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| **Shifts:** | **Local contact(s)**: **Jürgen Härtwig** | *Received at ESRF:* |


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# Report:

Remarkable progress has been achieved in the HPHT-synthesis of diamond and increasingly also in the surface preparation techniques, to develop diamond material for Bragg-diffracting X-ray optical elements that could conserve the coherence properties, however a lot of research and development still needs to be done. The crucial points are firstly, a bulk with a high structural quality – that means no dislocations, no micro-defects and precipitates, no inhomogeneities of impurity distributions that result in local relative lattice parameter changes larger than about $10^{-8}$. In addition to this the surfaces should be of high quality that is with rms roughnesses close to 1 or 2 Å. The best available specimens have now a "mosaicity" of typically 0 to 0.2 arcsec and smaller local regions with sufficient perfection. In measurements carried out in September 2006 at ID19 we were for the first time able to demonstrate (measurements done in the last few hours of the beamtime) on one sample the existence of smaller areas with residual strains close to few $10^{-8}$. However, such areas must be larger (nearly the whole plate), the strain level should even be lower and this bulk quality must be routinely reached. Consequently, the general long-range crystalline quality of the diamond crystal bulk must be improved and the necessary measuring strategy with high strain sensitivity and high spatial resolution must be developed. This was the focus point of this proposal. Practically the same proposal was submitted and accepted one year ago. The necessary key instrument was transferred from ID19 to BM05 together with other X-ray topography instruments it. Unfortunately the creation of a new X-ray topography station at BM05 and the re-installation of all instruments took a longer time than planned. It is well advanced but not yet finished even now. So unfortunately the instrument could not yet be used for proposal MA-742.

The proposal pannel asked also for information about other experiments that were carried out with the same main goal, the improvement of the bulk and surface quality of diamond for X-ray optical applications. Several sessions of inhouse reasearch beam time were used. Some results will be presented below.

## 1. Diamond Cooling Tests

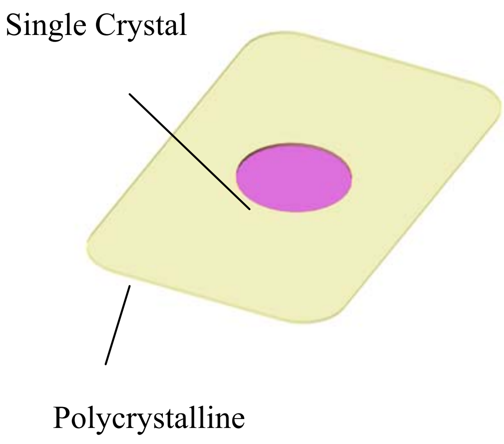
It appears that for most of the future diamond applications the cooling efficiency has to be improved; this will reduce the thermo-mechanical deformation of the crystal. We are working at ESRF on several approaches. One is to increase the surface of thermal exchange with the cooled support. The size of single crystal diamond plates (which are relatively easily available) is only 7x7 $mm^2$ (perfect central region of about 4x4 $mm^2$, 100-orientation). Therefore single crystal diamonds will be mounted on larger CVD diamond plates. The other approach is to improve the cooling efficiency of the copper block itself.

### Increase of Thermal Contact Area - The Hard Fixture Scheme

A test program was initiated to braze a single crystal diamond to a polycrystalline diamond heat-sink. Such ‘hard fixture’ schemes (i.e. metal brazing at high temperatures) lead to high levels of stress in the single crystal diamond. The goal of our tests was to minimize such stresses and so avoid degradation of the initially high optical quality of the single crystal. Two geometries were tested.

### The Hard Fixture Scheme – First Geometry

White beam topographs of single crystal test diamonds were taken before and after brazing. For the trial of the first scheme, a CVD grown single crystal diamond was used rather than an HPHT IIa diamond, simply for reasons of availability. A circular, single crystal of 4.98 mm diameter, 225 µm thickness, was brazed onto a rectangular, CVD grown polycrystalline diamond base plate 12x20 $mm^2$ and 230 µm thickness. A precise hole of 5.06 mm diameter was cut out to accommodate the single crystal diamond with a surrounding fine fillet of brazing material (see Figure 1). The brazing material used was Lucanex® 716 (alloy composition: Ag 71.5%, Cu 28%, Sn 0.5%) which had micron sized spheres of material. Brazing took place with flux and under vacuum.

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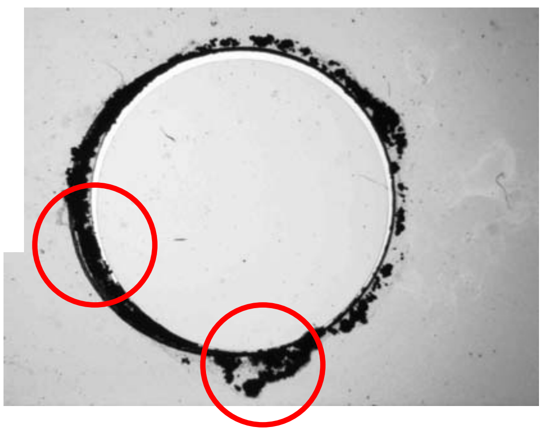

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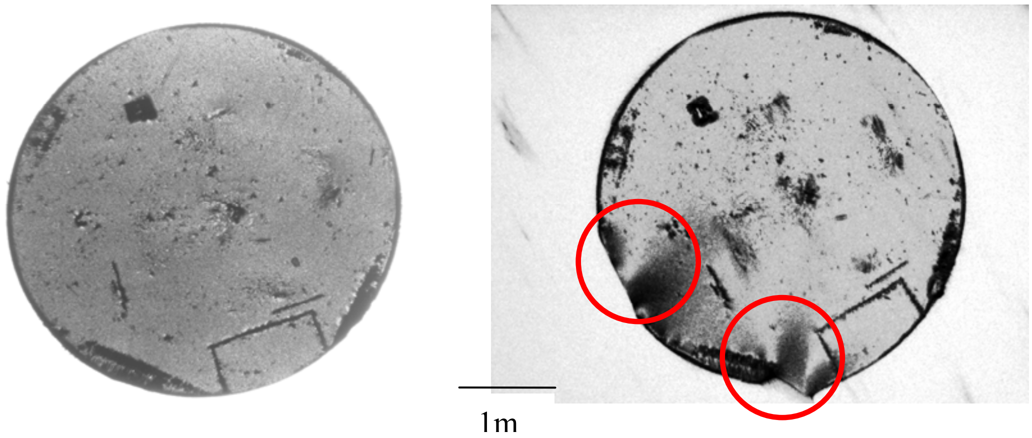


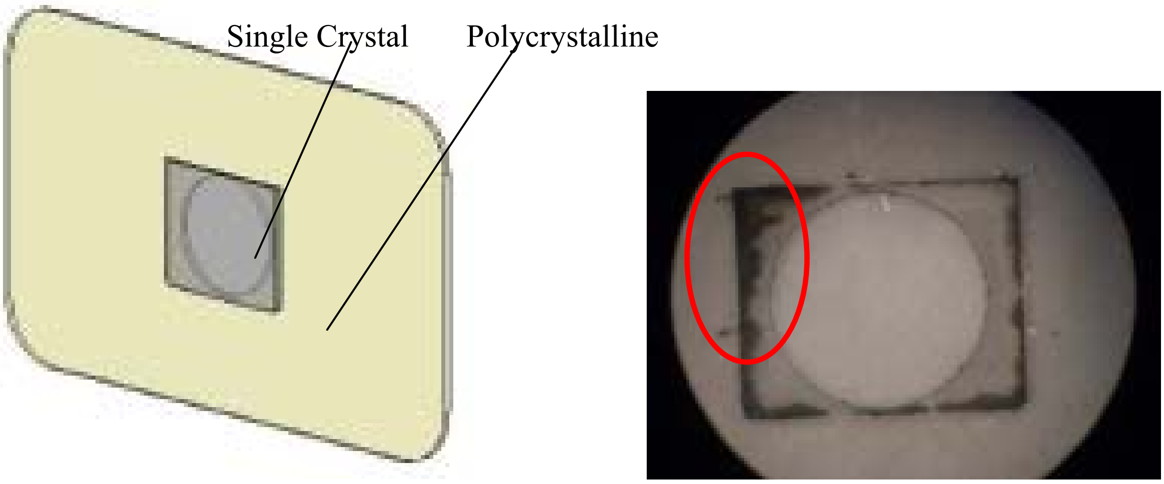

C D

Fig 1. A. Drawing of the two CVD diamond plates. B. Detail of the brazed single crystal diamond. C. White beam topograph of the single crystal CVD before brazing (in transmission; ID19), and D. after brazing

Comparing the pictures before and after brazing, we notice that no previously existing major crystallographic defects were enhanced, nor did new deformations appear in the central region. On the other hand, we observe two areas of strain (marked with circles on pictures 1.B and 1.D) where the crystal was strongly distorted following brazing. This might be explained by a non-uniform brazing seam (lower circle of picture 1.B) and/or an excess of brazing material (upper circle of picture 1.B). In the future, other diamonds will be brazed with this geometry to test different brazing techniques which might produce a more homogenous brazing seam and thus not distort the single crystal diamond.

**The Hard Fixture Scheme – Second Geometry**

For this second test, the polycrystalline diamond support plate had a dimension of 5x4x0.1 $mm^3$. A 5 mm diameter hole was laser cut in this plate to avoid interaction with the X-ray beam. Brazing paste was applied as a fillet along the edges of a rectangular, single crystal CVD diamond, and then this and the polycrystalline plate were pressed together in a jig during the brazing at high temperature. This was done to obtain a direct diamond to diamond contact and to avoid capillary migration of the paste between the two diamonds. However, as shown in Fig 2, the braze material did migrated between the two diamonds during the processing. Fig 2.D shows that this migration induced strong deformation of the crystal at the places where the migration is the most pronounced.

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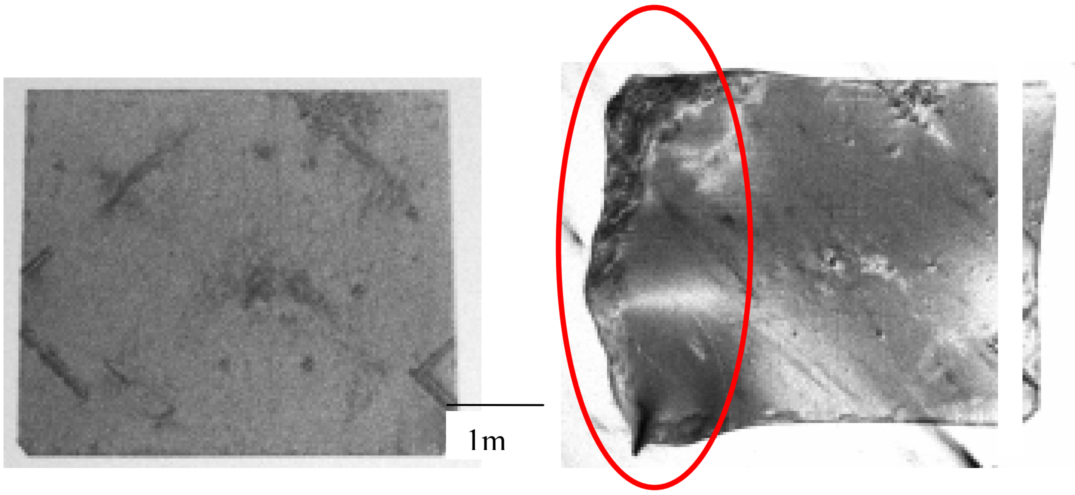


C D

Fig 2. A. Drawing of the two CVD diamond plates. B. Detail of the brazed diamond. C. White beam topograph of the single crystal CVD before brazing (in transmission; ID19) and D. after brazing

A future trial is planned using a proprietary *Element Six* process which might prevent this migration of the brazing paste between the two diamonds and which will therefore reduce the local stress. Besides this problem of induced stress, this brazing scheme is more interesting than the previous one because the firm pressing together of the diamonds during the process should result in obtain a better cooling of the single crystal due to the intimate diamond to diamond contact. Table 1 shows the thermal conductivity values for the different materials.

Table 1. Thermal conductivity and fusion point for materials used to bond two diamonds together

| | Thermal Conductivity at 297 K [$W.cm^{-1}.K^{-1}$] | Fusion point [°C] |
|---|---|---|
| Diamond IIa HPHT | 20-25 | 3700 |
| Diamond CVD | 4-18 | 3700 |
| Brazing paste *(LUCANEX 716)* | ~3 | ~900 |
| Indium | 0.82 | 150 |
| Eutectic In-Ga | 0.51 | 16 |

When we will have mastered brazing techniques which do not create unwanted additional stress, the brazed systems will be leak tested and used to build vacuum tight windows that with embedded HPHT grown single crystals. This is of interest to replace the existing polycrystalline diamond windows on beamlines where the coherence preservation of the X-ray beam is a concern.

### Increase of Thermal Contact Area - The Soft Fixture Scheme

Soft fixtures look very attractive to bond two diamonds together or to fix the diamond heat sink to the cooled copper block. They should bind the crystals without inducing internal stress. An ideal soft fixture also has to be made with a material that has a high thermal conductivity coefficient; with a fusion temperature point which is not too high to avoid induced stress during the bounding; and not too low which does not required a sophisticated, and costly, cooling system. The selected material has to have a low vapour pressure that will reduce the outgasing of the component. This will ensure a good compatibility with Ultra High Vacuum environment, as all of our optical elements are located in vacuum. In this respect Indium looks to be a good compromise. A trial was made to bind a single crystal diamond to a heat sink of polycrystalline diamond with a thin Indium layer. In order to avoid the Indium migration and to ensure good adherence to the crystal, the diamond surfaces were first metalized with Ti/Pt/Au. The Indium layer was inserted between the two crystals, then the whole system was heated up to the fusion temperature of Indium and pressed together before cooling down of the assembly.

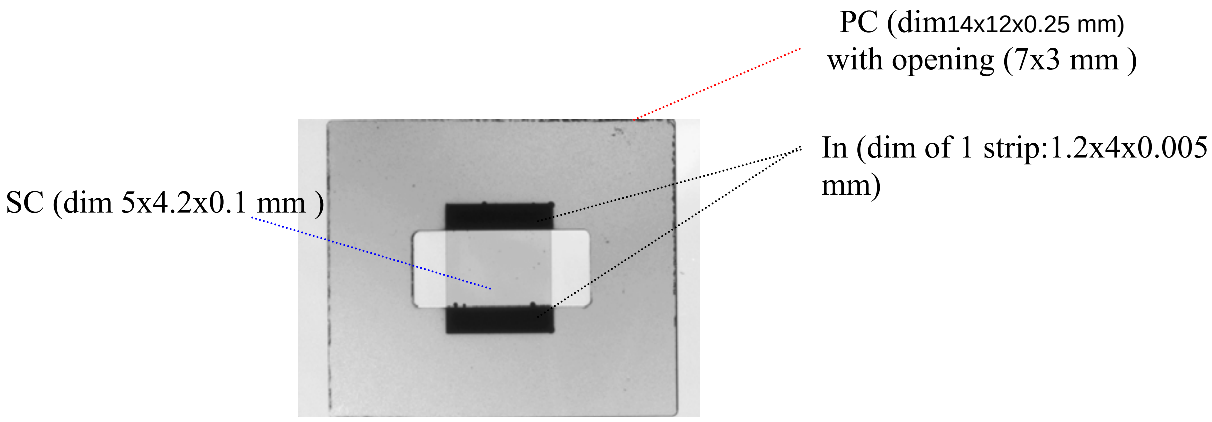


Fig 3. Close-up picture of a Single Crystal (SC) diamond fixed to a Polycrystalline (PC) heat sink with two thin strips of Indium

The Indium layer was 5 µm thick, which is a practical limit in terms of minimum material thickness. This thin layer thickness ensures a minimum thermal resistance of the fixture.

The system was put in the X-ray beam in order to obtain topographs of the single crystal. At the time of the experiment no cooling systems were available. As a consequence, the heat loading from the absorbed X-ray beam softened the Indium, causing the single crystal to move. This mounting will be remade with an adequate cooling system as shown in Fig 4.

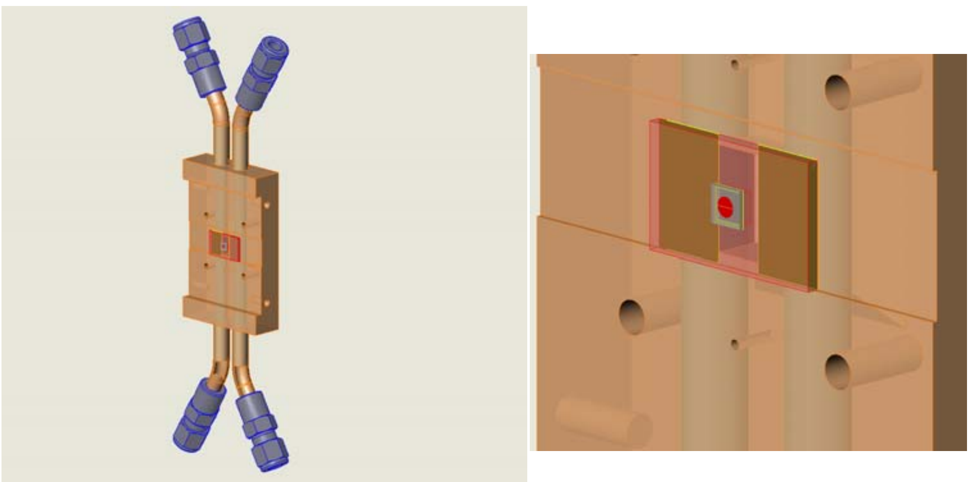

Fig 4. Global and extended view of the cooling system fitted with a heat sink, a single crystal and bound with Indium (the red circle represents the beam footprint)

Fig 5 shows finite element calculations of a quarter geometry of the above cooling system, with the single crystal bond directly to the copper cooled block, or with the diamond mounted to an intermediate polycrystalline diamond plate that is itself bonded to the cooled block. For the computation, the total absorbed beam power was set as 100 W; the temperature of the cooling pipes at 20 °C; and the beam given a diameter of 1 mm. With these boundary conditions, the reduction of the temperature increase at the centre of the crystal using the intermediate polycrystalline diamond heat spreader is nearly 10 %. More importantly, the temperature distribution in the single crystal is smoother with the polycrystalline heat spreader.

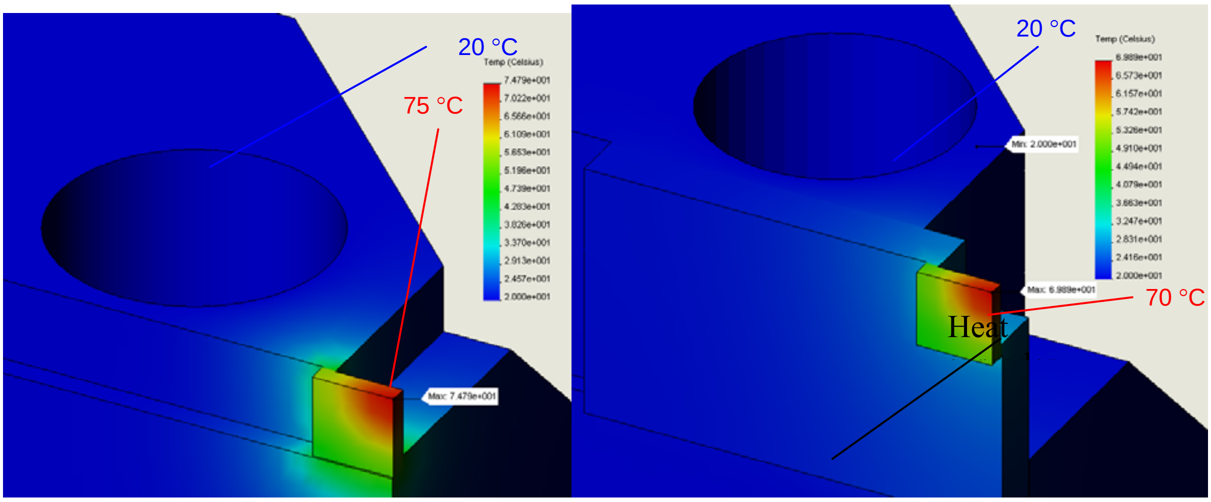


Fig 5. Quarter geometry, copper block mounting without and with a polycrystalline diamond heat spreader

**Increase of Thermal Contact Area - The Clamping Fixture Scheme**

Some fixtures have used a thin Indium foil pressed at room temperature between the diamond and the cooling system with a clamping system. This technique is extremely sensitive to the clamp pressure applied, with the value of the thermal contact resistance decreasing as the contact pressure increases. We are using extremely thin diamonds to reduce the amount of absorbed X-ray beam power in the material, and consequently such clamping techniques is not advisable because the diamond becomes deformed and stress is created in the crystal. Secondly, the contact surface of the single crystal diamond to the Indium foil is limited due to the small available dimensions of high quality IIa HPHT diamonds. This leads to a large temperature rise at the diamond-Indium interface (ΔT [K]), given by the following equation.

$$\Delta T = R.\Phi$$

where R is the Thermal Contact Resistance [$m^2$.K/W], and Φ is the Heat Flux [W/$m^2$].

The best R value that we can expect is in the order of 1 $10^{-4}$ [$m^2$.K/W]. For illustration, if we consider the geometry of Fig 4, where the Indium contact surface is 9.6 $10^{-6}$ $m^2$, then with an absorbed power of 100 W and the above R value, we obtain a temperature rise at the interface in the order of 800 °C if the system is only clamped. This will melt the Indium foil.

**Increase of Thermal Contact Area - The liquid Fixture Scheme**

Diamond plates might be bonded together and fixed to the cooling system by using an In-Ga eutectic. This compound is liquid at room temperature; it holds the crystal by surface tension and therefore induces no appreciable stress in the crystal. As shown in Table 1, its thermal conductivity value is lower than Indium. The eutectic induces corrosion of aluminium or copper supports, but this can be avoided by a nickel coating. The main drawback of this eutectic is that when it is applied on the diamond, it is extremely difficult to prevent liquid spillage onto the optical region of the diamond. Literature reports that with such spillage and in the presence of the intense X-ray beam, diamond oxidation might be initiated. Such oxidation would ruin the optical surface. It is possible to avoid the In-Ga spillage towards the central region, but this requests a delicate mechanical arrangement.

**Increase of Cooling Efficiency of the Cu support - The Micro-channel Scheme**

Different cooling schemes were modeled in a study intended to improve the design and thus the efficiency of the water cooling support for diamond crystals used as X-Ray monochromators. The immediate goal was to optimize the cooling support of the existing ESRF semi-transparent diamond monochromator design and to prepare the high-heatload diamond monochromator projects.

The parameters taken for the thermal model are the following: the crystal is 6 x 6 $mm^2$ with a thickness of 150 µm. The crystal is cooled on two lateral sides on a width of 1mm, i.e. the total cooling area is 12 $mm^2$.

An Indium-Gallium eutectic layer interfaces the diamond to the support without any stress. The total absorbed power from the X-ray beam is 20 W. The supports are in copper, coated with nickel. The temperature of reference of the cooling water is $T_{ref}$= 295K. The heat transfer coefficient between water and copper is taken to be 10 000 W/m$^2$.K, but for the micro-channels cooling design below the value is estimated to rise to 30 000 W/m$^2$.K due to turbulent flow effects. The prototype support is designed to work in Bragg or Laue geometry. It might accept larger crystals (see Figure 6).

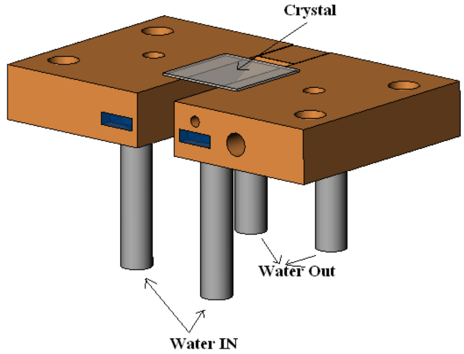


Figure 6. Prototype support

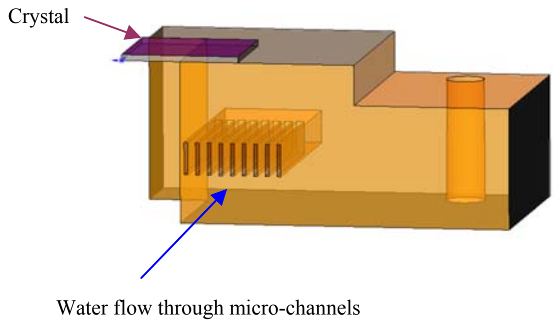


Figure 7. A quarter of a micro-channels support.

Five different schemes were considered: bottom cooling, pipe cooling, channel cooling with different geometries and micro-channels cooling (see Figure 7). For each design we report below the minimum temperature, the maximum temperature, the gradient of temperature through the support itself and the difference of temperature between $T_{min}$ and the water temperature. Table 2 compares the different cooling schemes.

Table 2: Results of the cooling scheme models

| ***Type of cooling scheme*** | ***$T_{max}$ [K]*** | ***$T_{min}$ [K]*** | ***$T_{max}$-$T_{min}$ [K]*** | ***$T_{min}$-$T_{ref}$ [K]*** |
|---|---|---|---|---|
| *1. Bottom cooling* | *322* | *311* | *11* | *16* |
| *2. Pipes Ø 2 mm cooling* | *320* | *310* | *10* | *15* |
| *3. Channel 0.4 x 0.8mm cooling* | *315* | *306* | *9* | *11* |
| *4. Micro-channels 0.1 x 0.8 mm cooling* | *307* | *298* | *9* | *3* |
| *5. Micro-channels 2x (0.1 x 0.8 mm) Cooling* | *304* | *296* | *8* | *1* |

The gradient of temperature, $T_{max}$ –$T_{min}$, across the support determines the extent of the internal deformation and bending of the support itself. $T_{min}$-$T_{ref}$ expresses the difference of temperature between the support itself and the surrounding. This difference of temperature is important because it may introduce stresses and a parasitic deformation such as a twist of the support.

The fifth scheme is clearly the best as regards the results from the model but this micro-channels design requires advanced manufacturing techniques. Therefore, as a first step, we have ordered a cooling support of the third type, with the wider cooling channels of 0.4 x 0.8 mm$^2$.

The support has now being manufactured and the water connectors has been implemented. The next step is to test under heat load this system with a 7x7x0.5 mm$^3$ diamond and compare it to the FEA results and with standard cooling devices (results expected before the end 2010).

### Thermometry

In order to assess the efficiency of the future diamond cooling systems presented here above, a thermometry method must be developed to measure the heating of the diamond sample. The selected method may also be used at the ESRF to monitor diamond based X-ray Beam Position Monitors, which are presently under development, as these are inserted in the intense white beam.

### Thermocouple Measurement

As a first step, a synthetic Ib CVD polycrystalline square diamond sample of 3.5x3.5x1.250 $mm^3$ was drilled on its side to accommodate a 0.25 mm thick thermocouple. This diamond, equipped with a miniature thermocouple fixed in this hole, will be placed in the white beam of an ESRF beamline. As the diamond is relatively thick it will heat up rapidly and the thermocouple method will give us a direct measurement of the diamond bulk temperature rise.

### Infra-red measurement

In engineering, contact-less IR measurement is a proven technique to determine the temperature of material surfaces. In the case of a heated diamond, however, it is difficult to get reliable measurements out of IR devices (e.g. camera, pyrometer). The main reason for this is the extremely low emissivity of diamond at IR wavelengths (around 0.03, to be compared with silicon emissivity which is around 0.6, and most of the IR cameras available on the market have a minimum emissivity threshold of typically 0.1). Secondly, as we want to keep the diamond at a temperature that does not induce noticeable thermal stress, the emitted IR flux is low: recall that for a black body the total emissive power is proportional to $T^4$.

An attempt will take place at a thermography laboratory (ENISE- Saint Etienne- France) where a diamond sample of will be heated with a $CO^2$ laser up to 100 °C and the temperature measured with an ultra-high sensitivity IR camera (FLIR ThermaCam Phoenix) and a pyrometer. These results will be crosschecked with the direct thermocouple measurement technique. If this camera or the pyrometer give reliable and repeatable measurements in the laboratory, then the technique will be tried on an ESRF beamline. A limit of this technique is that it will be extremely difficult to measure the temperature of the diamond once it is put in operation in the vacuum vessel, as the diamond IR signal measured by the camera will be confused with that of the room temperature vacuum window. Nevertheless this technique might be useful to assess, in air, the efficiency cooling of our diamond mounting systems.

### Optical measurement

A second contact-less technique will be tested at the ESRF. The method is based on the fact that when a diamond heats up, its refractive index is modified. The following relation links the variation of the refractive index to the local temperature of the diamond, where nd is the refractive index which is determined experimentally by laser interferometry.

$$(nd(T)-nd(25°C))/nd = -8.1E\text{-}5 + 3.02E\text{-}6 \cdot T + 2.91E\text{-}8 \cdot T^2 - 2.29E\text{-}11 \cdot T^3 + 9.52E\text{-}15 \cdot T^4 \qquad (T = 25, ..., 800°C)$$

Such a setup might be motorised to scan the diamond surface to determine the heat profile induced by the X-ray beam. We should be able to easily integrate this optical method in a vacuum system.

**2. Test of cleaved 111-oriented crystal plates by X-ray topography with long propagation distances**

For many setups using diamonds as beam splitters or double crystal monochromators it if of advantage to use crystal plates with the 111-orientation. Unfortunately this is the surface that is most complicated to polish with the classical mechanical diamond polishing methods. For plates with negligible miscut (angle between reflecting lattice plans and crystal surface) the polishing time tends to infinity. Therefore one has at least three choices with different drawbacks.

1. Mechanical polishing with several degrees of the miscut angle. This may have negative effects on the coherence properties as well for the possibility of extreme focussing. But it is possible to do. It is known that this introduces substantial sub surface damage, to the extent that it is not possible to obtain a Bragg diffraction at the Cuk$K_{\alpha 1}$ line.

2. Using alternative, non-mechanical polishing methods. They are not yet well established and still under development, but it is possible to obtain a low miscut angle (common R&D project of the ESRF and the University of Johannesburg).

3. Using cleaved crystal plates. This results in surfaces with low miscut angle, but with surface steps.

The idea was to check the influence of those surface steps on the beam quality at different propagation distances. One has to have in mind that in most cases the distance between monochromators and the sample may be many meters.

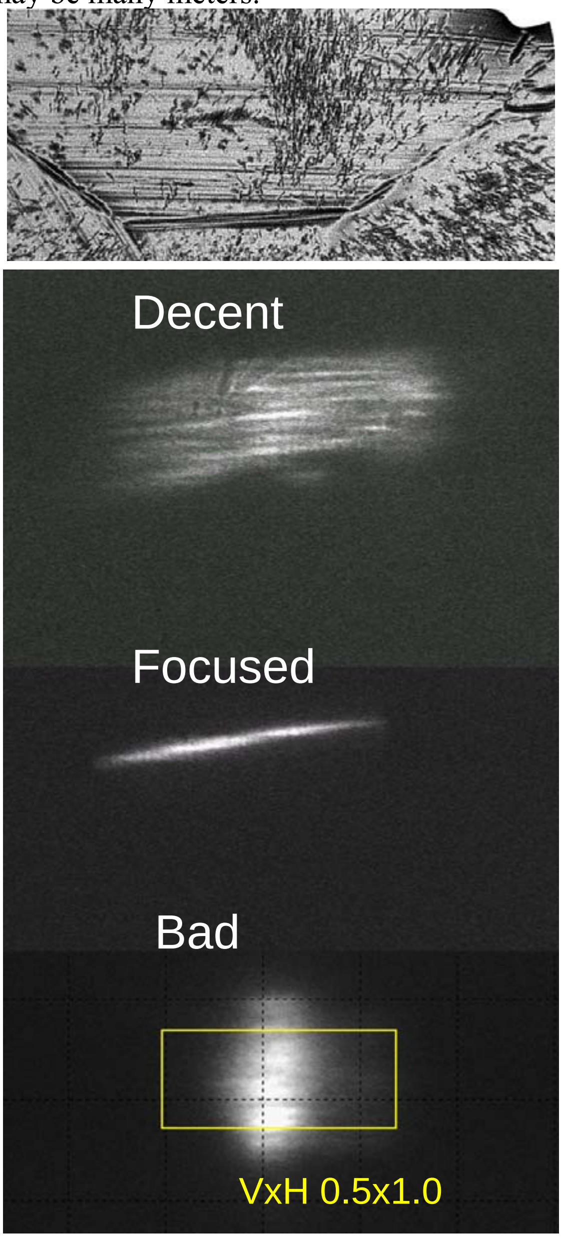


Figure 8. X-ray white beam topograph (in transmission) of a beamsplitter diamond plate installed at ID10B (above) and three pictures of the beam several meters after the crystal.

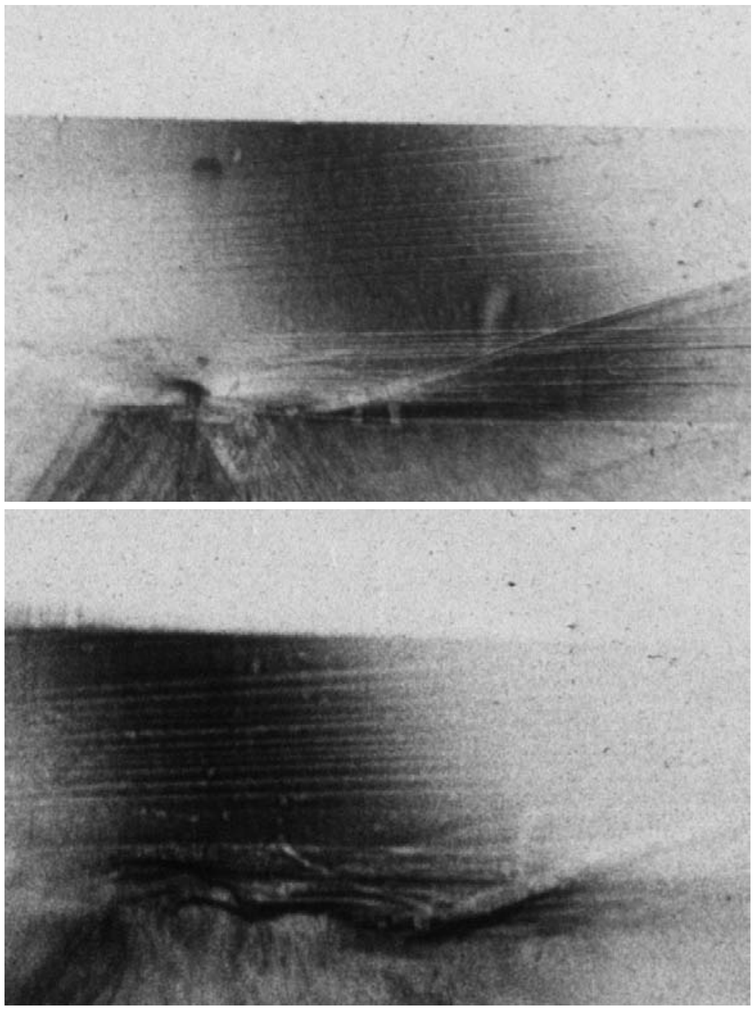

Figure 9. X-ray topograph with a monochromatic beam in reflection of a cleaved 111-oriented diamond plate (dispersive set-up, total image height 1mm, negative images).

On Figure 8 we presented four pictures. The upper one is a white beam topograph of a diamond beam splitter installed at ID10. This is the so called type Ib crystal that is rich in nitrogen impurities and it contains strong deformations due to growth sector boundaries, growth striations and dislocations. The three beam images under the topograph show a low quality beam. The upper beam image should show the rectangular profile of the diffracted beam. This is not the case.

From the diamond producer Elements Six we received a cleaved 111-oriented diamond plate of type IIa with very low nitrogen content and with local dislocation free zones. We checked the quality of the beam image after a short (0.28m) and a long (2.mm) propagation distance.
The phase contrast images of the steps of the cleaved surface (horizontal lines) become more distinct with the distance and images of deformed crystal parts (in the lower part of the images) deform rather strongly. However the images of the rather perfect crystal parts (upper regions) keep their form.
This result demonstrates that a cleaved crystal with high bulk quality that is visible in Figure 9, leads to much less beam deformation than that visible in Figure 8. So it appears to be very promising the use these crystals already now. An even bigger progress could be achieved when the steps could be polished away by alternative processing methods (R&D under way).

**3. Study of regions close to the surface of diamond plates by grazing incidence X-ray topography**
We also made a test if it is possible to detect surface damage due to the crystal processing by X-ray topography. The idea was to work with asymmetric Bragg cases in grazing incidence geometry. By changing the energy of the incident beam it is possible to change the Bragg angle for a given reflection. We selected a given set of reflecting lattice planes, in our case using the 224 reflection, the crystal had a 001-orientation. By tuning the energy to 12.4keV, 13.5keV and 14.4keV we changed the angle $\alpha_i$ between the incident beam (in Bragg position) and the crystal surface from 9.7 º, to 3.8 º and to 1.0º. This changed the extinction depths from 2.8μm, over 2.0μm to 1.1μm. We took whole scans with images. A quantitative analysis did not yet start, but on a first glance we do not see remarkable changes. Probably the surface quality of the selected sample was already too good.