Recent performance of laboratory-scale X-ray absorption fine structure instruments

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It is of importance to carry out X-ray absorption fine structure (XAFS) measurements not only at synchrotrons but also in ordinary laboratories. A breakthrough in the instrumentation for laboratory XAFS came with a new idea for an X-ray generator. This paper gives a summary of the instrumental designs and demonstrates the recent experimental performance, particularly with regard to the absorption spectra of 3d transition metals. Some results of rather advanced measurements, such as high-energy-resolution experiments and the fluorescent XAFS, are also shown. The laboratory-scale equipment is now sufficiently competitive to play a role in extending the opportunities of X-ray absorption studies and in the further development of X-ray spectroscopy.

Keywords: Laboratory XAFS; X-ray generator; Rotating anode; LaB₆ cathode; 3d Transition metals; Absorption spectrum; Fluorescent XAFS
1. Introduction

There were ambitious trials to measure X-ray absorption fine structure (XAFS) precisely in the ordinary laboratory several decades ago. Lytle’s pioneering instrument[1] greatly stimulated the new experimental trend in X-ray absorption spectroscopy. It was in 1971[2] that theoretical advancements first ensured the availability of XAFS as a tool for the analysis of atomic-scale structure around a specific atom. Since then, many instruments have been reported by several research groups[3-12]. In the 1980s in particular, significant improvements in spectrometer design were made. Tohji, Udagawa and their co-workers[9] developed the state-of-the-art spectrometer for XAFS experiments in an ordinary laboratory. On the other hand, since 1975, the advent of synchrotron sources has facilitated the application of XAFS. It started at Stanford, and then spread all over the world. In the case of Japan, the Photon Factory, KEK started in 1982. XAFS has very rapidly become one of the most popular techniques and still continues to grow.

In the 1990s, another breakthrough in laboratory XAFS came with the development X-ray generator that is suitable for XAFS experiments[13, 14], while most conventional X-ray tubes for industrial use had previously been designed for either diffraction or fluorescence experiments. With its dedicated design for XAFS experiments, the NRIM super XAFS[15], developed at the National Research Institute for Metals (NRIM), Tsukuba, Japan, can permit the highest tube current in spite of its very compact size. When combined with a Johansson-type spectrometer, it can produce an extremely intense monochromatic X-ray beam of $\sim10^7$ counts/s/mm$^2$ at the maximum. One should note that synchrotron radiation can provide a much higher intensity, of the order of $10^9$ to $10^{11}$ counts/s/mm$^2$, but for ordinary absorption measurements, even $\sim10^6$ counts/s/mm$^2$ intensity is sufficient to get good quality data from a viewpoint of counting statistics.
In the present paper, the main features of the NRIM super XAFS are first summarized, and then recent performances in practical measurements are described. Some trials of advanced measurements, such as high-energy-resolution experiments and fluorescent XAFS, are mentioned as well.

2. The NRIM super XAFS and the spectrometer

The problems of laboratory XAFS measurements have been discussed many times[12]: (1) the low intensity of the incident X-ray beam at the sample position, because XAFS uses monochromatic X-rays from a weak Bremsstrahlung part of the spectrum; (2) the degradation of the spectrum caused by second- or third-order harmonic reflections from the crystal monochromator, which is also significant at synchrotron sources and; (3) the effect of a non-smooth spectral distribution mainly due to the characteristic lines (7 ~ 12 keV) of tungsten, the conventional filament material which evaporates onto the anode. One might notice that all of these problems arise from the characteristics of the conventional X-ray source, and therefore the design of X-ray generator is important in solving these problems. That is, the essential specifications for an XAFS X-ray generator are as follows: (1) an extremely high tube current (e.g., more than 1000 mA); (2) a narrow line focus (e.g., less than 0.1 mm at 6° take-off); (3) operation at low tube voltage (e.g., 10-30 kV); and (4) a filament free of emission lines that contaminate the useful part of the spectrum and/or with little evaporation (e.g., LaB₆).

Fig. 1 shows schematic drawings of the NRIM super XAFS, the specifications of which are listed in Table 1. The present generator employs an LaB₆ cathode with a molybdenum anode. The diameter of the anode is 100 mm, and it rotates at 6,000 rev/min for cooling purposes by means of a motor installed inside the cup. Although LaB₆ is a promising electron emitter, because of its small work function[16] it is not always easy to get a good
filament for an X-ray tube. Being a ceramic, LaB$_6$ is difficult to form as a coil heater. In the present study, the filament was prepared by slicing an LaB$_6$ rod (1 in. diameter) and cutting with an electro-discharging wire. LaB$_6$ works at much a lower temperature (1750 - 2050 K) than a conventional tungsten filament; on the other hand, the current for heating is twice that of tungsten because of its small resistivity. The size of the electron emitter plane is 11 mm $\times$ 1.3 mm, and the shape of the filament has been optimized to get uniform heat distribution and to avoid the deformation caused by thermal expansion. The cathode structure has been designed especially for low tube-voltage operation[13], which is necessary to prevent the generation of high-energy X-rays that cause higher-order harmonics at the monochromator. For example, since the energy range for Cu-K XAFS measurements is usually 8.8 - 9.5 keV, when the tube voltage is set at 17.5 kV, one can avoid the effect of second-order reflection. As yet, conventional electron gun have not been designed for operation at less than 20 kV, and it is difficult to get a high tube current in these circumstances. Furthermore, the tube is equipped with two turbomolecular pumps for improving the vacuum to prolong the life of the LaB$_6$ filament, since it is very short under the moderate vacuum used for ordinary X-ray generation[17]. The shape of the tube is also carefully designed for this purpose. The system pressure is around $10^{-7}$ torr when operated at full power.

Fig.2 shows a photograph of the NRIM super XAFS and the spectrometer. The present X-ray source provides the maximum tube current of 1100 mA at low tube voltage (14.5 ~ 19.0 kV) with a narrow line focus (0.07 mm $\times$ 7 mm at 6° take-off). The tube voltage can be changed from 10 to 35 kV. When combined with a Johansson- or Johan-type spectrometer (Roland radius, 350 mm) shown in Fig.3, an intense monochromatic X-ray flux of $\sim 10^7$ counts/s/mm$^2$ at the maximum is available at the sample position, Although obviously it depends on the X-ray energy and the kind of monochromator. Because of such high incident intensity, a fast detector system with a YAP:Ce scintillator[18] and a specially
designed amplifier[19] were employed. The present X-ray source equipped with the LaB₆ cathode gives a very smooth continuum spectrum in the energy region between 6.5 and 33 keV except for the anode's (molybdenum) characteristic lines. Since the evaporation rate of the LaB₆ filament is extremely low, lanthanum emission lines (4 - 6.3 keV) in the spectrum are weak[20]. In the earlier stage of our development, the life of the filament was very short mainly because of poisoning by residual O₂ gas[21]. Later, the life was prolonged to more than 2500 h by improvement of the vacuum in the tube, controlling the surface condition by pre-heating and optimizing the operation temperature. The stability is excellent, and in the author’s laboratory, the machine is usually operated continuously for 3 - 6 weeks.

3. Performance in normal transmission XAFS experiments

Figs 4-7 show K-edge absorption spectra of pure compounds of the 3d transition metals manganese, iron, cobalt and nickel, respectively. Typical experimental conditions are listed in Table 2. Each sample was prepared in the form of pellets (13 mm diameter.) mixed homogeneously with fine cellulose powder. The weight of the sample powder was adjusted to give a moderate edge jump (~1) and post-edge absorption coefficient (not greater than 4). A Ge(220) Johansson-type crystal monochromator (commercially available from the Quartz and Silice Co., France) was employed for these measurements. The energy resolution at Fe Kα₁ (6.4 keV) is 6 eV, and is sufficient at least to see the extended X-ray absorption fine structure (EXAFS). In most measurements, both the incident and transmission intensities were accumulated for more than 10⁶ counts. For lighter elements like manganese and iron, however, we needed to compromise sometimes because of weak intensity due to lowering the tube voltage. Additionally, the rather large Bragg angle at the monochromator causes a longer X-ray path, resulting in further intensity loss. The time needed to obtain one complete spectrum depends on the specific element; it was shorter than 1 h for nickel, but 5.5 h for
manganese. An ordinary X-ray generator provides an X-ray spectrum with strong characteristic tungsten lines, and it degrades the absorption spectrum strongly in the energy region from 7 to 12 keV. In our previous study, the tube voltage had to be reduced below 10.2 kV so as not to generate tungsten L lines, resulting in an inevitable severe intensity loss. On the contrary, it is found from Figs 4-7 that specific fine structure, reflecting atomic arrangements, is clearly visible without any obstruction from the spectrum of the X-ray tube. Those spectra were analyzed successfully and a good agreement was achieved with the crystallographic data. The authors are now constructing a database and intend to display all data electronically via the Internet in the near future (http://inaba.nrim.go.jp/xray/).

Since the spectrometer employs linear motion of the crystal monochromator, as understood from Fig.3, the available angular range is not very wide and the lower limit (the closest distance position from the source) is sometimes a problem. Therefore, it is necessary to change the crystal monochromator when the energy of absorption edge becomes higher. Fig.8 shows the L_{III}-edge XAFS of lead compounds. In these measurements, a Ge(331) Johansson-type monochromator was used. To compensate for the low reflectivity, a rather high tube voltage was applied because second-order reflection is not caused for this plane. The oscillation at post-edge was rather weak for these samples, but the difference among them is clearly recognized. Through analysis of the data, good agreement was obtained with the structure determined by X-ray diffraction. The present measurement was extended to lead silicate glasses[22].

Cooling the sample is sometimes very effective to enhancing a weak XAFS oscillation signal, and in making it easy to obtain the excellent spectra in the laboratory. This is valid for samples with an atomic structure that does not change at low temperature. As seen in Fig.2, the authors use a cryorefrigerator (Cryomech, GB-15) weighing less than 3 kg. It can cool the sample down to around 10 K, but 30-50 K is usually chosen for convenience.
Fig. 9 shows the K-edge XAFS of a nickel foil at 45K, measured with a Ge(220) crystal monochromator. As temperature is lowered, the amplitude of the XAFS signal becomes larger, and the high-frequency components reflecting the contribution of scattering by far atoms become clearer. Another practical example at low temperature (30K) is given in Fig. 10. The sample was Cu_{30}V_{70} powder synthesized by 60 h of mechanical alloying, a non-equilibrium process exploiting a solid-state reaction in a high-energy ball mill. The data are in good agreement with the results obtained from synchrotron studies[23]. Lowering the temperature enabled the observation of sign of the formation of a bcc super saturated solid solution in spite of the immiscibility of copper and vanadium. The measuring time was only 40 min, which is almost the same as typical synchrotron experiments. Although in this case Ge(220) reflection was chosen as a monochromator to obtain high intensity, there is a limit at the high-energy (low-angle) side because of the linear motion of the spectrometer. When the sample is an ordered material and it is significant to see high-k region for Cu-K XAFS, we usually use Ge(311) and the generator is then operated at 20kV and 1000 mA. The measuring time is about 4 h in this case, but better energy resolution can be obtained. Although the energy resolution did not affect the results of XAFS data analysis, good resolution is sometimes useful to discuss the differences observed in the raw spectra.

4. Advanced measurements

The laboratory XAFS spectrometer is based on focusing optics and therefore the energy resolution is moderate, but sufficient for usual EXAFS measurement. However, it is sometimes important to observe XANES (X-ray absorption near edge structure) and such measurements require rather high resolution. Fig. 11 shows the XANES of copper foil measured with the monochromator of higher-order reflection. The resolution can be improved to almost the same standard as the usual synchrotron radiation experiments. In the
authors’ opinion, a high-resolution measurement does not fit very well for the laboratory XAFS because of low intensity. But when the application concerns pure elemental samples and not diluted systems, it is feasible enough.

Fluorescent XAFS measurements in the laboratory is another challenging direction[24], because there are many demands for structural analysis of trace systems and thin films that are not always easy to study by a transmission technique. Fig. 12 shows the results for a thin film (1000Å) of magnetic Ni$_{70}$Co$_{30}$ at room temperature. An NaI(Tl) detector (1 in. diameter) was used for measuring fluorescent X-rays, and about 5000 counts/s intensity was obtained at post-edge. It took 8 h 40 min to obtain the whole spectrum it represents the accumulation of $5 \times 10^5$ counts per points, but this is much shorter than the pioneering work using the conventional source[24]. When cooling the sample (20 - 50K), longer measuring time was required in our case because of the absorption loss at the cell window and the smaller solid angle. One could evacuate the X-ray path and also sometimes compromise on total counts, because $10^5$ counts/point is often considered sufficient. However, the authors believe it would be possible to get further strong X-rays at the sample position. Our preliminary experiments indicate the allowable load (21 kW at the present stage, already superior to the commercially available standard of 18 kW) can be improved to 22.5 kW or higher, by improving the cooling structure of the anode. Probably upgrading the X-ray source would plobably open further new opportunities for fluorescent XAFS and other advanced X-ray spectroscopic research. Generating further intense X-rays and also extending the X-ray energy to low-energy region[25] are interesting and important developments.

5. Summary

The NRIM super XAFS can overcome almost all of the problems encountered in XAFS measurements in the laboratory. As for a conventional transmission technique, it is
now possible to measure a spectrum to the same degree of quality as that obtained from a synchrotron in a reasonably short time. The laboratory XAFS has great advantages in cost and feasibility for both academic research and industrial applications. It has enabled us to have a good feedback through the research. It can be used for routine analysis and possibly can be applied to the on-line inspection of products in industry. Synchrotron radiation is still an attractive X-ray source, even if most XAFS experiments become achievable in an ordinary laboratory. Undoubtedly, the highly brilliant polarized beam is a very strong tool for especially difficult and advanced experiments in X-ray spectroscopy. The authors expect that laboratory equipment and synchrotrons will both play a roles in spectroscopic studies in the future, and are hopeful for further developments in the XAFS field.

6. Acknowledgements

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References


25) S. Munekawa, private communication.
Figure Captions

Figure 1
The X-ray generator specially designed for XAFS (top and side views)

Figure 2

Figure 3
Layout of the spectrometer for focusing optics. The X-ray focal spot (F), crystal monochromator (M) and receiving slit (RS) are linked with the bar so that they are always on the circle of 350 mm radius. The distance F-M and M-RS changes systematically when the X-ray energy is scanned. DS: divergence slit, C₁: proportional counter for measuring incident X-ray intensity, S: sample, C: cryorefrigerator, C₂: scintillation detector for measuring transmitted X-ray intensity.

Figure 4
X-ray absorption spectra of Mn compounds; Mn₃O₄ (tetragonal, I41/amd), MnO₂ (tetragonal, P42/mnm), MnO (cubic, Fm3m), MnB₂ (hexagonal, P6/mmm), MnCO₃ (trigonal, R-3c), MnF₂ (tetragonal, P42/mnm).

Figure 5
X-ray absorption spectra of Fe compounds; FeF₃ (trigonal, R-3c), Fe₂O₃ (trigonal, R-3c),
Fe₃O₄ (cubic, Fd3m), FeO (cubic, Fm3m), FeB (orthorhombic, Pnma), Fe₂B (tetragonal, I4/mcm), FeSi₂ (orthorhombic, Cmca).

**Figure 6**

X-ray absorption spectra of Co compounds; Co (hexagonal, P63/mmc), CoTiO₃ (trigonal, R-3), CoMoO₄ (monoclinic, P2/c), CoCl₂ (trigonal, R32), CoO (cubic, Fm3m), Co₃O₄ (cubic, Fd3m).

**Figure 7**

X-ray absorption spectra of Ni compounds; NiF₂ (tetragonal, P42/mnm), NiTiO₃ (trigonal, R-3), NiO (cubic, Fm3m), NiB (orthorhombic, Cmcm), NiS (hexagonal, P63/mmc), Ni₂Si (orthorhombic, Pnma).

**Figure 8**

(a) X-ray absorption spectra of Pb compounds; PbF₂ (orthorhombic, Pnma), PbO (orthorhombic, Pbcm), PbO₂ (tetragonal, P42/mnm), PbTiO₃ (tetragonal, I4/mcm), PbWO₄ (tetragonal, I41/a). (b) XAFS function extracted from the absorption coefficient shown in (a). (c) Magnitude of Fourier transform of k χ(k)s in (b). The k-range used are as follows: PbF₂ 2.643-9.975 Å⁻¹, PbO 3.075-9.556 Å⁻¹, PbO₂ 3.099-11.29 Å⁻¹, PbTiO₃ 2.649-11.82 Å⁻¹, PbWO₄ 2.448-11.28 Å⁻¹.

**Figure 9**

XAFS function extracted from the absorption spectra of metallic Ni foil measured at room temperature and low temperature (45 K). Magnitude of Fourier transform of kχ(k)s over the range 2.73-12.43 Å⁻¹ are also shown.
Figure 10
Absorption spectrum of 60 h mechanically alloyed $\text{Cu}_{30}\text{V}_{70}$ powder, measured at 30K with a Ge(220) monochromator, at 17.5 kV and 1000 mA. The measuring time was 40 min. XAFS function $k\chi(k)$ and the magnitude of Fourier transform of $k\chi(k)$ over the range 2.88-9.4 Å$^{-1}$ are shown in the inset; the asterisk indicates the position of the fourth neighboring atom of bcc structure, which demonstrates the formation of a bcc supersaturated solid solution in spite of the immiscibility of copper and vanadium.

Figure 11
Higher energy resolution measurements to see XANES. Absorption spectrum of Cu metallic foil with a Ge(440) crystal (Lab.). For comparison, a synchrotron data (SR) with a Si(111) is also shown in the figure.

Figure 12
Application to fluorescent XAFS. Absorption spectrum of $\text{Ni}_{30}\text{Co}_{70}$ thin film at room temperature with a Ge(220) crystal, 1 deg. divergence and 0.1 mm receiving slits, at 16 kV, 1000 mA. Magnitude of Fourier transform of $k\chi(k)$ over the range 3.19-11.55 Å$^{-1}$ is shown in the inset.
<table>
<thead>
<tr>
<th>Table I</th>
<th>Specifications of the NRIM super XAFS</th>
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<table>
<thead>
<tr>
<th>Anode</th>
<th>Molybdenum (10cm in diameter)</th>
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<tbody>
<tr>
<td>Filament</td>
<td>Lanthanum hexaboride (LaB$_6$)</td>
</tr>
<tr>
<td></td>
<td>Non-tungsten material to obtain smooth spectral distribution without strong contamination lines</td>
</tr>
<tr>
<td>Allowable Load</td>
<td>21 kW</td>
</tr>
<tr>
<td></td>
<td>Tube Voltage 10 ~ 35 kV</td>
</tr>
<tr>
<td></td>
<td>Tube Current 0 ~ 1100 mA</td>
</tr>
<tr>
<td></td>
<td>Special cathode structure for low voltage operation to suppress the generation of high energy X-rays.</td>
</tr>
<tr>
<td></td>
<td>Capable of supplying extremely high intensity due to high tube current.</td>
</tr>
<tr>
<td>Focus Size</td>
<td>0.07 mm (width) x 7 mm (height) at 6 deg. take off</td>
</tr>
<tr>
<td></td>
<td>Narrow line focus to obtain intense monochromatic X-rays without losing energy resolution</td>
</tr>
<tr>
<td>Vacuum</td>
<td>$1 \times 10^{-7}$ Torr (when operating at full power)</td>
</tr>
<tr>
<td></td>
<td>High vacuum tube to prolong life of filament</td>
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**Table II**

Typical measuring conditions in normal transmission experiments

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<tr>
<th>Absorption Edge</th>
<th>Tube Voltage</th>
<th>Tube Current</th>
<th>Monochromator</th>
<th>F-M-RS Distance (See, Fig.3)</th>
<th>Number of Points</th>
<th>Measuring Time</th>
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<tr>
<td>Mn –K (6.538 keV)</td>
<td>12.8 kV</td>
<td>750 mA</td>
<td>Ge(220)</td>
<td>28.298 deg</td>
<td>663.7 mm</td>
<td>336</td>
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<tr>
<td>Fe-K (7.111 keV)</td>
<td>13.8 kV</td>
<td>800 mA</td>
<td>Ge(220)</td>
<td>25.837 deg</td>
<td>610.1 mm</td>
<td>316</td>
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<tr>
<td>Co-K (7.710 keV)</td>
<td>15.0 kV</td>
<td>750 mA</td>
<td>Ge(220)</td>
<td>23.703 deg</td>
<td>562.8 mm</td>
<td>316</td>
</tr>
<tr>
<td>Ni-K (8.332 keV)</td>
<td>16.0 kV</td>
<td>450 mA</td>
<td>Ge(220)</td>
<td>21.837 deg</td>
<td>520.8 mm</td>
<td>306</td>
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<tr>
<td>Cu-K (8.980 keV)</td>
<td>17.5 kV</td>
<td>1000 mA</td>
<td>Ge(220)</td>
<td>20.188 deg</td>
<td>483.1 mm</td>
<td>244</td>
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<tr>
<td>Pb-LIII (13.041 keV)</td>
<td>25.5 kV</td>
<td>700 mA</td>
<td>Ge(331)</td>
<td>21.485 deg</td>
<td>512.8 mm</td>
<td>291</td>
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