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Preparation and characterization of single crystal samples for high-pressure experiments

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Abstract

To date, most research utilizing the diamond anvil cell (DAC) has been conducted with polycrystalline samples, thus the results are limited to addressing average bulk properties. However, experiments on single crystals can yield data on a range of orientation dependent properties such as thermal and electrical conductivity, magnetic susceptibility, elasticity and plasticity. Here we report new procedures to produce extremely high-quality metallic single crystal samples of size compatible with DAC experiments in the Mbar range. So far, we have produced samples of zinc, Al_2O_3, cobalt, molybdenum and cerium, and have evaluated the quality of the finished samples with white-light interferometry, synchrotron x-ray diffraction and inelastic x-ray scattering.

Keywords: single crystal, polishing, laser cutting, diamond anvil cell

1. Introduction

Detailed knowledge of the high-density physical properties of matter is an increasingly important aspect of modern experimental physics with applications ranging from solid-state physics, engineering science, to the earth sciences. Consequently, a great deal of effort has been devoted to the technical development of high-pressure generating devices and spectroscopic probes. The diamond anvil cell (DAC) is by now, after more than forty years of research and improvements, one of the most utilized tools for static high-pressure generation. Its use has revolutionized the study of condensed matter at elevated pressure, both in terms of the maximum achievable pressures, as well as the range of different techniques that can be used to probe the material contained within the DAC [1-15]. Today there exist specialized DACs for use with infrared absorption, Brillouin and Raman spectroscopy, impulsive stimulated light scattering, Mössbauer spectroscopy, diffraction and inelastic scattering of x-rays, x-ray absorption and magnetic dichroism, nuclear scattering, magnetic scattering, electric transport and magnetic susceptibility measurements, ultrasonic interferometry and other techniques. However, with few exceptions, comparatively little effort has been put into sample fabrication and sample environment. Due to the extreme difficulties with preparation of the small samples necessary for the DAC, most of the experiments in the DAC have been performed on powder samples. If the samples are properly prepared (perfectly random orientations in powders for example), and maintained under hydrostatic conditions at high pressures, it is possible to obtain from polycrystalline samples well averaged bulk material properties, such as the bulk modulus and its pressure derivative, from diffraction experiments, or the aggregate longitudinal and shear sound speeds, from velocity measurements. In practice however, this is very difficult to achieve at large compressions, where there are often undesired uniaxial stress components that induce strong lattice preferred orientations [16]. Thus, these bulk methods typically become biased by the non-random crystallographic orientations [17]. This problem can be circumvented by making measurements on single crystals along well-defined directions

and polarizations. In this case, the entire property tensor can be determined, and the aggregate properties derived from proper averaging processes.

More generally, when action and/or reaction are tensorial magnitudes and linearly related (such as stress and strain), the material property which links the exerted action with the associated reaction, also has a tensorial character. Linear relations between conjugate magnitudes usually arise when a quadratic expansion suffices to describe the energy. Beyond such range, either higher order terms may be required (*e.g.,* third-order elastic constants) or the property may not be tensorial in character (*e.g.,* yield stress). The physical manifestation of anisotropy is given by the difference in the reaction to the same action, when the latter is exerted along a different direction in the material. In the tensorial representation of the property, the anisotropy leads to differences amongst some of the tensor components which would, in the case of an isotropic material, be equal or exhibit a definite relationship. In practice, elastic, plastic, optical, thermal, electric, magnetic, and transport properties of crystals are always anisotropic, although sometimes only weakly so. Finally, the comparison between single-crystalline and aggregate properties can provide much richer information than the bulk properties alone. Indeed, the study of the averaging schemes that may connect the two scale lengths (single crystals to polycrystals) is an active area of research [18-22]. Thus, it is now critical to be able to measure tensor properties at high-pressure and thus to be able to prepare high-quality single crystal samples for these delicate measurements.

In the remainder of this communication we address a set of new techniques that starting from commercially available material have been developed for the production of extremely high-quality metal single crystal samples for use in ultra high-pressure DAC experiments. The main technical impediment to the use of single crystals in the DAC has been the required size and quality of samples. In order to achieve pressures in the range of Mbars in a DAC, single crystal samples must be approximately <30μm in diameter and <15μm thick while still maintaining a low mosaic spread. Thus, metals present an extremely challenging test for any proposed procedure. For this reason, the examples we discuss are metals, specifically cobalt and molybdenum.

2. Sample preparation method

Our starting materials are commercially available single crystals, either pre-oriented or in a random orientation. However, for our applications, we are concerned with a specific orientation and thus, for the non-oriented samples, the first step is to obtain an oriented wafer using standard Laue backscatter diffraction. For example, in the case of phonon measurements in the face centered cubic system (fcc), a sample cut with the surface normal parallel to the [110] direction, allows one to probe all the phonon branches: the three L and the T_1[110] mode by appropriate rotation around the sample surface normal in θ-2θ geometry, the T_2 [110] as well as the T[100] and T[111] modes in the χ-2θ geometry. It is worthwhile to note here, that the limited aperture of the DAC makes maintenance of the orientation during the sample preparation process a critical requirement during the remaining preparation steps. To date, with the process we outline here, we are able in most cases, to maintain the orientation within ~2°. The basic outline of our process is as follows: a) rough cutting of a thick slab; b) polishing the first side of

the cut crystal; c) cutting of the small samples as columns; d) impregnation of the as cut sample columns and final thinning and polishing of the opposite side to achieve the desired thickness. In the following sections we address some of the details of the processes involved.

2.a Cutting

The orientated samples are fixed on a stainless steel plate, placed in an orientation-preserving jig and mounted on the saw for rough cutting. In order to minimize both waste of material and damage to the crystal, to cut thick sections from the as-received sample we use a wire saw with a stainless steel wire in combination with boron-carbide slurry. Depending on the material, different combinations of wire diameter and boron-carbide particle size can be used. However, for most cases the combination of a 254 μm blade (0.010") with 23 μm boron-carbide slurry has been the most effective.

2.b Polishing

Following the rough cutting, the sample is placed in a mounting ring on an optical flat and epoxy resin is poured over the assembly. The epoxy serves to both hold the sample, as well as to prevent damage during the thinning and polishing process. Once the resin is cured, the now hardened puck is removed from the optical flat and the surface that was not in contact with the optical flat is ground parallel to the one that contacted the optical flat. This forms the two parallel reference planes (the top and bottom of the resin puck) coplanar with the crystallographic directions. Next, the surface that was in contact with the optical flat is polished utilizing an automated lapping and polishing machine in conjunction with descending combinations of standard alumina and diamond slurries (material dependent), and low nap polishing cloths. We have also incorporated the use of an appropriate chemical etch (specific to the material being prepared) between every polishing step. After each step, the surface is examined for etch pits and other signs of non-intrinsic defects in the bulk material. The final step before cutting the small sample disks is to polish the sample to a mirror finish using colloidal silica. The goal here is to remove any damaged layer that might contribute to an increase in the final sample rocking curves or, in the case of surface-dependent measurements such as impulsive stimulated light scattering, bias the final results. Polishing and etching proceed until the disturbed surface layer [23] is completely removed and the sample is either free of etch pits or their number stabilizes and thus reflects the actual intrinsic crystal defect density (Figure 1).

2.c Laser cutting

Once the initial surface has been prepared, the large sample slab is ready to have small samples roughed out from the now polished surface. The process and geometry is schematically illustrated in Figure 2.

We have used a number of techniques for the sample cutting, but have now settled on a procedure that uses a trepanned femtosecond laser to produce the micro-disks (Figure 3). The advantages of using a laser, more specifically a femtosecond laser as compared

to, for instance, coring with an electrical discharge machining unit are fourfold: 1) there are no thermal perturbations to affect the crystals; 2) we can control and change during the process, the size and shape of the samples from a remote computer; 3) sample production is relatively fast and highly reproducible from sample to sample; 4) the technique works on metals as well as semi-conductors and insulators.

We have chosen to cut circular shaped samples, as disk shaped samples dovetail well with the geometry of the sample chamber in a DAC. However, the techniques outlined here have been applied to producing many sample shapes (small ~100 μm dog-bones for tensile tests) and are well suited to cube shaped samples for apparatus such as the D-DIA. The diameters of our small samples range from 25 to 100μm. These samples are cut using motion controlled optics in conjunction with an ultra-short pulsed (1.5×10^{-13} seconds) laser focused to extremely small spot sizes, which ablates the sample material (Figure 4). Unlike longer pulsed lasers, ultra-short pulse lasers allow machining while producing minimal heating near the ablation zone. This laser technology is attractive for precision cutting of single crystals and other materials that are sensitive to heat produced in the cutting process. The process is also able to produce highly repeatable disk samples at the rate of hundreds per hour (compared to few samples per day using conventional electric discharge machining (EDM) methods).

2.d Thinning

Once the samples are cored, an EDM is used to drill holes of known depth in areas unused material around the laser cut columns, to serve as thickness indicators (in the case of non-metals a small amount of a metallic solid was placed around the sample to serve as the depth gauge). The sample is then impregnated with epoxy resin using a vacuum impregnator to insure complete saturation of the ablated region around the cores. This step is essential for preventing deformation of the cored material during polishing. The previously polished and cut surface is then re-polished using colloidal silica until any disturbed surface layer or sputtered material is completely removed. The now completed first sample surface is then replaced in a brass ring and covered with potting resin. Once the resin is cured, the puck is removed from the ring and as poured surface is ground parallel to the previously ground surface. Thus, again we have a resin puck with two parallel surfaces. Now the opposite face is polished using the same sequence previously described until the final desired sample thickness is achieved.

3. Sample quality measurement

To evaluate the surface quality of the produced sample we have performed white-light interferometric measurements (Figure 5). In the test case of 80 to 100 μm Co disks, we observed a root-mean-square (rms) roughness over the individual disks between 64.7 and 74.5 nm. The obtained low values of roughness clearly testify to the high quality in the sample surface.

The x-ray characterization of the crystal quality consisted of the acquisition of several Bragg reflections, the verification of the intensity profile and rocking curve of each reflection, and their correlation through the calculation of the orientation matrix of the single crystal in order to check the structure and the absence of twins. The first step in

this analysis was performed on individual cores at the high-pressure dedicated diffraction beamlines ID09A and ID30 of the European Synchrotron Radiation Facility (ESRF) using angular dispersive x-ray diffraction. This method has the advantage of being very fast, and the shape and intensity of the reflections provides a good qualitative check on sample quality. However, due to time constraints we did not obtain detailed rocking curve information. Figure 6 shows a typical diffraction pattern of a Mo sample recorded at 30keV using a mar 3450-type fast reading image plate detector. Based on the qualitative information obtained from the diffraction patterns, the samples with the highest quality were selected and loaded into the DAC using helium as pressure transmitting medium to ensure hydrostatic compression (Figure 7). The rocking curves of relevant reflections were than measured as a function of pressure. As an example of the quality of our samples we show the rocking curves of the [110] and [002] Mo reflections obtained at 3.2 GPa (Figure 8). Typical values of the mosaic spread are between 0.08° and 0.3°, which is consistent with the as-received crystal. Furthermore, we have not observed evidence of degradation in crystalline quality upon increasing pressure, up to the point of bridging of the sample between the diamonds at ~40 GPa.

A further indication of the crystalline quality of the produced samples can be obtained from the inspection of the collected inelastic x-ray scattering spectra (IXS) (Figure 9). IXS spectra are especially sensitive to crystalline quality. These spectra are characterized by the presence of the Stokes and Anti-Stokes phonon peaks, symmetric with respect to the quasi-elastic line, centered at the 0 energy position. For IXS spectra collected in a fixed scattering geometry, with increasing mosaic spread, the momentum transfer becomes ill defined and thus leading to a rapid broadening of the Stokes and Anti-Stokes phonon peaks and increased intensity in the quasi-elastic line. The very weak elastic contribution and sharp inelastic peaks (Figure 9) are a direct signature of the very-high crystalline quality of the samples.

4. Conclusions

We have described here a new technique to produce very high quality metallic single-crystalline sample of dimensions compatible with DAC constraints. The procedure involves standard polishing techniques in conjunction with femtosecond laser cutting.
Presently, we have produced crystals of zinc, Al_2O_3, cobalt, molybdenum and cerium, with diameters varying according to the experimental needs, from 25 to 100 μm diameter, and thickness between 20 to 25 μm. We optimized the different steps of our procedure using cobalt and molybdenum samples, and thus these metals have been considered as the most relevant examples. The final orientations were within 2° from the nominal value, with a mosaic spread (rocking curve) between 0.1° and 0.3° in the case of cobalt and better than 0.1° in the case of molybdenum. These values are comparable, if not better than the as-received crystals. The produced micro-samples have been characterized using white-light interferometry, x-ray diffraction at ambient conditions, as well as under hydrostatic compressions in the DAC. No significant degradation has been observed up to up to ~40 GPa. Our Co and Mo samples have been successfully used in challenging inelastic x-ray scattering experiments, yielding high quality data at the highest hydrostatic pressures (39 GPa) ever obtained with this technique on single crystals [24, 25]. The

collected spectra, both in the case of longitudinal and transverse modes, clearly highlight the extreme quality of the produced crystals. Impulsive stimulated light scattering measurements to 12 GPa have also been performed on our Co samples [26], further supporting the claimed high surface quality of our crystals. EXAFS experiments on our Zn samples are scheduled, and the application of the present methodologies to preparation of crystals for other techniques is straightforward.

In summery, we have illustrated a new technique for the production of single crystal samples for use in experiments at very high pressures in the DAC. These types of samples open the door to a range of high-pressure investigations of orientation dependent properties. Ultimately, it has been the sample thickness that has limited the measurements to pressures of <40 GPa. This is due to the strong increase in the mosaic spread when the samples are bridged between the diamonds. We are presently working on new techniques with which we aim to obtain thin samples (5 to 10 μm) for use in quasi-hydrostatic experiments at Mbar pressures.

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References

[1] P. Loubeyre, R. LeToullec, D. Hausermann, M. Hanfland, R. J. Hemley, H. K. Mao and L.W. Finger, Nature **383** 702 (1996).

[2] A. K. Singh, H. K. Mao, J. Shu and R. J. Hemley, Phys. Rev. Lett. **80** 2157 (1998).

[3] V. V. Struzhkin, Y. A. Timofeev, R. J. Hemley and H. K. Mao, Phys. Rev. Lett. **79** 4262 (1997).

[4] M. I. Eremets, K. Shimizu, T. C. Kobayashi and K. Amaya, Science **281** 1333 (1998).

[5] C. Gao, H. K. Han, Y. Z. Ma *et al.,* Rev. Sci Instrum. **76** 083912 (2005).

[6] P. Loubeyre, Occelli F. and LeToullec R., Nature **416** 613 (2002).

[7] G. Fiquet, J. Badro, F. Guyot, H. Requardt and M. Krisch, Science **291** 468 (2001).

[8] B. Li, J. Kung and R.C. Liebermann, Phys. Earth. Planet. Inter. **143-144** 559 (2004).

[9] A. P. Kantor, S. D. Jacobsen, I. Y. Kantor, L. S. Dubrovinsky, C. A. McCammon, H. J. Reichmann and I. N. Goncharenko, Phys. Rev. Lett. **93** 215502 (2004).

[10] A. F. Goncharov, J. Crowhurst and J. M. Zaug, Phys. Rev. Lett. **92** 115502 (2004).

[11] H. Shimizu, H. Tashiro, T. Kume and S. Sasaki, Phys. Rev. Lett. **86** 4568 (2001).

[12] M. Song**,** H. Yamawaki, H Fujihisa, M. Sakashita and K. Aoki, Phys. Rev. B **60** 12644 (1999).

[13] M. P. Pasternak, G. KH. Rozemberg, W. M. Xu and R. D. Taylor, High Press. Res. **24** 33 (2004).

[14] O. Mathon, F. Baudelet, J. P. Itié, A. Polian, M. d'Astuto, J. C. Chervin and S. Pascarelli, Phys. Rev. Lett. **93** 25503 (2004).

[15] E. Arakawa, M. Ito, N. Ishimatsu *et al.,* J. Phys. Chem. Solids **65** 2089 (2004).

[16] H. R. Wenk, S. Matthies, R. J. Hemley, H. K. Mao and J. Shu, Nature **405** 1044 (2000).

[17] S. Matthies, S. Merkel, H. R. Wenk, R. J. Hemley and H. K. Mao, Earth Planet. Sci. Lett. **194** 201 (2001).

[18] S. Matthies and M. Humbert, J. Appl. Cryst. **28** 254 (1995).

[19] G. C. Butler and D. L. McDowell, Int. J. Plastic. **14** 703 (1998).

[20] J. G. Berryman and H. F. Wang, Phys. Rev. E **64** 011303 (2001).

[21] L. Dormieux, A. Molinari and D. Kondo, J. Mech. Phys. Solids **50** 2203 (2203)

[22] T. G. Mayerhöfer, Spectr. Acta A **61** 2611 (2005).

[23] G. Petzow, Metallographic Etching, Am. Soc. for Metals (1978).

[24] D. Antonangeli, M. Krisch, G. Fiquet, D. L. Farber, C. M. Aracne, J. Badro, F. Occelli and H. Requardt, Phys. Rev. Lett. **93** 215505 (2004).

[25] D. L. Farber, M. Krisch, D. Antonangeli, D. Orlikowski, A. Beraud, J. Badro and F. Occelli, submitted.

[26] Crowhurst *et al.*, unpublished data, 2005

Figures

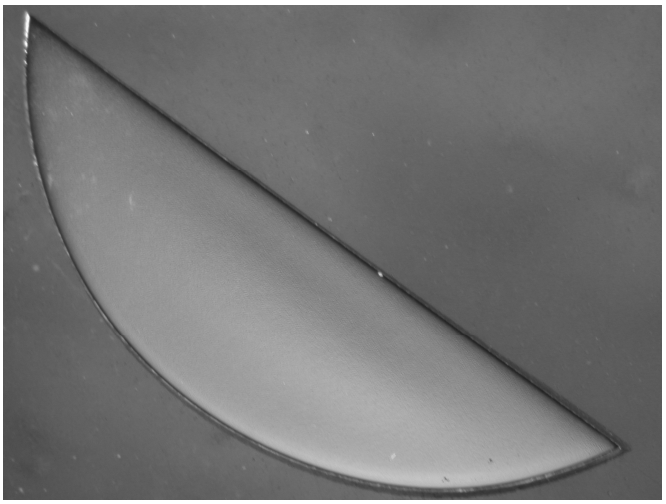

Figure 1. Top view of a thin (500 μm) single crystal of molybdenum as seen after initial polishing. The sample is oriented with [110] polished and the straight edge is approximately 0.8 mm.

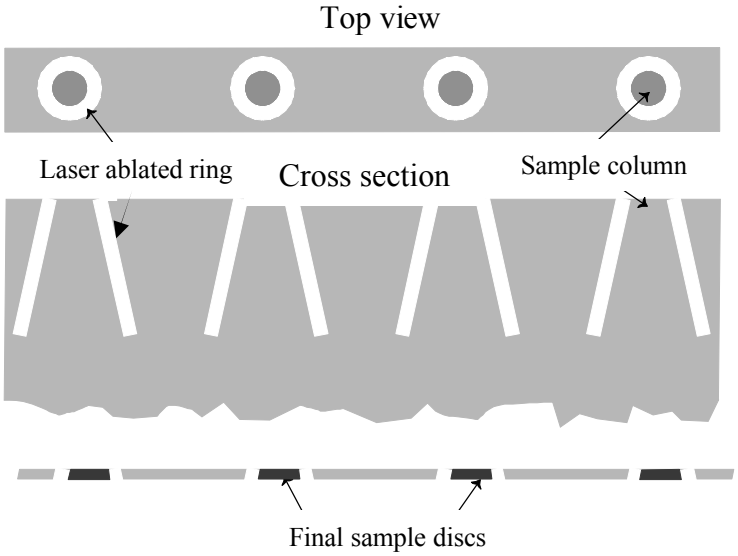

Figure 2. Schematic cartoon of the sample cutting and polishing processes. The angle of ablated rings in metals is approximately 10°.

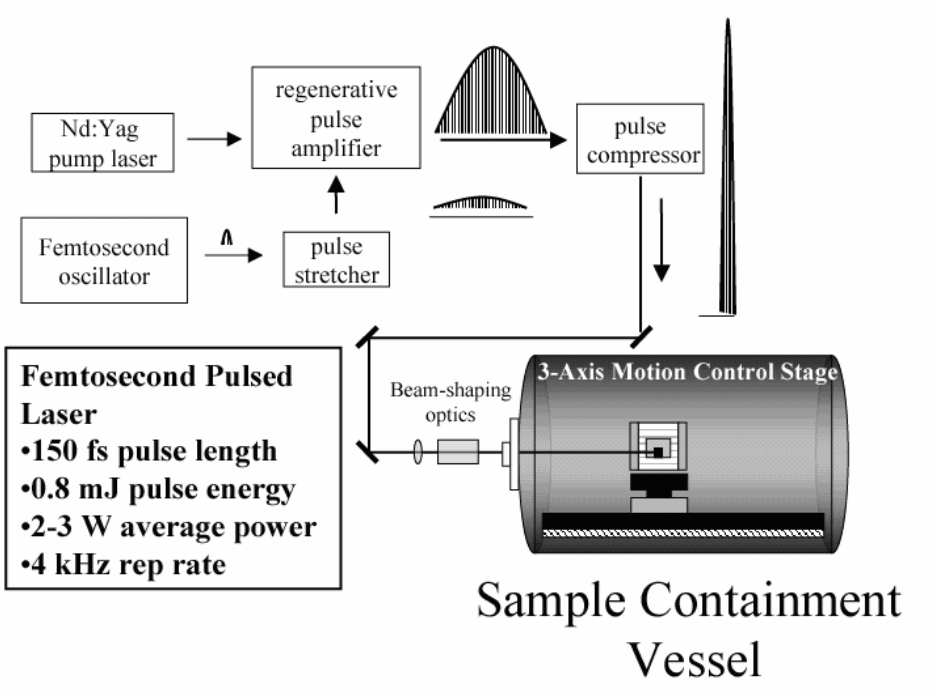

Figure 3. Schematic view of the laser ablation system used for cutting disks in the sample.

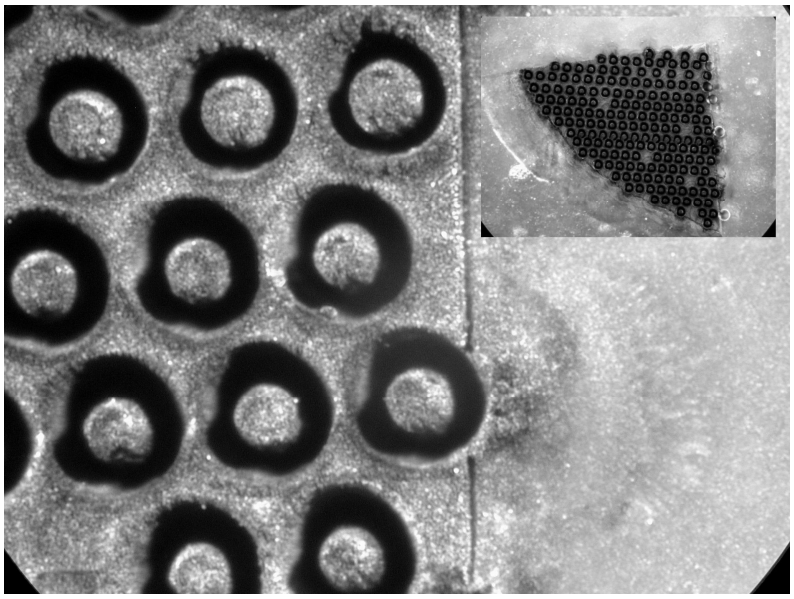

Figure 4. Map view of a cobalt thin plate after laser cutting and prior to re-polishing. The diameter of the inner cores is ~ 60 µm. In the inset: top view of the entire cored Co plate.

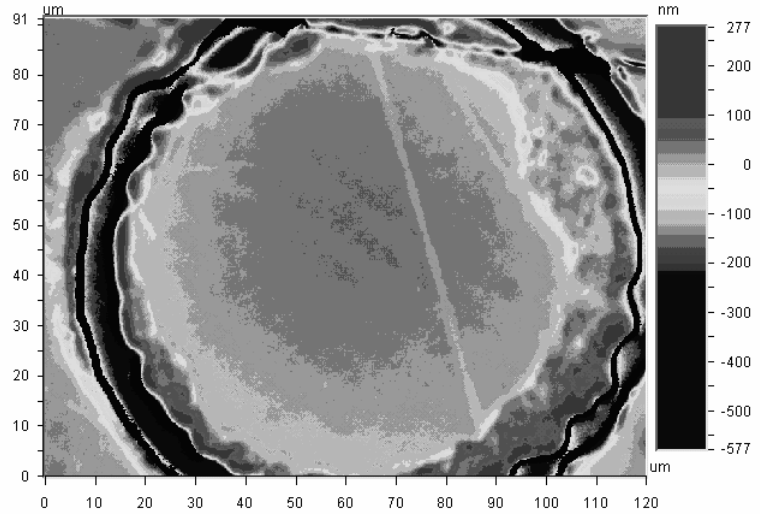

Figure 5. Surface characterization of a Co sample by white-light interferometry. The horizontal and vertical scales are in µm, while the z-scale (gray scale) is in nm. The rms roughness is 74.5 nm, with a maximum peak-to-valley roughness of 850.2 nm due to roll off around the edges of the samples.

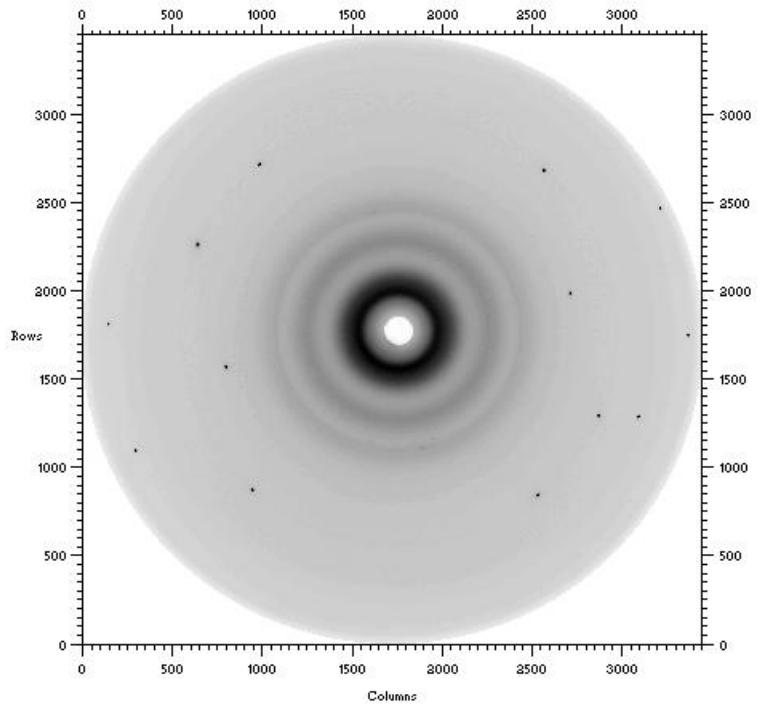

Figure 6. Typical angle dispersive diffraction pattern of a Mo sample (45 µm in diameter and 17 µm thick). The image was recorded by rocking the sample from -15° to +15°. Thirteen Mo reflections are seen. The circular shapes and small size of the spots are a qualitative indication of the high quality of the crystal.

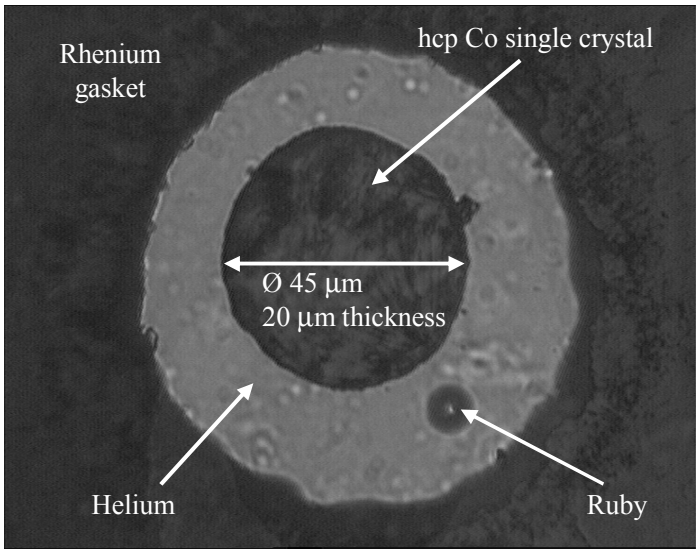

Figure 7. Co single crystal, 45 µm in diameter and 20 µm thick, loaded into a rhenium gasket and compressed within a DAC using helium as the pressure-transmitting medium.

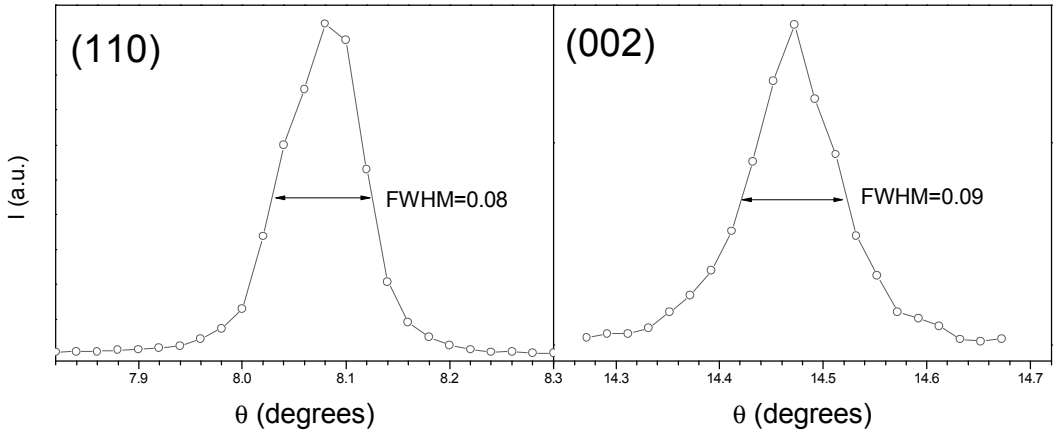

Figure 8. Rocking curves from a Mo sample in the DAC at 3.2 GPa recorded at the IXS-dedicated beamline ID28 of the ESRF. Their full widths at half maximum (FWHM) are both less than 0.1°.

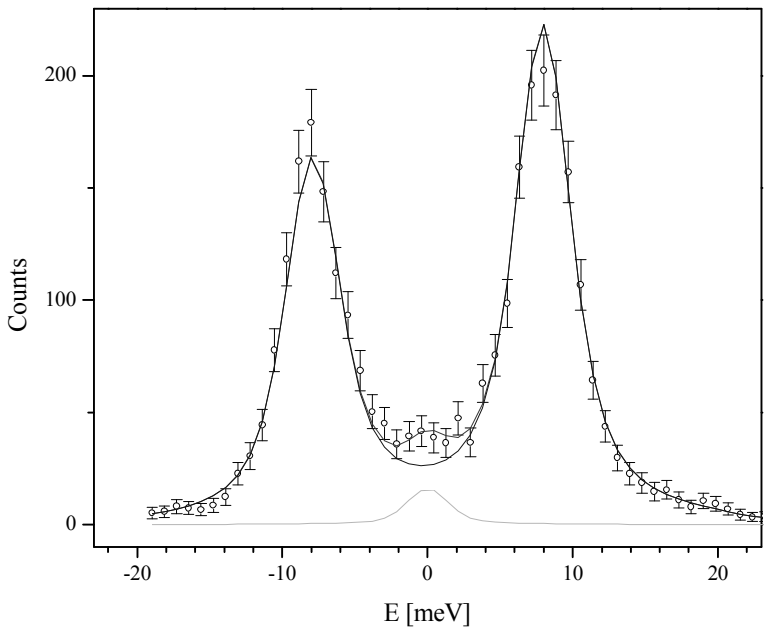

Figure 9**.** Typical IXS spectrum recorded on Mo at 3.2 GPa. Three peaks are recorded: the faint quasi-elastic line centered at 0 energy, surrounded by the Stokes and Anti-Stokes peaks corresponding to the creation and annihilation of acoustic phonons. The lack of a strong quasi-elastic line further supports the claim of the good crystalline quality of the sample.