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NEW MODULAR SQUEEZERS FOR MBAR PRESSURES

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Introduction

For high pressure experiments diamond anvil squeezers are being used worldwide. Two concepts best known are the Piermarini-type and the Mao-Bell-type, named after their first users: (Fig. 1). The basic difference is the point of rotation

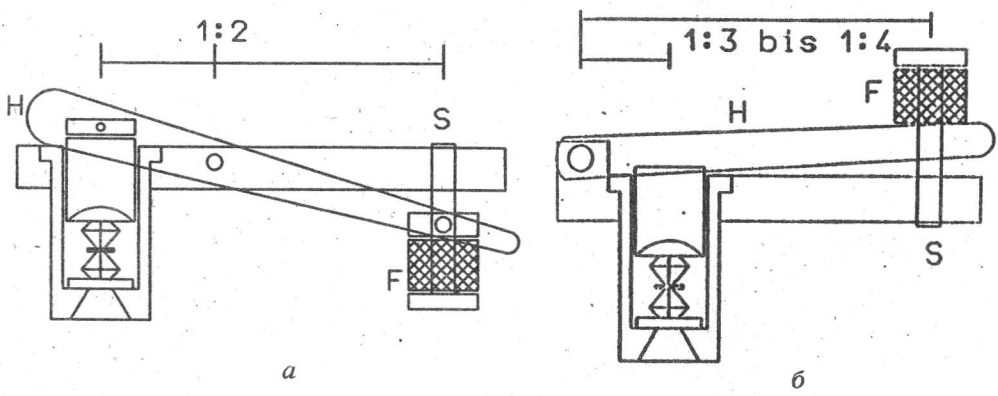

Fig. 1. Schematics of Piermarini (a) and Mao & Bell type (*b*) squeezers differing in the location of the sample with respect to the rotation point

between force and sample. In the Piermarini-type this point lies between sample and force, with a ratio R of about 1:2. In the Mao-Bell type the rotation point is behind the sample with a ratio of 1:3 to 1:4. In both types there is a set of springs F between screw and body. The diamonds are glued into a holder and basically unmovable with a maximum movement less than 100 μ. Pressure P is generated between the two diamonds when the screw (S) is turned:

$$P = R\frac{D}{A}s = R\frac{D}{A}hU. \tag{1}$$

A is the area on the diamonds, about 0.28 mm^2 with 600 μ diamonds, D the spring constant (~ 600 N/mm/sec), s the movement of the springs ($s \approx 1.3\,U$), h the pitch (1–3 mm with M13) and U the number of rotations of the screw. The pressure generated is roughly 31 to 46 kbar/revolution of the screw.

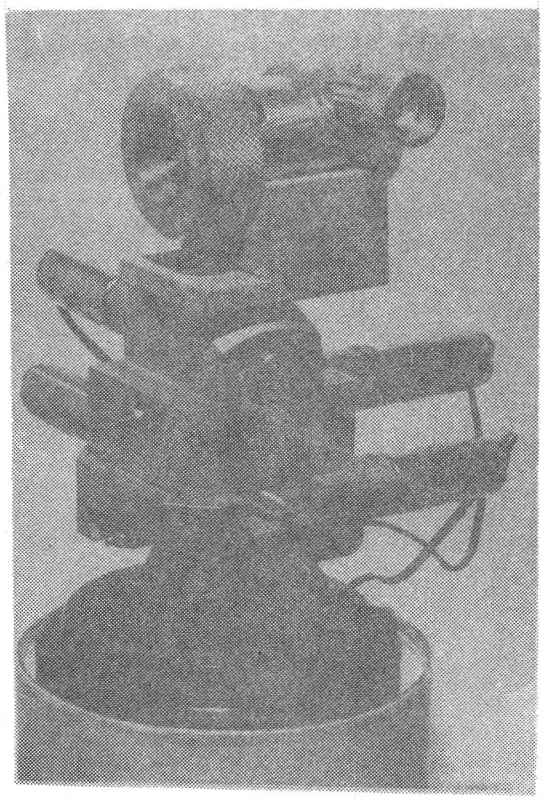

Fig. 2. (*a*) Diamond anvil squeezer built and used in Bonn with a direct force translation. Maximum pressure 250 kbar. (*b*) Photograph of this cell mounted on a remote controlled goniometer head for use with synchrotron radiation

Some types, also one of our earlier developments (Fig. 2) (Hinze and Will, 1980) use a direct force translation via a set of springs without a lever system. The pressure attainable here is less than with a lever system, however such cells are small in size and are being used for example on four circle single crystal diffractometers or in cryostats, etc. Our own squeezer mentioned above was mounted on a small goniometer head and used for the first experiments reported using synchrotron radiation and high pressure (Buras et al.,1977). The maximum pressure reached in that experiment was about 250 kbar (Will et al., 1980). For X-ray diffraction under extreme pressures in-situ with the aim to work routinely in the Mbar range and with sufficient sample volume for structure determinations we have followed new avenues for high pressure cells. This leads primarily to modified diamond mountings. Since the experiments were aimed for synchrotron rediation experiments control of the pressure was wanted, and this in turn leads to a hydraulic squeezer system. These developments and new techniques are reported here.

Modular Systems

The difficulty and overall disadvantages of all squeezers so far published is the general principle for fixing the diamonds (by glues). For pressures in the Mbar range, large forces, also shear forces act on the diamonds. In order to safeguard against cracking, the faces of the two diamonds must move exactly parallel to each

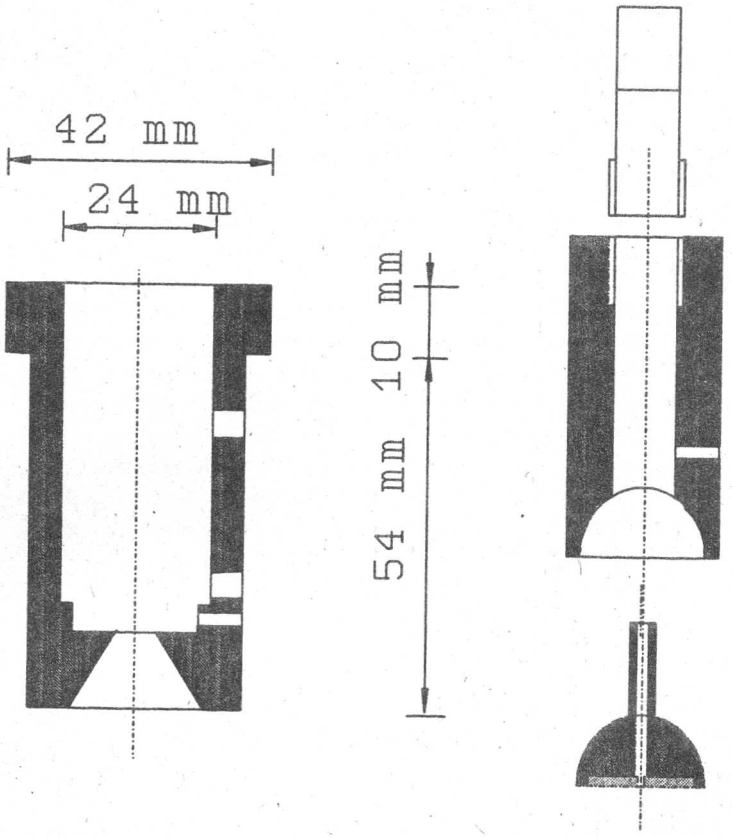

Fig. 3. Modular system for mounting the diamonds in high pressure devices. For details see text. The system can be exchanged easily between different cells

other, and therefore extreme precision in mounting the diamonds is needed. Another disadvantage is the fact that the mechanical setup has to be rebuilt completely even if only minor changes in the diamond settings are required. Mainly for those reasons we have developed a modular system, which is a system where the diamond settings can be easily exchanged between different types of squeezers or other high pressure cells. This modular system is shown in Fig. 3. This system has been incorporated in our laboratory in two different types of high pressure cells, a Mao-Bell-type squeezer and a completely new construction based on a hydraulic system (Fig. 6).

We are using a "long" cylinder (see Fig. 3) made of maraging steel, 51 mm long, outside diameter 42 mm, inside diameter 24 mm, which guarantees parallel movement inside the mounting cylinder. The diamonds are mounted inside this cylinder: one diamond is glued to a tungsten carbide plate in a fixed position, the second diamond is glued to a pin sitting on a half-sphere with some freedom for small tilting. This half-sphere fits into an equivalent space in the main cylinder.

Three screws through the maincylinder and acting on the pin allow one to adjust this piece to an exact parallel position.

To guarantee and also in order to check on parallel diamond faces we use initially AgI-powder. AgI changes color at two phase transitions, one at about 2.9 to 4.7 kbar (Hinze, 1969) and the second one at > 4 kbar (Schock and Jamieson, 1969). If the diamonds are parallel, coloured rings ceneterd around the center must be observed. The diamonds are adjusted under a binocular microscope with the setting screws until this criterion is met.

For extreme pressures in the Mbar range this does not suffice however, mainly because the AgI-grains may already cause very minute tilting. We have used therefore for the final adjustment the direct interference in air between the diamonds without any material between the diamonds, known as Newton's rings. Thereby the diamonds are in direct contact. A small misalignment acts like a wedge yielding the well-known colors. Under pressure, or vice versa when releasing pressure, those colors move. If the diamonds are parallel, the whole view shows only one color which changes with pressure.

Before we use such a cell for the first time in Mbar experiments the pressure is increased very slowly, held constant for several hours, released and relaxed, then increased again to higher pressures, released again and so on. This procedure takes several days. The same procedure is followed for mounting the gaskets: pressure, release pressure, cleaning, redrilling the gasket, opening and so on.

Gasket Material

Gaskets play a crucial role when Mbar pressures shall be reached. We have tested several materials to be used as gaskets, Fe/Cr/Ni/xx steel from Goodfellow

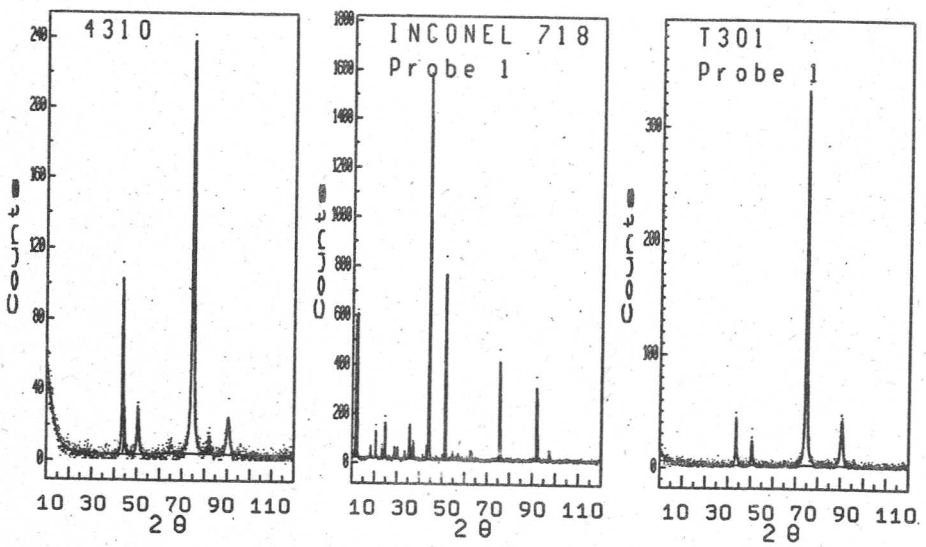

Fig. 4. Angle dispersive diffraction diagrams of three gasket materials: 4310, INCONEL 718 and T301; for details see text

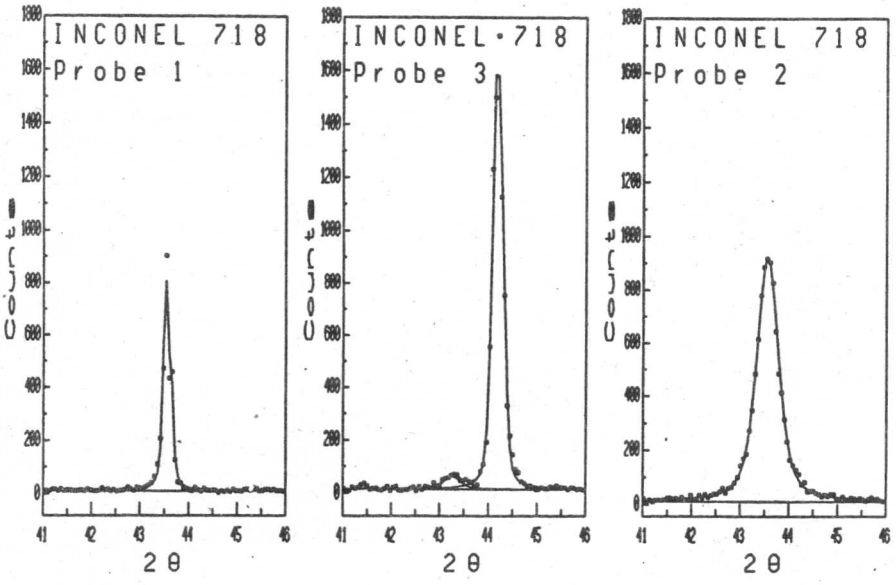

Fig. 5. Enlarged diffraction maxima around $2\theta = 43.5°$, 44.2° and 43.5° of three INCONEL 718 samples. Differences in peak position, peak height and FWHM are observed for the considered "same" gasket material, acquired at different times, e. g. from different manufacturing charges

(USA), INCONEL 600 and 718, a Ni/Fe/Cr/Nb alloy, and T301, a Fe/Cr(16-18)/Ni(6-8) steel (Stainless Steel Handbook, 1959) from "Ulbrich Stainless Steel and Special MMetals Inc. ". Fig. 4 shows diffraction diagrams of three of those materials measured on a conventional diffractometer in angle-dispersive mode. Fig. 5 gives enlarged sections of three Inconel samples. It is interesting to note, that the "same" INCONEL 718 samples, taken from different manufacturing charges, show significant differences in the half widths. The full width at half maximum (FWHM) increases directly with the gasket's hardness and the FWHM can be taken as a measure for the gasket to satisfy the requirements for ultra-high pressures. For such gaskets we need material with both high tensile- and compressive-strength, in order to withstand the pressure under a high load without flowing (Beresnev and Efros, 1986). Sample "Probe 2" of Inconel 718 (Fig. 5*c*) has the greatest FWHM. It seems to have the best properties and it was used in our experiments.

Mao-Bell-Type Modular Squeezer

For Mbar pressure large forced are needed. In the systems used today generally this force is obtained in diamond anvil squeezers either by large levers, or by using extremely small diamond areas (about 50 μ diameter) (remember $p = F/A$). The mechanical force on the diamonds is always formidable, which often leads to misalignment of the diamonds in such systems, resulting either in breaking the diamonds, or bringing the whole system out of alignment. The last point is especially frustrating when working with synchrotron radiation because it then requires a new alignment in the synchronous beam with all its time consuming

safety procedures. We have built and used such a Mao-Bell-type squeezer, however with our advanced diamond setting system described above. We have used it routinely in about 200 high pressure experiments with a maximum pressure of 1. 1 Mbar (see later).

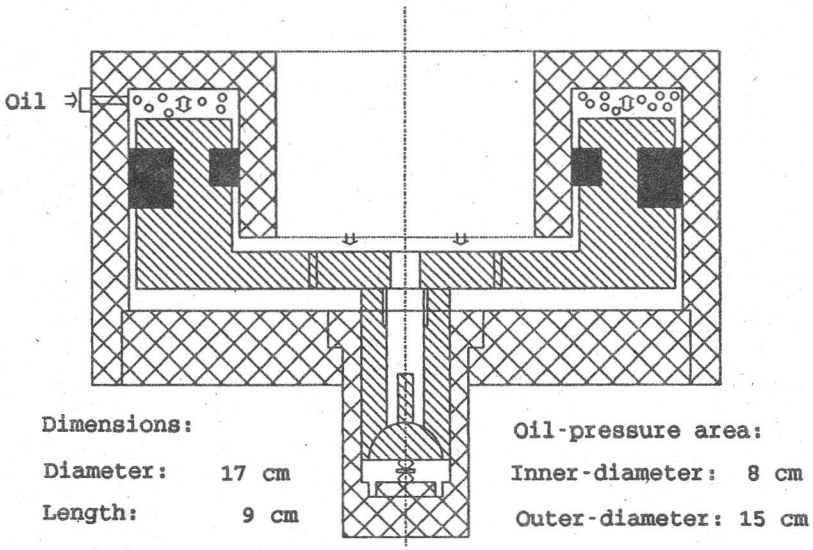

Fig. 6. Schematics of the hydraulic squeezer. For details see text

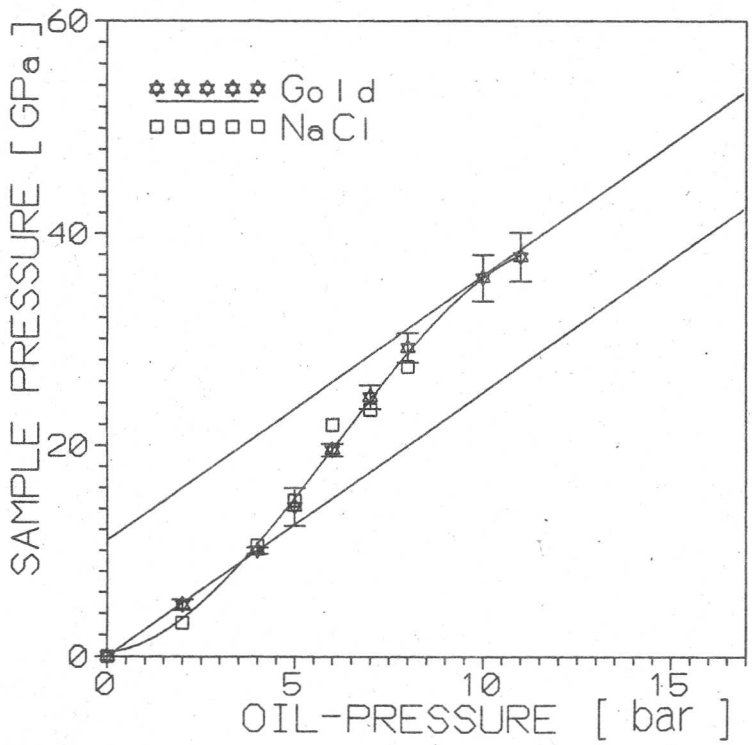

Fig. 7. Calibration curve of the hydraulic squeezer, sample pressure (GPa) versus oil pressure (hPa = bar). After over-coming an initial part of friction and compressing the gasket, the relation becomes linear again

The Hydraulic Squeezer

Parallel to the Mao-Bell type squeezer we have developed a new concept based on a hydraulic system (Fig. 6). The hydraulic squeezer consists of four cylinders of maraging steel, 1–2 cm wall thickness, and two seals. The outer diameter is 17 cm. The oil pressure area has 15 cm outer diameter and 8 cm inner diameter yielding

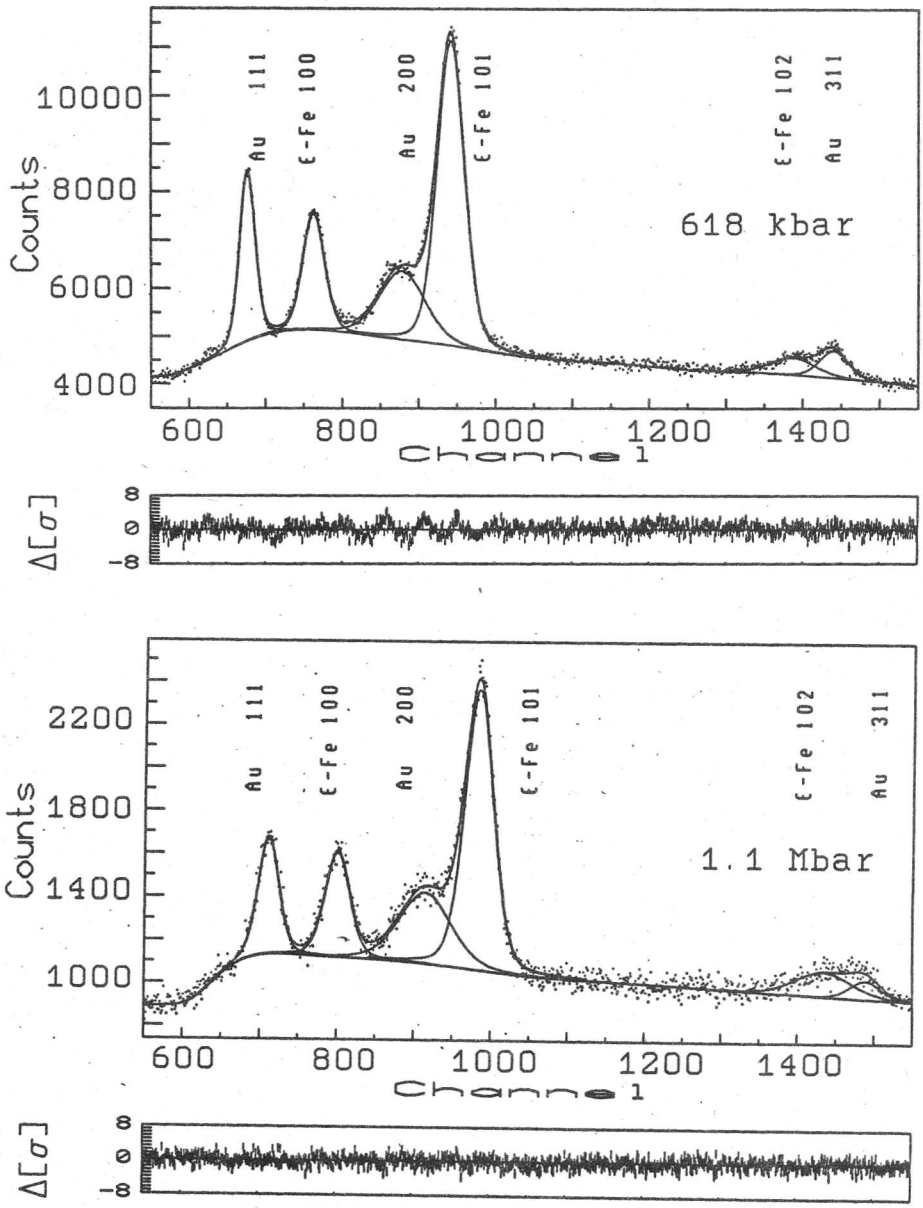

Fig. 8. Diffraction diagrams of Fe collected at HASYLAB/DESY at 618 kbar and 1.1 Mbar. The solid line give the results of the profile fitting analysis for determining peak positions and consequently lattice constant and the compressibility

126 cm^2. With 0.4 mm (400 μ) diamonds equal to 1.26×10^{-9} cm^2 we should reach 1 Mbar sample pressure at 10 bar oil pressure. Of course we have friction, therefore the actual oil pressure needed will be somewhat higher (about 25 bar for 1 Mbar). The hydraulic squeezer has been calibrated by using NaCl as well as gold with the compressibility data taken from literature. Thereby we have increased the oil pressure in steps of 1 to 2 bar. Fig. 7 gives the calibration curve up to 330 kbar (33 GPa) which was achieved with an oil pressure of 12 bar. The successful operation of these squeezers was made possible only, because we used a special new plastic 94AU925 from SIMIRIT for the sealings. This was not available in previous constructions several years ago, where we used rubber sealings which constantly failed at about 32 kbar.

The straight line through the origin in Fig. 7 represents the calculated calibration curve. The pressure in the cell follows initially this straight line. At about 8 kbar friction in the steel components increases and has to be overcome before further pressure is transmitted to the sample. Also, and perhaps more important, the gasket has to be compressed, before further pressure is brought onto the sample. After that initial stage the calibration curve is linear again. We have used this cell so far to a pressure of 400 kbar (40 GPa). Higher pressures can be obtained easily and we expect to go into the Mbar range in the near future.

The sample volume is about $1 \cdot 10^{-3}$ mm^3, which is fairly large, especially in comparison with diamond anvil squeezers. This should allow us to measure intensities for determining crystal structures in a reliable way without too many errors caused by preferred orientation in the sample (Will, 1993).

Table 1. Evaluation (profile fitting) of a diffraction diagram of Fe and Au taken at 202 kbar

PK	Position Channel	d-spacing	Height	FWHM Channel	R-Values [%] of sections
0	562.04 ± 2.27	2.449 ± 0.011	48 ± 11	20.3 ± 5.7	1.34
1	622.39 ± 0.02	2.285 ± 0.004	12550 ± 37	17.5 ± 0.1	
2	690.29 ± 0.19	2.125 ± 0.004	750 ± 14	22.9 ± 0.5	
3	760.79 ± 0.04	1.981 ± 0.003	6173 ± 24	23.6 ± 0.1	
4	791.63 ± 2.36	1.924 ± 0.007	131 ± 14	25.5 ± 0.3	
5	822.84 ± 0.10	1.870 ± 0.003	2238 ± 17	25.5 ± 0.3	
6	1152.93 ± 2.13	1.439 ± 0.004	63 ± 8	26.8 ± 0.2	1.04
7	1193.03 ± 0.09	1.400 ± 0.002	1720 ± 14	26.8 ± 0.2	
8	1395.65 ± 1.08	1.231 ± 0.002	111 ± 6	34.1 ± 0.3	0.95
9	1445.71 ± 0.14	1.195 ± 0.002	946 ± 9	34.1 ± 0.3	
10	1523.64 ± 0.41	1.143 ± 0.002	270 ± 5	34.1 ± 0.3	
11	1568.07 ± 2.45	1.116 ± 0.003	40 ± 5	34.1 ± 0.3	
12	1993.76 ± 1.33	0.907 ± 0.002	52 ± 3	43.5 ± 3.9	1.01

R-Values of the whole pattern
R(PF) : 1.22 R(STA)
R(STA) : 1.78 %

Experimental results

We have used both systems for many experiments. Using the Mao-Bell-type squeezer we have investigated the compressibility of iron and gold. Calibration was achieved by an internal standard. In synchrotron experiments we consider internal standards preferable, because the system, once carefully adjusted, can stay in the synchrotron beam and pressures can be increased continuously and even by remote control without removing the cell system to determine the pressure through the shift of the ruby fluorescence line. In our facility in the HASYLAB at DESY, as in general at most facilities, this must be done outside the synchrotron beam hutch. Fig. 8 gives as an example two diffraction patterns of Fe collected at 618 kbar and 1.1 Mbar (61.8 GPa and 110 GPa). Data were collected at the HASYLAB in DESY in Hamburg. The exposure time was 1000 seconds. The solid line gives the results of the profile fitting analysis, which was done with our program HFIT (Höffner et al., 1991; Will and Höffner, 1992). The profile fitting values were typically $R_{prof} = 1.8\%$, which is indeed very good. Table 1 gives the results of such an analysis, shown on a sample of a mixture of gold and iron measured at 202 kbar.

Table 2. Refinement of lattice constants for both components of Table 1

SYSTEM 1:	Au CUBIC						
SYSTEM 3:	ε−Fe HEXAGONAL						
PARAMETER				INITIAL	FINAL		
A		S1		3.955351	3.955		± 0.002
A		S3		2.457807	2.458		± 0.002
C		S3		3.926644	3.927		± 0.006
ID:	h	k	l	d-Value	--- Channel ---		Delta
				refined values	obs	calc (refined)	
Au:	1	1	1	2.284	622.39	622.43	−0.04
ε−Fe:	1	0	0	2.129	690.29	688.18	2.11
Au:	2	0	0	1.978	760.79	762.03	−1.23
ε−Fe:	1	0	1	1.871	822.85	821.28	1.57
Au:	2	2	0	1.398	1193.04	1193.64	−0.60
ε−Fe:	1	1	0	1.229	1395.65	1396.92	−1.27
Au:	3	1	1	1.193	1445.71	1447.99	−2.28
Au:	2	2	2	1.142	1523.65	1524.83	−1.18
ε−Fe:	1	0	3	1.115	1568.08	1568.31	−0.23
Au:	3	3	1	0.907	1993.76	1991.02	2.74

We can distinguish 12 lines, 10 of which were used for refinement: 6 coming from gold, 4 from iron. Table 2 gives the result of the refinement of the lattice constants: $a_0 = 3.955(2)$ Å for gold, $a_0 = 2.457(2)$, $c_0 = 3.926(6)$ for the hexagonal (high pressure) phase of iron. Standard deviations are given in paranthesis. Details and results will be published separately.

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