Anomalous dispersion neutron diffraction and its potential role in the elucidation of structure in glasses

VIEWPOINT

Anomalous dispersion neutron diffraction and its potential role in the elucidation of structure in glasses

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Abstract
The anomalous dispersion neutron diffraction method is briefly discussed in the context of structure elucidation in glasses. The method represents a novel contrast technique that might be applied more generally provided suitable isotopes with accessible and isolated absorption resonances are available.

Determining the structure of glasses represents a challenging problem in structural science. Unlike crystalline solids, where long-range order of the periodic lattice can be probed by standard diffraction methods, in amorphous solids the lack of periodicity necessitates a different approach to elucidation of the structure. In both types of solids powder diffraction represents a powerful technique, but data analysis differs significantly between the two. The powder diffraction patterns of crystalline solids are characterized by sharp Bragg peaks that can usually be modelled by Rietveld analysis yielding the asymmetric unit of the crystal structure. In contrast, the diffraction patterns of glasses exhibit broad diffuse features, and lack the detail and intensity of crystalline patterns. While the lack of periodicity in amorphous solids means that directional information on interatomic vectors is lost in their diffraction patterns, their magnitude is not and this information can be accessed in the form of a total correlation function via Fourier transformation. Analysis of these data is complicated by the fact that the total correlation function is a summation over all atoms and as such contains overlapping pair correlations, the number of which increases with radial distance. This means that analysis is often limited to relatively short-range correlations typically below 3–4 Å. Analysis is often aided by results from element-specific techniques such as EXAFS, XANES and solid state NMR, while vibrational spectroscopy can allow for interpretation of bonding interactions in the glass framework.

Deconvolution of medium- to long-range pair correlations in total correlation functions is key to an improved understanding of structure/property relationships in glasses and is particularly important in optoelectronic glasses, where metal–metal distances influence the optical and electronic properties. Since the total correlation function is a sum of individual

partial correlations it is possible, using suitable contrast experiments and subsequent first-order difference methods, to extract individual partial correlation functions. A number of interesting approaches have been used in this context. For example, a combination of x-ray and neutron diffraction methods involving reverse Monte Carlo simulation has been used successfully to resolve short- and medium-range correlations in divalent metal phosphate glasses [1]. Similarly, molecular dynamics simulations have also been employed to this end in Tb phosphate glasses [2]. Where appropriate, isotopic substitution can also be used to increase contrast [3]. A recent novel approach is that of magnetic difference neutron diffraction, where differences in the diffraction patterns with and without an external applied field yield a correlation pattern exclusively associated with metal–metal correlations [4].

Hot on the heels of the magnetic difference method is another novel contrast method, this time applied to Sm phosphates [5]. The anomalous neutron dispersion method exploits wavelength-dependent variations in the neutron scattering length of particular isotopes at an absorption resonance to provide contrast. The beauty of this method is that through generation of difference correlation functions not only can the metal–metal pair correlations be separated, but in addition all other correlations involving the metal can be obtained separately. While this work focuses on Sm phosphate glasses, its impact lies in the field of amorphous solids as a whole. The method described takes advantage of the 14% natural abundance of ^{149}Sm, its large neutron absorption cross-section, and in particular the accessibility of a suitable isolated absorption resonance within the wavelength range of the diffractometer. However, in principle, similar experiments could be performed on isotopes of other elements, provided their absorption resonances are within the operational range of the diffractometer. Indeed, the range of neutron wavelengths available is already quite large on reactor source instruments such as D4 at ILL, as well as time-of-flight instruments such as GEM at ISIS. This situation should be further improved with proposed instruments such as NIMROD on TS2 at ISIS.

In addition, the similarity of structural chemistry in rare earth phosphate glasses [6] means that distance correlations extracted for partial structure factor calculations on Sm could serve as initial values in the analysis of total correlation data from analogous systems involving other lanthanides. These could proceed using the isomorphic substitution method, which is based on the assumption that diffraction patterns in compositional analogues differ only in the coherent neutron scattering length of the modifying cations and have been used successfully in analysing Dy and Ho phosphates as well as La and Ce phosphates [7].

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