ESRF

Experiment title: Short range order in liquids	Experiment number: HS217 and HS528

Beamline: BM29	Date of Experiment: from: 22/01/97 (HS217) 25/01/98 to: 01/02/97 and 31/01/98	Date of Report: 15/02/1999
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Report:

This is the combined experimental report of projects HS217 and HS528 carried out at beamline BM29 during two separate runs in 1997 and 1998. As the projects and related experiments are intimately interconnected we present only one report for both projects focussed on "short-range order in liquids". Several papers, some of them cited in the reference list, already report about these experiments. Here we shall only recall the most important results obtained at ESRF taking advantage of the performances of the highly performant BM29 experimental set-up.
Due to the limited space we report about three successful experiments:
(a)
We have performed a careful investigation of phase transitions occurring in confined submicrometric Ga droplets, combining energy-dispersive x-ray diffraction (EDXRD), high resolution XAFS and single-energy x-ray absorption. Results have been published recently on Phys. Rev. Letters. [1] Accurate measurements at the Ga K-edge were performed using ionization chambers for photon counting, 40 % detuning of the monochromator and an automatized cryogenic sample environment set-up.
Our study shows that Ga droplets confined in epoxy resin experience sharp phase transitions both during cooling and warming processes. The undercooled liquid-solid transition is located at 150 K while melting takes place at about 254 K. Direct evidence for those transitions is obtained by using EDXRD, XAFS and single-energy x-ray absorption temperature scans which gave consistent and unambiguous results. Differences between bulk Ga and this restricted system appear to be largely controlled by geometrical confinement. In fact, the density of the stable α-Ga solid phase is lower than that of liquid Ga and freezing is observed to occur in denser solid phases, metastable in normal conditions.
Experimental techniques are found to be particularly sensitive for discovering and studying phase transitions and can be used on a variety of solid and liquid systems.

(b)
Among several succesful high-temperature measurements we report about the first XAS measurements on liquid Rhodium (melting point $T_m \sim 2236$ K) and on a liquid Rh-C alloy for which no diffraction measurements have been performed so far.
Good quality measurements of solid Rh covering a wave-vector range up to $k \sim 25 \AA^{-1}$ for temperatures in the 300-1900 K were obtained both by using both a 25 μm Rh foil and on pellets obtained by mixing and reducing fine powders of Ammonium hexachlororhodate (99.999 from Aldrich chemicals) into graphite. Successful measurements of pure liquid Rh just above the melting point were performed on pellets composed of fine Rh powders dispersed into a HfO_2 matrix. In particular, the reversible alloying of Rhodium into graphite was observed and several good quality high-temperature XAS spectra of the liquid alloy were recorded.
Results on high-temperature solid and liquid Rhodium are compared, as we have shown in a recent Letter [2] with structural models obtained using MD simulations performed using different pair functional models. The short-range part of the pair distribution function of liquid Rh at 2240 K was measured for the first time showing that the first peak is slightly broadened and shifted toward longer distances as compared to MD simulations.
We have verified that reliable very high-temperature XAS measurements of liquid metals and alloys are feasible using third generation synchrotron radiation sources and available experimental devices. Future efforts should be devoted to measurements of other important liquid metals and alloys.
(c)
A third line of interesting experiments regards ionic and superionic systems at high temperature and in the liquid phase. We performed very high-quality measurements at both Ag and I K edges of AgI in the 30-850 K temperature range exploiting the potential of BM29 fpr high photon energies.
Structural results on this molten superionic system (AgI) are compared with computer simulations based on published interatomic potentials. Results have been presented as an invited contribution to the international XAFS X conference. [3] In the case of silver iodide, XAFS is shown to able to give important information on local structure and on the short-range part of the atomic interaction.
We performed a simultaneous refinement of both Ag and I K-edge XAFS of liquid AgI starting from molecular dynamics (MD) results. Comparing the $g(r)$ reconstructed from XAFS data analysis results, we found a clear shift (of about 0.2 Å) toward larger distances an a narrowing of the peak are found, well outside the error limits. It is clear that the parametrization or the functional form of the potential are not accurate and present simulations do not describe the short-range structural properties of molten AgI. Our results are in agreement with previous investigations on CuBr and stimulate the development of new theoretical approaches taking into account non-ionic bonding in superionic compounds.

[1] A. Di Cicco, *"Phase Transitions in Confined Gallium Droplets"*, Phys. Rev. Lett. **81**, 2942 (1998).
[2] A. Di Cicco, G. Aquilanti, M. Minicucci, A. Filipponi, and J. Rybicki, *short-range interaction in liquid rhodium probed by x-ray absorption spectroscopy*, J. Phys.: Condens. Matter **11**, L43 (1999).
[3] A. Di Cicco and M. Minicucci, *Solid and liquid short-range structure determined by EXAFS multiple-scattering data-analysis*, J. Synchrotron Rad. (to be published, 1999).