



Experiment title: Zintl ions in liquid alloys under extreme conditions probed by X-ray absorption spectroscopy

Experiment number:
HE-513

Beamline: BM29	Date of Experiment: from: 3-Mar-1999 to: 10-Mar-1999	Date of Report: 16-Aug-1999
Shifts: 18 (3 in single-bunch)	Local contact(s): M. Borowski	<i>Received at ESRF:</i>

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Report:

during beam time allocated for the experiment HE-513, we have performed a successful x-ray absorption spectroscopy experiment to investigate the local atomic arrangement in several liquid semiconductors under high temperature and high pressure.

The systems we considered in our studies were the so-called Zintl compounds [1]. One can produce Zintl phases by alloying alkali metals with post-transition metals: because of the high difference in the electronegativities of the components, the resulting compounds show peculiar polyanionic clustering. In particular, the occurrence of these polyanions in such alloys is necessarily accompanied by the formation of covalent bonds, from which it originates the semiconducting behaviour. Upon melting, several neutron diffraction (ND) studies performed in the last decades [2] showed the persistence of these negatively charged units in the liquid state (at least up to a certain temperature), together with the conservation of the semiconducting character of the compounds.

Aim of the experiment was to probe the local structure in the solid and liquid state of KTe, RbTe, RbSn and KPb, possibly probing the eventual dissociations of the polyanions, as a function of temperature and pressure.

The high temperature / high pressure conditions were applied through a two-anvil large-volume press of the Paris Edinburgh type [3]. The XAS measurements were performed in transmission mode. A 1 m long collimator was set on the sagittal plane of the press, between the sample and a NaI scintillator, to collect the scattered beam from the sample. Scanning the monochromatic energy impinging on the sample, it was possible to collect complete diffraction patterns in the energy dispersive mode, with extremely high resolution and reproducibility. Combining the known equations of state of two calibrants (BN and Pd), it was possible to determine the actual experimental point in the P/T space with high accuracy. Also, the diffraction patterns demonstrate the absence of any contamination of the sample from impurities or reagents during the P/T cycles.

Differently from a ND measurement, an x-ray experiment has to deal with the absorption of the sample

environmental conditions of the measurement have posed severe constraints to the scientists, and very poor attempts [4] were made up to our experiment.

Facing these difficulties, we develop a technique which was suitable to protect the sample from oxygen and moisture, but allowed us to satisfy the necessary requirements to perform a proper x-ray absorption spectroscopy (XAS) experiment (such as sample homogeneity and optical thickness). We preloaded, then, a powder mixture of the sample and boron nitride, which acts as an inert matrix and pressure transmitting medium, in expressly made BN capsules inside a glove-box (our special acknowledgement goes to Dr. H. Müller, from the ESRF chemistry laboratory, for the helpful assistance in operating the glove-box). The sealed capsules were then fitted in the boron/epoxy gaskets (fairly transparent to x-rays) and set between the anvils of the press.

With this experimental set-up we collected for the first time XAS spectra at several temperatures and pressures of solid and liquid Zintl compounds.

The quality of the data is very good, as shown in Fig. 1, and already preliminary results are extracted. In particular, in the KTe system, we confirm the results of Fortner [5] who observed a high degree of structural ordering in the liquid at ambient pressure. Our data indicate the persistence of Te dimers in the molten state up to 3 GPa. In addition, our measurements show a clear edge shift, at the Te K-edge, of about 1.5 eV upon melting at the constant pressure of 3 GPa (see Fig. 2). This is a clear indication of the covalent band gap filling at the Fermi level, possibly due to the superposition of bonding and anti-bonding states of the polyanions. This interpretation is strongly supported from the observation of analogous behaviour occurring in well known elemental semiconductors, such as Ge or Te [6]. The role of pressure in this electronic and structural transition, as well as the coupling between the atomic arrangement and the electrical properties, must be of fundamental importance, and it deserves further investigation.

References:

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- [5] J. Fortner et al., *Phys. Rev. Lett.* **69**, 1415 (1992).
- [6] S. De Panfilis and A. Filipponi, *Europhys. Lett.* **37**, 397 (1997).

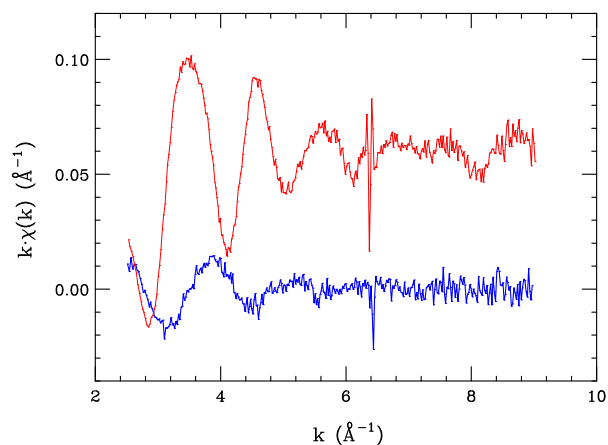


Figure 1: EXAFS signals in the solid (room temperature, upper curve) and in the liquid (730 K, lower curve) state of KTe at 3 GPa.

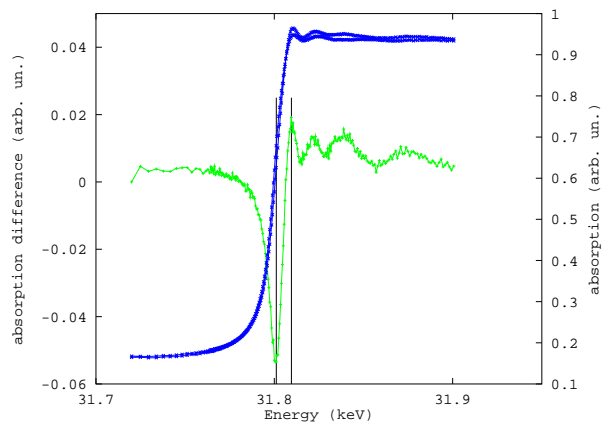


Figure 2: Rough Te K-edge spectra of KTe at 3 GPa in the liquid and solid state together with their difference to put in evidence the edge shift occurring upon melting.