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# HIGH POWER X-RAY GENERATOR FOR XAFS EXPERIMENTS

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A new X-ray generator has been developed for X-ray absorption fine structure (XAFS) experiments. Over the years, much research has been performed at synchrotron radiation facilities, and it has been believed that the measurements in an ordinary laboratory are not of a competitive standard. In this report, we describe the basic idea of a laboratory X-ray source dedicated to XAFS and show how our generator is a powerful and practical alternative. It realizes a very high tube-current of 1,100 mA at low tube-voltage of 18 kV, and therefore provides extremely intense monochromatic X-rays, which are completely free from higher order reflections. It enables the measurement of a spectrum with the same quality as that using a synchrotron in a reasonably short time, typically 30 min to 2 h. This X-ray generator is now available in a normal laboratory, and a new phase of laboratory XAFS is now beginning.

## 1. Introduction

X-ray absorption fine structure (XAFS) provides information on the atomic-scale structure around a specific atom, and has become an essential analytical tool in materials, biology and many other sciences [1, 2]. The availability of a synchrotron source has facilitated the application of XAFS, because a strong smooth spectral distribution is important for the measurements, and synchrotron radiation is eminently suitable. However, as is often the case in materials study, the difficulty in obtaining quick feedback ready for the next sample preparation is one of the big disadvantages. In addition, as the number of scientists involved in this field increases rapidly, many problems, including the strictly limited beam time of the facility become significant.

Instruments for carrying out measurements in an ordinary laboratory have been continuously developed and improved since the middle of 1970s [3-6]. Above all, a lot of work has been devoted to developing a spectrometer [7-12], to produce monochromatic X-rays efficiently from a continuum spectrum generated in a tube. However, from a practical point of view, performance so far has not always been satisfactory. A long measuring time was usually required, and sometimes there was a problem with the quality of the data.

The authors consider that further scope for improvement comes with the development of an X-ray generator [13-17] that is suitable for XAFS experiments. Most X-ray generators for industrial use have been designed for either X-ray diffraction or X-ray fluorescence analysis, and no X-ray source has been specially designed for XAFS so far. This report describes the necessary specifications for such a source and show how the present new X-ray generator has raised the standard of laboratory XAFS experiments.

## 2. Design Considerations

Since XAFS is absorption spectra in the X-ray region, a simple transmission technique is generally used as an ordinary measurement. One has only to measure X-ray intensities before and after transmitting the sample as a function of incident X-ray energy scanned by a monochromator. However, this is not easy because XAFS is a small oscillation of the absorption coefficient and therefore precise measurements are needed. The main problems are as follows: (1) the low intensity of incident X-ray flux at the sample position, resulting in insufficient count statistics of the signal, because XAFS uses monochromatic X-rays from a weak bremsstrahlung component, (2) the degradation of the spectrum caused by 2nd or 3rd order harmonic reflections from a crystal monochromator, and (3) the effect of non-smooth spectral distribution mainly due to the characteristic lines of tungsten, which is the filament material and which evaporates on the anode.

XAFS experiments need high intensity monochromatic X-rays free from high energy components and contamination lines. The expression 'high intensity' is ambiguous and may sometimes lead to misunderstanding. Tube power is obviously important for obtaining high intensity, but the size and divergence of the beam at the sample position should be considered at the same time. The XAFS equipment uses a monochromator, often a curved crystal monochromator, and the energy resolution is mainly determined by geometrical factors such as focal size and receiving slit width. Thus, in order to obtain high intensity with reasonable resolution, one should consider not only the tube-current but also the shape of the X-ray focus. These requirements are similar to the conditions for focusing optics in X-ray diffraction. Therefore the narrow intense line focus is important [13, 14], although the authors never think X-ray diffraction tube is suitable for XAFS.

Diffraction experiments use characteristic X-rays from the anode, and therefore the tube-voltage is usually set rather high, typically 40-60 kV. Conversely, XAFS uses the weak bremsstrahlung and therefore the typical tube-current of 200-300 mA from an X-ray diffraction source is not enough for XAFS experiments. In addition, high energy X-rays are unnecessary and should be eliminated. Low tube-voltage operation is a perfect way to suppress higher order harmonics, as long as sufficient intensity can be obtained. That is, a completely different design is necessary compared with a diffraction generator. Furthermore, to be free from the tungsten lines, new filament materials that contain no tungsten should be employed [18]. Otherwise, tungsten lines from the anode would have to be rejected by means of some other techniques.

As a result of these points, the following specifications have been considered essential for an XAFS X-ray generator: (a) an extremely high tube-current (e.g. more than 1,000 mA), (b) a narrow line focus (e.g. about 0.1 mm at 6 deg. take off), (c) low tube-voltage operation (e.g. 10-30 kV), and (d) $LaB_6$ or other non-tungsten filament. We started with a tungsten filament because of the ease of design, and therefore specifications (a), (b) and (c) were taken into consideration for our X-ray generator then, although very recently we succeeded in developing a new $LaB_6$ filament [19]. This article reports on the earlier stage where a tungsten filament was employed. However, even when a tungsten filament is used, tungsten lines can be completely suppressed by low tube-voltage operation.

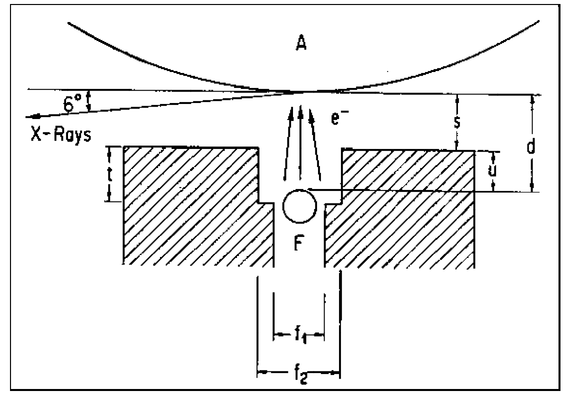


**Fig. 1** Schematics of the electron gun. A: rotating anode, W: Wehnelt electrode, F: filament. Parameters for the present X-ray generator are as follows: d: 10.75 mm, s: 5.25 mm, u: 5.5 mm, t: 5.8 mm, $f_1$: 8.0 mm and $f_2$: 9.0 mm.

## 3. X-ray generator for XAFS

Figure 1 shows a schematic drawing of the electron gun in the X-ray generator developed for the dedicated use of XAFS experiments. The electron gun is the most important component, as almost all the specifications discussed in the previous section come with this new electron gun. It allows an extremely high tube-current and a narrow line focus at a low tube-voltage. The maximum allowable tube-current between the filament (**F**) and the anode (**A**) depends on the work function of the filament materials, the size of the filament, the tube-voltage between **F** and **A**, and the distance (**d**) between them. In the present generator, the filament employed is a tungsten coil, and the entire coil length, coil diameter, and wire diameter are 17.7, 5, and 0.6 mm, respectively. This is much larger than a conventional filament to ensure a high filament-current which results in high thermoelectronic emission (i.e., tube-current) from **F** to **A**. Since lowering the tube-voltage works against an increase in the tube-current, it is necessary to shorten **d** to compensate. When **d** is shortened, focusing becomes difficult in general, but in the present case, the geometrical parameters (**s**, **u**, **t**, $\mathbf{f_1}$, $\mathbf{f_2}$) of the Wehneit electrode (**W**) and the bias voltage applied between **W**and **F** are optimized. These conditions were experimentally determined through the observation of the shape and size of the focal spot, including the degree to which the sub focal spot was suppressed.

Another important feature of the present X-ray generator is the use of a compact rotating anode. A molybdenum anode is 100 mm in diameter, and rotates at 6,000 rpm for cooling purposes by means of a motor installed inside the cup. Though such a small anode has been widely used for X-ray diffraction equipment, it has never been tried to combine with an extremely high power generator with a tube-current of more than 1,000 mA. In fact, even the authors themselves em-ployed a large rotating anode of 250 mm in diameter in an earlier study [13-15], because it is equipped with Rigaku, RU1000 (60 kV, 1,000 mA), which is a commercially available super high power X-ray generator allowing an extraordinary tube-current around 1,000 mA. However, the size of the anode required is essentially related not to the tubecurrent but to the total heat load (i.e., the product of the tube-voltage and current). This means a compact rotating anode can be used for a high tube-current generator if the voltage is lowered as in XAFS experiments. The reason why the maximum tube-current for 100 mm anodes has been limited at 200-300 mA, or at most 450 mA, is simply that the tube-voltage is usually set at 40-60 kV in order to obtain intense characteristic X-rays for diffraction experiments.

Figures 2 (a) and (b) show the top and side views of the present X-ray generator, respectively. A tube is evacuated to around $10^{-6}$ Torr, and inside its housing, the molybdenum anode and the electron gun are installed. The take off angle of X-rays is set at 6 deg. The controller and the power source are essentially the same as those for the RU-1000, but were slightly changed to permit a maximum tube-current of 1, 1 00 mA.

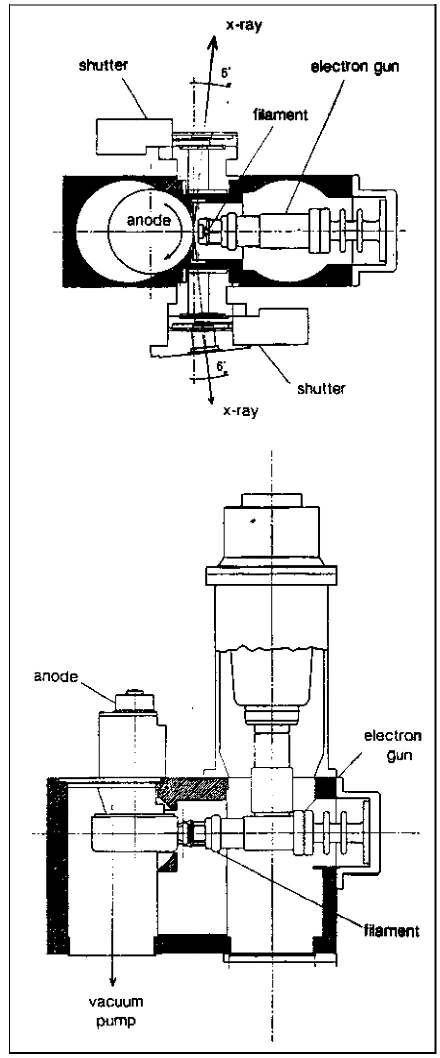


**Fig. 2** Top and side view of the X-ray generator for XAFS.

## 4. Performance

The present X-ray source is operated at low tube-voltage so as not to generate 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 the 2nd order reflection. As yet, a conventional electron gun has not been designed for operation at less than 20 kV, and it is difficult to get a high tube-current in these circumstances. The new design for the X-ray gener-ator realizes both a high tube-current and a narrow focus at low tube-voltages.

The dependence of the focal width on the tube-current and the bias voltage at 18 kV was measured and is listed in Table 1. These data were obtained by directly measuring the projection on X-ray film through a 10 μm pinhole placed at an exit angle of 6 deg. A narrow line focal spot of 0.1 - 0.13 mm in width was formed by applying a bias voltage of about -600 V. This is sufficient for the use of a Johanson-type focusing spectrometer for XAFS experiments. Figure 3 shows the relationship between the maximum tube-current and tube-voltage, when the focal width was fixed at around 0.1 mm. The present X-ray generator provides an extremely high tube-current in the low-voltage region, compared with a conventional X-ray diffraction source, although the total heat load on the anode is similar (around 20 kW). It enables higher X-ray intensity than any other previous ordinary in-house source, at low tube-voltages. In fact, this is the first time that a high tube-current of 1,100 mA was achieved at 18 kV with a line focus of approximately 0.1 mm.

**Table 1** Effective focal width (mm) at an exit angle of 6 deg. Tube-voltage was fixed at 18 kV

| | No bias | -200 V | -400 V | -600 V |
|---|---|---|---|---|
| 600 mA | 0.14 | 0.13 | 0.12 | 0.10 |
| 800 mA | 0.14 | 0.14 | 0.12 | 0.11 |
| 1,000 mA | 0.16 | 0.14 | 0.13 | 0.12 |
| 1,100 mA | 0.16 | 0.14 | 0.13 | — |

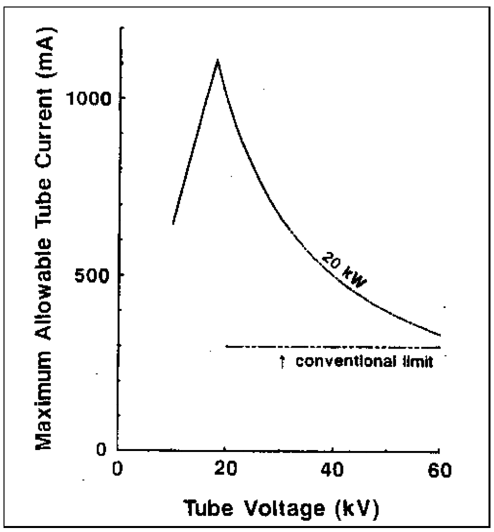


**Fig. 3** Dependence of the maximum allowable tube-current on tube-voltage. The conventional limit for commercially available X-ray generators is shown as well by the double-dotted-dashed line.

The present X-ray source has been applied to perform XAFS measurements, combined with the Johanson-type spectrometer [16] as shown in Fig. 4. Intense monochromatic X-ray flux of 3x $10^6$ to $10^7$ cps, completely free from higher order harmonics, was available at the sample position. In future, X-ray intensity may be further increased by use of a two-dimensional focusing monochromator [21]. The measuring time for a sample of between 2 and 4μt thickness is estimated to be usually less than 1 h and at most 2 h for a difficult sample, when the accumulation count of transmitted X-rays and the point number of the spectrum are set as $10^6$ and 300, respectively.

Figure 5 shows the Cu-K absorption spectrum of $Cu_{30}V_{70}$ powder. The sample was synthesized by 60 h of mechanical alloying, a non-equilibrium process using a solid state reaction in a high-energy ball mill. The X-ray generator was operated at 17.5kV and 1,000 mA, and measurement was done at 30K. The magnitude of Fourier transform of $k\chi(k)$ is shown in the inset of Fig.5, and is in good agreement with the results obtained from synchrotron studies [20]. The measurement time was 40 min, which is almost the same as with typical synchrotron experiments.

To avoid the effect of strong characteristic X-rays of tungsten which might evaporate from filament and adhere to the anode, a low tube-voltage operation is sometimes effective. Figure 6 shows the transmitted X-ray intensity of nickel foil around the Ni K absorption edge. Intense tungsten Lα lines, which significantly degrade the absorption spectrum, were

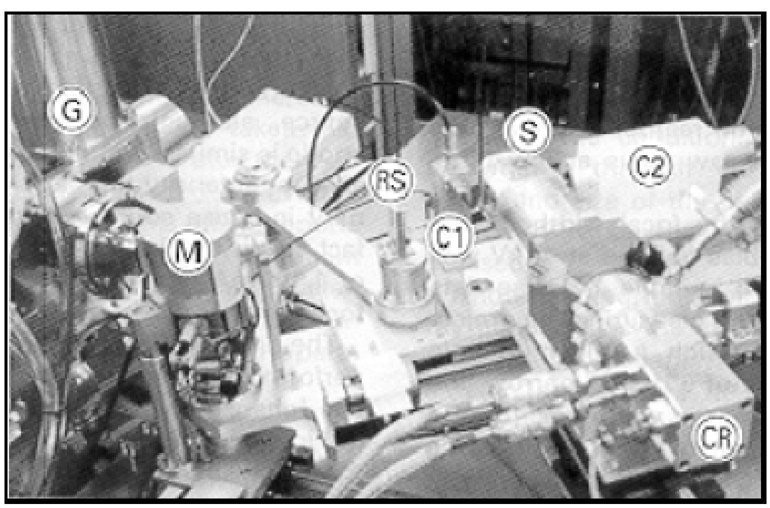


**Fig. 4** The X-ray generator and spectrometer. G: X-ray generator, M: crystal monochromator, RS: receiving slit, C1: proportional counter for measuring incident X-ray intensity, S: sample, CR: cryorefrigerator, C2: scintillation detector for measuring transmitted X-ray intensity.

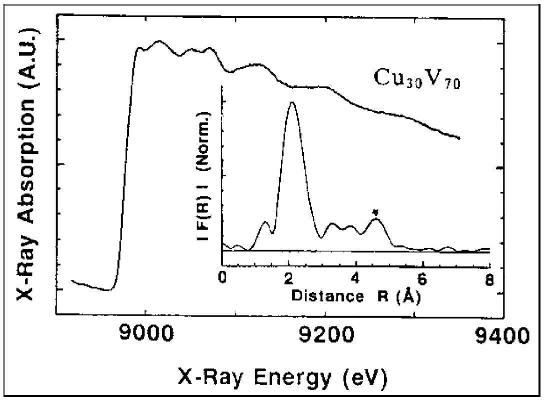


**Fig. 5** Absorption spectrum of 60h mechanically alloyed $Cu_{30}V_{70}$ powder. Magnitude of Fourier transform of $k\chi(k)$ over the range 2.9-9.4 $A^{-1}$ are shown in the inset; the asterisk indicates the position of the fourth neighboring atom of bcc structure, which demonstrates the formation of a bcc supersaturated solid solution in spite of the immiscibility of copper and vanadium.

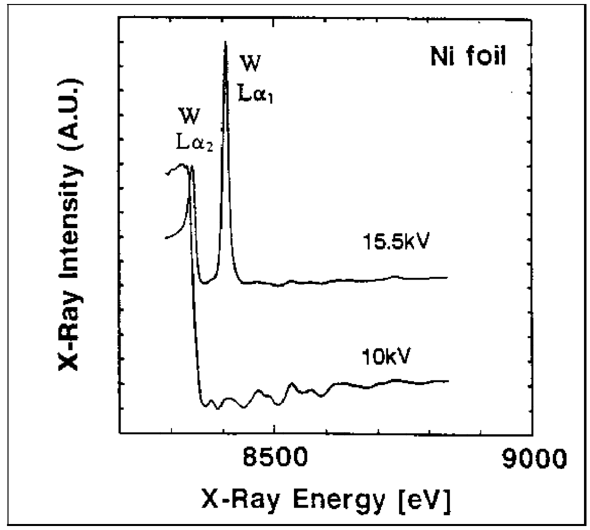


**Fig. 6** Spectrum of transmitted X-ray intensity of nickel foil around nickel K absorption edge.

observed at the usual operation of 15.5 kV. However, tungsten Lα lines are not emitted at a tube-voltage of less than 10.2 kV, which is necessary for the excitation of the 2p electron of tungsten. The present generator provides a relatively high tube-current of about 600 mA even at a very low tube-voltage of 10 kV, and it is possible to suppress tungsten lines with only moderate intensity loss. This procedure works well in the present case of nickel foil, however, the authors by no means consider it the best way. As an alternative solution for suppressing tungsten lines, the use of $LaB_6$ filament is very promising [18, 19].

## 5. Concluding Remarks

In conclusion, a new intense X-ray source for XAFS experiments was developed by combining a compact rotating anode with an electron gun specially designed for providing a high tube-current at low tube-voltage with a narrow line focus. The maximum allowable current was 1,100 mA, and undesirable high energy X-rays were completely eliminated. The capacity to control the continuum spectrum of the X-ray source by tuning the tube-voltage is an important feature which not even synchrotron radiation can provide. It is now possible to measure spectrum to the same degree of quality as that obtained from a synchrotron in a reasonably short time, typically 30 min-2 h.

Synchrotron radiation is still an attractive x-ray source, even if most XAFS experiments become achievable in an ordinary laboratory. Undoubtedly, it is a very strong tool for specially difficult experiments in X-ray spectroscopy. The authors expect that laboratory equipment and synchrotrons will both play a role in spectroscopic study in the future, and are hopeful for further development of the XAFS field.


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