ROBL – the ROssendorf BeamLine at the ESRF

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1. Introduction

The ROssendorf BeamLine (ROBL) is a collaborating research group (CRG) beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The beamline was built and is operated by the Forschungszentrum Rossendorf. ROBL has been designed for performing experiments on two different experimental stations: a Radiochemistry Hutch (RCH) and a Materials Research Hutch (MRH), both operating alternatively. X-ray absorption spectroscopy and X-ray diffraction and reflectometry are the main experimental techniques used in RCH and MRH, respectively. Most of the beamtime is used by the FZR for in-house research devoted to:

- Radioecological research as scientific background for risk assessment and development of remediation strategies for areas contaminated by radionuclides. Determination of the chemical speciation of radionuclides interacting with geological material, natural and anthropogenic organics, and micro-organisms. Study of the influence of these interactions on radionuclide migration and retardation in the environment.
- Structural identification and characterisation (including texture) of modifications of surfaces and interfaces produced by ion beam techniques for applications as hard covers, sensors or in semiconductor technology. Study of interfaces in thin films and nanometer-multilayers. Structural investigations of melts and amorphous solids.

The beamline is also available to outside users to perform experiments either in collaboration with the FZR or by submitting a proposal to the ESRF: one third of the ROBL beamtime will be allocated by the ESRF for peer-reviewed experiments.
This paper gives an overview about the beamline design and describes the standard experimental equipment of both experimental stations [#].

2. Beamline optics

The beamline is located at the bending magnet port BM 20 of the ESRF. The overall layout of ROBL is shown in the title page of the report. The beamline optics uses horizontally a fan of 2.8 mrad of synchrotron radiation from the hard edge of the ESRF bending magnet (0.8 T range, critical energy 19.6 keV) [1]. The layout of the optics is sketched in Fig. 1. The main elements are a fixed-exit double crystal monochromator located between two mirrors. The beamline is designed for an energy range from 5 to 35 keV. The lower energy limit is given essentially by the mandatory Be-windows. The upper energy limit was chosen to allow X-ray absorption spectroscopy (XAS) experiments on all chemical elements from Ti onward, since at least one absorption edge is in the energy range 5 to 35 keV.
The two mirrors, with the same grazing angle of 2.5 mrad suppress the higher-order harmonics in the monochromatic beam, reduce the heat load on the monochromator, and provide a parallel or vertically focussed beam at the experimental stations at a fixed height.

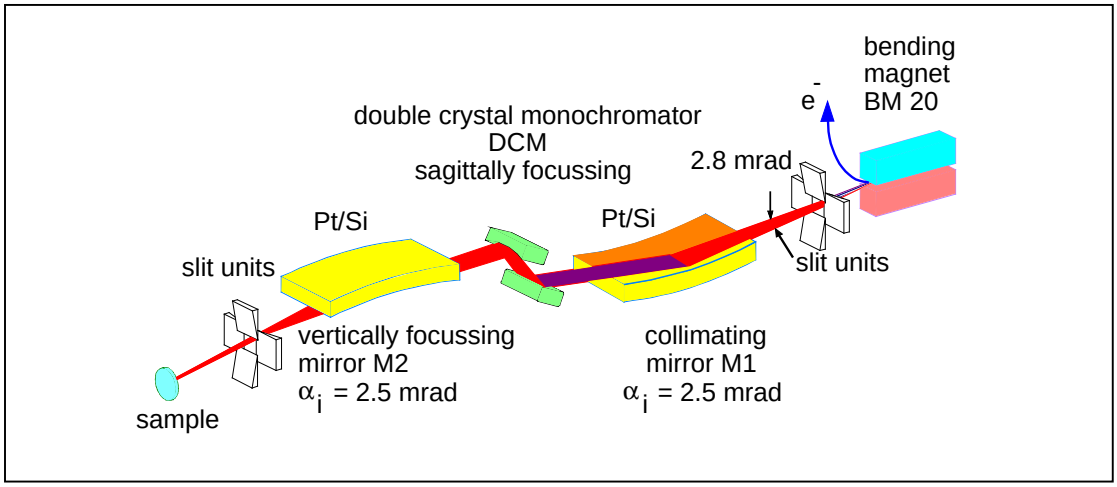

Fig. 1: Scheme of the X-ray optics of ROBL. A mirror - double crystal monochromator – mirror arrangement selects a monochromatic beam for the two experimental end-stations

The X-ray mirrors including cooling and bending mechanisms were purchased completely. The first mirror is made of a single Si crystal which is water cooled. The second mirror uses a ZERODUR substrate without cooling. Both mirrors are equipped with pneumatic benders. The first is bent with a radius of 20.8 km to collimate the incident radiation onto the first monochromator crystal. The second with an adjustable bending radius down to 8 km focuses the beam vertically to the two experimental end-stations. The mirror substrates were coated with two parallel stripes of silicon and platinum that are used alternatively. The harmonic suppression is better than $8x10^{-4}$ for all energies when using the silicon stripes. For the platinum stripes, it is of the same order of magnitude for energies above 13.5 keV.
The calculated spectral flux for the two cases is shown in Fig. 2. The intensity decrease below 10 keV, is due to the absorption of the beryllium windows.

The double crystal monochromator (DCM) provides a fixed-exit beam with a vertical offset of 18 mm. It operates with either Si(111) or Si(311) crystal sets. The mechanical construction allows to reach 25 keV using Si(111) crystals and 35 keV using Si(311) crystals. The design is mainly a commercial one. The axis of a high-precision rotation table is fed into a vacuum vessel. A crystal cage mounted on this axis carries both crystals. The first crystal is mounted with the rotation axis on the reflecting surface. The second crystal can be moved relative to the first one, parallely and perpendicularly to the beam direction. The combined motion of both drives realises a fixed-exit beam. The first crystal is water cooled. The second crystal will be equipped with a bender for sagittal focussing; in the beginning it will be available only for Si(311).
For Quick-EXAFS, a pseudo channel-cut mode of the monochromator is possible by keeping fixed the position of the second crystal relative to the first one. In this mode only the Bragg angle of the DCM is changed during a scan; for energies above 14 keV the beam height variation during a 500 eV wide scan is less than 0.6 mm.
A feedback system is installed, which compensates intensity modulation during XAS scans, by fine tuning the orientation of the second crystal on the base of a signal coming from a monitor in front of the sample.
The overall energy resolution of ROBL is shown in Fig. 3. This resolution allows to study the near-edge structure at all absorption edges within the accessible energy range with a resolution better than the core hole width.

In addition to the mirrors and the monochromator, the optics contains various slit units, filters, and beam position monitors.

The motions of nearly all optical components are motorised, mostly with stepper motors, controlled by an UNIX workstation based system. Many standard ESRF software applications are used in the control programs, which utilise SPEC© code package [4].
The control system includes also interlock components for the vacuum, beam shutters and the cooling of components exposed to the white beam.
The characteristics of the monochromatic beam are summarised in Table 1.

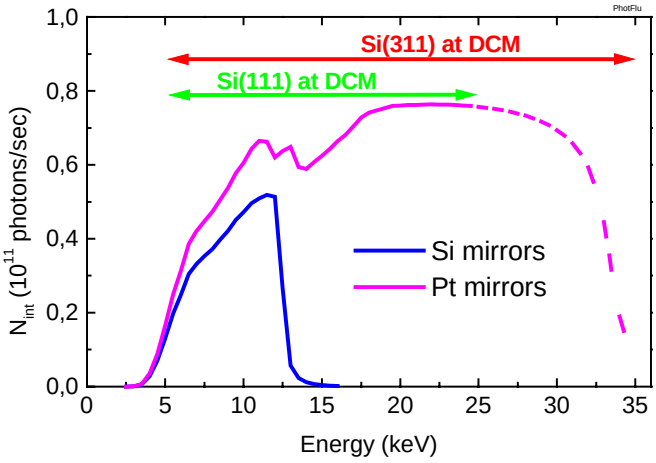

Fig. 2: Calculated flux of focussed radiation with silicon and platinum coated mirrors and silicon (111) crystals in the double crystal monochromator obtained using the SHADOW code [2,3]. The attenuation from beryllium windows of the total thickness of 1.5 mm is included. The maximum energy of 35 keV can be realised only with Si(311) monochromator crystals. Geometrical constraints of the DCM design limit the accessible energy range for Si(111) crystals to about 25 keV.

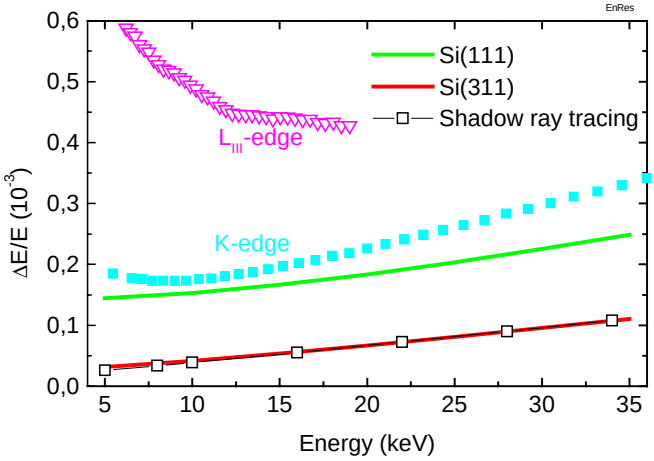

Fig. 3: Calculated energy resolution of the double crystal monochromator with silicon crystals and parallel incident beam. For comparison the natural line widths of the absorption edges of the elements are shown. Besides the analytically calculated values, results obtained with SHADOW code are included for Si(311).

Table 1: Characteristic data of monochromatic synchrotron beam

energy range	5 - 35 keV
energy range with Si-mirrors	5 -12 keV
energy resolution with Si(111) crystals	1.5 – 2.5 x 10^{-4}
energy resolution with Si(311) crystals	0.5 – 1.0 x 10^{-4}
integrated flux for focussed beam (calc.)	6x10^{11} ph./s @ 20keV, 200 mA
standard beam size	20 mm (w) x 3 mm (h)
focussed beam size	$\leq$ 0.5 mm x 0.5 mm

3. Radiochemistry end-station

The radiochemistry end-station is designed for studying radionuclides of environmental importance such as Tc, U, Th, Np, Pu, Am. X-ray absorption spectroscopy is a powerful technique to obtain information on the molecular and electronic structure of these radionuclides in solids and liquids. It is an element specific method and provides information about the oxidation state as well as the bond lengths and numbers of neighbouring atoms in the first, second and even third coordination shell of the absorber. Such knowledge is essential to understand complexation and speciation of radionuclides and also absorption processes from solutions. Actinides are known to exist in many oxidation states which are difficult to be determined by chemical or optical methods. In contrast XAS can distinguish the oxidation state from the shift of the absorption edge, providing also information if different states are present in one sample. Another advantage of XAS for radiochemical investigations is the possibility to use solid or liquid samples as well as very dilute ones (micro-mol region).

The ROBL-CRG obtained a license from the French authorities to perform XAFS experiments with the isotopes listed in Table 2. Under this license the maximum allowed activity at any given time present at ROBL is 185 MBq (5 mCi). These elements emit mostly alpha and beta particles and only weak gamma radiation. Therefore, the heart of the radiochemistry end-station is a glovebox without additional lead shielding (see Fig.4). To ensure a safe handling of the radionuclides, the entire experimental station is built as a radiochemistry laboratory according to legal safety requirements.

Table 2: List of radioactive elements which can be investigated at ROBL and the maximum amount of material to remain below the activity limit of 5 mCi

Isotope	Half-Live (years)	Amount (g)	Isotope	Half-Live (years)	Amount (g)
Np 237	2.1×10^{6}	6.97	Pu 239	2.4×10^{4}	0.08
Am 241	433	1.4×10^{-3}	Pu 242	3.75×10^{5}	1.27
Am 243	7370	0.025	Ra 226	1600	0.005
Po 208	2.9	8×10^{-6}	Tc 99	2.1×10^{5}	29.1
Po 209	103	3.01×10^{-4}	U nat	4.47×10^{9}	1000
Pa 231	3.28×10^{4}	0.106	Th nat	1.4×10^{10}	1000

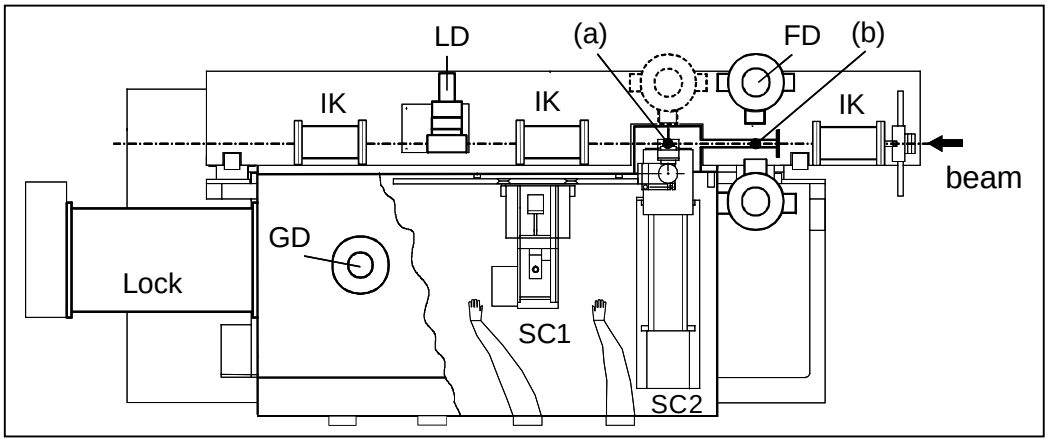

Fig. 4: Principal layout of the glovebox. (a) standard sample position for XAFS experiments; (b) sample position for fluorescence radiation detection from dilute liquid samples. The ionisation chambers (IK) are mounted on an optical bench and can also be used for non-radioactive samples while the box is moved out of the beam. FD- fluorescence detector; LD – Lytle detector; GD – gamma detector for measurement of sample activity, SC1,2 - sample changers.

The XAFS spectra can be measured both in transmission and fluorescence modes. For transmission mode the sample is placed perpendicular to the photon beam between two ionisation chambers (IK in Fig. 4). In fluorescence mode, the sample is inclined by 45^{o} with respect to the beam and the fluorescence radiation is detected with Ge solid state detectors (FD in Fig. 4) positioned perpendicular to the beam. The radioactive samples are positioned inside the glovebox equipped with 125 µm thick Kapton (polyimide) windows which are transparent to hard X-rays. All detectors, e.g., gas ionisation chambers and fluorescence detectors, are mounted on an optical bench outside the glovebox. This arrangement allows a direct and easy access to the detectors and avoids bringing signal cables, gas and power supply lines into the glovebox. In addition, even in the unlikely case of a contamination inside the glove box, the detectors will not be affected.
Inside the glovebox it is possible to use sample holders at different positions. Two, marked (a) and (b), are indicated in the schematic glovebox layout of Fig. 4. At position (a) a larger space is available so it is possible to mount either an automatic sample holder which provides room up to eight solid or liquid samples or a closed cycle He cryostat. The samples in position (a) can be measured both in transmission and fluorescence modes. For measurements on very dilute samples, a special single sample holder can be placed at position (a). The rotating arm of this positioning system moves the sample to position (b), between two Kapton windows and rotates it of 45^{o} with respect to the beam: two Ge solid state detectors record simultaneously the fluorescence signals.
Since the samples are safely contained in the glove box, it is possible to change some of the sample conditions during the experiment. With the closed cycle He cryostat the sample temperature can be varied between 10 K and 295 K. It is also possible to modify the chemical conditions of liquid samples just before or during the XAFS measurements by adding non-radioactive substances like acids, bases or complexing agents.
The glovebox is mounted on a support frame which allows to move the glovebox in the horizontal direction out of the beam leaving the position of the optical bench and of the detectors unchanged. So, non-radioactive samples can be easily measured outside the glovebox by mounting them on the optical bench between the first and second ionisation chambers. For energy calibration purpose a non-radioactive reference sample can be placed between the second and third gas ionisation chamber. The reference sample is inside a fluorescence X-ray ion chamber detector (Lytle detector) to have the possibility to record the XAFS also in fluorescence mode.
When measurements take place downstream in the MRH, the box and the optical bench are moved out of the beam horizontally and vertically, respectively, and the beam path in the RCH is closed by a vacuum pipe to reduce the loss of beam intensity.

In order to guarantee a safe operation of the experiments with radioactive samples a number of safety installations was made to monitor the actual status. Basically a multi-barrier concept is realised here as usual for radiochemical work [5]. No preparation of radioactive samples is possible at the ESRF. Ready for measurement samples will be transported to the experimental end-station in certified transport containers.

To check the energy calibration of the Si(111) double crystal monochromator, the X-ray absorption near-edge structure (XANES) spectra of several metal foils in the energy range of 5 – 30 keV were measured in transmission mode. The absorption edges values found for Ti, Cr, Co, Zn, Zr, Nb, and Sb foils were compared with the values given by [6]. The data evaluation showed that the standard deviation of the Bragg angle was less than 0.002^{o} in the entire energy range indicating an excellent linearity of the monochromator mechanics. Figure 5 displays single sweeps of K-edge XANES spectra of three representative elements. The features of the Ti and Zr K-edges are well resolved, as expected from the high resolution of the beamline, that is lower than the material core-hole lifetime.

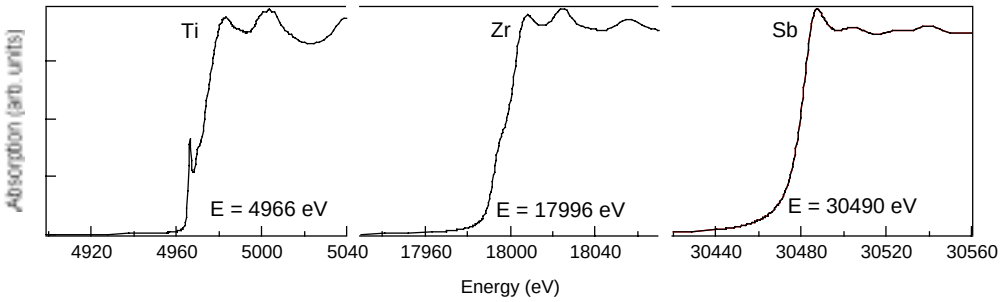

Fig. 5: K-edge XANES spectra of metallic Ti, Zr, and Sb. The energy scale was calibrated using the edge energies given in [6]. The natural line widths of the Ti, Zr, and Sb K shells are 0.94, 3.84, and 9.16 eV, respectively [7].

4. Materials research end-station

The materials research end-station is mainly devoted to structural studies of solids and melts by diffraction and reflectometry. The field of interest for the in-house research are crystalline phases and structural changes in thin near-surface regions of solids. Mainly samples produced or modified by ion beam techniques will be investigated. But, the diffractometer is versatile enough to allow for a wider range of applications than thin film studies. First single crystal diffraction studies have been performed [8]. A special design was made for the diffraction on melts with free surfaces.

The goniometer (Fig. 6) in the MRH is a six-circle built from standard components. The arrangement of two parallel circles each with horizontal and vertical axes, respectively, allows experiments in both scattering planes. The sample position can be equipped with an x-y-z-slide or, alternatively, with special sample environment chambers which are mounted directly on the ϕ-circle. The layout is made for a load up to 15 kg at the sample position and the χ-circle has an inner diameter of 400 mm so that even huge and heavy chambers (e.g. a high temperature chamber) can be used without difficulties. All axes are equipped with stepping motors and gear boxes which allow a minimum angular step of 0.0001°. The z-translation of the x-y-z-slide has a step width of 1 µm while the two other translations have 10 µm. Additionally, sample holders for single crystal samples and capillary sample containers are available.
The goniometer is fully computer controlled by a workstation and the programs are based on the SPEC© code [4].
Different detection systems can be mounted at the detector arm. As standard, a high load, high linearity scintillation detector is used. In front of the detector, interchangeable fixed single or soller slits can be mounted. Other detection systems are a two-dimensional CCD-camera or an energy-dispersive pin-photodiode. Optionally, a secondary monochromator unit (crystal analyser) may be mounted in front of the detector.

The resolution of a diffraction experiment depends not only on the energy resolution of the monochromator but also on the beam divergence. The experimentally achievable resolution was measured using silicon single crystals and powders. At present, radiation with the natural horizontal divergence of the synchrotron radiation beam from the source is used since the sagittal focussing option at the monochromator is not yet installed. The vertical divergence is reduced by the first collimating mirror.
Using the Si(111) monochromator and the Si mirrors, at 12 keV and a vertically parallel beam, the FWHM of a Si(004) single crystal reflection was measured to be $\Delta\vartheta = 0.003°$ (10 arcsec). This corresponds approximately to a resolution $\Delta d/d = 1.3 \times 10^{-4}$. Vertical focussing

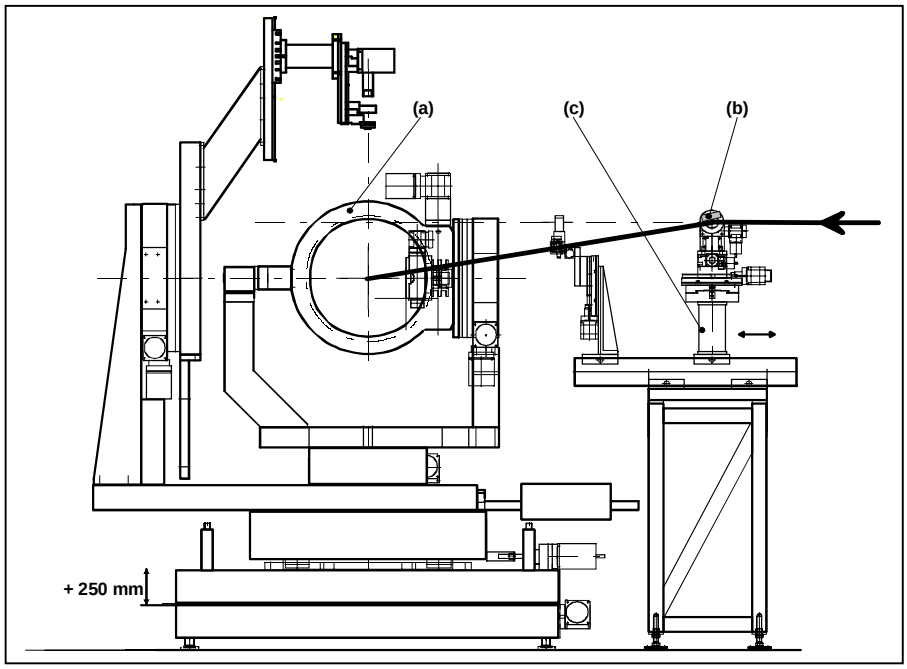

Fig. 6: Scheme of the goniometer (a) in the materials research end-station and of the deflector unit (b) for the study of melts with free surfaces. The small goniometer head with the deflecting multilayer mirror (b) can be positioned at different distances to the sample by a translation slide (c).

with the second mirror raises the FWHM up to 0.0051° but increases the incident radiation intensity significantly. It follows from these results, that ROBL´s optics allows optimising the intensity by vertical focussing without significant loss in resolution for polycrystal diffraction experiments.
For powder diffraction, the instrumental contribution to the intrinsic FWHM of Bragg peak was estimated. The angular resolution in the case of Si(111) sample is entirely determined by the convolution of the incident and receiving slit apertures. The profil fitting of the measured Si(111) peak from a powder sample with a pseudo Voigt function ($F_{PsV} = \eta * F_L + (1-\eta) * F_G$) gives a FWMH of 0.0528° which agrees with the value of 925 µrad = 0.0530° estimated from the apertures. The very small η-parameter (η=0.0485) indicates that the instrumentally determined Gaussian part dominates over the sample broading effects expressed by the Lorentzian term.
To get the full possible resolution for powder diffraction (0.01°-0.03°) it is possible to use a narrower receiving slit or a perfect crystal analyzer.
Typical Si-powder resolution curves $\Delta d/d$ for different energies are given in Fig. 7. These data show that the materials research end-station is also suitable for high resolution X-ray powder diffraction and for the study of line broadening effects [9].

The study of melts (or more general liquids) with free surfaces by diffraction requires an incident beam inclined to the horizontal, to hit the horizontal surface of the melt. The additional demand to tune the energy in order to make use of anomalous scattering led to the installation of a deflection unit (b) as displayed in Fig. 6. A suitable multilayer mirror of 40x100 mm^2 is mounted on a circle with a horizontal rotation axis perpendicular to the incident beam and deflects the beam downwards. The reflecting efficiency of the deflecting multilayer mirror is 50% at 8 keV. In order to make the deflected beam to hit the sample the goniometer has a motorised height adjustment. The sample position can be set 250 mm below the primary beam from the monochromator. When changing the energy of the incident beam, the deflection angle of the mirror and the height of the sample have to be changed. To avoid height adjustment of the huge diffractometer where the sample is mounted, the

multilayer-mirror deflection unit is mounted on an additional translation stage (c). So leaving fixed the sample height the adjustment is performed by translation and rotation of the deflecting mirror alone, for an energy range of 5 keV when working at 10 keV and of 11 keV when working at 25 keV.

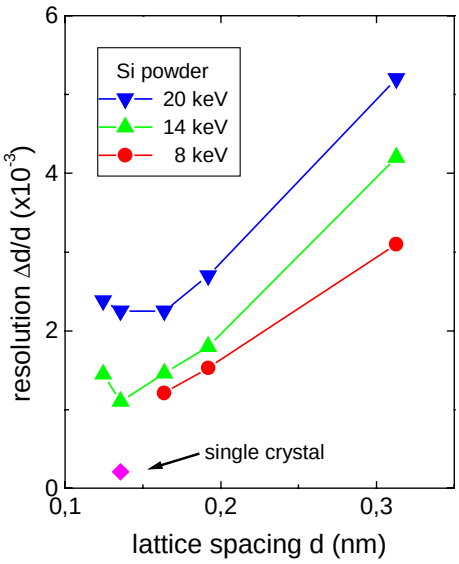

Fig. 7: Experimental resolution Δd/d obtained on silicon powder inside a glass capillary (diameter 0.4 mm; wall thickness 0.01mm). For comparison the value from a single crystal sample is indicated. The Si(111) monochromator crystals are used.

5. Conclusion

The ROBL beamline with both end-stations became fully operational in fall 1998. First experiments show a reliable performance of the entire beamline and its components. This CRG beamline adds new experimental possibilities to the ESRF.
The advantages of the ROBL radiochemistry station when compared to the other synchrotron radiation beamlines are manyfold: (i) the maximum allowed amount of radioactive material is 5 mCi which is higher than at most other synchrotron light sources, (ii) it is the only dedicated end-station for XAFS experiments of actinides in Europe. In addition, as to our knowledge, ROBL is the only XAFS station in the world where it is possible to manipulate the chemical and physical properties of the sample in a glove box on site and during the experiment at a third-generation high-energy synchrotron radiation source. Dedicated beamlines for the study of radioactive materials have become operational in Japan at the Photon Factory (PF) and Spring-8, but working in lower energy region [10,11]. At SSRL (USA) the maximum allowed quantity of ^{237}Np in the experimental X-ray hutch at one time must be less than 50 µCi. The total amount of Np material that can be shipped to and be at SSRL must be less than 500 mg (325.5 µCi) [12].

The materials research hutch (ROBL-MRH) offers horizontal and vertical scattering planes as well as off-plane diffraction possibilities. The dedicated ESRF powder diffraction beamline (BM16) or the powder diffraction set-up of Swiss-Norwegian-Beamline (BM1) are equipped with goniometers which are restricted to one scattering plane [13-15]. For powder or polycrystalline samples we provide the same diffraction resolution and nearly the same wavelength range as the mentioned beamlines. Concerning the study of liquids with free surfaces the ROBL-MRH setup is complementary to the BM32 one, but the latter uses a silicon crystal in Laue geometry as beam deflector [16]. The arrangement at ROBL-MRH reduces the necessary movements of the goniometer and makes the arrangement of samples in chambers with small radiation windows easier.

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[#] The extended version of this contribution will appear in J. Synchrotron Rad. **6** (1999). It is also available as Technical Report FZR-256, April 1999.
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