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Magnetic differences on GEM – direct observation of closest R...R approach in rare-earth phosphate glasses

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Rare-earth (R) phosphate glasses have shown great promise in the laser and optoelectronics industry. Their structure plays an important role in their physical characteristics, with the R...R closest approach affecting their optical and magnetic properties. A novel characterisation method for amorphous materials which makes use of magnetic field effects has enabled the first direct experimental evidence of nearest-neighbour R...R separation in these materials.

The optical applications of rare earth phosphate glasses with compositions in the metaphosphate-ultraphosphate region $(R_2O_3)_{0.25}(P_2O_5)_{0.75}$ - $(R_2O_3)_{0.166}(P_2O_5)_{0.833}$ are made possible by two effects: the rare-earth ions possess the required energy levels for achieving successful population inversion; and the non-linear refractive index is large enough to exhibit the desired optical effects without causing beam breakup and damage. The glasses' physical properties are heavily influenced by the atomic structure. In particular, knowledge of the closest R...R approach in these materials is very desirable since too close a separation impairs their optical and magnetic properties.

Conventional x-ray and neutron diffraction, EXAFS, XANES and solid-state NMR have, in combination, been used to piece together the local structure of these materials out to an interatomic distance, r , of about 4 Å (see fig. 1). Beyond this limit, no further structural information can be obtained directly using these standard characterisation techniques, owing to (i) increasing numbers of overlapping pair-wise correlations in conventional diffraction, making it impossible to

Fig. 1
A model of rare-earth meta-phosphate glass. Green, red, and purple circles represent the rare-earth, oxygen and phosphorus atoms, respectively (distances in Å).

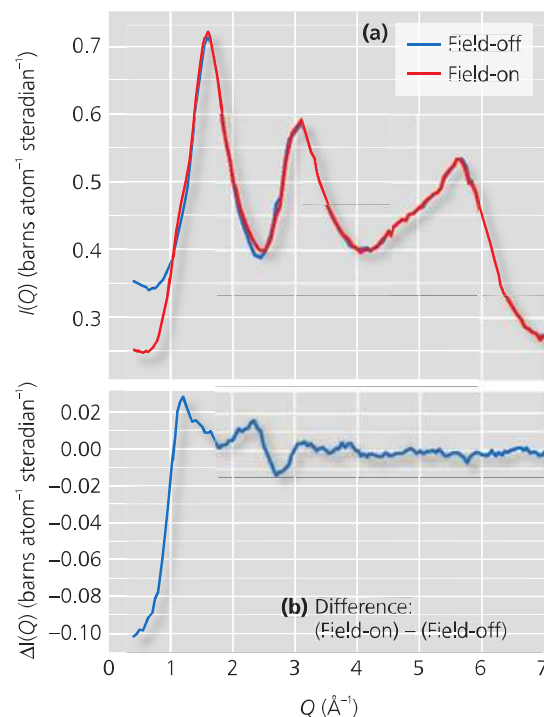
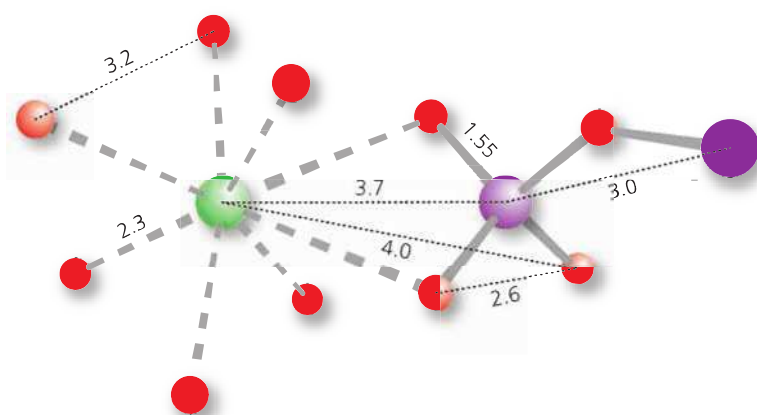


Fig. 2
a) The diffraction pattern with and without the applied magnetic field, **b)** the difference between the field-off and field-on data.

deconvolute individual correlations; (ii) a progressively damped signal, and obscuring multiple scattering effects in EXAFS; (iii) the inherent short-range J - J coupling effects in NMR, and heavily broadened signal due to the paramagnetic nature of rare-earth ions. The all-important nearest-neighbour R...R separation lies beyond 4 Å, and therefore remains elusive by conventional structural probes.

The first such information has now been obtained by means of a magnetic difference neutron diffraction experiment on GEM. The experiment relies on the intrinsic paramagnetism of the rare-earth ions, such that a large magnetic field, applied to a He-cooled sample, yields an increase in the sample magnetisation. There is thus an increase in the degree of alignment of the moments of the magnetic ions in the sample. Or, in other words, there is an increase in the correlations between the directions of the moments of the magnetic ions,

and this is apparent as an enhancement of the contribution to the diffraction pattern arising from the interference between the scattering from the magnetic ions. Neutron diffraction data on the sample were recorded with and without an applied magnetic field, so that the difference of the two datasets isolates the magnetically-induced perturbation of the R...R contribution to the scattering. The Fourier transform of this difference then yields a signal corresponding exclusively to R...R correlations in real space, as required.

This is the first time that the application of a magnetic field to an amorphous material has been used in order to isolate a specific interatomic correlation. This is primarily because it is an intrinsically low-contrast difference experiment - the weak and wholly diffuse scattering of an amorphous material (often comparable to background level), combined with the four-fold increase in required statistics when generating difference data, means that there are few neutron diffractometers worldwide that could cope with the experimental demands of such an experiment.

GEM was used to collect data on a glass sample, $(\text{Tb}_2\text{O}_3)_{0.246}(\text{P}_2\text{O}_5)_{0.722}(\text{Al}_2\text{O}_3)_{0.032}$, cooled to 4 K, first without an external magnetic field applied and then with a field of 4 Tesla. The difference between the two interference functions, $\Delta(Q)$, 'field on - field off', was subsequently calculated for data from each detector bank and showed a characteristic oscillatory structural signature. Fig. 2 shows the magnetic difference obtained by combining data from the different detector banks. The numbers on the vertical axis indicate the small size of the effect, which is roughly 1% of the total signal from the sample. Fig. 3 shows the Fourier transform of the magnetic difference, which yields a real-space correlation function, the peaks of which represent frequently occurring distances between two rare earth ions. The magnetic difference has its first peak at about 6.2 Å and this corresponds to the shortest Tb...Tb distance in the glass. The negative linear region at shorter distances than the first peak arises from the absence of shorter Tb...Tb distances.

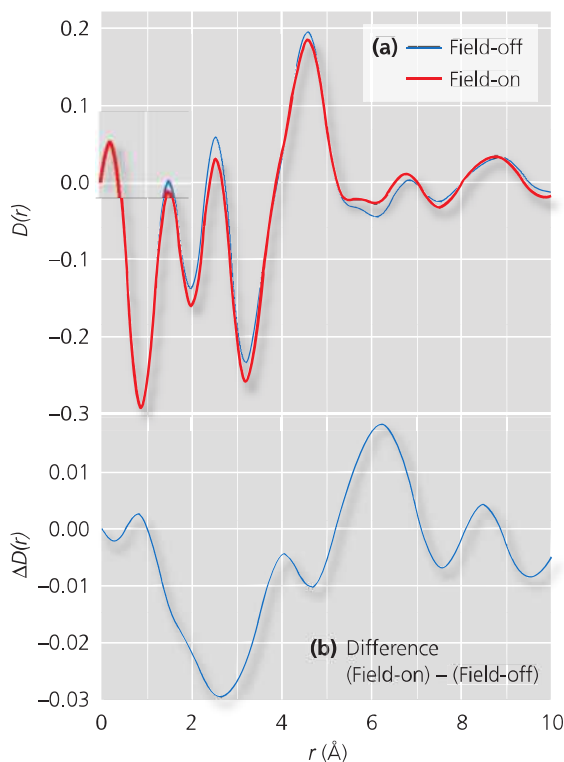


Fig. 3
a) The correlation function with and without the applied magnetic field,
b) the difference correlation function.

The magnetic difference technique is element-specific, with only the Tb^{3+} ions making any contribution, and hence the peak at about 6.2 Å may be reliably assigned to the closest average approach of Tb^{3+} ions to each other. This Tb...Tb distance is similar to a value recently deduced by an 'isomorphous' comparison of diffraction data for glasses containing different rare earth ions. An average Tb...Tb separation of 6.2 Å corresponds to a homogeneous distribution of Tb^{3+} ions in these glasses, as calculated purely from density and stoichiometric grounds. Together with the observation that there are no close Tb...Tb correlations, this indicates that there is no clustering of the ions in the material, which has important implications for laser and optoelectronic applications.

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Further reading: J.M Cole et al, *Journal of Physics: Condensed Matter* 11 (1999) 9165