

The improvement of G3 beamline for diffraction imaging of solid-liquid phase transitions

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Motivation

X-ray diffraction is a common method to investigate crystalline substances. Since interatomic distances in solids have an order of angstroms, crystal lattice behaves as a diffraction grating for the radiation of X-ray region ($\lambda=0.01\text{ nm}-10\text{ nm}$).

The main equation combining the parameters of crystalline material and the wavelength of incident beam is Bragg's equation:

$$2d_{hkl}\sin\theta = n\lambda$$

Here d_{hkl} is an interplanar distance between crystal planes with corresponding indices. The position of a peak in Θ -scale (or in practice in 2Θ -scale) determines the interplanar distance. Moreover, the broadening of x-ray powder diffraction peaks gives information about crystallite size and strain in case of polycrystalline specimens.

However, X-ray diffraction in general case reveals only mean crystalline structure or phase composition.

Real crystals can be inhomogenous due to residual stresses, deviations of crystallite sizes and complicated distributions of phases.

X-ray diffractive imaging allows investigating small areas of a crystalline material by measuring a signal from a variety of spots on the surface [1, 2, 3].

In principle there are two ways to accomplish such experiment. The first possibility is to use a microbeam to illuminate small areas of a sample. This implies high intensity and low emittance sources to be used.

The second way is to illuminate a specimen with an extended beam (so that a large area is irradiated) and to perform the spatial discrimination behind the sample [1].

At G3 beamline (HASYLAB, DESY) the second approach is used.

G3 uses DORIS III synchrotron as a source of radiation (fig. 1)

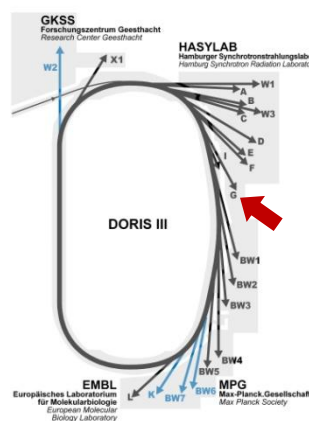


Figure 1. G3 beamline at DORIS

The scheme of a measurement is given in fig. 2. A monochromated beam illuminates a sample fixed on an x-y-z-table of the four-circle MAXIM (MATERIALS X-ray diffraction Imaging) diffractometer. The 2Θ -circle carries a CCD detector with a microchannel plate (MCP) as collimator array. Small capillaries used as collimator tubes have the diameter of 10 μm and the length of 4 mm. The angular acceptance of such collimator system is 2.5 mrad. Since this angle is small the spatial resolution can be given as:

$$r = ad,$$

Where a is the acceptance angle and d is the distance between the sample and the detector.

The pixel size of the CCD is 13 μm and the number of pixels is 1024^2 . An additional detection system consisting of a scintillation counter is inclined 20.4° relative to the MCP/CCD combination [1, 3].

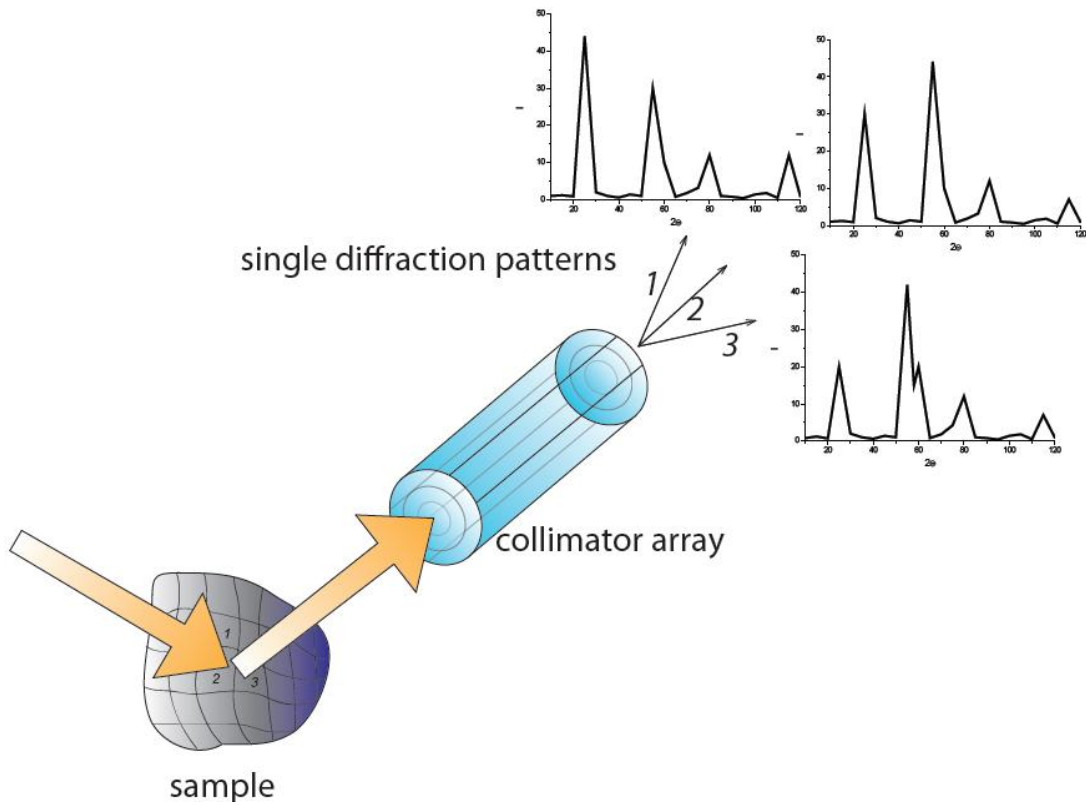


Figure 2. Diffraction imaging experiment

The goal of the current work is to improve the experimental set-up of G3 beamline to make it possible to carry on diffraction imaging measurements in wide temperature ranges including solid-liquid phase transitions.

Experimental Set-up

The hutch of G3 beamline is completed with MAXIM diffractometer (described above) and the source of the beam (fig. 3).

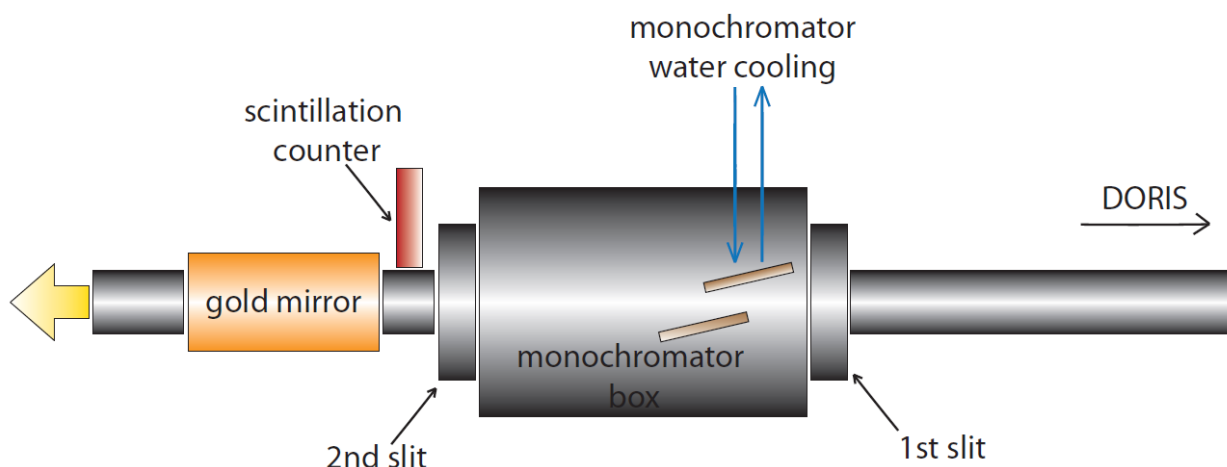


Figure 3. The scheme of G3 beamline

The white beam produced in synchrotron ring hits the germanium monocrystal (111) at Bragg's angle. Consequently the beam with desired wavelength goes out of the monochromator box (after the second reflection).

The cross-section of the beam (and thus the irradiated area of a sample) can be adjusted by the second slit system.

The tilted gold mirror is used for the suppression of higher harmonics (i.e. the reflections with $n > 1$ in Bragg's equation). Higher harmonics are absorbed while the first harmonic passes further. In all our experiments the gold mirror was tilted at 7 mrad.

As it is not possible to treat liquid samples using the common geometry of MAXIM diffractometer with the tilted x-y-z-table (fig. 4), the following upgrade was made.

A germanium monocrystal (111) was mounted on the way of the synchrotron beam in order to reflect it downside so that the sample fixed in horizontal position could be irradiated from above (fig. 5).

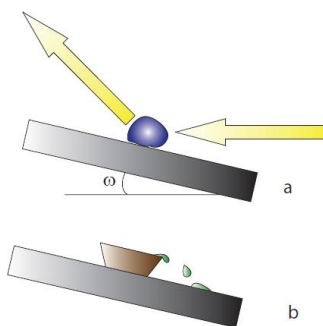


Figure 4. a) Solid sample b) Liquid sample

The work on project was started during the DORIS shut-down so there was no beam to adjust the position of the monocrystal . At first we used a laser beam for rough adjustment.

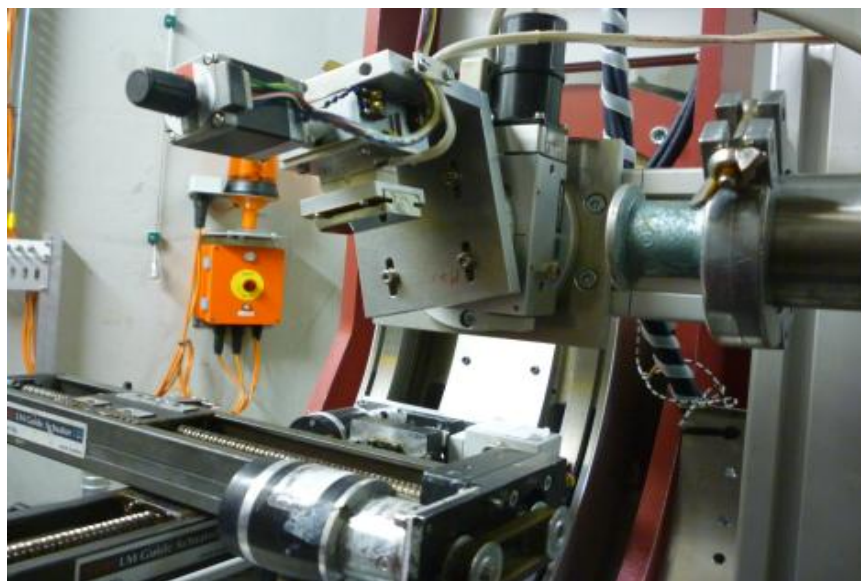


Figure 5. Germanium monocrystal mounted above the x-y-z-table

A He-Ne laser was put on a moving table in the monochromator box. The moving table was controlled by a motor, so the height of the beam could be adjusted precisely while the other variables (the angles and the position in horizontal plane) were tuned manually. We used a spot on the wall corresponding to the precise height of the synchrotron beam as the reference point.

As we had planned to use Cu $K\alpha$ radiation for our measurements the Bragg's angle of the monocrystal was 13.642° which corresponds to 111-reflection of germanium at this wavelength. The position of the monocrystal was adjusted so that the laser beam hit the center of rotation.

When the synchrotron beam became available we managed to adjust the position of the monocrystal more precisely. In order to see the reflection we fixed a small fluorescence screen on the x-y-z-table in the sample position and observed the screen during a 2Θ -scan using a camera connected to the display outside the hutch.

LaB₆ calibration

Since the direction of the synchrotron beam changed after the monocrystal installation we had to recalibrate the detector position (fig. 6). The position of -23.482° was calibrated as zero. Before the calibration the tilt of the gold mirror was taken into account.

To calibrate the 2Θ -offset more precisely and to check whether the wavelength had been properly adjusted we performed a 2Θ -scan of lanthanum hexaboride as this compound has sharp reflections with highly reproducible peak positions.

The diffraction pattern of LaB₆ is given in figure 7. One can see that the positions of peaks are not significantly shifted.

To calculate the 2Θ -offset we used the modified Bragg's equation:

$$2d_{hkl} \sin(\theta + \Delta\theta) = \lambda,$$

where $\Delta\theta$ is the theta-offset. With the calculated offset we managed to calibrate the detector position accurately.

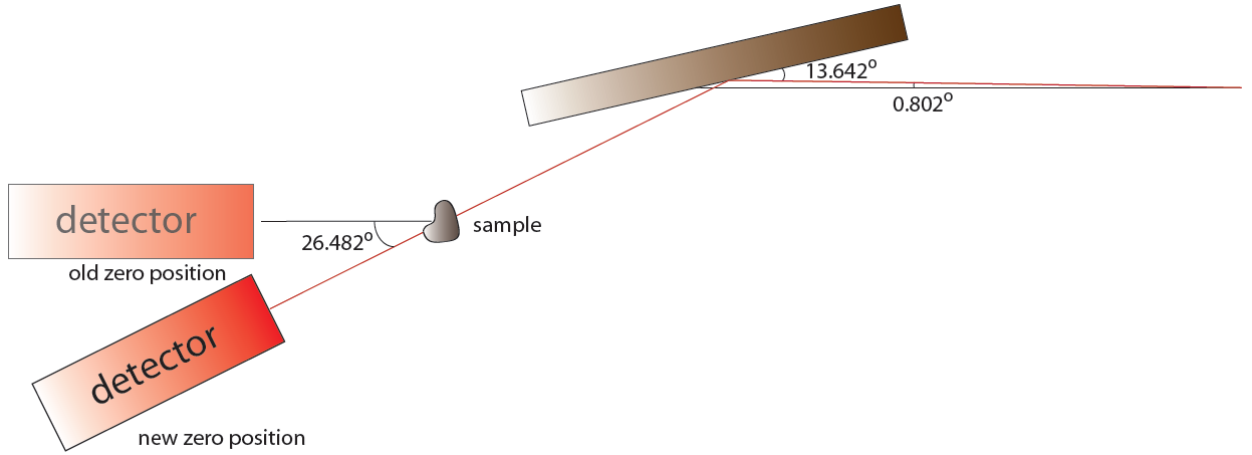


Figure 6. Calibration of the detector position

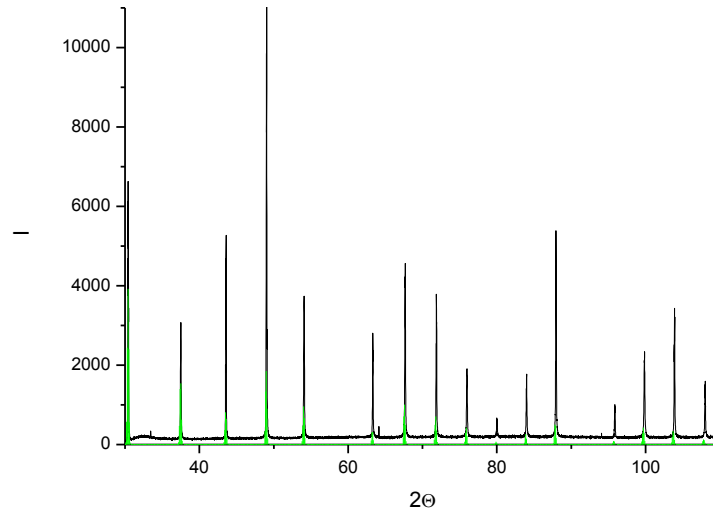


Figure 7. LaB₆ diffraction pattern. Green lines correspond to calculated peak positions

Ice measurements

When the calibration was finished we started our measurements. Ice was chosen as the first sample since it has low melting point.

To control the temperature of the specimen we used the Peltier cooler with Pt100 sensor.

A Peltier cooler is a thermoelectric cooler using the Peltier effect to create a heat flux between the junction of two different types of materials. Peltier cooler, heater,

or thermoelectric heat pump is a solid-state active heat pump which transfers heat from one side of the device to the other side against the temperature gradient (from cold to hot), with consumption of electrical energy [4]. We used a simple power supply as a source of energy. The scheme of a Peltier cooler is given in figure 8. In our experiments the Peltier cooler was connected to the water cooling system in order to cool the hot side at high currents.

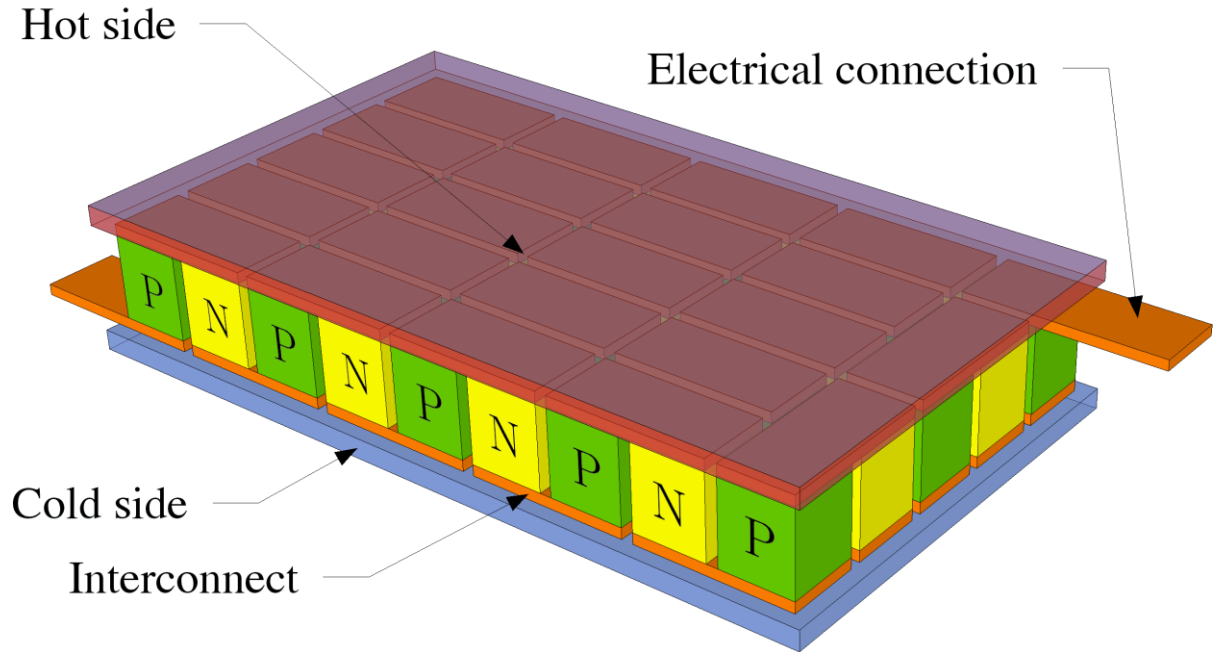


Figure 8. Peltier cooler (from http://en.wikipedia.org/wiki/Thermoelectric_cooling)

The ice sample was prepared in a brass pot on the Peltier cooler and was covered with a plastic film to prevent water condensation from air during the measurements (fig. 9). The diffraction pattern of ice obtained at -20°C showed that the specimen was highly textured as it contained only one strong peak (fig. 10).

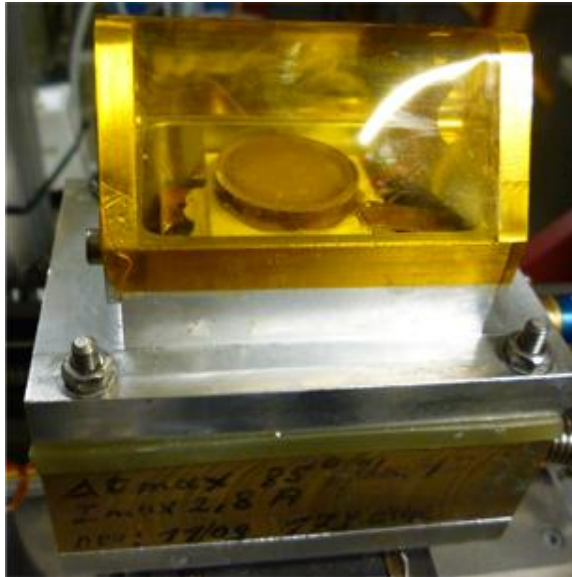


Figure 9. Ice sample under the cover on the Peltier cooler

The texture of crystalline materials is accounted for the preferred orientation of crystallites.

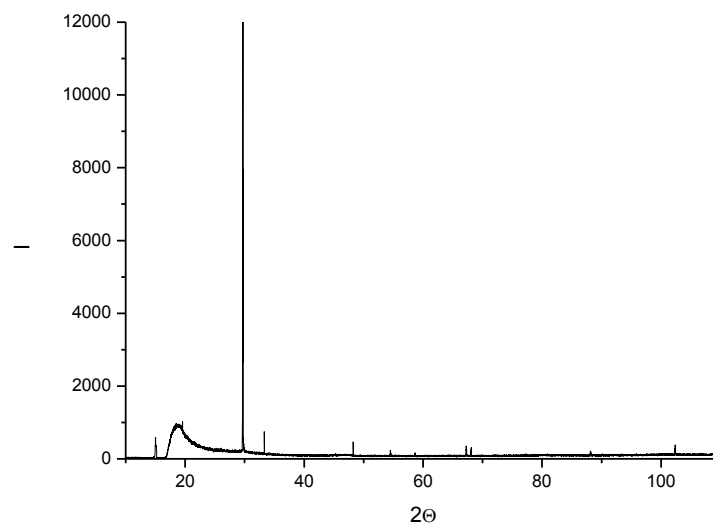


Figure 10. Diffraction pattern of ice

To get more peaks we mixed a small amount of baking flour with the water before freezing. The particles of the flour were expected to act as centers of crystallization which would lead to fast crystallization of water and thus – to random orientation of the crystallites.

As we expected there appeared more peaks in 2Θ -region of 30° - 50° . To investigate the behavior of ice at various temperatures we used only this region of angles. The obtained set of diffraction patterns is shown in figure 11.

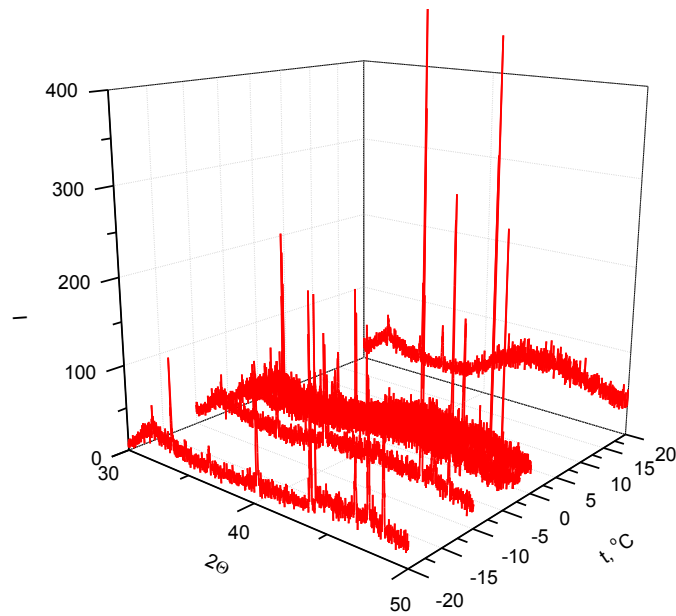


Figure 11. Diffraction patterns of water at different temperatures

One can see that the peaks vanish at temperatures higher than 0°C due to ice melting. The other feature is the texture change near the melting point as it is obvious that some peaks appear in the region of 30°-40°. The peaks which are visible even in case of liquid water (at 20°C) correspond to the material of the pot.

Gallium measurements

Gallium is a silvery white metal with unexpectedly low melting point of 29.78°C. As it is not considered highly toxic and is not rapidly oxidized in air it can be used as a convenient sample to investigate solid-liquid phase transitions.

Gallium is a highly textured crystalline solid which is a usual feature of many metals. To make it less textured the gallium sample was molten from the top and rapidly frozen on the Peltier cooler with the addition of several small pieces of gallium as centers of crystallization (see fig. 12).

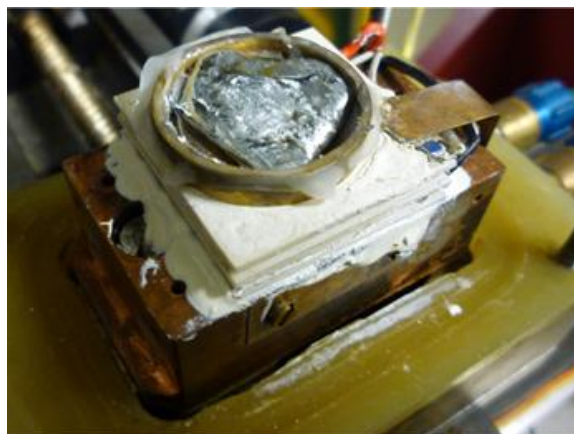


Figure 12. Gallium sample on the Peltier cooler. Since gallium is corrosive the brass pot is covered with parafilm which is visible at the edges of the pot

Prepared as described above the sample had one strong peak at about 46.7° which turned out to be four close peaks and some less intensive peaks (fig 13.)

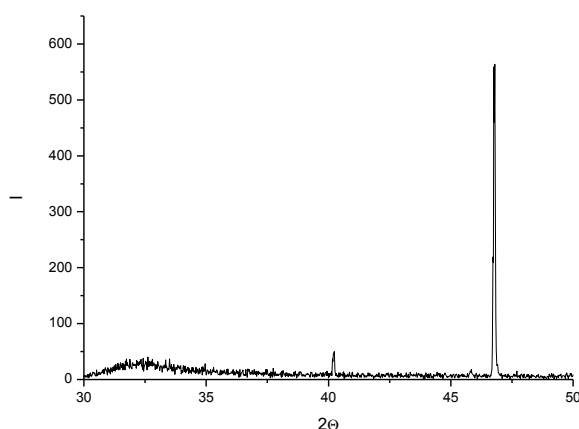


Figure 13. Diffraction pattern of gallium

The x-ray diffraction study was conducted the same way as in case of water. The temperature was controlled with the Peltier cooler and the region of 46.6° - 47.5° was investigated. It is necessary to notice that the Peltier cooler can only create a temperature gradient. As the melting point of gallium is near the room temperature it is not possible to adjust the temperature of the sample precisely because of the small gradient and consequently the low current.

The temperature dependent x-ray diffraction patterns of gallium are presented in figure 14.

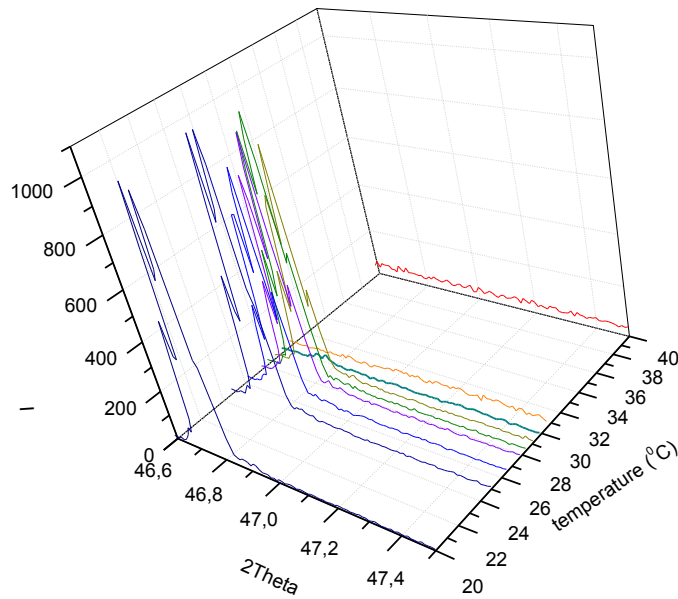
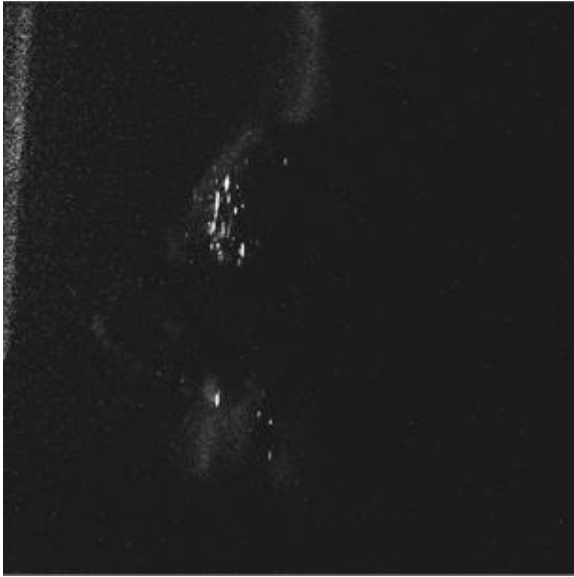


Figure 14. XRD patterns of gallium at various temperatures

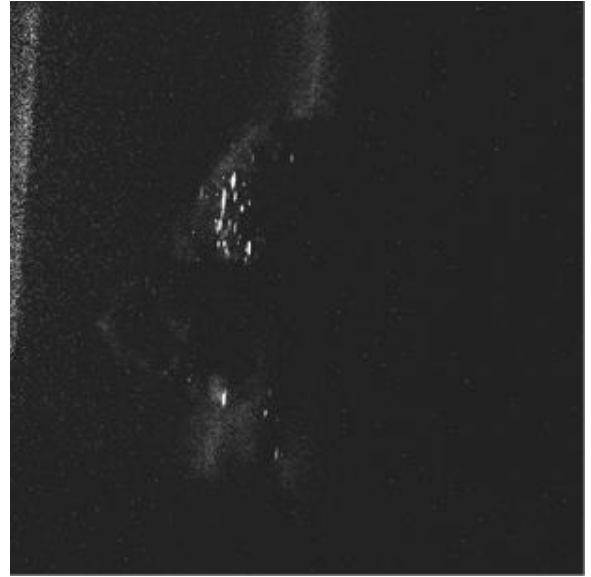
The strong multiple peak at about 46.7° becomes practically invisible at the melting point of gallium (dark cyan). Yellow and red patterns correspond to the liquid phase and contain no peaks. Nevertheless there are no significant changes of texture in the observed temperature region below the melting point.

To see whether there were any changes of grain size or internal stresses the x-ray diffraction imaging measurements were performed.

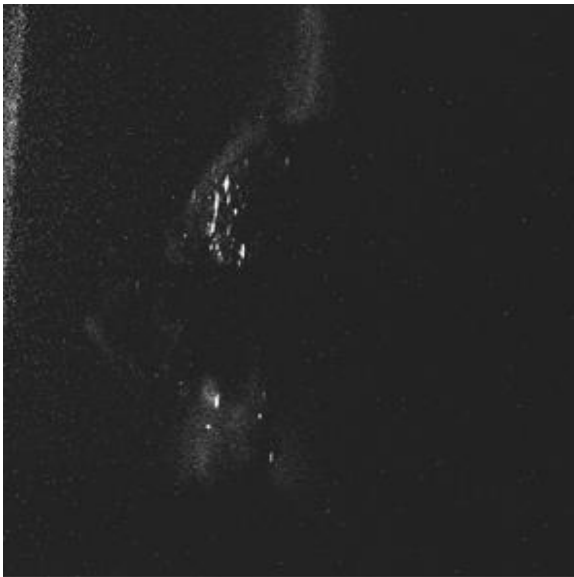
The CCD camera was moved to the position of the peak and several images were made in temperature range between 20°C and 30°C . Because of the small intensity of the peak we used high exposure time (15 min). Several grains (white spots) can be seen below the melting point (fig. 15).



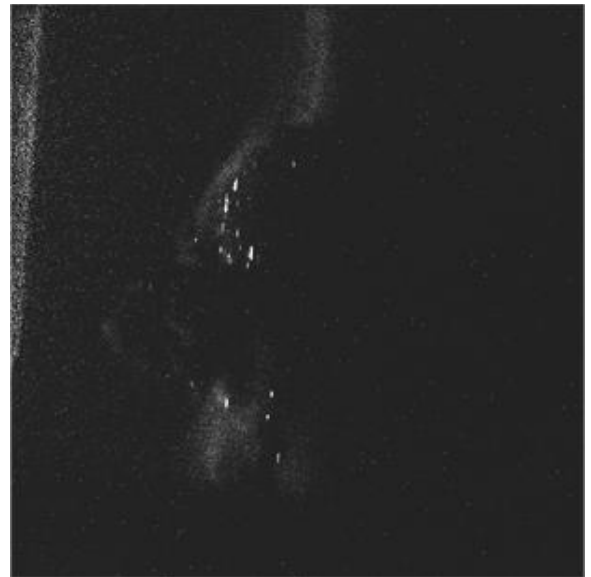
20°C



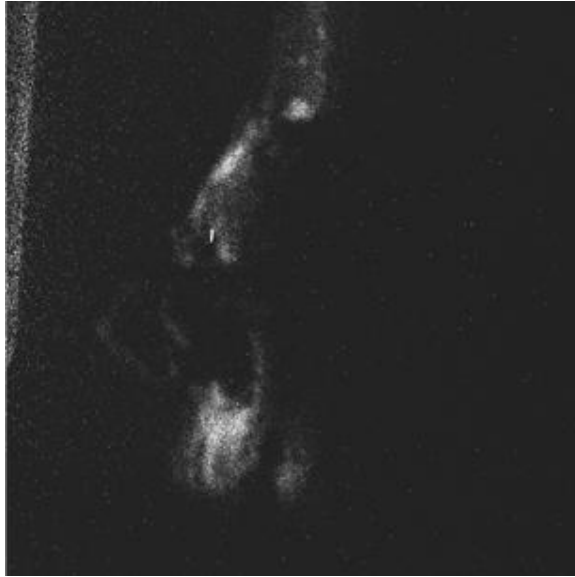
25°C



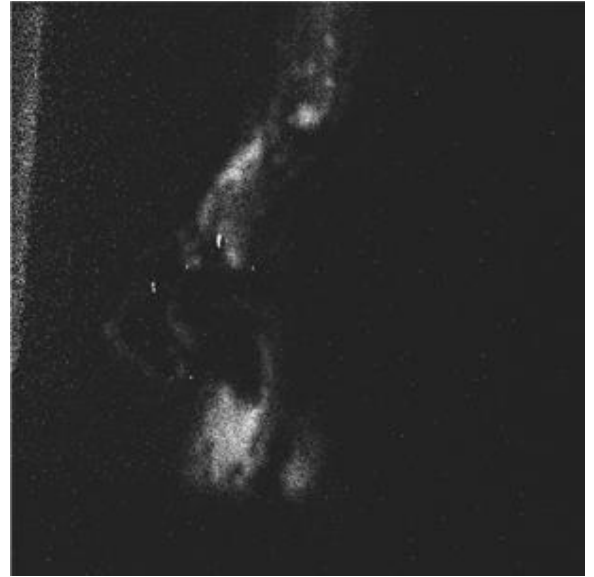
27°C



29°C



29.5°C



29.7°C

Figure 15. Diffraction imaging of gallium

The spots corresponding to single grains become considerably smaller at 29°C. At 30°C there are no white spots since the gallium is liquid (fig. 16).

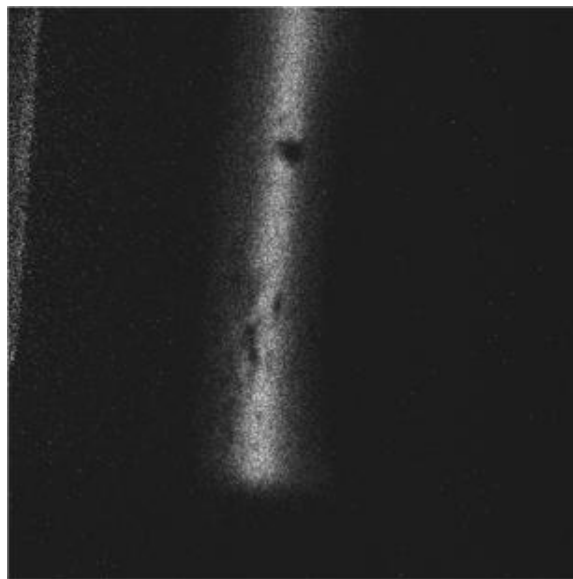


Figure 16. Image of liquid gallium

Conclusions

The improvement of G3 beamline described above gives an opportunity to perform measurements of samples in wide temperature ranges including melting points. With the beam going from above it is possible to keep the horizontal position of a sample while the diffraction imaging experiment. Grain sizes, changes of phase distributions and residual stresses near the melting point can be investigated with new geometry.

References

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