Local Ordering in Disordered Systems under Extreme Conditions

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Abstract. Recent advances in data-analysis and instrumentation allowed us to perform x-ray absorption (XAS) studies of liquids, undercooled liquids and glasses under high-temperature and/or high-pressure conditions. The experimental set-up used for combined XAS and x-ray diffraction with synchrotron radiation at the ESRF is briefly shown. Advances in XAS data-analysis allowing detailed structural insight about pair and higher-order distributions are also mentioned. Applications to liquid and undercooled liquid metals like Cu, and Sn under pressure are briefly discussed.

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INTRODUCTION

Recent advances in experimental and data-analysis techniques using synchrotron radiation have allowed us to study the structural properties of liquids and solids under high-temperature and/or high-pressure conditions. In particular the XAS sensitivity to local structure has been exploited to study liquid and undercooled liquid metals (see for example [1] and a review paper [2]). Full reference to previous and parallel works of scientists contributing in this field can be found in those papers.

In particular, an experimental set-up dedicated to structural studies under extreme conditions has been developed at the ESRF (Grenoble) (see [3, 4] and ref. therein). The x-ray absorption spectroscopy (XAS) is used as a probe for the local structure, x-ray diffraction (XRD) for measuring long-range ordering, checking the sample status and determining relevant environmental parameters (pressure), while single-energy (SE) x-ray absorption temperature or pressure scans are used to detect and study phase transitions.

These techniques can be combined and used at third generation synchrotron sources on samples under extreme thermodynamic conditions, due to the high flux and reduced size of the x-ray spot, and are able to give information about aggregation state and local structure of unprecedented accuracy. Recent applications regarded undercooled liquids and glasses under high temperature and/or high-pressure conditions, like liquid Ga and Bi [5, 6], metal alloys [7, 8], amorphous Ge[9].

Advances in experimental techniques have been accompanied by improvements in data-analysis methods. Reliable reconstruction of the structure of disordered systems by combining XAS and XRD can be now obtained using Reverse Monte Carlo (RMC) simulations implemented into modern XAS data-analysis algorithms (RMC-GnXAS)[1, 10].

In this communication we shall review some important characteristics of the techniques showing their potential in measuring and understanding disordered matter under extreme conditions, and show new results on liquid Sn under pressure as compared to liquid Cu[1].

METHODS

The experimental set-up for combined XAS and XRD measurements under extreme high-temperature and high-pressure conditions has been developed in the last decade at the ESRF (bending magnet source, BM29)[3, 4] High-temperature measurements up to about 2500 K are possible using a special furnace (L’Aquila-Camerino[11]) while high-pressure/high-temperature measurements in the 0.1-10 GPa/300-1800 K domain can be performed with a large-volume press (Paris-Edinburgh[12]). The highly automated set-up allows us full remote control and measure of the pressure and temperature of the sample environment and performance of the various x-ray measurements (XAS, energy-scanning XRD, angular XRD, SE temperature scans). [3, 4]

Techniques for preparation of samples suitable for XAS/XRD measurements under extreme conditions have been developed. A mixture of fine specimen powders (µm or sub-µm size) with selected low x-ray absorbing materials (see Fig. 1, left) is a convenient choice
FIGURE 1. The sample (left) is usually dispersed into a "chemically inert" matrix, low x-ray absorbing and high-temperature resistant (like BN, C, Al₂O₃, ZrO₂). Micrometric powders of pure materials can be easily undercooled. In some cases the sample can be obtained as a film in a container made by inert material (right).

for several reasons: 1) provides a stable container for liquid matter also under high temperature or pressure; 2) homogeneous liquid samples of suitable thickness in the 10 µm range can be obtained; 3) substances with known equation of state (EOS) can be used in the mixture for in-situ XRD pressure measurements; 4) micrometric and sub-micrometric droplets can be easily undercooled and this gives access to XAS/XRD measurements under metastable conditions.

Usually, the sample for high-temperature measurements is a compressed pellet to be positioned in the crucible along the x-ray beam. The sample assembly for high-pressure measurements with the Paris-Edinburgh cell is much more complicated as it is composed by a low x-ray absorbing gasket (B-epoxy) and several small parts providing the electrical contact for the furnace (graphite), the confinement of the sample and the insertion of a thermocouple. Details on samples for XAS/XRD measurements can be found in the literature (see [11, 2] and ref. therein).

A typical configuration for combined XAS/XRD measurements at high temperatures is shown in Fig. 2. In this configuration the furnace is positioned along the beam and the sample is centered in order to collect several XRD patterns at fixed angle (here we see 5 channels, see arrows in Fig. 2), using the monochromator for scanning the energy of the photon beam.[4] This setup has been used for measurements of several liquid systems including Cu[1] and allows collection of XRD patterns in a wide q range in a reasonable elapse of time. This configuration is now often used in combination with an image-plate 2D detector (MAR345), positioned at a side in place of the multichannel detectors, which can collect angle-dispersive fixed-energy XRD with very high statistics in times of the order of minutes and is very useful for an immediate identification of the phase structures.

FIGURE 2. Typical setup for high-temperature experiments at BM29 (ESRF) using the L’Aquila-Camerino oven for combined XAS and XRD. The multi-channel collimator for energy-scanning x-ray diffraction (ESXD) can be installed in the vertical and horizontal directions (arrows indicate pathways for scattered photons). Here is shown the horizontal set-up used also for high-pressure with the Paris-Edinburgh cell (horizontal slit of ~1 mm).

Several accurate measurements of substances under extreme conditions have been realized so far using the above mentioned experimental set-up and suitable data-analysis approaches have been developed and used for their understanding (see [2] and ref. therein). In particular, it has been shown that the application of modern XAS data-analysis techniques (GnXAS[13]) incorporated into a RMC algorithm are able to produce realistic tridimensional models of the average structure, compatible with XAS data and pair distribution functions obtained by diffraction or computer simulation techniques.

RESULTS

Here we report, as an example, new results of a recent experiment on liquid Sn under high-pressure showing the potential of the techniques.

In Fig. 3 we report the temperature scans collected at selected energies near the K-edges of Cu and Sn, at different pressures. Depending on the selected energies, different sensitivity and features of the phase transitions, monitored by smoothed discontinuities in the absorption signals, can be observed. Using the temperature scans we have been able to discover that the undercooling range in liquid Sn is reduced by application of pressure, practically disappearing when the underlying solid phase is Sn-III (stable above 3 GPa). This can be observed looking at the upper curves of the lower panel of Fig. 3 where the transition to the Sn-III phase is associated...
FIGURE 3. Upper panel: SE temperature scan of Cu obtained using the L’Aquila-Camerino furnace. The hysteresis cycle show that undercooled liquid Cu (u-Cu) is obtained upon cooling. The inset shows selected XRD data at various temperatures, confirming occurrence of melting and solid phases. Lower panel: temperature scans of Sn at two pressures showing the absence of undercooling in presence of the Sn-III phase.

In the last viewgraph shown in Fig. 4, we report several low-noise XAS signals obtained at high pressures. The measured XAS signals clearly show that there are important differences in the local structure of solid Sn-I, Sn-III and liquid Sn. In particular, even in absence of a detailed structural analysis (subject of a separate paper), we notice that the Sn-I XAS signal is much stronger in amplitude and has a different phase as a consequence of the different first-neighbor coordination, distances and mean-square displacements. On the other hand, the Sn-III and liquid and undercooled Sn XAS signals are much more similar in amplitude and phase reflecting their similarity in the first-neighbor distribution. This finding provides an interesting key for understanding the variation in undercooling properties as a function of pressure. In fact, nucleation to the underlying solid phase is favored when the consequent rearrangement of atoms is facilitated by similar local arrangements, and the fluctuations sampling the phase space are able to find their way toward a stable or metastable thermodynamic configuration.

These results, selected by those coming of our long-standing research efforts, show the potential of the combination of x-ray techniques presently available at synchrotron radiation facilities for studying and understanding the local structure of substances under extreme conditions.

REFERENCES