate (albeit with largish errors) the expected small decrease with increasing pressure.

The values at 4.42 GPa correspond to a 4% decrease of the root-mean-square amplitudes of both Ca and F – changes similar to those measured for NaCl by Finger & King (1978) who found the Na and Cl amplitudes reduced by 4 and 8%, respectively, at 3.2 GPa.

Concluding remarks

The main advantages of the M-B cell are its simple construction and its ease of use on a four-circle diffractometer. The present study shows that the M-B cell can be used to obtain reliable structural parameters, provided care is taken to prevent shadowing of the sample crystal by the gasket edges. This can be achieved at pressures up to 3.0 GPa by modifying the gasket shape, while at higher pressures the shadowing of the crystal, as explained above, should not occur. (The problem of shadowing can also be overcome by using beryllium or carbon-fibre gaskets, which have very low X-ray absorption. However, the use of X-ray absorbing gaskets has certain advantages: besides the difficulties in machining very poisonous beryllium and its high cost, the 'normal' metal gasket absorbs part of the incident beam, significantly reducing scattering from the diamond anvil and beryllium disc on the side of the M-B cell facing the X-ray detector and so reducing the background.) Some other limitations in the cell's construction are not so readily overcome. First, the steel housing restricts the volume of reciprocal space accessible to measurement, and so limits the precision with which structural parameters – especially thermal parameters – can be determined. Secondly, there is substantial background scattering from the beryllium discs supporting the diamonds. And, although one can partly reduce these problems by using the shorter Ag \( K\alpha \) wavelength (Finger & King, 1978) this involves other difficulties.

If results significantly more precise than those obtained here are required, it will be necessary to turn to a different cell construction or to a different technique. Malinowski (1984) has recently designed a diamond-anvil cell in which the incident and diffracted beams pass through the same diamond: almost unrestricted data collection is then possible and, owing to the elimination of beryllium discs, the background level is significantly lowered. In this cell, Dieterich, Glinnemann, Koepke & Schulz (1984) have successfully used beryllium gaskets to overcome the shadowing of the sample. Then, the use of a synchrotron radiation source appears very promising for high-pressure structural studies (Hatton, 1984; Skelton, 1984): the limitations of the M-B cell on a conventional four-circle diffractometer are significantly reduced by the high collimation and brightness of the incident beam, and by the white-beam energy-dispersive technique (Hatton, 1984).

Nonetheless, for many purposes careful use of the M-B cell on a four-circle diffractometer affords an attractive and adequately reliable method for undertaking high-pressure crystal-structure studies.

This work is supported by a research grant from the Science and Engineering Research Council.
References