SPring-8 Beamline Review Committee Report
on
XAFS
(BL01B1)

Report to the Director General of Synchrotron Radiation Research Laboratory

M. Nomura (IMSS,KEK), Chairman
N. Kosugi (IMS)
K. Sudo (Mitui Chemical Analysis & Consulting Service Inc.)
T. Murata (Kyoto University of Education)
J.Goulon (ESRF)

Japan Synchrotron Radiation Research Institute (JASRI)
Hyogo, Japan

0. Introduction

The beamline BL01B1 is characterized as a beamline for XAFS experiments across a wide energy range, serving the needs of a variety of research fields. Beamlines having similar characteristics can be found in many other synchrotron radiation (SR) research facilities and are used by a number of users. There is also high demand for XAFS spectroscopy from industrial fields. In contrast with conventional XAFS beamlines at other SR facilities, BL01B1 has positively supported the XAFS studies in an energy region above 20 keV using a light source with a high critical energy. Among SPring-8 XAFS beamlines include BL38B1 for R&D, BL10XU using an undulator light source, BL19B2 for industrial use, BL39XU using phase retarders, and BL28B2 for energy-dispersive XAFS using a white X-ray, BL01B1, in particular, has played a pivotal role in XAFS experiments for public use.

1. Technical status of the beamline and experimental stations

BL01B1 has sufficient performance for standard XAFS experiments and is highly competitive with other XAFS beamlines. Since the light source of BL01B1 is a bending magnet, and it is often the case that XAFS does not necessarily require high brilliance, it is safe to say that BL01B1 has not taken full advantage of the characteristics of the third-generation SR light source. However, BL01B1 has put the characteristics of the high-energy light source into practical use by covering a wide energy range from 3.8 to 113 keV.

The optics system is relatively complicated for an XAFS beamline, where the light from the source is collimated in the vertical direction by the first mirror, then monochromatized by a double-crystal monochromator, and subsequently focused at the sample in the vertical direction by a second mirror. The monochromator crystals can be switched between Si(111), Si(311) and Si(511)without breaking the vacuum. In addition, a computer aided adjustment system for the X-ray optics has been developed. The beamline has achieved its goal of easily covering the wide energy range afforded by these systems. In addition, it has achieved high-energy resolution in the low and medium energy regions, which is attributed to the aforementioned optics and the small vertical size of the light source.

By optimizing the setup of the two mirrors, the problem of the contamination of the higher-order harmonics from the high-energy light source has been solved. Now a third mirror system has been developed for a quick change of X-ray cut-off energy between high and low energy regions without complicated realignment of the other beamline optics. This mirror system has enabled comparative XAFS measurements both at K-edge and at L-edge in a short time. Judging from the small fluctuations of the beam position during energy scanning, it would be fair to say the optics are sufficiently stable. The high level of performance mentioned above is largely attributable to the efforts of the facility staff, not to mention the beamline scientists.

Some points to be considered regarding the beamline are:

a) It is desirable to consider the equipment for the horizontal focusing. During energy scan, the sagittal focusing monochromator needs to adjust the bending radius and easily causes tuning errors; therefore, it is better to use a focusing mirror than a focusing monochromator. To keep full advantage of the characteristics of BL01B1 mentioned above, careful consideration should be given to introducing the horizontal focusing optics. However, it is also possible to do such experiments at BL38B1 or other beamlines instead of BL01B1. Thus the SPring-8 facility should manage the optimal use of each beamline.

b) Because of the efforts of the beamline scientists, much of the time spent to adjust the parallelism between the double crystals during the energy scan has been significantly reduced, and the beamline is being well received by its users. However, considerable dead time still remains, which should be reduced as proposed by the beamline scientists.

The beamline is equipped with ionization chambers, an ionization chamber for the fluorescence mode, a detector for conversion electron yield mode and a multi-element SSD, which is time-shared with other beamlines. The beamline also has sample positioning systems for a grazing incidence, a cryostat and electric furnaces. Now that the beamline is fully equipped with necessary detectors and devices for adjusting the experimental conditions of samples, it will be each user's task to further improve the environment for their respective samples.

The experimental hutch has a large space that cannot be found in other facilities, helping users to perform XAFS experiments that employ special experimental apparatus such as a vacuum chamber. However, the number of experiments taking advantage of this is still small. The efforts of the facility to support such research will help users benefit from the advantages of SPring-8.

The development of the automatic adjustment system for the beamline optics is well under way and the user's manual has already been prepared on the Web. Considering most users can do their experiments by themselves with a basic knowledge of XAFS, we rate the user-friendliness of BL01B1 highly.

The permanent installation of a multi-element SSD should be ensured if the budget permits, since the frequent installation and removal of the SSD increases the burden on the beamline scientists and tends to cause deterioration of the detector. Since it is conceivable that the number of users who use XAFS as a tool for analysis will keep increasing, especially in industry, it is desirable to develop the automatic measurement system for many samples at a reasonable cost.

In improving the beamline and its equipment, it is important that the beamline scientists obtain the maximum use and utility of the beamline; in this sense, it can be judged that a frequently reserved beam time warrants the improvement of BL01B1.

2. Research activity

Since BL01B1 is a XAFS beamline intended to meet the demand of users in various research fields, it is inappropriate to compare it on the same level with beamlines dedicated for one particular scientific purpose. Research into catalysts accounts for a large proportion of beamtime, and recently environmental research using BL01B1 has been increasing. Furthermore, the number of published papers resulting from research conducted on BL01B1 has also been increasing steadily.

BL01B1 has a special significance in the sense that it has put XAFS measurements in the high-energy region into practical use. In particular, it is very useful for having enabled K-edge XAFS experiments on 4d atoms (especially $Z>=45$) and on lanthanides, which are frequently used for catalysts and semiconductors.

Before BL01B1 came into use, XAFS spectra of 4d atoms were measured at Photon Factory with 3-GeV operations; however, a long time was needed for data accumulation due to a limited photon flux. BL01B1 made these XAFS measurements easier. A case in point is a study for Pd catalysts supported on hydroxyapatite, which are used for the oxidation of alcohols and amines. It was revealed that the active site structures differ with different catalytic activities, which depend on the Ca/P ratio in the hydroxyapatite.

Before BL01B1 commenced operation, it was necessary to measure XAFS spectra for lanthanide at the L-edge. However there were some problems such as significant errors in structural analyses caused by the small energy difference between the L_{III}-edge and the L_{II}-edge, interference with the K-edge of 3d transition metals which exist in the same energy region as the lanthanide L-edge, and strong multi-electron excitation, which was frequently observed in L-edge XAFS of lanthanide, increasing the inaccuracy of analysis. BL01B1 uses K-edge XAFS to help overcome these problems. The analysis of CeO_2-ZrO_2 used as a three-way catalyst for automobile exhaust systems would be a good example. From the analysis of the Ce L-edge XAFS, CeO_2-ZrO_2 was considered to take a random structure, which did not depend on its composition, and did not reflect the difference of activity. However, the Ce K-edge XAFS revealed the structural difference because the wavenumber (k) range for the L-edge XAFS was limited, and the scattering waves from Ce and Zr atoms canceled each other due to their phase difference in the small k range. The K-edge XAFS possessed the structural information reflecting medium-range order appearing in a large k range, and could be used to analyze the correct structure. Furthermore, X-ray absorption coefficients at the K-edge are small, which makes it possible to prepare thicker and thus more uniform samples. Consequently, data with good S/N ratio can be obtained up to a large k range.

On the other hand, it is difficult to obtain useful information from K-edge XANES due to restrictions on the energy resolution arising from the finite lifetime of a core hole. However, it is expected that information can be obtained on structures and electron states by using K-edge EXAFS and L-edge XANES, respectively. BL01B1 is suitable for these types of experiments. We believe that such positive characteristics should be proclaimed in a way that users can easily understand.

Judging from the list of papers, some proposals have not produced enough results despite using a substantial amount of beamtime. This might reflect the fact that the beamline is still young. However, in the management and operation of such a large facility, it is important to have results published extensively, and this point should be clearly communicated to users. Indeed, it is often the case that the results obtained by company users do not take the form of papers. Therefore, it is conceivable that it will become increasingly important for the facility to obtain feedback on whether and how research conducted at SPring-8 has served the purpose of its users.

3. Utilization and support system for users

There have been large fluctuations in supply and demand of beamtime, which is partly because SPring-8 invites proposal applications every six months. However, from 2001A to 2002A, the acceptance rate was high and almost all the beamtime requested for the accepted proposals was allocated. It is fair to say that SPring-8 has sufficiently met demand. Until 2000B, both the acceptance rate and beamtime allocation rate were low, so it is necessary to see if the low acceptance rate in 2002B was a resurgence or a peculiar case. It is recommended for the facility to rouse demand a little more and select really active research groups from among them.

We deem it reasonable that a lot of proposals originate from the Kinki region, since it reflects the location of the facility. On the other hand, company proposals come mainly from Kanto and Koshin region. This is probably because unlike other existing SR facilities, SPring-8 has been promoting its industrial applications, and companies can use the beamline free of charge for non-proprietary proposals.

For research methods such as XAFS, which have already become established to some extent, it is fair to presume that a number of users would wish to use the beamline as an analytical tool for analysis when they want. If SPring-8 wishes to further encourage industrial use, it is important to achieve a shorter turnaround, and keep some beamtime, a day or two a month, to meet their demand.

It is undeniable that the beamline is facing a serious staffing shortage when compared with the global standard, so it will become increasingly important to place emphasis on promoting the employment and performance review of "researchers," who expand research fields and "engineers," who improve the performance and user-friendliness of apparatus - especially software engineers. Moreover, it will be advisable to consider supporting the researchers in the form of outsourcing, which will relieve them of time-consuming routine work and free them to focus on their developmental research.

4. Future technical and scientific developments

The upgrading of the beamline optics and fundamental experimental apparatus is mentioned above. The issue then transforms into the following points: the upgrading of focusing optics or the separation of roles among beamlines, and the permanent installation of the multi-element SSD.

It would be safe to say that BL01B1 is optimized for XAFS experiments with a bending magnet as its light source. It is now necessary to make it easier to create a special environment of samples (to create such an environment itself is the experimenters' duty) which is important as a point of materials science. For that purpose, a large hutch, a large experimental plate and sufficient workspace outside the hutch can be significant advantages. We call for efforts to create better conditions for users to perform chemical and biological experiments, *in-situ* experiments, gas handling and wet sample preparation easily and safely. The proposed exhaust system can be a plus for the experiments, and such environmental considerations will help create new demand, as will the environment in which users can prepare and dispose of wet samples in a nearby lab.

It may be a good idea to make total reflection fluorescence XAFS a centerpiece for the beamline, taking advantage of the low beam divergence in the vertical direction, but BL10XU is more suitable for that purpose if conditions permit.

So far, each user has set different standards for deciding absolute energy in XAFS experiments. To make the comparison between XANES spectra easier, however, it is desirable to establish an absolute energy scale, while another possible solution is to create a database for spectra, which will require the consultation with the international XAFS society for its efficient operation.

5. Conclusion

With regard to the beamline optics, it was suggested that the focusing optics be upgraded, the allotted tasks of each beamline be clearly identified, and that a multi-element SSD be permanently installed. Another necessity is the building of an infrastructure that assists in the preparation of various sampling conditions.

To make use of the beamline's characteristics and to produce distinctive research results, SPring-8 must invite research groups that will play a central role in promoting the research and establish a more solid support system for them, which will include joint research with the beamline scientists. To ensure the success of research using the beamline, it would be better to implement a system in which users lay a mid-term plan in order to attract their investment.

Considering that industrial use is the main pillar of SPring-8 activities and that XAFS is in great demand, it is worthwhile to further enhance user-friendliness, such as by shortening the turnaround time. On the other hand, since research results for industrial use do not necessarily take the form of papers, it is worth considering a feedback system for non-proprietary industrial use.

We are under the impression that the complicated optics are fully utilized, and that the survey and statistical analyses of the realities of public use have been properly conducted. We share the view that the credit for that goes to the facility's staff, at both the SR research institute and the administration sector with the beamline scientists first on the list, who have been making serious efforts to make better use of synchrotron radiation.