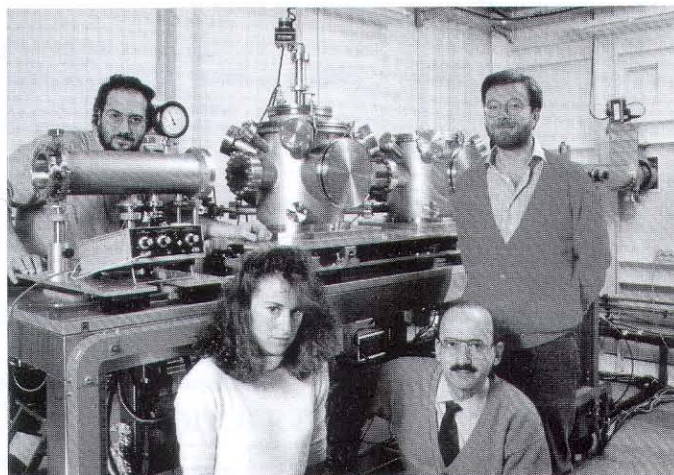


D8: GENERAL PURPOSE ITALIAN LINE FOR DIFFRACTION AND ABSORPTION

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The Italian CRG beamline GILDA became operational in autumn 1994, with the opening of its X-ray absorption station to public users. In September 94, less than a year from the beginning of hutch construction, the line was delivering a sagittally focused monochromatic beam in the 7-26 keV energy range, working in one of the two optical configurations foreseen. This article gives a brief description of the beamline and presents some of the results obtained during the first user runs.

BEAMLINE DESCRIPTION

The GILDA beamline has been financed by INFN (Istituto Nazionale Fisica Nucleare), INFN (Istituto Nazionale Fisica della Materia) and CNR (Consiglio Nazionale delle Ricerche) in order to give the Italian scientific community access to a third generation synchrotron radiation facility to perform X-ray absorption and diffraction experiments in a large energy range. The beamline will work in two optical configurations covering a full energy range from 5 to 50 keV. The optics at energies below 28 keV consist

of a monochromator and two mirrors, allowing the beam to be focused in both the horizontal and vertical planes in three experimental stations. At higher energies, mirrors are removed and the beam is not focused in the vertical plane.

Figure 1 shows a schematic view of the optics hutch. The common element in both configurations is a fixed exit, double crystal, sagittally focusing monochromator. Si(311) and Si(511) crystals are used to cover the whole energy interval with an energy resolution in the 10^{-4} to 10^{-5} range. At low energies (5 - 28 keV) a first collimating mirror

allows a good matching of the vertical divergence of the beam to the Darwin width of the crystal. The focal length of a vertically focusing mirror placed downstream the monochromator can be adjusted between 5 m and 15 m. In this configuration, expected focal spot dimensions should be smaller than 1 mm^2 , with an average flux of the order of 10^{11} phot/sec. At energies higher than 28 keV mirrors shall be removed from the beam; the radiation will therefore not be focused in the vertical direction and spot sizes will be two to three times larger than in the low energy configuration.

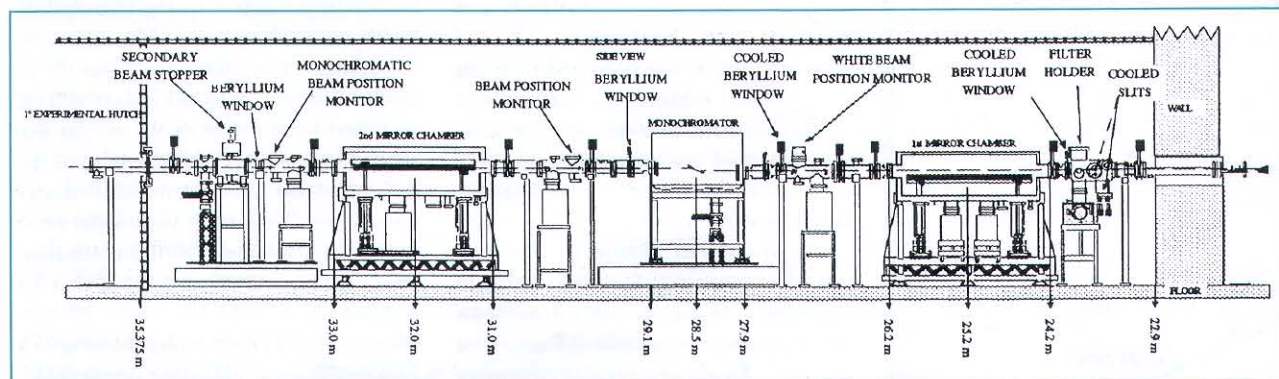


Fig. 1:
The GILDA
optical
hutch.

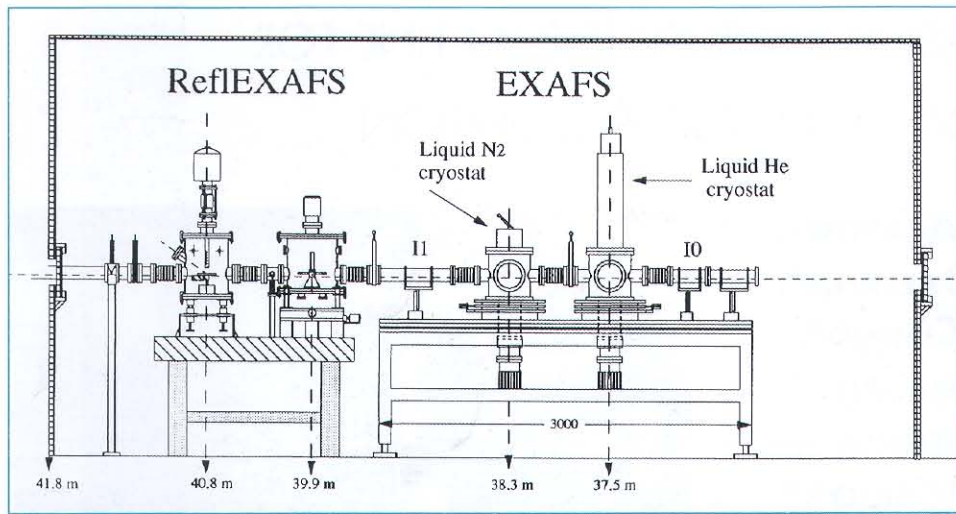


Fig. 2: Schematic picture of the X-ray absorption hutch.

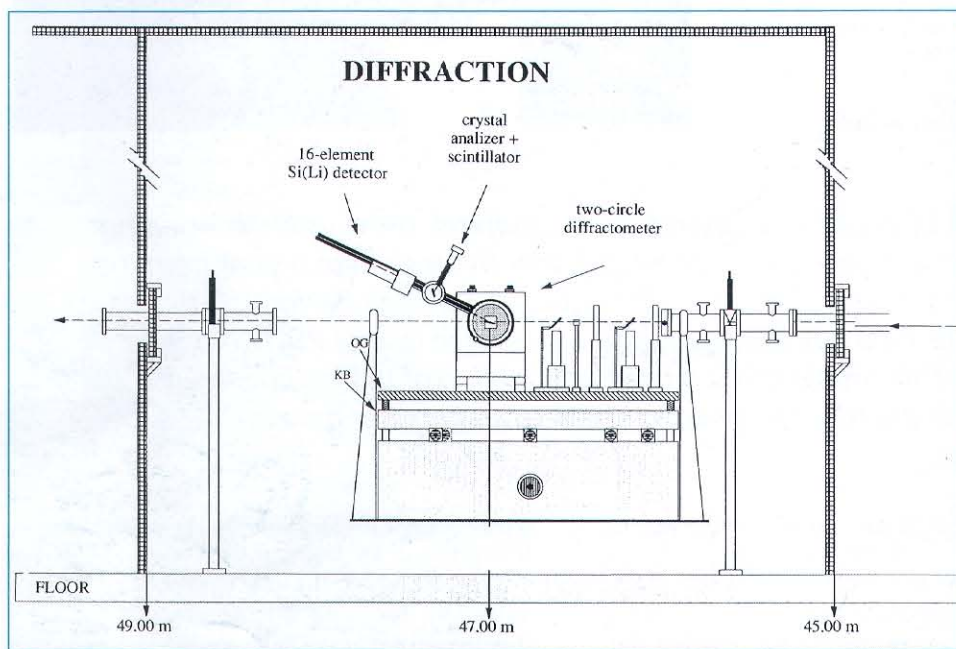
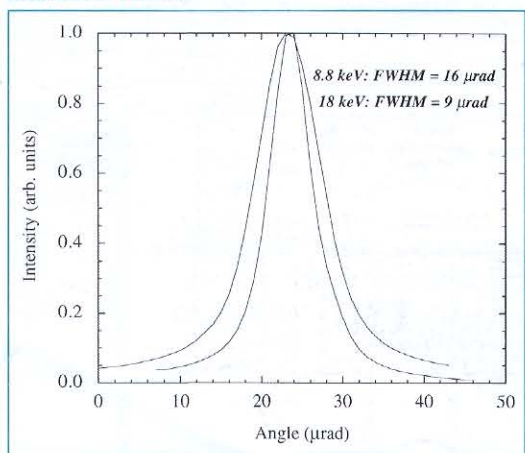


Fig. 3: Schematic picture of the X-ray diffraction hutch.

Fig. 4: Si(311) rocking curves at $E = 8.8 \text{ keV}$ and $E = 18 \text{ keV}$. The measured FWHM are very close to theoretical values.



The GILDA beamline is equipped with a first experimental station dedicated to X-ray Absorption Spectroscopy (XAS) in the transmission and fluorescence modes, and will soon be ready for XAS in the reflection mode (refLEXAFS). The high flux available at the ESRF is particularly useful in the study of dilute systems, surfaces and interfaces. A second station is dedicated to wide angle X-ray scattering on amorphous materials, anomalous scattering and powder diffraction. Finally a third station will be available for non-standard and non-permanent experiments.

As shown in Figure 2, the XAS station is equipped with two vacuum chambers, the first for ultra-clean environment experiments and the second for general purpose

experiments, including biological studies. A liquid He cryostat as well as a liquid N₂ cryostat are available, yielding a global temperature range from 4 K to 550 K. Besides the two ionisation chambers which are now being used, the detector facilities available in the final configuration consist of photodiodes, plastic scintillators and an electron yield detector.

The wide angle scattering and powder diffraction set-up are shown in Figure 3. The two circle diffractometer has an angular step of 0.28 arcsec and a reproducibility of 2 arcsec. A 16-element Si(Li) detector is available to perform anomalous scattering with an energy resolution of 300 eV at 5 keV, while a crystal analyser and a scintillator allow powder diffraction patterns to be recorded with an instrumental angular resolution better than 0.01 degree. A high temperature cell is available to study recrystallisation processes up to $T = 1800 \text{ }^\circ\text{C}$.

PROGRESS REPORT

The monochromator was installed in February 94 and was commissioned using Si(311) crystals. Rocking curves were recorded and were found to be equal to theoretical curves, as can be seen in Figure 4. The first absorption edge was recorded in April, while the first sagittally focussed beam was obtained in September. In October, the XAS station was commissioned and allowed EXAFS spectra to be routinely recorded. The mirrors are expected to be installed and commissioned in 95, allowing the line to be fully operational in the two optical configurations by the end of the year.

While the XAS apparatus is operational, the refLEXAFS station will be installed by the end of 95. As for the second station, the optical bench and the diffractometer have been installed and aligned while the Si(Li) multi-detector is being commissioned. The first anomalous scattering experiments are scheduled for Summer 95.

A total of 51 shifts (corresponding to 5 proposals) were allocated public ESRF

Fig. 5: Pd K-edge EXAFS recorded at $T = 77$ K on a nanostructured Pd sample: raw data and extracted EXAFS signal.

beam time on GILDA during the period November - December 1994. The proposals (Chemistry, Hard Condensed Matter and Earth Science) all dealt with EXAFS experiments in the temperature range from 77 K to 300 K. Two examples of these user experiments are briefly described and some illustrative results shown in the following section.

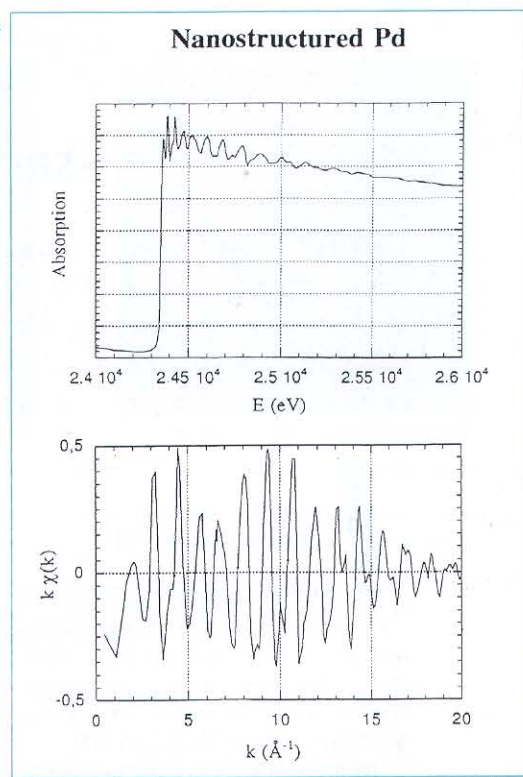
Finally, the USM scheduling for 1995 foresees 1/3 of the total for public user - experiments, 1/3 for private user - experiments, and the remaining 1/3 for beamline installation and commissioning.

FIRST RESULTS

On 10 November GILDA welcomed its first ESRF users with a collaborative group from the University of Saarlandes (Germany) and INFN (Italy). They studied the local structure in nanostructured Palladium deposited by the inert gas condensation technique, by recording EXAFS spectra as a function of temperature, from $T = 77$ K to room temperature. Nanostructured materials are characterized by a grain size in the 10 nm range and thus contain a very high density of grain boundaries. In recent years there has been increasing interest in such materials because of the relationship between grain size and physical properties. One of the fundamental properties which has been investigated is the local structure of the grain boundaries, with controversial conclusions by various groups and claims of either completely ordered grain boundaries or totally disordered atomic arrangements. Temperature dependent XAFS spectra have been recorded on a number of samples which have undergone various treatments such as ageing, annealing and hot pressing. Figure 5 shows an example of raw XAS data relative to one of the samples as well as the EXAFS spectrum extracted from it. The latter shows that oscillations can be observed up to and above a photoelectron wavevector of 20 \AA^{-1} with a very good S/N ratio. The picture arising

from a preliminary analysis of the set of data is consistent with an ordered grain boundary structure.

The second example is relative to a collaboration between the University of Malaga (Spain), the University of Montpellier (France) and CNR (Italy). This group studied the local structure in micro- and meso-porous sorbent and catalyst materials at liquid N_2 temperature. In particular they were interested in the structure of oxide-pillared layered solids. These are sorbent, sieving and catalyst materials, properties that are conferred on them by their porous character, which bridges the gap in the continuum between zeolites and larger pore materials (typical pore radius 7-10 \AA). The measurements performed were mostly aimed at i) identifying extended aggregates or clusters in the precursor intercalation compound and ii) determining the local structure of the metal nanoparticle oxide, forming the pillar, both before and after the calcination step. Experiments were performed at the Ga, Cu and Fe edges in heteroatomic pillared phosphates containing Ga-Cr, Fe-Al and Si-Cu pillars. Figure 6 shows an example of raw XAS data at the Ga k-edge relative to an intercalation compound containing the precursor to a Cr-Ga pillar and to the corresponding porous solid after calcination at 400 $^\circ\text{C}$. The Fourier Transforms (FT) of the extracted EXAFS show distinct modification in going from the precursor to the corresponding calcined phases. This modification, induced by thermal treatment, is accompanied by a loss of long range order beyond the second coordination shell. Moreover the first maximum of the FT relative to the calcined sample with higher Ga content closely resembles both in the intensity and position that of Ga_2O_3 , confirming the presence of nanoparticles of gallium oxide in the structure of the pillared phosphate. ■



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Fig. 6: Ga K-edge EXAFS recorded at $T = 77$ K on an intercalation compound and the corresponding porous solid after calcination at 400 $^\circ\text{C}$.

