Definition of Partial Structure Factor

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Abstract

The structure of several network-forming liquids and glasses is considered, where a focus is placed on the detailed information that is made available by using the method of neutron diffraction with isotope substitution (NDIS). In the case of binary network glass-forming materials with the MX_2 stoichiometry (*e.g.* GeO_2, $GeSe_2$, $ZnCl_2$), two different length scales at distances greater than the nearest-neighbour distance manifest themselves by peaks in the measured diffraction patterns. The network properties are influenced by a competition between the ordering on these "intermediate" and "extended" length scales, which can be manipulated by changing the chemical identity of the atomic constituents or by varying state parameters such as the temperature and pressure. The extended-range ordering, which describes the decay of the pair-correlation functions at large-r, can be represented by making a pole analysis of the Ornstein–Zernike equations, an approach that can also be used to describe the large-r behaviour of the pair-correlation functions for liquid and amorphous metals where packing constraints are important. The first applications are then described of the NDIS method to measure the detailed structure of aerodynamically-levitated laser-heated droplets of "fragile" glass-forming liquid oxides ($CaAl_2O_4$ and $CaSiO_3$) at high-temperatures (~ 2000 K) and the structure of a "strong" network-forming glass (GeO_2) under pressures ranging from ambient to ~ 8 GPa. The high-temperature experiments show structural changes on multiple length scales when the oxides are vitrified. The high-pressure experiment offers insight into the density-driven mechanisms of network collapse in GeO_2 glass, and parallels are drawn with the high-pressure behaviour of silica glass.

Keywords: Liquid and Amorphous Metals; Network Properties; Temperature and Pressure.

Introduction

The investigate by means of diffraction experiments the mutual distribution of the components in the metallic glass $Fe_{go}B_{20}$- Eor this purpose three independent diffraction experiments have to be performed, in each of which the ratio of the scattering powers of Fe and B must be different. This can be achieved either by applying different radiations or by using isotopes with different scattering lengths in preparing samples with the same chemical composition for neutron scattering experiments. In the present work both methods have been combined.

The knowledge of the atomic structure of disordered binary systems described by three partial structure factors (PSF) is necessary for the calculation of their electronic density of states and more generally for the understanding of their electronic properties. At the moment, we focus our attention on the structure of liquid transition metalaluminium alloys. The discovery of icosahedral phases of AIMn [1] and the large scattering contrast brought by the isomorphous substitution between Mn atoms and the σ-FeCr mixture in neutron diffraction (used previously in quasicrystalline phases [2]) have encouraged us to study the structure of the pseudo-binary liquid $AI_{80}(Mn_x(FeCr)_{1-x})_{2O}$ alloys. Of course, one of the first points will be to confirm the isomorphous behaviour between Mn atoms and the σ-FeCr mixture in the liquid phase by performing four neutron diffraction measurements with different Mn to σ-FeCr atomic ratios; the fourth measurement allows us to check the consistency of the 3 PSFs extracted from the three others. It will be interesting to compare the local order of the liquid phase with those previously determined by neutron diffraction in the icosahedral $Al_{74}Si_5Mn_{21}$ and decagonal $A1_{80}Mn_{2O}$ phases [3, 4] and also in their crystalline hexagonal β–AI_9SiMn_3 [3] modification. Actually, if an icosahedral bond orientational order has been shown in computer experiments on supercooled liquids [5], such an order has not yet been observed above the liquidus. There exist several definitions of partial structure factors for a binary liquid. Here, we will be interested in the determination of the Bhatia Thornton $S_{N, C}$ (Q)'s [6] and the Faber Ziman I_{ij} (Q)'s [7]. There are related to the coherent scattering cross-section per atom, $d\sigma_{coh}/d\Omega$ (Q), as follows:

$$S(Q) = \frac{d\sigma_{coh}}{d\Omega}(Q)/\langle b^2 \rangle = \sum_{N,C} W_{NC}\, S_{N,C}(Q)$$

more explicitly :

$$S(Q) = \frac{\langle b \rangle^2}{\langle b^2 \rangle} S_{NN}(Q) + \frac{2\,\Delta b\,\langle b \rangle}{\langle b^2 \rangle} S_{NC}(Q) + \frac{c_T\, c_{Al}(\Delta b)^2}{\langle b^2 \rangle} S_{CC}(Q) \qquad (1)$$

where $\langle b \rangle = \sum_{i=T,Al} c_i\, b_i$, $\langle b^2 \rangle = \sum_{i=T,Al} c_i\, b_i^2$ and $\Delta b = b_T - b_{Al}$ (T = Mn, σ-FeCr) c_T and

b_T are the average atomic concentration and the average coherent scattering length of transition metal atoms ; c_{Al} and b_{A1}, for Al atoms.

$$I(Q) = \left[\frac{d\sigma_{coh}}{d\Omega}(Q) - (\langle b^2 \rangle - \langle b \rangle^2) \right]/\langle b \rangle^2 = \sum_{ij=T,Al} W_{ij}\, I_{ij}(Q)$$

$$I(Q) = \frac{c_T^2\, b_T^2}{\langle b \rangle^2} I_{TT}(Q) + \frac{c_{Al}^2\, b_{Al}^2}{\langle b \rangle^2} I_{AlAl}(Q) + \frac{2\, c_T\, c_{Al}\, b_T\, b_{Al}}{\langle b \rangle^2} I_{TAl}(Q) \qquad (2)$$

S (Q) and I (Q) are two definitions of the total structure factor. In the following we will use preferentially the function $S(Q)$ which remains defined even for a zero alloy (i.e., when $\langle b \rangle = 0$). For a liquid mixture, in the long wavelength (Q - 0) limit, the number-concentration structure factors $S_{N,C}(Q)$ are related to the thermodynamic quantities following statistical mechanics [6] :

$$S_{NN}(0) = \rho k_B TK_T + \delta^2 c_T c_{Al} S_{CC}(0)$$
$$S_{NC}(0) = - c_T c_{Al} \delta S_{CC}(0) \tag{3}$$
$$S_{CC}(0) = \mathcal{N} k_B T / c_T c_{Al} \left(\frac{\partial^2 G}{\partial c_T^2} \right)_{T,P}$$

where p is the atomic number density, K_T the isothermal compressibility, G the Gibbs free energy per mole, k_B the Boltzmann constant, N the Avogadro number and δ is a dilatation factor defined by :

$$\delta = \frac{1}{V} \left(\frac{\partial V}{\partial c_T} \right)_{T,P},$$ V being the molar volume of the mixture.

From relations (1) and (3), the limit at $Q = 0$ of the total structure factor is given by :

$$S(0) = \frac{\langle b \rangle^2}{\langle b^2 \rangle} \rho k_B TK_T + \frac{(\langle b \rangle \, \delta - \Delta b)^2}{\langle b^2 \rangle} c_T c_{Al} S_{CC}(0) . \tag{4}$$

Using the linear relations between $I_{ij}(Q)$ and $S_{N, C}(Q)$ established by Bhatia and Thornton [6], the long wavelength limits of the Faber-Ziman PSFS are defined by :

$$I_{TT}(0) = \phi - c_{Al}/c_T + c_{Al} c_T S_{CC}(0) \times (\delta - 1/c_T)^2$$
$$I_{AlAl}(0) = \phi - c_T/c_{Al} + c_{Al} c_T S_{CC}(0) \times (\delta + 1/c_{Al})^2$$
$$I_{TAl}(0) = \phi + 1 + c_{Al} c_T S_{CC}(0) \times (\delta - 1/c_T)(\delta + 1/c_{Al}) \tag{5}$$

where ϕ is the product $p^k{}_B TK_T$.

The paper is arranged as follows : in section 2, the characteristics of the pseudo-binary liquid alloys (x, b_T) will be given, then the experimental and data analysis will be detailed. Particular attention will be paid to the determination of the long wavelength limit of $S(Q)$ which allows us to estimate the magnetic moment of transition metal atoms and the paramagnetic scattering correction. In section 3, the total structure factors, the Faber-Ziman and Bhatia-Thornton PSFs will be presented as well as their respective Fourier transforms. Finally, in section 4 given the average interactomic distances and partial coordination numbers, a comparison between the local orders in the liquid, quasicrystalline and crystalline phases will be attempted.

Experimental Technique and Data Analysis

Four cylindrical samples of $Al_{80} (Mn_x (FeCr)_{1-x})_{20}$ alloys with $x = 1, 0.639, 0.304$ and 0 were prepared, about 5.8 mm in diameter and 65 high. The largest contrast in neutron diffraction is obtained between the $AI_{80}Mn_{20}$ and $Al_{80}(FeCr)_{20}$ alloys ; the coherent scattering lengths of Mn atoms and the (FeCr) mixture which are of opposite signs are equal to $- 0.373 \times 10^{-12}$ cm and 0.659×10^{-12} cm, respectively. For $x = 0.639$, the alloy is characterized by an average transition metal atom coherent scattering length (noted b_T) which is equal to zero ; therefore the measurement of its structure factor yields directly the partial structure function 1_{A1A1} (see Eq. (2)).

The composition of the fourth alloy (x = 0.304) was chosen so that bT became equal to the coherent scattering length of Al atoms, giving directly the number structure factor S_{NN} (see Eq. (1)).

For these four studied alloys, the contributions of the partial function S_N, $C(Q)$ or $I_{ij}(q)$ to the total structure factors are given by the weights W_{NC} or W_{ij} listed in table I.

Table I. - Weights of the partial functions defined in equations (1) and (2). (T = Mn, σ-FeCr).

Alloy	W_{NN}	W_{NC}	W_{CC}	W_{TT}	W_{TAl}	W_{AlAl}
$Al_{80}Mn_{20}$	0.33	− 2.35	0.67	0.137	− 1.015	1.878
$Al_{80}(Mn_{0.639}(FeCr)_{0.361})_{20}$	0.8	− 2	0.2	0	0	1
$Al_{80}(Mn_{0.304}(FeCr)_{0.696})_{20}$	1	0	0	0.04	0.32	0.64
$Al_{80}(FeCr)_{20}$	0.913	1.407	0.087	0.104	0.437	0.458

The atomic density of the liquid $Al_{80}(Mn_x(FeCr)_{1-x})_{2O}$ alloys was estimated as 0.058 at/$Â^3$ from the density measurements of liquid AlCr and AlFe [8].

Conclusion

The results presented in this Perspective demonstrate that, by matching carefully designed experiments with suitable neutron diffraction instrumentation, it is possible to use NDIS to probe the detailed structure of liquids and glasses on multiple length scales. Moreover, it is now possible to apply the NDIS method even when the samples are small, as in high-pressure Paris-Edinburgh press experiments and in high-temperature aerodynamic-levitation experiments, or when the neutron scattering length contrast is small, as in experiments on water using oxygen isotope substitution. The different length scales that were discussed are associated with e.g. (i) intermediate versus extended-range ordering in network glass-forming systems, where there is a competition that affects the relative fragility of a material; (ii) changes in the local structural motifs on vitrification in the fragile glass-former $CaAl_2O_4$, which are accompanied by the development of extended branched-chains of Ca-centred polyhedra; and (iii) intra-molecular versus inter-molecular ordering in liquid water, where there is a competition between the associated quantum effects. The results obtained from carefully performed NDIS experiments play an important role in helping to assess e.g. the accuracy of various theoretical schemes that are employed to make atomistic models for different classes of disordered materials. This is illustrated by (i) first-principles investigations of liquid and glassy chalcogenide materials at ambient pressure, where the progression from use in self-consistent calculations of the local density approximation (LDA) to a generalised gradient approximation using the Becke–Lee–Yang–Parr (BLYP) functional to describe the electron exchange and correlation, has led to models that are in better agreement with the NDIS and other experimental results; (ii) classical molecular dynamics simulations of network-forming oxide glasses, where the

parameterisation of a polarisable ion model for GeO_2 using *ab initio* results has led to transferrable potentials that can be used to accurately predict, for the first time, the material properties under high-pressure conditions; and (iii) path integral molecular dynamics investigations of liquid water, where flexible anharmonic models best account for the measured difference between the intra-molecular O–H and O–D bond distances in light and heavy water, thus giving support to the hypothesis of competing intra-molecular *versus* inter-molecular quantum effects. Once the correct theoretical scheme has been established, these simulations can be used to enrich the information about a material that can be extracted, and they can also be used to predict the changes in material properties that occur when *e.g.* new chemical species are added or the state conditions are varied.

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