

Temperature Scanning Techniques with Tunable X-Ray Photons

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Abstract. The concept of combining x-ray absorption spectroscopy with suitable temperature scanning techniques has been sporadically exploited for various research purposes whenever structural or electronic transformations take place in the sample as a function of T . Fixed (single) energy T -scanning techniques have been introduced about 10 years ago and their usefulness has been widely assessed. Not only they allow for a qualitative appreciation of the occurrence of a phase transition in a sample but they resulted a valuable source of information in the case of binary systems, in the presence of metastable states of matter, and for high pressure research.

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INTRODUCTION

The x-ray absorption cross-section $\sigma(E, T, P)$ of a given substance can be regarded as a function of the energy E and of the thermodynamic state parameters (i.e. T, P) of the sample. Far from x-ray absorption edges the dependence on T, P is negligible being σ established by atomic properties only, however, close to the edges the threshold shape (and resonances) and the interference XAFS effect make the T, P dependence quite important. A very well known case is the thermal damping effect of the XAFS usually referred to as “Debye-Waller factor”. More specific to the topic of the present article is the change occurring in the case of first order phase transitions such as solid-solid, solid-liquid, (or possibly liquid-liquid). In those cases it is expected that at the state parameters T, P corresponding to a coexistence (transition) line between phase 1 and phase 2 the cross sections associated with the two phases are different $\sigma_1(E) \neq \sigma_2(E)$; therefore in any path through the thermodynamic states of the sample which cross a transition line the cross-section will exhibit a discontinuity. The simplest paths involve isobaric temperature changes performed in vacuum, at ambient pressure, or at high pressure conditions (in this latter case the transformation is usually made at constant load, which can be regarded as equivalent to constant pressure with some approximation), where melting transitions and sometimes also solid-solid transitions can be crossed.

Here it should be stressed that in transmission geometry the physical quantity which is monitored is actually the x-ray absorption coefficient $\mu(\hbar\omega, T, P) = \sigma(E, T, P)\rho(T, P)d(T, P)$ given by the product of the

substance cross-section times the product of the sample thickness d and the atomic density ρ . The product ρd represents the atomic surface density orthogonal to the beam direction and is itself a function of the thermodynamic state which may reflect the occurrence of phase transitions. For instance ρ is discontinuous at first order phase transitions, however, what is actually measured mostly depends on the sample nature. For a bulk liquid sample in a container d is defined by the container walls and its change may reflect the thermal expansion of the container material but not of the sample, on the other hand ρ changes following the substance property. If the sample is made as a dispersion of finely ground powder in a powder matrix, the effective ρ in the above equation will depend on how the sample is concentrated in the volume of the matrix and it will mostly reflect the thermal expansion of the latter.

Now, in order to highlight the cross section discontinuity at phase transitions it is clearly possible to sample in various details the E and T variables. It is possible to collect full x-ray absorption spectra at various temperatures in successive scans, also using a continuous monochromator movement (energy read on the fly, QuickEXAFS mode) or a dispersive setup. However, if the greater interest is in the temperature parameter the deepest insight into the sample transformations can be given also by fixed energy temperature scans. Here, clearly the energy has to be tuned to a spectral feature (threshold, peak, valley, shoulder, ...) which exhibit a great contrast between the two phases. On the other hand the temperature resolution can be very fine (even in the sub K range) thus providing high resolution information into the sample behavior as a function of temperature.

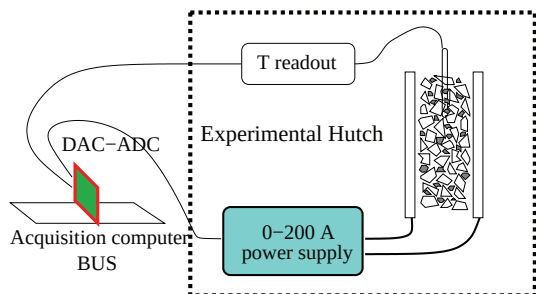


FIGURE 1. Schematic diagram of the hardware and sample environment involved in a temperature scanning facility

The principle of such temperature scanning techniques is quite simple and they have been sporadically used in pioneering experiments [1]. Our systematic implementation was initiated at the ESRF-BM29 beamline¹ and resulted in the publication of an extended paper on the subject [2]. The technique has been now developed for over 10 year and resulted to provide useful quantitative information. At present it constitutes a fundamental, ancillary technique available at the BM29 experimental facility for the investigation of condensed matter under extreme conditions of high-temperature and high-pressure [3, 4].

HARDWARE IMPLEMENTATIONS

The hardware implementations to be added to a standard EXAFS acquisition system represent a small additional effort (also for the budget) considering the added value to the facility, and are often available. Basically (see Fig. 1) the sample environment has to be of small heat capacity type (the rule for x-ray absorption experiments) to allow for a typical thermal time constant in the 1 s range. The heat (in the simplest and most versatile version a resistive graphite heater [5]) has to be fed by a remotely controllable power supply (typically a high current model 200 A is the most appropriate). The power supply is regulated by a pilot voltage signal generated by the acquisition computer through a D/A (digital to analog converter) channel. The sample temperature is monitored by a low heat capacity contact probe (an insulated thermocouple embedded in the sample gives the best results) or a fast non contact (pyrometer) probe. The time resolution of the system is limited by the thermal time constant of the sample/probe system, which is hardly below the 1 s range, therefore there is not really a need for a high speed A/D D/A card for control and readout, while a 16 bit resolution may be useful. The sample temperature is

varied by suitable heating/cooling ramps which can be also performed in a step by step method (heating power change followed by an x-ray absorption acquisition for a typical time interval of 0.5-5 s). There is no need for a PID temperature regulation system, the sample temperature will closely follow the heating power ramp and will equilibrate according to the heat dispersion. The key feature is to read the sample temperature in a region close to the one probed by the x-ray beam. If the heating ramp is too fast, a mismatch between the actual sample temperature and the one read by the thermocouple will result. The acquisition software can be implemented with the suitable commands to invert the heating power ramp and change its rate following what is observed to occur in the sample.

APPLICATIONS

This technique has been widely applied by us in connection with the XAFS investigations of the liquid state of matter [6], in particular:

- For a qualitative appreciation of the occurrence of undercooling in a liquid sample [2, 7, 8, 9];
- For a quantitative investigation aimed at the determination of the crystalline nucleation rate in an undercooled sample composed of a large number of micrometric droplets[10];
- For the investigation of simple eutectic phase diagrams [2, 11, 12]

An additional novel application that we wish to describe here regards the investigations of water salt phase diagrams under high pressure. Water and water-salt systems have enormous scientific importance. In particular high-pressure salted water is widely present in planetary interiors (Earth crust, icy satellites) but the knowledge of the relevant phase diagrams is very poor in spite of valuable efforts[13].

A typical water salt phase diagram at a fixed pressure is shown in Fig. 2. Typically the ice melting point $T_m(x)$ will decrease with increasing salt concentration x till the eutectic temperature T_e . For higher salt concentration typically one (or more) hydrated salt phases exist which undergo an incongruent melting. Many of the features of this phase diagram can be investigated by x-ray absorption techniques and temperature scans play an important role. We assume that the salt contains an ion whose edge is accessible. The spectrum at or above this edge will mostly reflect the environment of the ion being considered. For a low salt concentration at $T \leq T_e$ the sample is composed of a mixture of crystalline ice and crystalline hydrated salt (a) in Fig. 2. At T_e (b) the hydrated salt component melts together with the amount of water required to form molten droplet at the eutectic concentration surrounded by residual water ice. $\alpha(E, T)$

¹ Project HC-517 entitled "Single wavelength X-ray absorption detection in liquid metals: hunting supercooling thresholds and liquid-liquid phase transitions" was awarded 21 shifts and scheduled in June 1996.

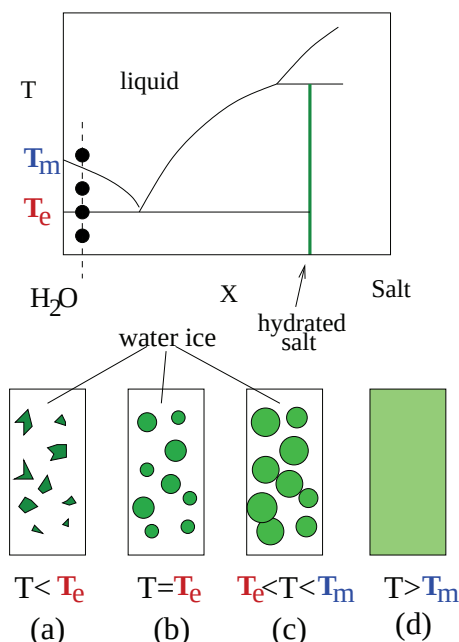


FIGURE 2. A typical binary water-salt phase diagram with a single crystalline hydrated phase. Sample conditions through a temperature ramp for a diluted solution.

must change dramatically at this temperature since the ions will move from a solid to a solution phase. Upon increasing temperature the ice component melts progressively (c) diluting the solution till $T_m(x)$ (d) when the sample is turned into a single phase solution at concentration x . During step (c) of this process, the droplets coalesce and the system becomes mechanically unstable and separates due to immiscibility of one phase on the other. This phenomenon is shown in the temperature scans reported in Fig. 3, where it is clear that a higher x-ray absorbing solution phase concentrates at the height of the x-ray beam. It is only with the complete melting that the absorption recovers a reproducible level. The temperature scans shown in Fig. 3 were performed at increasing pressures up to about 5 GPa. The values for T_e and $T_m(x)$ which can be clearly determined experimentally provide a unique information on how the phase diagram (shown schematically in Fig. 2) evolves with pressure; an information that would have been very hard to obtain by other means.

Temperature scanning techniques with tunable x-ray photons resulted extremely useful to provide information on the thermodynamic state and sample phase. They are also valuable to exclude any sample contamination and to perform temperature (and pressure) calibration. The quantitative analysis of the $\alpha(T)$ curves can tell precisely the mass fraction of molten sample which can be used to measure the crystalline nucleation rate in under-

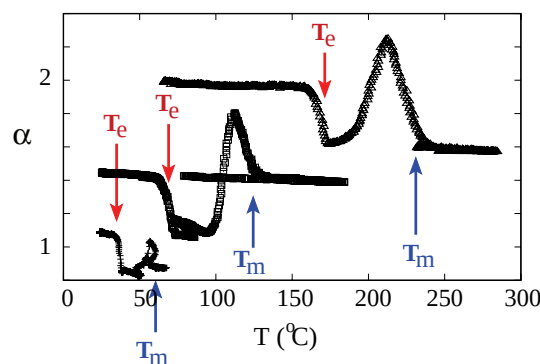


FIGURE 3. X-ray absorption temperature scans of a RbBr aqueous solution at the Br K-edge as a function of temperature at different pressures

cooled samples. However the most promising applications appear to regard binary phase diagram under extreme conditions of high-pressure and temperature, including the case of water-salt phase diagram just illustrated. The possibility to perform such temperature scans should be routinely available in world class facilities for XAS and these scans should be requested (at least as important support material) in XAFS investigation involving systems undergoing phase transitions.

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