Local ordering and metastable phenomena in liquids under extreme conditions

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Abstract.
Recent results obtained using the x-ray absorption spectroscopy (XAS) on liquids under high-pressure are presented. Advanced instrumentation combining XAS and x-ray diffraction and RMC XAS data-analysis techniques allowed to study and discuss the presence of metastable states in Bi and Sn at high pressures. Differences in the average local structure of liquid metals are briefly discussed.

1. Introduction
Recent advances in instrumentation and data-analysis allowed us to perform x-ray absorption spectroscopy (XAS) studies of liquids, undercooled liquids and glasses under high-temperature and high-pressure conditions[1, 2, 3, 4, 5, 6, 7]. XAS has been 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 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[5] and Bi[6], metal alloys[4], amorphous Ge [6]. 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, 8] In this communication we shall review some important characteristics of the techniques showing their potential in measuring and understanding phase transition and metastability under extreme conditions, taking as an example some new results on liquid Sn[7] and Bi[6] under pressure.

2. Experimental techniques and data-analysis methods
XAS measurements of systems under extreme and metastable conditions are able to give accurate information about the average local structure of disordered and ordered matter. XAS measurements in transmission mode are in principle very simple and suitable techniques for measuring samples under extreme and metastable conditions have been developed in recent times (see [9, 2] and ref. therein) combining XAS, XRD and single-energy x-ray absorption temperature scans (T-scan) into automated procedures. In Fig. 1 we see an example of the
Figure 1. Upper panel: T-scans of Bi at fixed energy and pressure. The arrows indicate the temperature of the occurring phase transitions. Upon lowering the temperature, undercooling and nucleation of the liquid to a new phase (Bi $\beta$) prior to crystallization to th Bi-I stable phase are clearly visible. Lower panel: Detail of the Bi $L_3$ near-edge structures where the differences in the shape of the x-ray absorption spectra are clearly visible. The absorbances of Bi-I and liquid Bi at 13465 eV are indicated by horizontal lines.

sensitivity of x-ray absorption to changes of the local structure, as detected in pure Bi at a pressure of 1.2 GPa. The sample was a dispersion of micrometric Bi droplets into a suitable solid matrix acting also as a pressure marker. The $L_3$-edge XAS spectra of the high-temperature liquid and of the stable solid phase (Bi-I) are shown in the lower panel of Fig. 1. Their different shape is related to the different average local structure of the two phases. Single-energy T-scans can be obtained by tuning the photon energy where changes in the x-ray absorption are maximized.

The result obtained by tuning the energy at 13465 eV is shown in the upper panel of Fig. 1, indicating the presence of undercooling and of nucleation to a different solid phase upon lowering the temperature. These findings are corroborated also by combined XRD experiments (see [6] for further details).

The XAS structural signal $\chi(k)$ contains reliable quantitative information about the local structure, but appropriate methods for data-analysis must be used for data-analysis especially for disordered systems. In particular, $\chi(k)$ is defined as the modulation of the photoabsorption cross-section $\mu$ with respect to the atomic one $\mu_0$ above the excitation edges of core electrons: $\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$. Here $k = \sqrt{2\mu(E - E_0)}$, where $E_0$ is the edge energy, is the wave-vector of the outgoing photoelectron. XAS is chemically selective and sensitive only to the local structure, due to the limited photo-electron mean free-path ($\approx 5-6$ Å). Modern interpretation of the XAS theory is based on an expansion in series of irreducible $\gamma^{(n)}$ signals associated with $n$-body atomic configuration[10] including the photoabsorbing atom, from which follows:

$$
\langle \chi(k) \rangle = \int_0^\infty dr 4\pi r^2 \rho_1 \rho_2 \gamma^{(2)}(r, k) + 
+ \int dr_1 dr_2 d\theta 8\pi^2 r_1^2 r_2^2 (\sin \theta)^2 \rho_1^2 \rho_2^2 g_3(r_1, r_2, \theta) \gamma^{(3)}(r_1, r_2, \theta, k) + \cdots
$$

where the $\chi(k)$ structural signal is given by integrals of the $n$-body distribution functions $g_n$. The unique short-range sensitivity and the possibility of measuring three-body correlations, makes XAS a highly valuable technique complementary to diffraction. In standard data-analysis,
Figure 2. Phase diagrams of Bi (lower) and Sn (upper) obtained from analyzing the x-ray T-scan patterns collected in a wide pressure-temperature range. The solid lines (lower) indicate the Bi stable phase diagram adapted from [11]. The dashed line mimics the melting line of metastable solid Bi proposed by [12]. The dotted line is an hypothetical transition line between Bi $\beta$ and Bi II at low pressures. The boundaries of the liquid (l-Sn) and solid phases (Sn-I, Sn-III) are superimposed on those reported in the Tonkov handbook [13].

Figure 3. In the upper panel the model signal calculated from the RMC atomic coordinates (green) is compared with the experimental signal (Expt, blue). The agreement can be appreciated looking at the residual curve (red). Normalized angular distributions $f(\theta)$ of liquid (l-Sn) and undercooled (u-Sn) liquid Sn at 0.05 GPa and 2.5 GPa, where the nucleation of the Sn-III phase takes place. The distribution obtained for a close-packing liquid metal like Cu,[1] different from those of liquid Sn at both pressures, is shown for comparison.

The $n$-body distributions are assumed to be a superposition distinct peaks (“shells”) whose structural parameters are refined against the experimental data. More advanced techniques based on simultaneous refinement of short and long-range order (XAS and diffraction) through the Reverse Monte Carlo algorithm (RMC-GnXAS) were recently shown to be succesful in measuring the local bond-angle distribution in liquids and undercooled liquids under extreme conditions.[1, 8, 7]

3. Metastable states and structure at high pressures

Several high-temperature XAS experiments on undercooled liquids have been performed by our group, and recently techniques ad methods described in the preceding section were applied to polymorphic metals under pressure such as Bi and Sn.[6, 7]

In Fig. 2 we report the phase diagrams of Bi and Sn including the appearance of metastable states obtained cooling the liquid. Those states are easily obtained by cooling micrometric droplets of those liquids (our typical XAS samples) at selected pressures and their lifetime...
is much longer than typical measurement times. Looking at Fig. 2, it is inferred that maximum undercooling temperatures and presence of metastable solid phases are related to the characteristics of the underlying stable solid phases. In particular, we notice that undercooling is not obtained in Bi around 2 GPa, in presence of the stable solid Bi-II phase, while it is observed again at higher pressures. For Sn, undercooling is prevented above 2 GPa by appearance of the Sn-III solid phase. As discussed also in ref. [7], XAS spectra of liquid Sn are similar to those of Sn-III while are remarkably different from those of Sn-I. This suggests that an important role is played by the local structure, leading to high undercooling rates and nucleation preferential selection when the transition implies important changes of the average atomic environment.

XAS data of liquid Sn under pressure were analyzed using RMC-GnXAS, looking for possible modifications of the liquid local structure for increasing pressures. In Fig. 3, upper panel, we show that the agreement between the RMC simulation and the experimental data (0.05 GPa) is excellent. We remark that RMC-GnXAS structural refinement is done including both XAS and g(r) data obtained by XRD, constraining both short-range and medium-range structure simultaneously. The normalized bond-angle distribution shown in Fig. 3, lower panel, shows that the average local structure of liquid tin is very different from that of a typical close-packing metal (Cu, shown in the figure). In particular, the Sn liquid is found to be composed of a mixture of tetrahedral and close-packed configurations, with the weight of the latter increasing at higher pressure (as shown by the deepening of the minimum around 90 degrees in the bond-angle distribution).

4. Conclusions
New combined x-ray absorption and diffraction experimental techniques, associated with advanced data-analysis methods, allowed us to obtain reliable unique data and information about metastable states under high-pressure and high-temperature conditions. Our results on Bi and Sn under pressure shows that we are able to study the details of the local structure of the liquid phase and of occurring metastable states as well as possible relationships with phase selection mechanisms.

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