An in-situ heater for the XAS beamline (12-ID) in Australia

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Abstract. To accommodate for a growing number of requests by our user community an in-situ heater has been commissioned for the X-ray absorption spectroscopy (XAS) beamline 12-ID at the Australian Synchrotron. Here, we present an in-situ method for calibrating the temperature of the heating stage based on an anharmonic, correlated Einstein model. Specifically, we show that a temperature-dependant study of a bulk metallic foil (7.5 µm Cu) can be used to accurately calibrate the temperature of the heater. We also present the temperature-dependant coordination number, bond length, Debye-Waller factor, and third order cumulant to the bond length distribution function of the material from 18K to 1074K. At the higher temperatures we find that the atomic structure is comparable to that of an amorphous or liquid material indicating a gradual transition from crystalline to disordered atomic structure.

1. Introduction
Temperature-dependant X-ray absorption spectroscopy (XAS) is now a sought after technique in a range of fields, including solid-state physics to investigate issues such as vibrational properties of Co nanoparticles [1], chemical disorder in bulk amorphous GaSb [2], and the bonding environment in InN epilayers [3]. Many XAS beamlines around the world now have in-situ heaters enabling measurements to be performed at above room temperature, including beamline BM23 at the European Synchrotron Radiation Facility (controlled atmosphere oven, 300 – 3000K [4]), beamline 5-BM-D at the Advanced Photon Source (displex cryostat, 15 – 600K [5]), and beamline BL01B1 at Spring-8 (muffle furnace, 205 – 1870K [6]).

In response to a growing number of requests by our expanding user community, the XAS beamline at the Australian Synchrotron has recently commissioned an in-situ heater for high temperature XAS studies. A water-cooled, controlled-atmosphere Linkam TS1500 heating stage has been integrated into the second beamline experimental end station (Hutch C), see figure 1.

Certainly, one of the most critical parameters associated with any heating device is its temperature and the calibration of the said parameter. Commonly, a thermocouple is used to report the temperature of the sample; however, it is necessarily an inaccurate method limited by imperfect thermal equilibrium between the sample and the thermocouple, which is affected by the distance between them and the source of heat. Here, we present a method for accurately determining the sample temperature based on an anharmonic, correlated Einstein model.
Figure 1. Photographs showing the Linkam heating stage; (a) operating at an elevated temperature and situated between two ion chambers on the optical table, (b) ceramic sample cup, (c) ceramic sample cup with Cu foil held in place by Ir wire and stainless washer.

2. Methods

A bulk Cu foil (7.5 µm) was measured in transmission mode at beamline 12-ID at the Australian Synchrotron as a function of temperature. The extended X-ray absorption fine structure (EXAFS) was collected at the Cu K edge (8979 eV) whilst controlling the temperature first using a Gifford-McMahon type cryostat from 18K to 280K and then using the Linkam heater from 300K to 1200K (as reported by an in-built thermocouple). The heater was used under a flowing Ar atmosphere with water-cooling and with the Cu foil held in place underneath a stainless washer with an Ir wire (see figure 1).

The spectra were analyzed using the IFEFFIT program package [7], and with a forward Fourier Transform (FT) from 3.0 to 10.7 Å⁻¹ (see figures 2 (a) and (c)) and backward FT from 1.2 to 2.8 Å (see figures 2 (b) and (d)). We observe in figure 2 that the EXAFS and FT amplitudes decrease gradually as the measurement temperature increases. This is indicative of a reduction in coordination number and / or increase in atomic disorder. The amplitude reduction factor and threshold energy were determined at 18K and kept constant when fitting spectra at all other temperatures. The photoelectron scattering-path amplitudes and phases were calculated ab initio using FEFF8 [8]. From the first nearest neighbouring shell of atoms structural parameters were extracted, specifically the coordination number, bond length, Debye-Waller factor and third order cumulant to the bond length distribution function [9].

The Debye-Waller factor \( \sigma^2 \), or mean square relative displacement of the bond length distribution, consists of a static and a dynamic component. The former originates from inherent crystallographic disorder, while the latter describes thermal vibrations of the atoms around their equilibrium position. In order to quantify the thermal component an anharmonic, correlated Einstein model is often used. The Debye-Waller factor can then be written as [10]:

\[
\sigma^2 = \frac{1}{2\mu\omega^2} \left[ 1 + \exp \left( \frac{\hbar \omega}{k_B T} \right) \right] + \sigma_s
\]

where \( \mu \) is the reduced mass, \( \theta_E \) the Einstein temperature, \( \omega \) the Einstein frequency, and \( \sigma_s \) is the static component of the Debye-Waller factor.
Figure 2. EXAFS data of a bulk Cu foil, (a) and (b) using a cryostat, and (c) and (d) using an in-situ heating stage. The EXAFS and Fourier Transform amplitudes decrease gradually with increasing measurement temperature.

3. Results and Discussion

Figure 3 shows the Debye-Waller factor as a function of temperature. Clearly, as the temperature increases the Debye-Waller factor increases, consistent with increasing thermal lattice vibrations. For the cryostat measurements the data were fitted using equation (1). From the fit the Einstein temperature was determined to be (244.3 ± 1.4) K. This is in excellent agreement with literature [11, 12] and as such one can then justify extrapolating the fit to beyond 280K (the highest measurement temperature using the cryostat).

It is evident that the extrapolated fit does not match with the measured data points using the in-situ heater and the reported temperature. Specifically, the reported temperature ($T_{\text{Reported}}$) is greater than that for the extrapolated fit, which is a more precise measure for the real sample temperature ($T_{\text{Real}}$). This is readily understood when inspecting the design of the heater and noting that the heater element and the thermocouple are both separated from the sample by a ~ 2 mm thick ceramic wall.

The discrepancy between the reported and real temperatures gives rise to the following temperature calibration equation:

$$T_{\text{Real}} = 68 + 0.87T_{\text{Reported}}$$  \hspace{2cm} (2)
Figure 3. Debye-Waller factor as a function of (reported) temperature. Measurements were performed both in the cryostat and the heater. The solid line indicates an extrapolated Einstein temperature fit to the cryostat data.

Figure 4 shows the temperature-dependant evolution of the four structural parameters that were extracted from the system after applying the calibration to the reported temperature (equation (2)). Specifically, we find that as the temperature increases the coordination number (eventually) decreases, while the bond length, Debye-Waller factor and third order cumulant all increase. This finding is equivalent to a broadening of the bond length distribution function related to a low degree of correlations between atoms. Again, this is in excellent agreement with previous studies up to ~ 500K [11]. At higher temperatures the structure of the Cu foil is comparable to that of an amorphous or liquid material (though we note that the bulk Cu melting point was not reached) [13, 14].

Figure 4. Cu foil structural parameters as a function of sample temperature; (a) coordination number, (b) bond length, (c) Debye-Waller factor, and (d) third order cumulant of the bond length distribution.
4. Conclusion
We have shown that the temperature of an in-situ heating stage can be accurately calibrated using XAS irrespective of where the in-built thermocouple is located relative to the sample. For a bulk Cu foil we have extracted the coordination number, bond length, Debye-Waller factor, and third order cumulant to the bond length distribution function. We found that while the coordination number decreased above ~ 600K, all the other parameters increased gradually and this is consistent with a highly disordered structure typically observed for amorphous or liquid materials, though we note that the maximum Cu foil temperature was below the bulk melting point. This indicates, as far as atomic structure is concerned, that there is a gradual transition from the highly ordered crystalline structure to the highly disordered and thermally excited structure.

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