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Laboratory-scale X-ray absorption spectroscopy approach for actinide research: experiment at the uranium L_3-edge.

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Abstract

We report that by using crystal optics and laboratory-based X-ray source, one may perform easily X-ray Absorption Spectroscopy (XAS) state-of-the-art measurements at the U L_3-edge. Our results are in excellent agreement with synchrotron-based studies for UO_2, KUO_3 and β-UO_3. The laboratory scaled approach constitutes an inexpensive solution to the limited availability of the XAS beamlines for actinide research. Moreover, our results allow for the development of many future applications addressing actinide f-electron chemistry and nuclear energy-related physico-chemistry, such as advanced nuclear fuel development and safe long term disposal of nuclear wastes.

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1. Introduction

X-ray Absorption Spectroscopy (XAS) is a well established non destructive method for determining both the oxidation state and the local environment of a given element in the studied compound. Major strengths of this technique include that no special sample preparation is usually required, and that it is bulk sensitive due to the long penetration depth of X-rays in matter. The sensitivity of XAS to the local order makes it useful not only for crystalline materials but also for liquids, gases, or amorphous matter. For example, XAS is regularly applied in actinide research such as actinide chemistry in molten salts [1], nuclear fuels [2, 3], nuclear waste [4] and environmental [5] studies. Indeed, by taking the advantage of the long penetration depth of the X-rays, XAS allows measurements under highly constraining environments and especially when studying radioactive matter such as actinide bearing materials.

XAS experiment requires a monochromatic and tunable X-ray beam. After the advent of synchrotron radiation sources, XAS experiments strongly focused at using synchrotron facilities for the obvious advantages of synchrotron light, most important difference to conventional x-ray sources being the several orders of magnitude higher brightness. However, the limited access to synchrotron beam-time access reduces and nearly excludes a large number of potentially important scientific research to be performed. This is especially true for actinide research, which at synchrotrons requires dedicated beamlines, and specific authorizations. Furthermore, high costs of radioactive sample transport and the limited number of dedicated beamlines strongly limits the experimental possibilities. In Europe, only few beamlines are clearly dedicated to actinide research: the MARS beam-line [6] at the French synchrotron radiation facility SOLEIL (Saint Aubin, France), the ROBL beamline [7] at the European Synchrotron Radiation Facility (ESRF,

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Grenoble, France), and the INE [8] and CAT-ACT beamlines [9] at the ANKA synchrotron radiation facility at the Karlsruhe Institute of Technology (KIT, Karlsruhe, Germany). Consequently, the development of alternatives is mandatory to compensate the currently lacking beamtime.

Studies of the XAS fine structure using conventional x-ray sources started rather soon after the discovery of x-rays [10], and in the mid-1970's the advent of synchrotron storage rings as x-ray sources made several advances in the XAS as a technique. However, XAS using laboratory-based sources and crystal optics have been continuously reported until today [11–21], because even owing to less intense x-ray source, the ability to perform experiments in home laboratory setting is convenient for many reasons such as easier access. Especially the recent development in SBCA optics [19, 22–24] has improved the quality of such spectrometers now considerably. Typical geometries are of Von Hamos and Johansson and Johann types using cylindrically [11–18, 20] and spherically [19, 21] bent analyzer crystals (CBCA and SBCA respectively). Compared to CBCA, SBCA's offer a relatively larger collection solid angle and a better resolution in the hard x-ray regime depending on the considered configuration and energy range [19]. Most of the reported laboratory scale XAS devices covers energies ranging between 5 and 12 keV, which do not include the actinide M and L-edges. However, the Mo K-edge (about 20 keV) obtained using a Laue-type DuMond curved crystal spectrometer [25] or a double-crystal monochromator [26], the Rh K-edge (about 23 keV) using a double-crystal monochromator [26] and the Zr K-edge (about 18 keV) collected using a transmission dispersive arrangement [27] can be found in literature. Therefore, the actinide L-edges are, in principle, reachable, and studies using them have already been done at Los Alamos National Laboratory [28] with an SBCA and Rowland-circle geometry instrument similar to the one here and by [19], but not reported in literature. Despite the obvious need of actinide L-edges for

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routine experiment in nuclear material research or radiochemistry dedicated laboratories, the absence of publication in the field has strongly limited the promotion of the technique to the researchers in the field, leaving the synchrotron radiation facility without alternative. In this work we finally report that by using efficient and cost-effective crystal optics, following the recent designs of Seidler et al. [19] with laboratory-based sources as an alternative to synchrotron XAS measurement at the uranium L_3-edge, i.e. between 17 and 18 keV, one may perform easily routine experiments. It is foreseen that this demonstration is highly valuable for further development of laboratory-scale XAS addressing actinide f-electron chemistry and nuclear energy-related physico-chemistry, such as advanced nuclear fuel development and safe long term disposal of nuclear waste.

2. Material and experimental methods

2.1. Sample preparation

All samples were prepared from depleted nuclear grade UO_{2+x}, supplied by FBFC International (Dessel, Belgium). Assessment of the impurity content of this powder has been reported elsewhere [29]. Sample processing parameters for various samples were determined via simultaneous thermal analysis (Netzsch STA 449 F1 Jupiter). A short description regarding the chosen parameters is given below for clarity [30].

The preparation of $UO_{2.00}$ was realized by reducing the supplied UO_{2+x} powder down to stoichiometry by heating it at 700°C under a flow of an Ar/H_2 (96:4 vol %) mixture. KUO_3 was prepared by mixing stoichiometric amounts of U_3O_8 and K_2CO_3 (Sigma-Aldrich, Belgium) powders and annealing at 800°C for 10 h under reducing conditions. A wet-chemical route was employed to produce β-UO_3. As-received UO_{2+x} powder was first dissolved in nitric acid and subsequently titrated

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with an excess of ammonia aqueous solution, which results in precipitation of ammonium diuranate (ADU). β-UO_3 was then obtained by calcining the ADU powder at 550°C for 30 min.

Phase purity of all samples was confirmed via X-ray diffraction. About 30-50 mg of compound powders were intimately mixed with boron nitride powder and pressed into thin pellets. These pellets were then doubly confined in kapton and polyethylene.

2.2. Synchrotron radiation experiments

X-ray Absorption Near Edge Structure (XANES) were first measured at the Rossendorf Beamline (ROBL, BM20) [7] located at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The storage ring operating conditions were 6.0 GeV and 170-200 mA. A double-crystal monochromator mounted with a Si(111) crystal coupled to collimating and focusing Rh-coated mirrors was used. U L_3-edge (17.166 keV) XANES spectra of all samples were recorded in transmission mode between 17 and 17.3 keV. The energy calibration was carried out measuring an Y foil (K-edge, 17.038 keV) in transmission mode simultaneously with each sample. A step size of 0.75 eV was used in the edge region. The energy E_0 of the edge absorption threshold position was taken at the first inflection point of each spectrum by using the first node of the second derivative. Several acquisitions were performed on the same sample and summed up to improve the signal to noise ratio. However, the spectra presented here are for comparison purposes, and contain only 4 scans of approximatively 30 min each. The ATHENA software (Version 0.9.18) [31] was used to remove the background and to normalize the spectra.

2.3. Laboratory-scale experiments

The benchtop XAS instrumentation at University of Helsinki is based on the use of SBCA which allows simultaneous monochromation and focus of the X-ray

beam to the sample. The schematic of the set-up [32], similar to the one presented in [19] is shown in Figure 1.

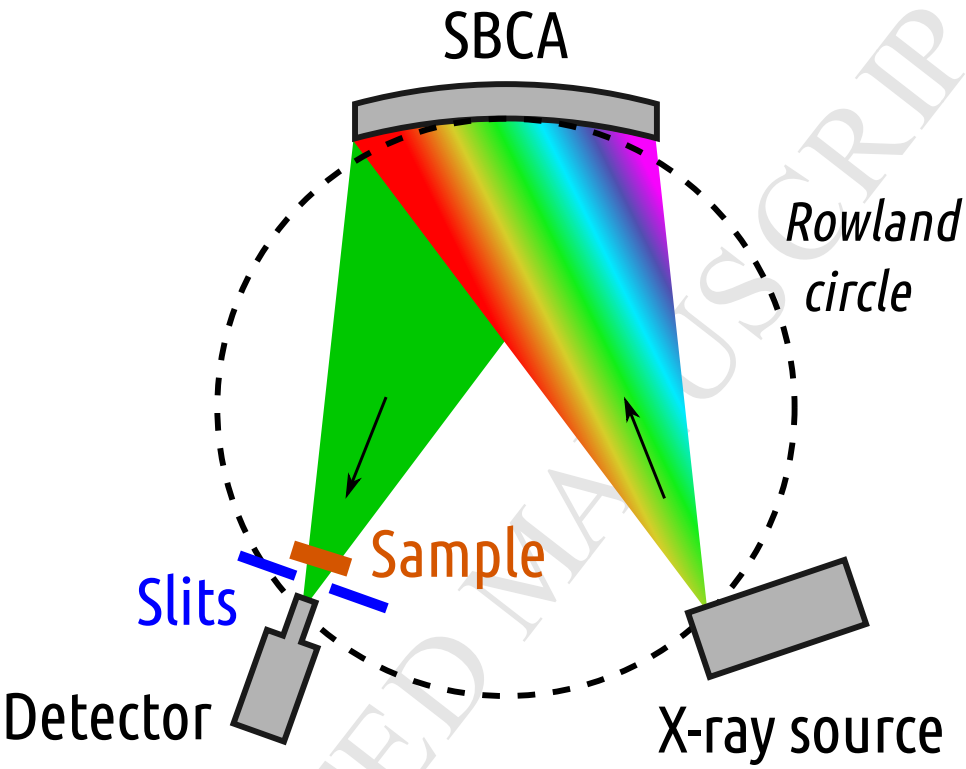


Figure 1: Laboratory scale instrument principles and configuration as for X-ray Absorption Spectroscopy.

The sample, the X-ray source, and the SBCA are positioned on the Rowland circle. When scanning the energy, both crystal and sample move synchronously to track the corresponding Rowland circle. The broadband x-ray radiation from the laboratory X-ray source directly illuminates the SBCA which monochromatizes and focuses the corresponding wavelength into the sample. Slits are applied to reduce the ambient X-ray background arising from elastic scattering and to limit the undesired wavelengths for hitting the sample. Then, the detector collects only

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the X-rays transmitted through the sample.

The X-ray source was a fine-focus Ag anode X-ray tube (Seifert/XRD Eigenmann) with 0.4 x 0.8 mm^2 effective source size (Horizontal x Vertical). The accelerating potential and electron current was fixed to 30 kV and 10 mA, respectively. A CdTe detector (Amptek XR-100T) with an active area of approx. 3 mm in diameter was used. An integrated signal electronic processing including Multi-Channel Analyser (Amptek, Inc.) was coupled to the detector. The good energy resolution of the CdTe solid-state detector allowed to reject the unwanted Ge(nnn) harmonics other than n=9. A Johann type Ge(111) SBCA, from XRS TECH LLC. [22], with the bending radius of 0.5 m was used to monochromatize and focus the radiation. Using that X-ray source-SBCA configuration, good count rates were achieved for energies above 12 keV as reported in Table 1. These count rates allow to measure slightly diluted uranium samples in transmission mode in still reasonable time. However, the fluorescence mode seems still out of reach at actinide L-edges. In addition, other actinides L_3-edges and Tc K-edge will be also possible.

The U L_3-edge (17.166 keV) XANES spectra of all samples were recorded in transmission mode between 17 and 17.3 keV. This energy range corresponds to the (999) reflection of the Ge(111) SBCA with Bragg angle between 81°and 86°. The intensity of lower harmonics were intentionally suppressed or reduced using Al filter, in order to not saturate the detector with undesirable counts. The XANES spectra reported here have been collected during 24 hours by repeating 30 min long scans.

The energy dependence of the incident flux can be determined by removing the sample and repeating the energy scan [19]. However, we found impossible subtract efficiently the additional background created by the elastic and inelastic scattering occurring to the doubly confined sample holder, making the standard procedure difficult in our case. To overcome this difficulty, one solution consists in placing

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Table 1: Count rates measured at sample position for energies above 12 keV. Note that these count rates are here order of magnitude due to the effect of high deadtime and degraded energy resolution when the detector was placed in direct beam, i.e. in the absence of any sample. *The count rate for the Ge(13 13 13) harmonic was measured below the energy range were X-ray source Ag Kβ_3 and Ag Kβ_1 fluorescence lines at 24.910 keV and 24.941 keV respectively were found.

Used harmonic	Energy (keV)	Count rate (s^{-1})
Ge(7 7 7)	13.4	1600
Ge(8 8 8)	15.3	2400
Ge(9 9 9)	17.2	700
Ge(11 11 11)	21.0	150
Ge(12 12 12)	22.9	100
Ge(13 13 13)	24.8	20

the sample directly in front of the X-ray source. In our case, we developed another method which relies on the presence of harmonics in the incoming beam as shown in Figure 2. With this approach the acquisition no longer requires repeating the experiment without the sample to obtain the incident-beam spectrum. Assuming that in the absence of a sample, both Ge(888) and Ge(999) harmonics behave similarly upon the probed Bragg angle range, one can simultaneously measure the incoming beam intensity and the U L_3-edge absorption spectra. In the absence of any edge or variations of the incident-beam spectrum at the energy range covered by the chosen harmonics, absorption decreases linearly with energy increase which justifies the validity of our approach. Such validity is clearly demonstrated by the comparison of harmonics behaviour relatively to Ge(888) with and without sample as shown in Figure 3. These intensities have been deduced by fitting the different harmonics using gaussian functions. Ge(7 7 7), Ge(9 9 9), Ge(11 11 11) and Ge(12 12 12) harmonics behave linearly relatively to Ge(8 8 8) as a function of energy without

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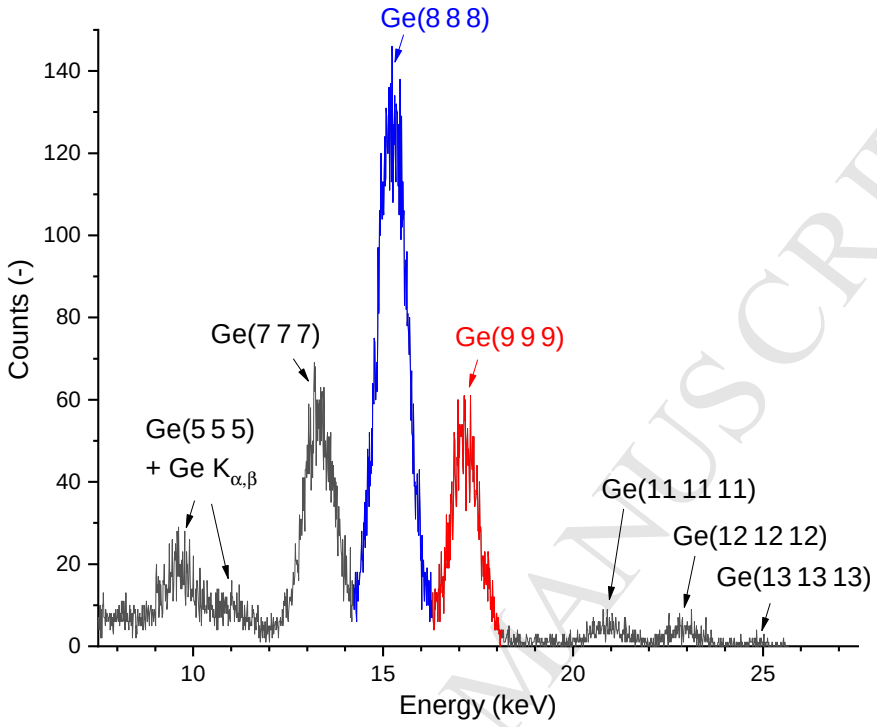


Figure 2: X-ray spectra of the incoming beam collected through the slits, without any sample. The different harmonics due to the Ge crystal as well as the resulting Ge fluorescences are also indicated. The Ge(888) reflection (in blue) was used as a measure of the incoming beam intensity while the Ge(999) reflection (in red) was the interesting signal.

sample. With a sample, for instance UO_2 here, the Uranium L_3-edge and L_2-edge are clearly visible through the Ge(9 9 9) and Ge(11 11 11) behaviours respectively. In both cases, the Ag Kβ_3 and Kβ_1 fluorescence lines at 24.910 keV and 24.941 keV are seen through the Ge(13 13 13) behaviour.

3. Results and discussion

Uranium L_3-edge XANES spectra for UO_2, KUO_3 and β-UO_3 were collected using both the laboratory-scale set-up and the ROBL beamline at ESRF. They are

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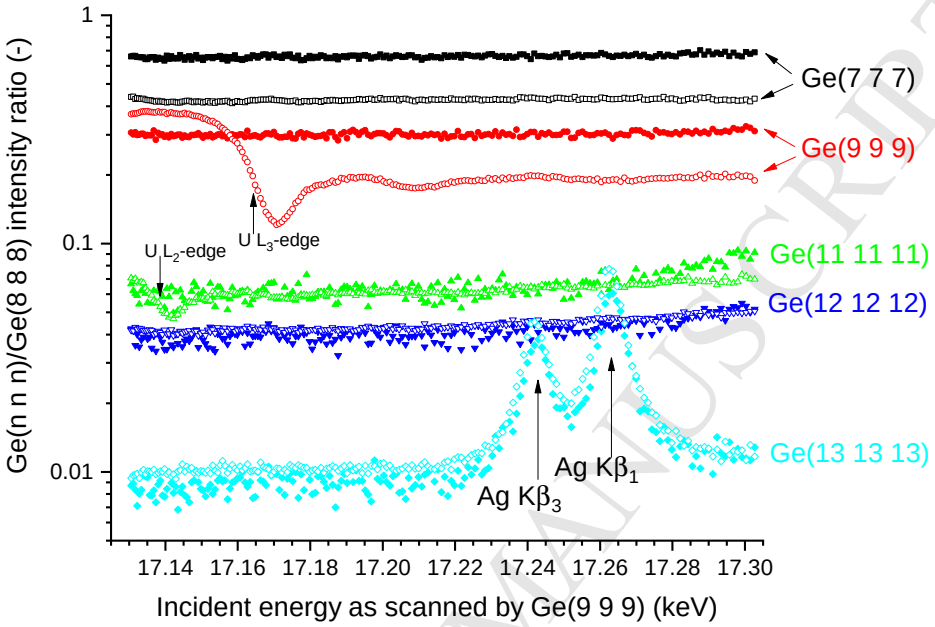


Figure 3: Harmonic Ge(n n n)/Ge(8 8 8) intensity ratio as scanned during the experiment with (open symbols) and without (closed symbols) the UO_2 sample.

shown in Figure 4. The Uranium L_3-edge XANES spectra are usually composed of one intense peak, the so-called white line, and additional resonance and/or shoulders at different energies. Both energy position and intensity of the white-line and the resonances depend on the uranium oxidation states and uranium local environment, i.e. the nature, number and geometrical arrangement of the neighbouring atoms.

The two datasets are in excellent agreement. Most notably, all the spectral features are well reproduced for all samples when using the lab-scale instrumentation. Statistical noise is clearly more pronounced in the laboratory-scale XAS spectra as compared to the synchrotron-XAS. The noise originates from several orders of

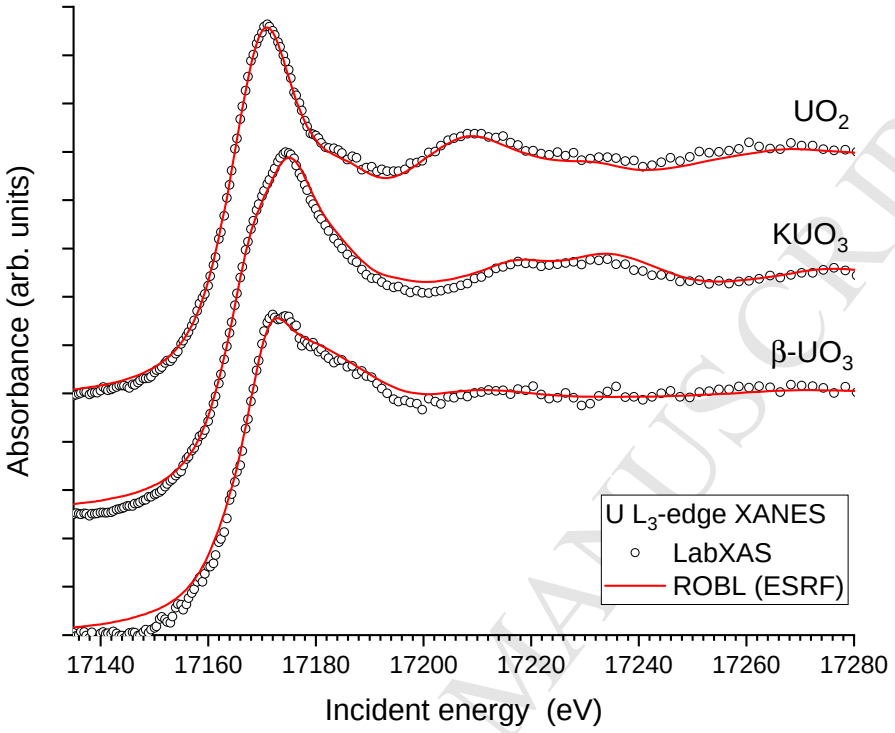


Figure 4: Uranium L_3-edge XANES spectra obtained for UO_2, KUO_3 and β-UO_3 and collected in transmission mode using both the laboratory-scale set-up (open symbols) and the ROBL beamline at ESRF (full lines). The spectra are vertically shifted for clarity.

magnitude photon flux difference between synchrotron radiation and standard X-ray tube source, which is not completely compensated by longer integration time per spectra. However, collection time is not a limiting factor for laboratory experiments and further improvements are expected when it is increased. One can also observe a slight discrepancy in the pre-edge region for some of the samples arises from ineffective background subtraction. Indeed, we found the Ge(8 8 8) signal being sensitive to the confinement layers and to any slight misalignment between the slits-sample-detector and the SBCA focal point. Improvements are currently being developed, e.g. additional shielding and new sample holder design to min-

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imize this discrepancy in the spectra. Nonetheless, the results between these two XAS methods are comparable and clearly demonstrate the proof of principle for laboratory-scale XAS set-up in actinide research.

While the low photon flux in our laboratory-scale XAS device increases the statistical noise, it also allows measurements for radiation-sensitive samples. There are also possibilities to highly dedicated sample environments for e.g. in-situ measurements. The laboratory-scale XAS device is also an ideal solution for preliminary investigations prior to synchrotron experiments. This approach will strongly benefit the actinide research in the dedicated facilities worldwide in the near future.

4. Conclusion

We have reported that measuring U L_3-edge XANES in transmission mode at laboratory-scale constitutes a credible, efficient and affordable alternative to synchrotron for actinide research by avoiding the high costs and lack of beamtime associated with such facilities. We found an excellent agreement with the synchrotron-based studies using reasonable acquisition time. Improvement and optimization of the described experimental device are currently ongoing to ensure faster acquisition and lower statistical noise in the near future, but the approach described here can be already applied in other laboratories for routine experiments. Consequently, the versatile laboratory-scale XAS device complements the synchrotron radiation experiments, allowing many applications to be developed in the field of actinide research, including f-electron chemistry and nuclear energy physico-chemistry, such as advanced nuclear fuel development and long term disposal of nuclear waste.

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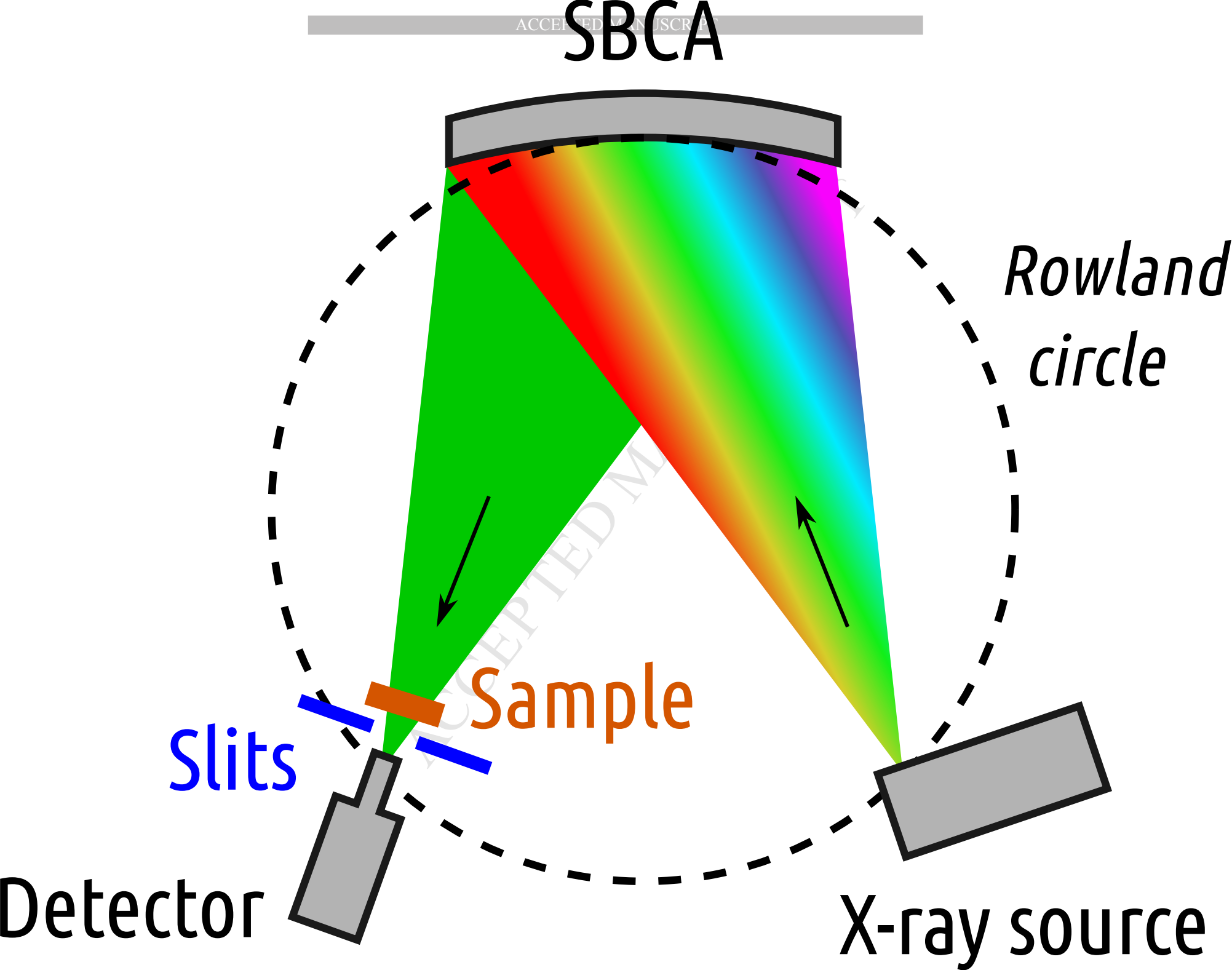
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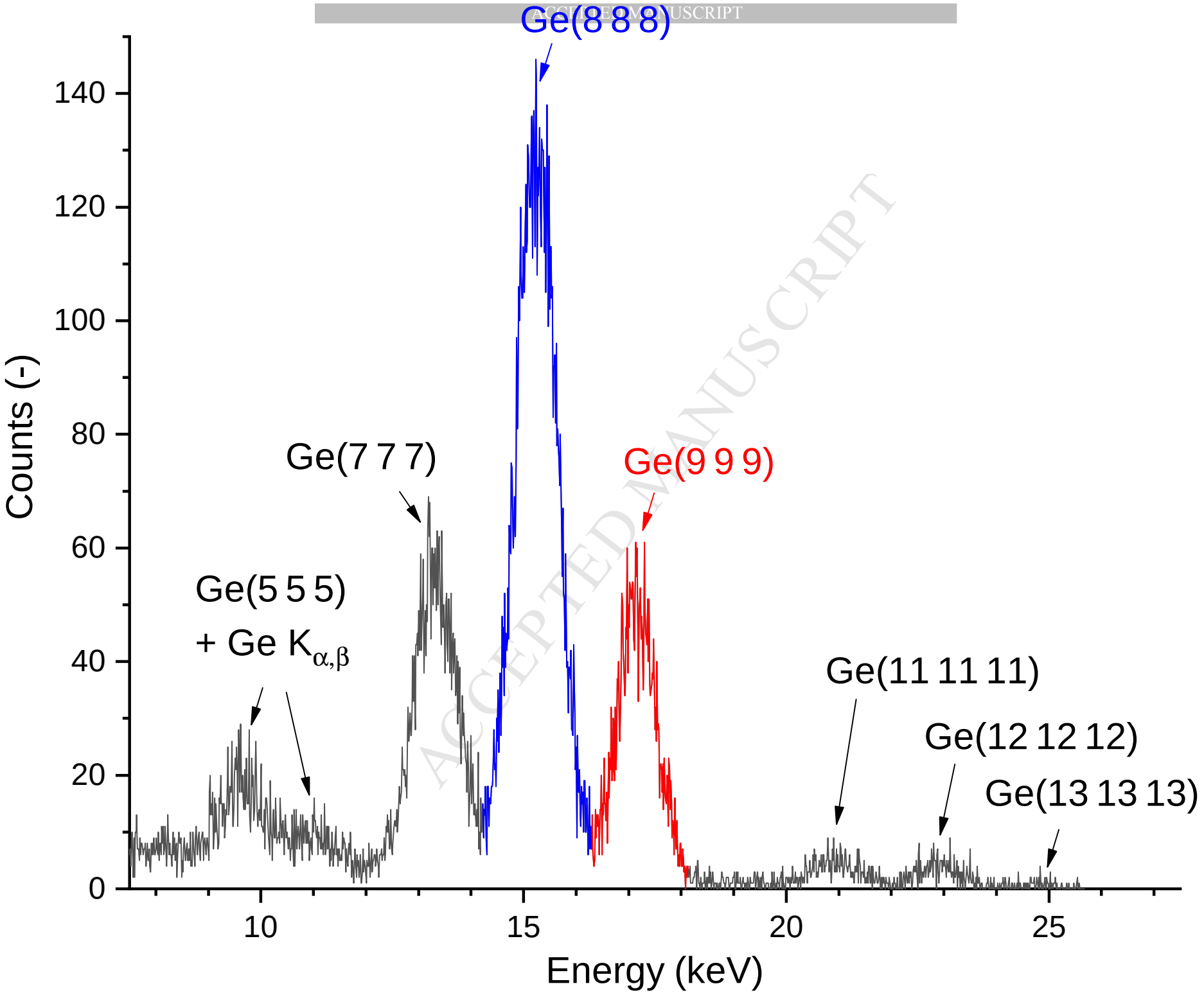
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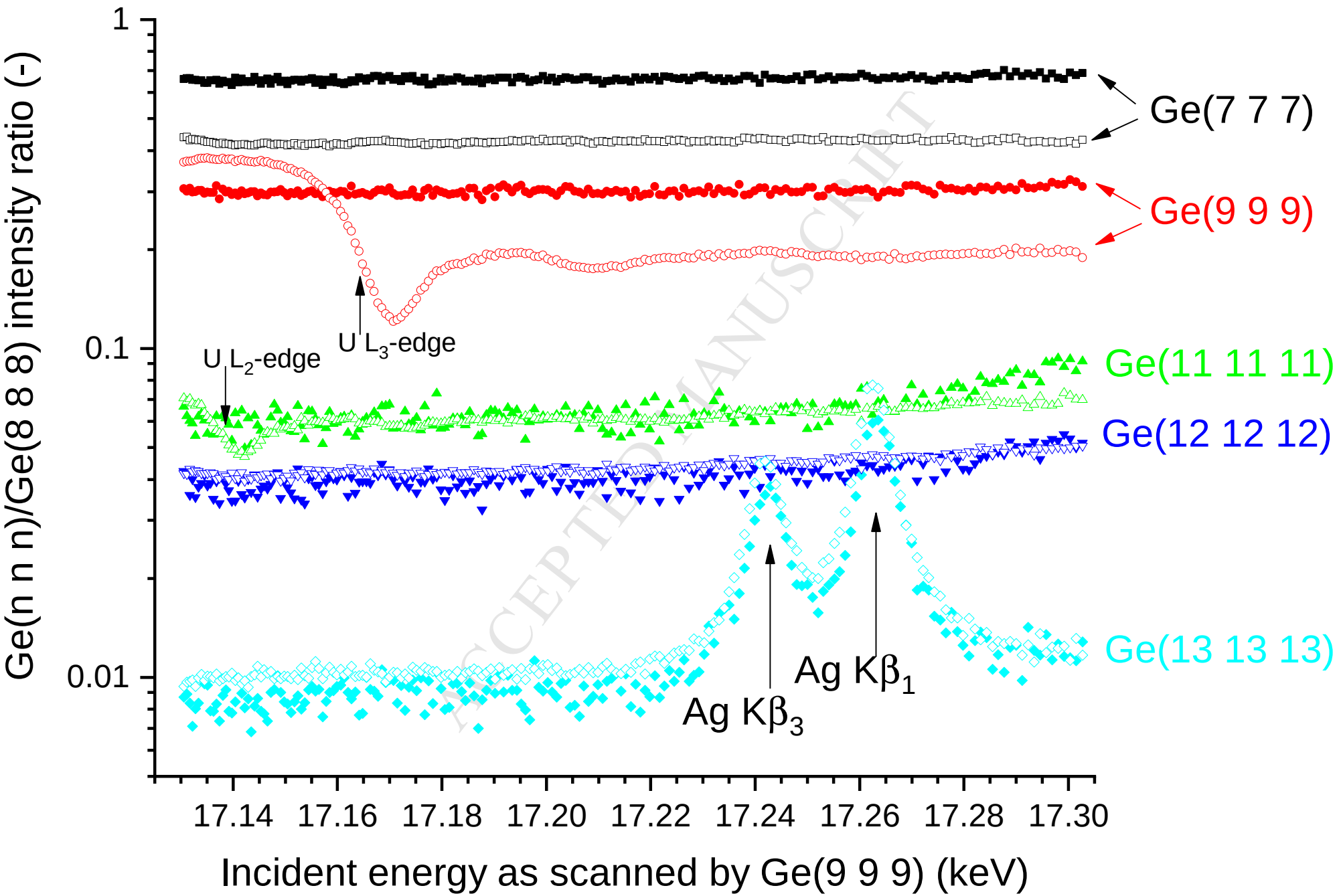
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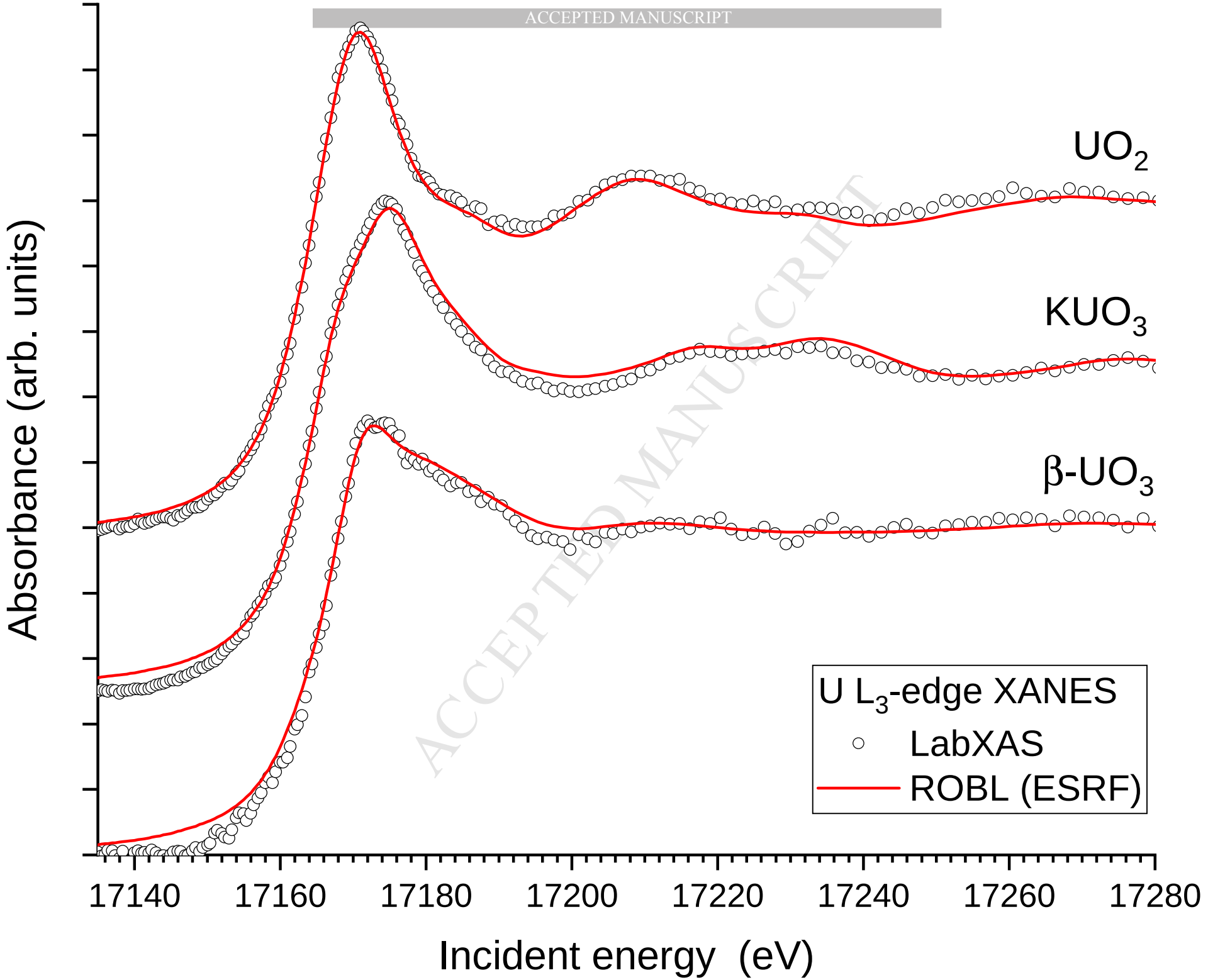


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