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Local structure in binary liquids probed by EXAFS

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Abstract. An overview of recent EXAFS measurements on binary liquids, including molten ionic and superionic salts, is given. Multiple-edge EXAFS data analysis using multiple-scattering theory is shown to be able to give accurate and reliable information on short-range structure, complementary to that obtained using diffraction techniques. Structural results on alkali bromides (KBr, RbBr) are illustrated and shown to be in agreement with computer simulations based on well established interatomic potentials. EXAFS results of liquid CuBr, for which a neutron diffraction study using the isotopic substitution method is available, are presented. Evidence for a narrower Cu–Br bond-length distribution is found. The usefulness of the performance of EXAFS measurements on binary liquid systems is addressed.

1. Introduction

In the last three decades, the study of the structure of binary liquids has been an important subject of research in liquid state physics. Several experiments on molten binary salts and metal alloys were performed using x-ray and neutron diffraction techniques. In some interesting cases the individual partial structure factors and distribution functions could be derived from diffraction data, principally using the isotope-enrichment technique (see for example [1–5]). Binary liquids, and in particular molten salts, have been also studied using computer simulation methods (see for example [6] and references therein). In simple binary salts, a good agreement between experiments and simulations was achieved using well established pair potentials.

However, reliable experimental determination of partial pair distribution functions in binary liquids is not a simple task. Quite often, independent measurements of the partial structure factors are hindered by practical difficulties in using suitable isotopes or mixture of isotopes. A few complete neutron diffraction (ND) experiments are available for molten binary systems.

In this paper, some interesting results on molten binary systems obtained using x-ray absorption spectroscopy (XAS) are presented. In fact, recent successful applications in some monatomic liquid metals [7–10] showed that reliable short-range structural information can be derived from EXAFS (extended x-ray absorption fine-structure) data provided that accurate experiments and data analysis are carried out.

Low-noise EXAFS spectra of high-temperature solid and liquid systems can be easily recorded at any core-level edge, excluding only light elements [11]. In a binary system, it is often possible to measure two independent EXAFS spectra related to both atomic species a and b probing the a-all and b-all short-range correlation functions.

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Advanced *ab initio* multiple-scattering calculations [12] and multiple-edge [10] EXAFS data-analysis methods are able to give accurate two-body short-range partial distribution functions which can be directly compared with computer simulation results or other experiments, complementing existing neutron diffraction measurements. In the presence of covalent or nearly-covalent bonding, three-body correlations can be also studied by EXAFS.

In the last five years, a long-standing research project on XAS measurements of liquid systems using synchrotron radiation produced a vast amount of results on both monatomic systems and binary salts and alloys. In this short paper recent results on several molten binary salts are summarized.

2. Experimental results

X-ray absorption measurements were performed in transmission mode at LURE (Laboratoire pour L'Utilisation du Rayonnement Electromagnètique, Orsay, France) on the EXAFS I (D-42) and EXAFS IV (D-44) beam-lines equipped with channel-cut Si (331) and double-crystal Si (311) monochromators respectively. Details of preparation of liquid samples and high-temperature measurements have been already given elsewhere [11, 13].

Several low-noise XAS measurements were performed on the entire series of alkali bromides in the liquid and solid phases for which raw data and experimental details have been already discussed [14]. In the following, results on KBr and RbBr ionic melts will be presented.

Accurate measurements were performed also for some other binary systems including 'mainly ionic' compounds and metal alloys (like Cu_xSn_{1-x}). In particular, low-noise Cu and Br K-edge EXAFS measurements of solid and liquid CuBr were performed and will be presented as an example of not purely ionic systems. Full details of these investigations are given elsewhere [15, 16].

Liquid KBr and RbBr are examples of molten alkali halides, an important class of binary systems studied for a long time using both experimental and theoretical means. Reliable expressions for the interatomic potential have been developed and utilized to investigate microscopic properties, mainly using computer simulations. Monte Carlo (MC) and molecular dynamics (MD) calculations of almost all alkali halides have been performed since the seventies (see references [6, 17]). Experimental studies of local structure of liquid alkali chlorides were carried out using neutron diffraction (ND) taking advantage of the different scattering lengths of the isotopes. Partial structure factors and correlation functions were derived from experimental measurements. However, such detailed studies were performed only in a limited number of systems. In particular, no ND measurements are available for alkali bromides.

In figure 1(a), upper panel, the $k\chi(k)$ Br K-edge EXAFS experimental signal (Expt) of liquid KBr at about 750 °C is compared with the best-fit calculated one (Fit, bold line). Calculations are performed using the methods described in [12, 7–10], using a decomposition of the two-body terms into short-range and long-range components. The EXAFS signal is dominated by a low-frequency contribution associated with the first-neighbour distribution. Therefore, EXAFS data are especially sensitive to the shape of the first peak of the g_{BrK} distribution (up to 3.5–4.0 Å). In figure 1(a), lower panel, the partial g_{BrK} pair distribution reconstructed from EXAFS data is compared with the result of a MD simulation obtained using a standard Tosi–Fumi potential. The estimated error bar [10] in the reconstructed g_{BrK} is quite low especially below 3.2 Å. EXAFS and MD results are in good agreement. Details on present MD calculation and EXAFS data analysis on solid and liquid KBr are reported elsewhere [15].

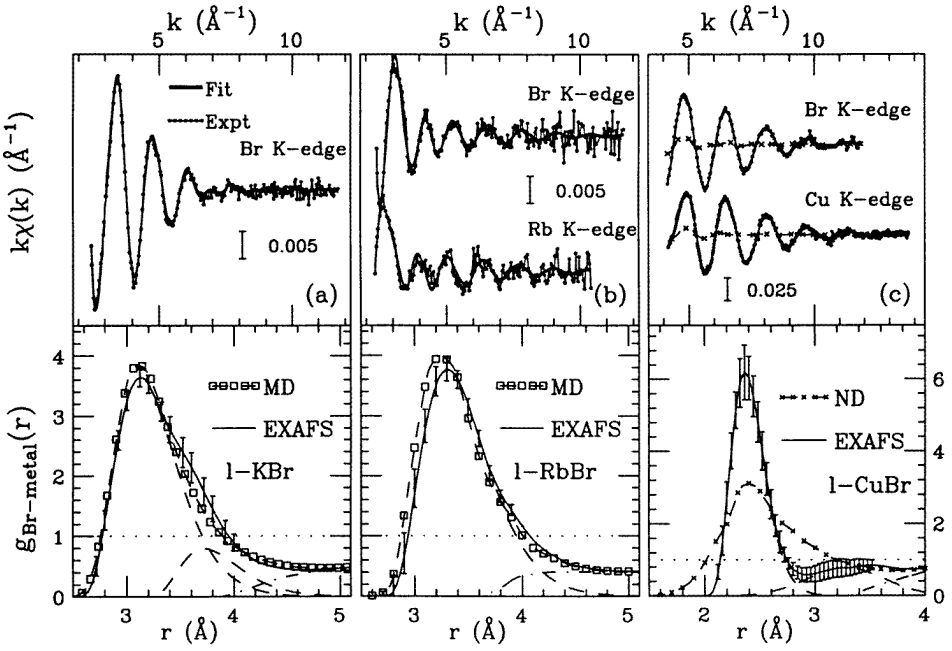

Figure 1. Upper panels (a),(b),(c): experimental (Expt) and best-fit (Fit) calculated $k\chi(k)$ EXAFS signals of liquid KBr, RbBr, and CuBr respectively. In RbBr and CuBr both the Br K-edge and the metal K-edge EXAFS signals were measured and calculated. The agreement between calculated and experimental signals is excellent. In liquid CuBr the $k\chi(k)$ EXAFS signal associated with previously published distribution functions is also shown (crosses, dashed). The amplitude of the experimental EXAFS signals is almost five times bigger. Lower panels (a),(b),(c): $g_{Br-metal}$ partial distribution functions reconstructed from EXAFS data compared with results of MD simulations (□, dashed in l-KBr and l-RbBr) and previously published ND data (crosses, dashed in l-CuBr). Dashed and dot–dashed curves are respectively the short-range peaks and long-range tails of the distribution. The agreement with calculated data is excellent. In l-CuBr the first-neighbour distribution is narrower than previously published.

Another nice example of structural refinement in molten alkali bromides is shown in figure 1(b), upper panel, where the Br and Rb K-edge EXAFS spectra (Expt) of liquid RbBr at 730 °C are compared with best-fit calculations (Fit, bold line). In this case a multiple-edge simultaneous EXAFS refinement was performed using the same g_{BrRb} distribution. Again, the short-range partial g_{BrRb} is measured with good accuracy. In figure 1(b), lower panel, the g_{BrRb} distribution reconstructed from EXAFS data is compared with that calculated using MD simulations [18]. The shape of the first peak is exactly reproduced, although a shift of about 0.07 Å, slightly larger than the estimated error bar, is found.

A third interesting example of EXAFS data analysis is represented by liquid CuBr. Partial distribution functions obtained by ND experiments performed using isotopic substitution of copper are available [5]. CuBr local structure was found to differ from those of molten alkali halides [4, 5] with a featureless Cu–Cu pair distribution and Cu–Br and Br–Br distribution of essentially ionic character. Although interaction models including imperfect ionicity of the bond were developed, complete theoretical explanation of this behaviour is still to be found.

In this case, as shown in figure 1(c), upper panel, the EXAFS $k\chi(k)$ spectrum obtained

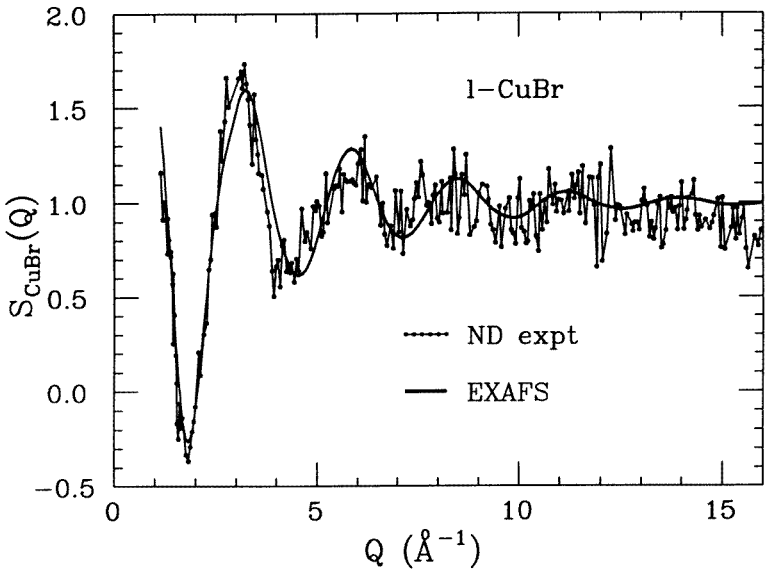

Figure 2. Partial structure factor $S_{CuBr}(Q)$ as obtained by ND measurements [5] compared with that derived by present EXAFS experiment. The agreement is remarkable.

using the partial pair distribution functions measured by ND (crosses) is not in agreement with the experimental signal (dots). The intensity of the calculated signal is of the same order of magnitude as found in the l-KBr and l-RbBr ionic liquids, but that of the experimental spectrum is at least five times bigger (note change of scale). A refinement of the short-range structure is clearly necessary to get an agreement with the experimental EXAFS data. The best-fit calculated signal (bold line) shown in figure 1(c), upper panel, follows closely the experimental data and cannot be easily distinguished on this scale. Again, the EXAFS signal is dominated by the first-neighbour Cu–Br contribution.

In figure 1(c), lower panel, the reconstructed g_{CuBr} (solid line) is compared with that obtained using ND (crosses, dashed). The EXAFS g_{CuBr} is accurately determined below about 2.8 Å (see error bars) and shows a narrower well defined first-neighbour peak. The sensitivity of the EXAFS spectrum can be appreciated looking at the difference in the EXAFS signals in the upper panel. The reconstructed g_{CuBr} is, however, perfectly compatible with the original ND data, within the noise level. In figure 2 we compare the experimental $S_{CuBr}(Q)$ ND measurement with the curve obtained from the g_{CuBr} reconstructed by EXAFS (bold line). The two g_{CuBr} curves of figure 1(c), lower panel, are both compatible with experimental data. This is a typical case where very precise structural information can be gained using EXAFS taking advantage of its exceptional short-range sensitivity. Details and consequences of the present study of liquid CuBr are presented elsewhere [16].

3. Conclusions

Several low-noise x-ray absorption measurements on several liquid binary systems have been performed. Advanced methods (GNXAS) for data analysis, including simultaneous

fitting of EXAFS spectra related to cation and anion sites, were used for the first time on liquid binary salts. The local anion–cation pair distribution function is derived in KBr, RbBr, and CuBr.

EXAFS short-range refinement of the $g_{Br-metal}$ distribution in KBr and RbBr is shown to be in agreement with computer simulations, confirming the reliability of present theoretical models.

Accurate EXAFS data on liquid CuBr are compared with previous results obtained by neutron diffraction measurements. The Cu–Br bond-length distribution is found to be narrower than previously reported giving direct evidence for nearly covalent bonding. The partial structure factor $S(Q)$ derived from EXAFS is shown to be in agreement with the available experimental neutron diffraction data, showing again the reliability of the EXAFS results. EXAFS data, due to their exceptional short-range sensitivity, are able to give us additional information on the shape of the first-neighbour distribution.

Further EXAFS experimental studies of molten binary liquids are stimulated by the present results.

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