

## EXAFS study on liquid gallium under high pressure and high temperature

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EXAFS (Extended X-ray Absorption Fine Structure) spectra of liquid gallium near the Ga *K*-edge have been collected in wide pressure and temperature ranges. Reliable short-range pair distribution functions have been determined using advanced ab-initio calculations (GNXAS) taking into account the medium and long-range structure obtained by previous neutron and x-ray-scattering studies.

**Keywords:** EXAFS; High pressure; High temperature.

## 1. Introduction

The atomic arrangement in liquid gallium (*l*-Ga) has been widely investigated at ordinary pressure using neutron and x-ray diffraction (see for example Narten, 1972 and Bellisent-Funel *et al.*, 1989). The principal peak of the structure factor  $S(q)$  is found to be characterized by a large asymmetry and a shoulder on the high- $q$  side just above the melting temperature. This anomalous feature merges into the principal peak increasing its asymmetry at very high temperature. Therefore, a large number of computer simulations have been performed in a wide range of temperature at ambient pressure in order to explain the anomalies in the structure factor and improve the knowledge of the electronic properties of liquid gallium (see for example Gong *et al.*, 1993 and Holender *et al.*, 1995). On the other hand, the only combined experimental investigations of liquid gallium at high temperatures and pressures have been performed using x-ray diffraction (Tamura & Hosokawa, 1993 and Tsuji, 1990) up to 1570 K, 0.07 GPa (Tamura & Hosokawa, 1993) and up to 393 K, 6.1 GPa on the high-pressure side (Tsuji, 1990). In spite of these investigations, a comprehensive picture of the structural properties of liquid Ga at extreme conditions is still lacking. In order to shed light on the characteristics of the local structure of liquid Ga we performed an EXAFS study of *l*-Ga in wide pressure and temperature ranges. In fact, as it has been shown previously, the unique short-range sensitivity of the XAS (x-ray absorption spectroscopy) technique has been found to provide unambiguous information about the local structure of both ordered and disordered systems. (Di Cicco *et al.*, 1996, Itié *et al.*, 1997 and Buontempo *et al.*, 1998)

## 2. Experimental

Ga *K*-edge XAS measurements as a function of pressure at high temperature were collected in two separate experiments using the dispersive setup available at LURE (D11 and DW11A beamlines) (Dartyge *et al.*, 1986) and synchrotron radiation emitted by the DCI storage ring operating at 1.85 GeV with typical currents of 300 mA.

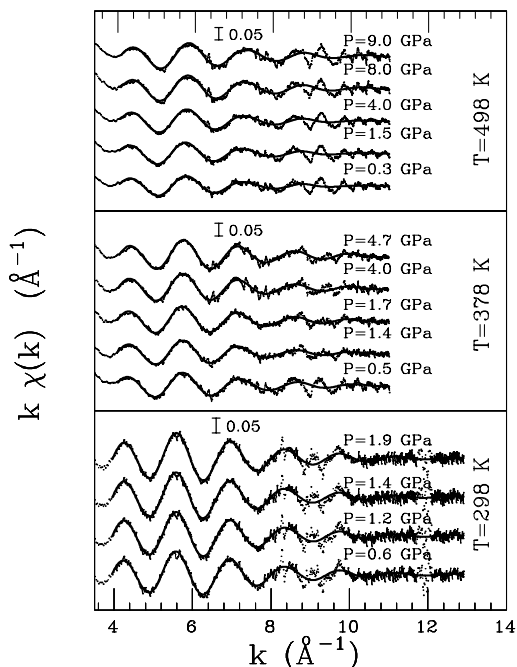
XAS spectra covered the 0.6–1.9 GPa, 0–5 GPa and 0–9 GPa pressure ranges at room temperature,  $T=378$  K and  $T=498$  K, respectively. A standard diamond anvil cell (DAC) equipped with an external heater was used as pressure device. Pure gallium was loaded into the cell equipped with stainless steel gaskets without pressure-transmitting medium. The size of the sample (hole of the gasket) was about 150  $\mu\text{m}$ . Particular care was taken to improve the quality of the spectra minimizing the appearance of extra absorption peaks associated with Bragg reflections from the diamonds by optimizing the position of the cell and of the two diamonds. Pressure was measured before and after each XAS scan by using the standard ruby fluorescence technique with a typical 0.1 GPa error bar for the room temperature measurements. Because of the large broadening of the ruby fluorescence peak at high temperature we also used as a pressure calibrant the fluorescence of the  $\text{Sm}^{2+}$ -doped  $\text{SrB}_4\text{O}_7$  which is nearly independent of the temperature. Temperature, excellently stable due to the mass of the cell including the heater, was monitored by a thermocouple placed on the rear of the cell with an estimated uncertainty of 5 K. Low noise spectra were obtained by summing 5 spectra (1024 pixel data), each recorded with a total integration time of about 90 s. XAS experiments were performed during two separate runs and the energy scale resulted to be always a linear function of the pixel number:  $E = a + bn$ . The energy step  $b$  was about  $b = 0.853$  eV and  $b = 0.670$  eV while the parameter  $a$  was about  $a = 10203.6$  eV and  $a = 10289.6$  for room temperature and high temperature scans respectively. The scale was obtained comparing the *K*-edge pure Ga and GaSb spectra at ambient conditions collected using the dispersive technique with analogous spectra recorded in the same conditions on a conventional spectrometer with a channel-cut (311) monochromator (beamline D42 at LURE).

## 3. Results and Discussion

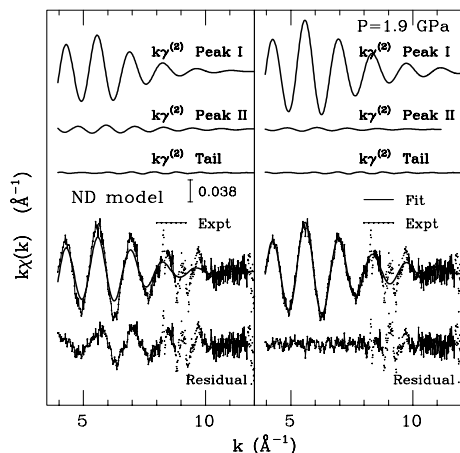
Experimental XAS  $k\chi(k)$  structural signals of liquid Ga at room temperature, 378 K and 498 K are shown in Fig. 1 as a function of pressure (lower, middle and upper panel, respectively). The XAS structural signal is particularly sensitive to the first coordination shell and therefore the  $k\chi(k)$  is extremely sensitive to the shape of the first-neighbor peak. For the data-analysis we followed the efficient method described in ref. (Filipponi, 1994) using the  $g(r)$  long-range asymptotic behavior contained in the  $S(k)$  measured by neutron or x-ray diffraction or determined by theoretical model. As described elsewhere (Filipponi, 1994, Di Cicco *et al.*, 1997 and Di Cicco *et al.*, 1999) it is useful to decompose the  $g(r)$  into a short-range peak and a long-range tail. In the present case, a suitable decomposition of the  $g(r)$ , obtained from x-ray and neutron diffraction experiments (Narten, 1972 and Bellisent-Funel *et al.*, 1989) for liquid gallium, has been made: a short-range peak, modeled as a couple of  $\Gamma$ -like distributions due to its large asymmetry, and a long-range tail have been used to represent accurately the model. Fitting procedure of XAS spectra of liquid gallium has been performed considering the constraints imposed on the long range part of  $g(r)$  by scattering data.

In Fig. 2 (left panel) the  $k\gamma^{(2)}$  signals related to the  $\Gamma$  functions ( $k\gamma_I^{(2)}$  and  $k\gamma_{II}^{(2)}$ ), and the tail  $k\gamma_T^{(2)}$  are shown for the spectrum at 1.9 GPa and room temperature. The total structural signal obtained by summing the three  $k\gamma^{(2)}$  terms is compared with the experimental  $k\chi(k)$  of *l*-Ga at various pressures. The calculated signal is in qualitative agreement with experimental data. However, the evident oscillation in the residual curve (bottom in Fig. 2, left panel) indicates that a refinement is still required. In the short-range refinement of *l*-Ga, the parameters of the  $\Gamma$  distributions were allowed

to float, while the signal associated with the tail was kept fixed. In order to take into account the compressibility sum rule and asymptotic behavior at long distances, we introduced two constraints (on the coordination number and on the second moment of the distribution) in the refinement process (Filipponi, 1994). Following this procedure, the shapes of the first and second peaks are not independent.



**Figure 1**  
Experimental XAS signals compared with best-fit calculated spectra for liquid Ga as function of pressure at room temperature (lower panel), at 378 K (middle panel) and 498 K (upper panel).

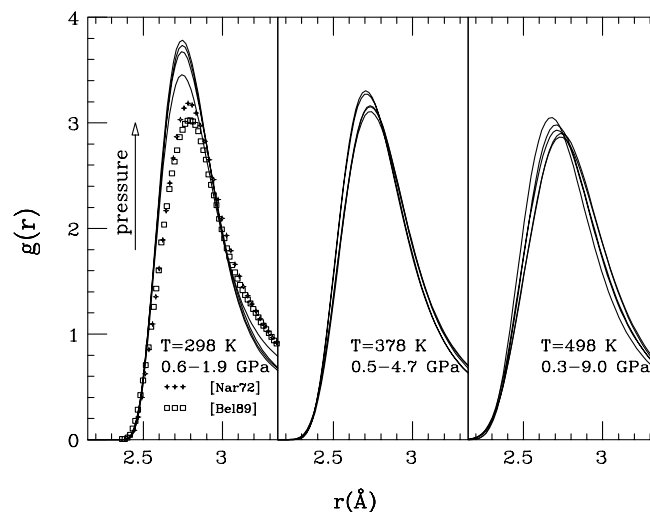


**Figure 2**  
Left panel: Multiple scattering pair contributions  $k\gamma^{(2)}$  associated with the two first-neighbors shells describing the first  $g(r)$  peak and the long-range tail (ND model). The total  $k\gamma^{(2)}$  signal is compared with the  $k\chi(k)$  experimental spectrum of liquid Ga at 1.9 GPa and room temperature. The residual curve indicates that a structural refinement is necessary. Right panel: Best-fit  $k\gamma^{(2)}$  signals for the  $l$ -Ga  $k\chi(k)$  spectrum at 1.9 GPa and room temperature. The agreement with experimental data is excellent.

XAS data-analysis at room temperature has been performed using those constraints in the 0.6–1.9 GPa pressure range (see Fig. 1, lower panel). Experimental points shown as small dots in Fig. 1 (see region around  $9 \text{ \AA}^{-1}$ ) contain spurious structures related to weak Bragg peaks coming from the diamonds of the cell and have not been considered in the refinement process. Structural data-analysis of  $l$ -Ga at high temperature has been performed using the same method described for the room temperature data. In this case the decomposition of the  $g(r)$  obtained from neutron diffraction experiments into a short-range part and a long range tail has been made considering the different macroscopic densities for each temperature defining the proper constraints for the coordination numbers. Realistic densities of  $l$ -Ga have been evaluated starting from the usual linear approximation for liquid metals:  $\rho = \rho_m + \Lambda(T - T_m)$ , where  $\rho_m = 6.103 (10^3 \text{ Kg m}^{-3})$ ,  $\Lambda = (\partial\rho/\partial T)_p = -6.2 (10^{-1} \text{ Kg m}^{-3} \text{K}^{-1})$  (Iida & Guthrie, 1993) and  $T_m = 302.9 \text{ K}$ . The  $\Lambda$  parameter is expected to be almost constant as a function of temperature (and pressure) in the present ranges. In Fig. 1 best-fit calculations (thick lines) are compared with the experimental spectra (thin lines) in the 0.5–4.7 GPa ( $T=378 \text{ K}$ , middle panel) and in 0.3–9.0 GPa pressure ranges ( $T=498 \text{ K}$ , upper panel). The excellent agreement between theoretical and experimental signals is evident.

### 3.1. XAS $g(r)$ reconstruction in liquid gallium

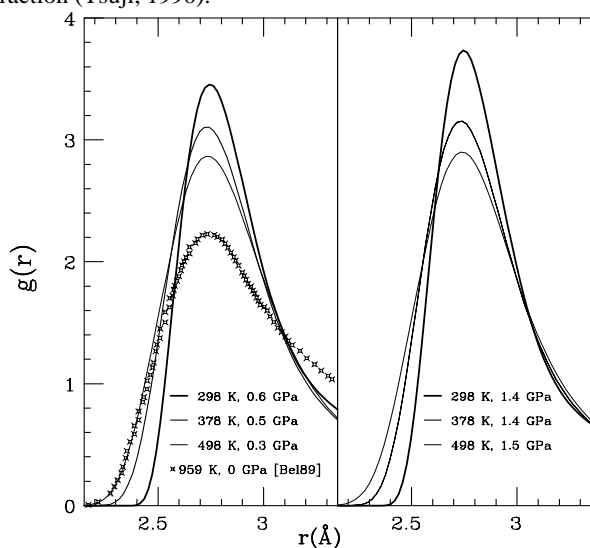
The pair distribution  $g(r)$  functions have been reconstructed for liquid gallium in a wide range of pressure and temperatures starting from the structural parameters determined by means of XAS data-analysis (Filipponi, 1994 and Di Cicco *et al.*, 1999). The typical error bar on the calculated  $g(r)$  functions is of about 0.1 on the first-peak rise and increases for longer distances (see Di Cicco *et al.*, 1997, Di Cicco *et al.*, 1999 and ref. therein). In Fig. 3 the pair distribution  $g(r)$  functions obtained by XAS results are shown for liquid Ga as a function of pressure at room temperature (left panel), at 378 K (middle panel) and 498 K (right panel). In the same plot (left panel), we also show the  $g(r)$  functions at ambient pressure reported in ref. (Narten, 1972 and Bellisent-Funel *et al.*, 1989) for comparison.



**Figure 3**  
Pair distribution functions  $g(r)$  reconstructed by XAS data-analysis for  $l$ -Ga shown as a function of pressure at room temperature (left panel),  $T=378 \text{ K}$  (middle panel) and  $T=498 \text{ K}$  (right panel).

For what concerns the room temperature curves, it is found that the height of the first-neighbor peak is affected by the pressure increase while no appreciable distance changes are detected. The  $g(r)$  peak height increases from about 3.5 (0.6 GPa) to 3.8 (1.9 GPa) at 298 K. The position of the maximum is at about 2.76 Å.

For the high temperature functions, a slight enhancement of the peak is observed increasing the pressure (see Fig. 3, middle and right panel). The  $g(r)$  peak intensity is found to increase from about 3.1 (0.5 GPa) to 3.3 (4.7 GPa) at 378 K (middle panel) and from about 2.8 (0.3 GPa) to 3.0 (9.0 GPa) at 498 K (right panel). Moreover, the position of the maximum of the distribution moves toward shorter distances from about 2.72 (0.5 GPa) to 2.70 (4.7 GPa) (see middle panel in Fig. 5) at 378 K and from about 2.72 (0.3 GPa) to 2.68 (9 GPa) (see right panel in the same figure) at 498 K. The slight decrease of the distance on increasing the pressure is in qualitative agreement with previous results obtained using x-ray diffraction (Tsuji, 1990).



**Figure 4**

Left panel: Pair distribution functions  $g(r)$  reconstructed by XAS data-analysis for  $l$ -Ga at 298 K and 0.6 GPa, 378 K and 0.5 GPa, 498 K and 0.3 GPa. The  $g(r)$  function at ambient pressure and  $T=959$  K reported by Bellissent-Funel *et al.*, 1989 is also shown for comparison. Right panel: Pair distribution functions of  $l$ -Ga at 298 K and 1.4 GPa, 378 K and 1.4 GPa, 498 K and 1.5 GPa.

Finally, we report in Fig. 4 the short-range  $g(r)$  functions for  $l$ -Ga as a function of temperature at given pressures. The peak height decreases from about 3.8 to 3.0 temperature from 298 K to 498 K at about 1.5 GPa (right panel). At lower pressures (around 0.5 GPa) the same trend is obtained (decrease from 3.5 to 2.9 increasing the temperature, see left panel). A dramatic temperature dependence of the  $g(r)$  shape is observed at given pressures, in agreement with the trend of previous neutron diffraction results at ambient pressure. In fact, comparing the  $g(r)$  at room temperature and at about 959 K at ambient pressure (see Fig. 4) one can see that the first rise of the  $g(r)$  moves toward shorter distances, the height decreases dramatically, and the asymmetry of the distribution increases. We obtain a similar behavior on our  $g(r)$  distributions at higher pressure. The position of the peak maximum does not move appreciably as a function of temperature in agreement with previous works (Tamura & Hosokawa, 1993).

## 4. Conclusions

A detailed study of the high-pressure and high-temperature  $K$ -edge x-ray absorption spectra of liquid gallium has been carried out. XAS data-analysis has been performed using the advanced GNXAS multiple-scattering method using constraints provided by neutron, x-ray diffraction and density data. The short-range pair distribution function  $g(r)$  for  $l$ -Ga has been reconstructed for the first time in a wide range of pressures and temperatures. The local average structure of  $l$ -Ga under pressure (up to 1.9 GPa) at room temperature is found to be compatible with that of  $l$ -Ga at ordinary pressure measured by neutron diffraction. The maximum of the first-neighbor distribution is slightly shifted toward short distances and its height increases with the pressure. At higher temperatures, both a slight contraction of distances and enhancement of the first-neighbor peak have been observed as a function of pressure. By increasing the temperature the height of the first-neighbor peak decreases while the first rise in the  $g(r)$  functions moves to shorter distances showing a modification in the average local structure for the liquid phase as function of temperature, in agreement with previous results obtained at ambient pressure. The present study can stimulate new theoretical and computational investigations of short-range potentials and electronic properties for  $l$ -Ga under extreme conditions. Moreover, advances in the data-analysis method allowed us to obtain results in quantitative agreement with diffraction measurements. Therefore, XAS technique is confirmed to provide complementary information compared to those achieved with diffraction techniques and can be used in the refinement of the short-range structure in disordered systems in high-pressure and/or high temperature conditions.

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