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Solid and liquid short-range structure determined by EXAFS multiple-scattering data analysis

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Reliable determination of local structure in ordered and disordered matter can be obtained by using advanced data-analysis methods (GNXAS) taking proper account of multiple-scattering terms and atomic background shapes. We report about recent XAFS application on liquid and solid systems at high temperature taking advantage of the performances of the BM29 experimental installation at the ESRF. Results on a molten superionic system (AgI) and a pure metal (Rh) at very high temperatures (up to about 2300 K) are compared with computer simulations based on published interatomic potentials. XAFS is shown to be able to give important information on local structure and on the short-range part of the interatomic interaction.

Keywords: XAS; EXAFS; GNXAS; liquid structure.

1. Introduction

Recent advances in x-ray absorption fine structure data-analysis using "ab-initio" calculations (GNXAS, see ref. Filipponi & Di Cicco, 1995) allowed us to obtain reliable determination of the local structure in ordered and disordered systems. In particular, the short-range part of the low-order distribution functions can be reconstructed and compared with computer simulations and x-ray or neutron diffraction results. Proper account of multiple-scattering (MS) and of atomic background shapes related to the opening of double-electron channels are essential ingredients for a reliable data-analysis.

XAFS has proved to be particularly useful for obtaining reliable structural measurements in extreme high-pressure and temperature conditions, and to put to a test model interatomic potentials. Pair-distribution functions obtained using GNXAS data-analysis on simple ionic solid and molten systems (KBr, RbBr, see Di Cicco *et al.* 1996, 1997) at high temperature were found to be in substantial agreement with molecular-dynamics (MD) simulations confirming the accuracy of present theoretical models. A detailed MS investigation on solid and liquid Kr at 300 K as a function of pressure (Di Cicco *et al.*, 1996) showed that Monte-Carlo (MC) simulations based on pair empirical potentials are in good quantitative agreement with XAFS experimental results up to about 10 GPa but deviations were found for higher pressures. It was shown that XAFS is able to give unique information about anharmonic vibrations in simple noble-gas and ionic systems, even at moderate temperatures. Similar results were obtained quite recently on solid Kr at low temperatures (Yokoyama *et al.*, 1997) and solid Cu at moderate temperatures (Edwards *et al.*, 1997) by comparing XAFS with MC or MD results.

A recent high-temperature multiple-edge (Di Cicco, 1996,1997) XAFS investigation (Di Cicco *et al.*, 1997) on a superionic system (CuBr) has also shown that previous results obtained using the isotope substitution neutron diffraction technique have to be reconsidered. In fact, the very short-range partial pair distribution function $g(r)$ derived by XAFS was found to be much more accurate than that obtained using diffraction. Of course, medium and long-range ordering are better investigated by diffraction, but XAFS allowed us to get a deep insight on the ion-counterion interaction at short-distances where only partial ionicity is present.

These recent results stimulated us to conduct an extensive investigation on relatively simple metal and ionic systems for which interatomic force models have been developed but no detailed experimental tests were carried out. Our aim is to show the important new information on interatomic interaction and short-range structure that can be obtained by XAFS study using advanced data-analysis technique. To this purpose, high-resolution and low-noise experimental data recorded at the European Synchrotron Radiation Facility (ESRF, BM 29) have been used (Filipponi *et al.*, 1998) taking advantage of the novel high-temperature devices recently installed. In this paper we present the first multiple-edge XAFS study of liquid AgI, considered the prototype of solid superionic systems, comparing experimental results with published MD simulations (Shimojo & Kobayashi, 1991). We also show novel high-temperatures XAFS measurements of liquid Rh which have been compared with MD simulations performed using published pair functionals (Cleri & Rosato, 1993) developed for transition metals.

2. Experimental

We report about high-temperature XAFS experiments for which a longstanding research project was developed at LURE (Orsay) at beamlines D42 and D44 during the last eight years. Improved high-temperature devices have now been installed at the ESRF, beamline BM29, taking advantage of the the excellent flux and energy resolution due to the brilliance of the source and of the highly automated experimental setup (Filipponi *et al.*, 1998). Present experiments on AgI and Rh samples at the Ag, I, and Rh K-edge were performed using the BM29 double-crystal fixed-exit monochromator equipped with a Si(311) crystal. XAFS spectra were measured in transmission mode using ionization chambers. An improved version of the furnace originally installed at LURE (Filipponi and Di Cicco, 1994) was used for the present high-temperature experiments. The furnace is able to work under high-vacuum conditions with automatic temperature readout using a small-spot infrared pyrometer and/or thermocouples.

AgI and Rh samples suitable for high-temperature measurements were prepared by pressing into pellets homogenous dispersions of suitable amounts of finely powdered chemical precursors and inert substances. In this way, a sufficiently uniform sample layer of typical 10-30 μm thickness can be obtained (Filipponi and Di Cicco, 1994). The AgI sample was obtained by mixing high-purity AgI and graphite. The high temperature crucible was a 100 μm graphite foil. Rh samples suitable for measurements above $T = 2000$ K were obtained mixing a Rh salt with high-purity HfO_2. The Rh salt was decomposed and reduced by an *in-situ* heat treatment into micrometric size metallic grains. Other more common matrices were found to interact with Rh at high-temperature. We used a 5 μm W crucible. Further details on the Rh experiment are described elsewhere (Di Cicco *et al.*, 1998).

3. Results

3.1. "ionic" melts: AgI

Silver iodide is classified as a mainly ionic compound showing a well-known solid-solid transition at about 420 K to a fast-ion conductor phase. XAFS spectra of solid AgI have been extensively studied and evidence for anharmonic vibrations of the first-neighbor shell were found (see Dalba *et al.*, 1995 and ref. therein). Present Ag and I K-edge XAFS measurements cover the 30-850 K range of temperatures including liquid AgI (melting point $T_m \sim$ 830 K). Here we present a simultaneous refinement (Di Cicco, 1996,1997) of both Ag and I K-edge XAFS of liquid AgI starting from MD results (Shimojo & Kobayashi, 1991) obtained using pair potentials (Parrinello *et al.*, 1983). Suitable modeling of Ag and I background shapes was used (Filipponi and Di Cicco, 1995, Buontempo *et al.*, 1997).

In Fig. 1(*a*) the partial $g_{AgI}(r)$ obtained by MD simulation is decomposed in a short-range peak (solid) and a long-range tail. XAFS is sensitive only to the shape of the short-range peak which can be eventually refined following a scheme already applied in several molten systems (Filipponi 1994, Di Cicco *et al.*, 1996). The calculated XAFS signals obtained starting from all of the $g_{AgI}(r)$, $g_{AgAg}(r)$ and $g_{II}(r)$ MD partial distribution functions are shown in Figs. 1(*b*) and 1(*c*), respectively. There is no quantitative agreement between experimental and calculated spectra indicating that a structural refinement is necessary. XAFS signals associated with the $g_{AgI}(r)$ tail, $g_{AgAg}(r)$ and $g_{II}(r)$ are very weak. They have been kept fixed during the refinement process of the $g_{AgI}(r)$ peak. Peak shape was refined using only three parameters (R, σ^2 and β) taking into account the appropriate long-range constraints (Filipponi, 1994).

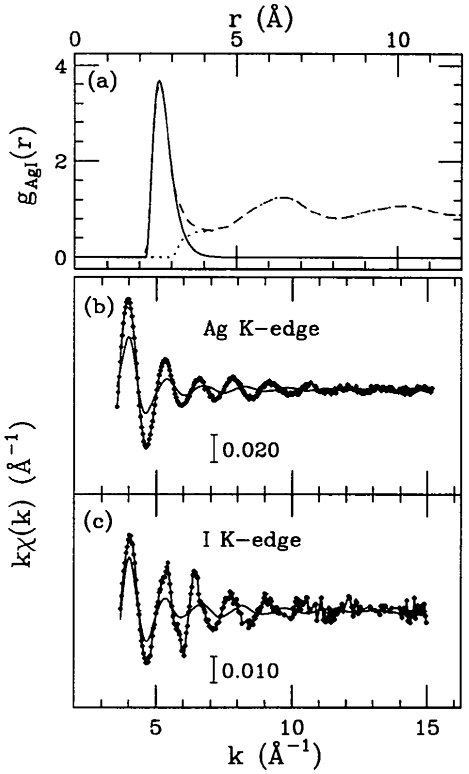

Figure 1
Partial $g_{AgI}(r)$ for liquid AgI (*a*) simulated by MD decomposed into short-range and long-range components. Ag (*b*) and I (*c*) K-edge XAFS signals calculated starting from MD simulations compared with experimental XAFS data of liquid AgI.

Best-fit Ag and I K-edge calculated spectra are compared with experimental data in Figs. 2(*a*) and 2(*b*), respectively. The agreement is very good. The reconstructed $g(r)$ is compared with the original MD curve in Fig. 2(*c*). Error bars have been calculated looking at the family of $g(r)$ curves obtained by varying the structural parameters within their statistical error limits (95 % confidence level) taking into account correlations. A clear shift (of about 0.2 Å) toward larger distances and a narrowing of the peak are found, well outside the error limits. It is clear that the parameterization or the functional form of the potential are not accurate and present calculations do not describe the short-range structural properties of molten AgI. Similar but less evident discrepancies between calculated and experimental $g_{AgI}(r)$ were already observed for solid $\alpha-$AgI taking into account the work of Boyce and Hayes (see Parrinello *et al.*, 1983 and ref. therin). Present results are in agreement with previous investigations on CuBr (Di Cicco *et al.*, 1997) and stimulate the development of new theoretical approaches taking into account non-ionic bonding in superionic compounds.

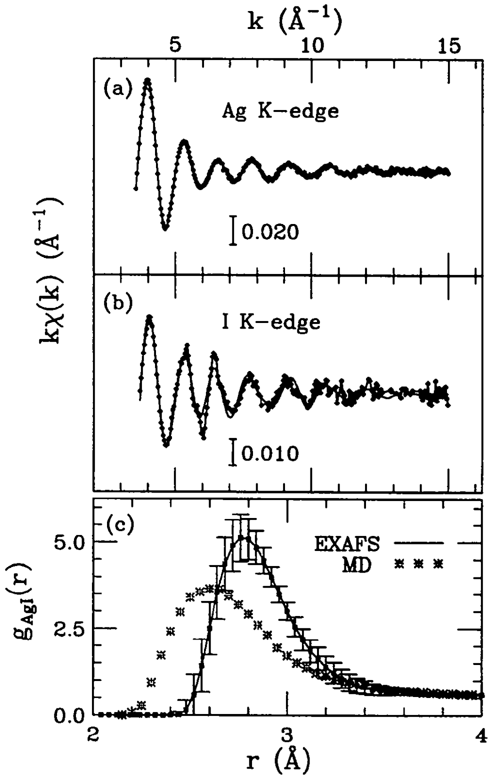

Figure 2
Best-fit Ag (*a*) and I (*b*) K-edge XAFS signals compared with experimental XAFS data of liquid AgI. (*c*) Partial $g_{AgI}(r)$ reconstructed by XAFS compared with previously published MD results for liquid AgI.

3.2. metallic melts: Rh

Structural properties of metallic melts are usually investigated by diffraction techniques (see for example Waseda, 1980). Only recently, following the initial efforts of Crozier and Seary (1980), XAFS investigations were recognized to give a unique insight into the short-range structure of liquid and undercooled liquid metals, as well as of high-temperature solids. Detailed applications regarded solid and liquid Ga, (Di Cicco, 1994) Ge, (Filipponi and Di Cicco, 1995), Sn (Di Cicco, 1996,1997).

Here, the results of a challenging experiment on liquid Rh (melting point $T_m \sim 2236$ K) are compared with MD simulations. Full report and original data of this experiment are given elsewhere (these proceedings, Di Cicco *et al.*, 1998). Due to the difficult experimental conditions, no diffraction measurements have been reported for liquid Rh so far. Model interaction potentials for transition metals are usually expressed as pair functionals (see Carlsson, 1990) incorporating many-body interactions for which the attractive part is computed using a tight binding scheme. A square-root dependence on the pair distribution with a short-range cut-off is often assumed for the attractive interaction, which is related to width of the valence *d* band in transition metals. A convenient parameterization of a square-root pair functional for solid Rh (Cleri & Rosato, 1993) has been used for present classical high-temperature MD simulations performed with 864 atoms. Comparison of MD and XAFS results for solid Rh are contained elsewhere, including the use of different functional forms for the interatomic interaction.

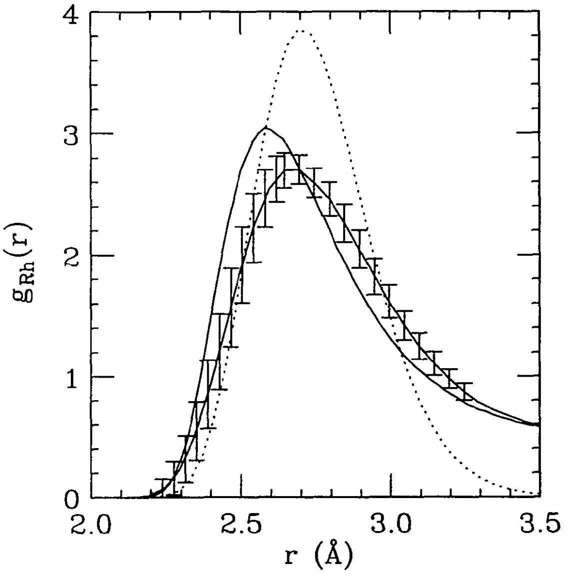

Figure 3
Pair distribution function of liquid Rh determined by XAFS (curve with error bars) compared with Molecular Dynamics simulations (continuous line) and with the first-shell distribution of solid Rh at 1890 K (dots).

Here we only note that the Cleri & Rosato parameterization of the potential gives a short-range structure in qualitative agreement with XAFS data of solid Rh up to about 2000 K and that anharmonic vibrations are increasingly important and not negligible even at moderate temperature. In Fig. 3 we compare pair distributions of liquid Rh obtained by MD simulations at 2500 K (continuous line) and measured by XAFS at 2240 K (curve with error bars). As usual, only the short-range peak was refined by XAFS. The first-shell $g(r)$ of solid Rh at 1890 K reconstructed by XAFS, showing a large degree of asymmetry, is also reported (dots). Comparison with high-temperature solid Rh indicates that in the liquid phase, besides the obvious filling of the gap between first and second-shell peaks, there is a slightly increased chance to find atoms at very short distances. In spite of the density decrease, the most probable value of the g(r) is slightly displaced toward shorter distances. The first peak is instead shifted toward longer distances with respect to the MD result. The foot of the distribution remains approximately at the same distance but the rise of the peak is less steeper than that calculated by MD. The agreement can be considered satisfactory at a qualitative level, however present results indicate that a softer effective interatomic potential would better reproduce the local structure of liquid rhodium.

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References

U. Buontempo, A. Di Cicco, A. Filipponi, M. Nardone, and P. Postorino, J. Chem. Phys. **107**, 5720 (1997).
A. E. Carlsson, Solid State Physics **43**, 1-91 (1990).
F. Cleri and V. Rosato, Phys. Rev. B **48**, 22 (1993).
E. D. Crozier and A. J. Seary, Can. J. Phys. **58**, 1388 (1980).
G. Dalba, P. Fornasini, R. Gotter, and F. Rocca, Phys. Rev. B **52**, 149 (1995).
A. Di Cicco and A. Filipponi, Europhys. Lett. **27**, 407 (1994).
A. Di Cicco, Phys. Rev. B **53**, 6174 (1996).
A. Di Cicco, M. J. Rosolen, R. Marassi, R. Tossici, A. Filipponi, and J. Rybicki, J. Phys.: Condens. Matter **8**, 10779 (1996)
A. Di Cicco, A. Filipponi, J. P. Itiè, and A. Polian, Phys. Rev. B **54**, 9086 (1996).
A. Di Cicco, J. Phys. IV (France) **7**, C2-171 (1997).
A. Di Cicco, M. Minicucci and A. Filipponi, Phys. Rev. Lett. **78**, 460 (1997).
A. Di Cicco, G. Aquilanti, M. Minicucci, A. Filipponi, J. Rybicki, J. Phys.: Condens. Matter **11**, (1999).
A. B. Edwards, D. J. Tildesley, and N. Binsted, Mol. Phys. **91**, 357 (1997).
A. Filipponi, J. Phys. Condens. Matter **6**, 8415 (1994).
A. Filipponi and A. Di Cicco, Nucl. Instr. & Methods for Phys. Res. B **93**, 302 (1994).
A. Filipponi and A. Di Cicco, Phys. Rev. B **52**, 15135 (1995).
A. Filipponi and A. Di Cicco, Phys. Rev. A **52**, 1072 (1995).
A. Filipponi and A. Di Cicco, Phys. Rev. B **51**, 12322 (1995).
A. Filipponi, M. Borowski, P. W. Loeffen, S. De Panfilis, A. Di Cicco, F. Sperandini, M. Minicucci, and M. Giorgetti, J. Phys.: Condens. Matter **10**, 235 (1998).
M. Parrinello, A. Rahman, and P. Vashishta, Phys. Rev. Lett. **50**, 1073 (1983).
F. Shimojo and M. Kobayashi, J. Phys. Soc. Jpn. **60**, 3725 (1991).
T. Yokoyama, T. Ohta, and H. Sato, Phys. Rev. B **55**, 11320 (1997).
Y. Waseda, *The Structure of Non-Crystalline Materials*, McGraw-Hill, New York, 1980.

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