Experimental report

21/01/2016

Proposal: **6-05-956** **Council:** 10/2014

Title: Neutron diffraction with isotope substitution study of levitated liquid $Ca_3Al_2O_6$

Research area: Materials

This proposal is a new proposal

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Samples: $Ca_3Al_2O_6$ (44 Ca)
$Ca_3Al_2O_6$ (Nat Ca)
$Ca_3Al_2O_6$ (50% 44 Ca + 50% nat Ca)

Instrument	Requested days	Allocated days	From	To
D4	5	5	17/06/2015	22/06/2015

Abstract:

We propose to measure the structure of levitated liquid $Ca_3Al_2O_6$ using the method of neutron diffraction with 44-Ca isotope substitution. Difference function methods will provide detailed insight into the local Al-O and Ca-O structure. Moreover, a second order difference function will enable the experimental determination of the Ca-Ca partial pair distribution function. $Ca_3Al_2O_6$ is the Ca-rich limit of the glass forming region in the CaO-Al_2O_3 system. The results will therefore provide important insight into the role of structure on constraining glass forming ability, an important unresolved problem. The results will be used as a rigourous constraint for molecular dynamics computer simulations, which will allow for the complete determination of the structure and dynamics of the liquid.

Neutron diffraction with isotope substitution study of levitated liquid $Ca_3Al_2O_6$

Introduction

In the three component $(\mathrm{CaO})_x(\mathrm{Al_2O_3})_{1-x}$ liquid system, the local aluminium coordination environment can be readily determined using conventional neutron and x-ray diffraction combined with aerodynamic levitation methods [1, 2]. However, it is difficult to determine the local calcium environment as Ca-O correlations suffer considerable overlap from other atom-atom interactions and the Ca-Ca interactions are unresolvable [2]. It is therefore desirable to employ Ca-atom selective methods in order to accurately determine the local calcium environment in these liquids by experiment. Despite the relatively low neutron scattering length contrast between the various calcium isotopes, NDIS with ^{44}Ca has previously been employed to determine $S_{\mathrm{CaCa}}(Q)$ in $(\mathrm{CaO})_{0.48}(\mathrm{SiO_2})_{0.49}(\mathrm{Al_2O_3})_{0.03}$ glass [3, 4]. We have also previously combined the NDIS method with aerodynamic levitation and laser-heating to investigate the structure of liquid and glassy $\mathrm{CaAl_2O_4}$ [5]. However, although the latter measurements were of suitable quality to allow for the experimental determination of $S_{\mathrm{CaCa}}(Q)$ in the glass, the liquid $S_{\mathrm{CaCa}}(Q)$ was indiscernible above the statistical noise [5].

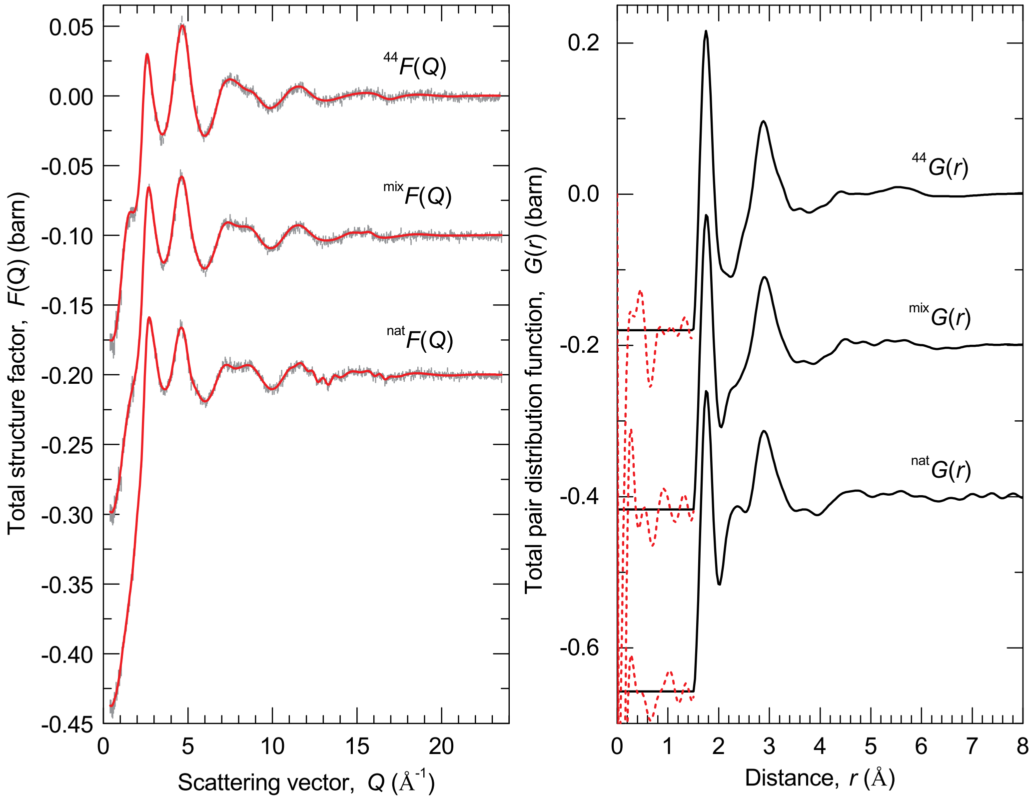
In this experiment, we made NDIS measurements of aerodynamically levitated and laser heated liquid $\mathrm{Ca_3Al_2O_6}$ at 2073 K. The results are of high statistical accuracy and enable the accurate determination of the local Ca coordination environment, including a measurement of the liquid $S_{\mathrm{CaCa}}(Q)$ and $g_{\mathrm{CaCa}}(r)$ partials.

Experiment

We measured the diffraction patterns for three samples of liquid $\mathrm{Ca_3Al_2O_6}$ that were identical in every respect except that they contained either $^{\mathrm{nat}}$Ca (i.e. Ca in its natural isotopic abundance), ^{44}Ca, or a 50:50 mixture of the two. The coherent neutron scattering lengths $b(^{\mathrm{nat}}\mathrm{Ca}) = 4.70(2)\,\mathrm{fm}$, $b(^{44}\mathrm{Ca}) = 1.42(6)\,\mathrm{fm}$ and $b(^{\mathrm{mix}}\mathrm{Ca}) = 3.06(3)\,\mathrm{fm}$, are sufficiently different for the Ca correlations measured in the experiment to have observably different weighting factors. Diffraction patterns were taken for the liquid samples at 2073(30) K using an aerodynamic levitation and $\mathrm{CO_2}$ laser heating device [6] installed at the D4C diffractometer with an incident neutron wavelength of 0.4979 Å. The wide scattering angle accessibility of 1.3-140 ° gives rise to a scattering vector range of $0.3 < Q\,(\mathrm{\AA}^{-1}) < 24$. Additional measurements were made for the empty levitation device inside the diffraction chamber with a continuous flow of Arcal (Ar + 3% $\mathrm{O_2}$) levitation gas and a solid vanadium sphere of 3 mm diameter for calibration purposes. In order to attain good counting statistics from the relatively small sample volume, a total counting time of 24-48 hours per sample was necessary.

Results and conclusions

The measured total structure factors $^{44}F(Q)$, $^{\mathrm{mix}}F(Q)$ and $^{\mathrm{nat}}F(Q)$ and corresponding total pair distribution functions $^{44}G(r)$, $^{\mathrm{mix}}G(r)$ and $^{\mathrm{nat}}G(r)$ for liquid $\mathrm{Ca_3Al_2O_6}$ are shown in figure 1. In reciprocal-space, the results show the progressive appearance of a pre-peak at $Q \approx 1.5\,\mathrm{\AA}^{-1}$, indicative of ordering on an intermediate length-scale, as natural Ca is substituted by ^{44}Ca. In real-space, the first peak at 1.75 Å corresponds to the nearest neighbour Al-O bond distance. The second peak at 2.3 Å in $^{\mathrm{nat}}G(r)$ function arises from Ca-O correlations and is more strongly probed in the natural sample for which the Ca scattering length is higher. A coordination number $\bar{n}_{\mathrm{Al}}^{\mathrm{O}} = 4.4(3)$ was determined from the area of the Al-O peak in $^{\mathrm{nat}}G(r)$, while a value $\bar{n}_{\mathrm{Al}}^{\mathrm{O}} = 4.3(3)$ was determined by integrating over the Al-O peak in $^{\mathrm{mix}}G(r)$ and $^{44}G(r)$. This



(a) (b)

Figure 1: (a) The measured total structure factors ${}^{44}F(Q)$, ${}^{\rm mix}F(Q)$ and ${}^{\rm nat}F(Q)$ for liquid $\rm Ca_3Al_2O_4$ at 2073 K and (b) the total pair distribution functions ${}^{44}G(r)$, ${}^{\rm mix}G(r)$ and ${}^{\rm nat}G(r)$ as obtained by Fourier transforming the corresponding $F(Q)$ functions in (a).

difference in $\bar{n}_{\rm Al}^{\rm O}$ is attributed to a stronger overlap into the Al-O coordination shell by Ca-O correlations. We find that integration over the region of the Ca-O peak results in a significant underestimate of the coordination number $\bar{n}_{\rm Ca}^{\rm O} \approx 4$ due to a large degree of overlap from O-O correlations, thereby demonstrating the need for difference function methods to be applied.

The reciprocal-space and real-space difference functions, as defined in Ref. [5], are shown in figure 2. The correlations involving only matrix μ (Al,O) atoms are entirely eliminated in $\Delta^{\rm Ca}(Q)$ and $\delta_{{\rm Ca}\mu}(Q)$, while the Ca correlations are eliminated in the $\delta_{\mu\mu}(Q)$ and $\Delta^{\mu}(Q)$ functions. The difference functions yield the coordination numbers $\bar{n}_{\rm Al}^{\rm O} = 4.2(2)$ and $\bar{n}_{\rm Ca}^{\rm O} = 5.7(3)$. The partial structure factor $S_{\rm CaCa}(Q)$ and pair distribution function $g_{\rm CaCa}(r)$, extracted directly from our measurements, are shown in figure 3. The measured $S_{\rm CaCa}(Q)$ exhibits a first sharp diffraction peak at 1.2(1) Å^{-1}, and a principal peak at 2.2(1) Å^{-1}. The position of the clearly defined first peak in $g_{\rm CaCa}(r)$ gives a Ca-Ca bond distance of $r_{\rm CaCa} = 3.68(4)$ Å. Integration over this peak gives an average coordination number $\bar{n}_{\rm Ca}^{\rm Ca} = 7.0(5)$.

References

[1] Mei Q *et al.* 2008 *J. Phys.: Condens. Matter* **20** 245107

[2] Drewitt J W E *et al.* 2011 *J. Phys.: Condens. Matter* **23** 155101

[3] Eckersley M C *et al.* 1988 *Nature* **335** 525

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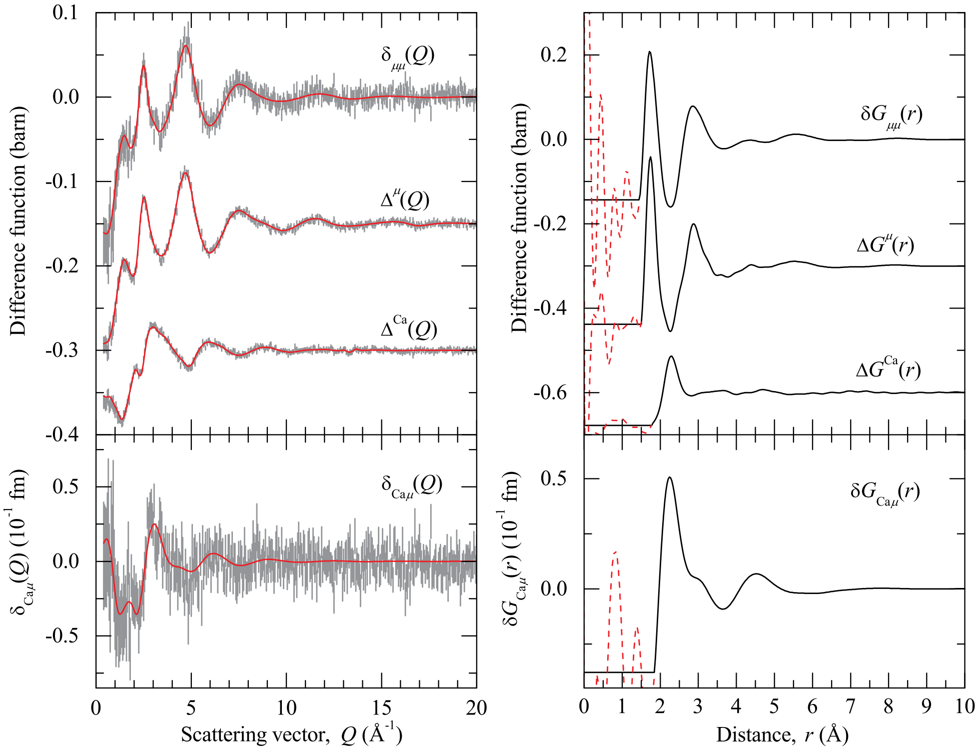
[5] Drewitt J W E *et al.* 2012 *Phys. Rev. Lett* **109** 235501

[6] Hennet L *et al.* 2006 *Rev. Sci. Instrum.* **77** 053903



(a) (b)

Figure 2: (a) Reciprocal-space difference functions for liquid $Ca_3Al_2O_6$ at 2073 K and (b) the real-space difference functions as obtained by Fourier transforming the corresponding reciprocal space functions.

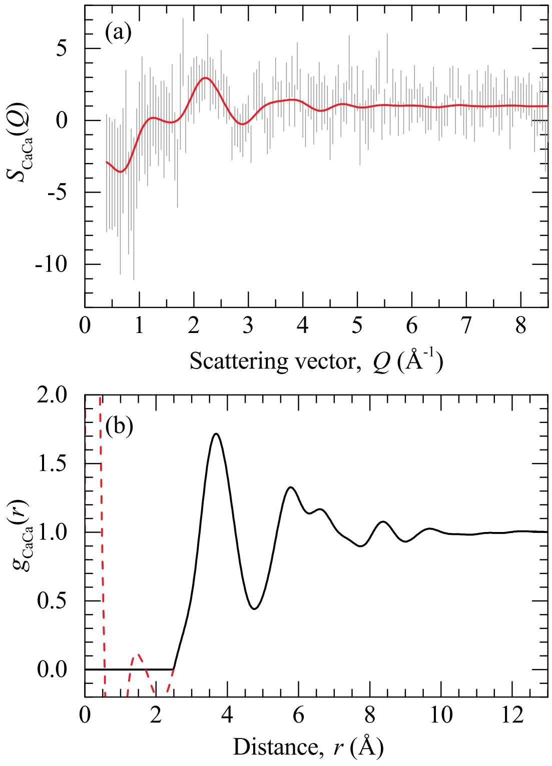


Figure 3: (a) The partial structure factor $S_{\mathrm{CaCa}}(Q)$ and (b) pair distribution function $g_{\mathrm{CaCa}}(r)$ directly determined by difference function methods from the diffraction measurements obtained in this experiment.