Anharmonic phonons and negative thermal expansion in ScF$_3$ and Ag$_2$O

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We report progress towards understanding how phonon anharmonicity contributes to negative thermal expansion (NTE). Some contribution to the NTE is from "quasiharmonic" behavior, where phonon frequencies decrease as a crystal expands. A second "anharmonic" effect from phonon-phonon interactions is sometimes calculated by perturbation theory, but sometimes the anharmonic effects are too large to be treated as perturbations. Both ScF$_3$ and Ag$_2$O, which exhibit large NTE, have some highly anharmonic phonons.

Inelastic neutron scattering experiments were used to study the temperature dependence of the phonon densities of states (DOS) of ScF$_3$ from 7 to 750 K. The measured phonon DOS showed a large thermal stiffening of modes around 25 meV, which is the energy of quartic phonons. (A thermal stiffening of quartic modes is expected from the unequal level spacings of the quartic oscillator.) The large transverse displacements of the F atoms in the quartic modes are responsible for much of the NTE of cubic ScF$_3$.

The material Ag$_2$O shows similar behavior, with anomalous stiffening of some phonon modes, but a large softening of others. The temperature dependence of the phonons was calculated by ab-initio molecular dynamics, which includes anharmonic behavior. It was possible to calculate accurately the NTE, which is partly from quasiharmonicity and partly from quartic anharmonicity. The calculations predicted the thermal shifts of phonons measured by infrared spectrometry. Neutron scattering experiments on Ag$_2$O are scheduled for ARCS at the end of February.

(invited) Jahn-Teller transition and orbital disorder in LaMnO$_3$

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Lanthanum manganate, LaMnO$_3$, occupies a special role in the field of strongly-correlated oxides not least because it is the parent compound of the colossal magnetoresistance (CMR) family La$_{x}$Ca$_{1-x}$MnO$_3$ [1]. The delicate balance in these systems amongst orbital, spin, and lattice degrees of freedom gives rise to a series of phases harbouring unusual physics. This is true even for the LaMnO$_3$ end-member itself, which exists in a poorly-understood orbital-disordered phase at temperatures between 735 and 1010 K [2]. On doping with Ca, it is from this disordered phase that CMR emerges and hence a rigorous microscopic description of this state has a number of important ramifications.

Total scattering measurements are an ideal tool with which to probe structural correlations in disordered materials such as LaMnO$_3$ [3], and indeed a series of earlier neutron total scattering measurements have played a crucial role in developing our collective understanding of structural distortions in this system [4,5]. The focus in these earlier studies has been primarily on characterising Mn–O bond length distributions, which are sensitive to the presence of local Jahn-Teller distortions but which do not yield a microscopic picture of longer-range orbital correlations.

We have recently used a series of neutron and X-ray total scattering measurements, analysed using reverse Monte Carlo refinement, to derive nanoscale atomistic models of LaMnO$_3$ at a range of temperatures that span the emergence and eventual disappearance of the orbital disorder. Here we present the results of that analysis,
providing evidence that the disordering process involves a change in type of Jahn-Teller distortion to a state that includes Mn off-centering. Our results are discussed in the context of previous studies sensitive to local distortions, including neutron total scattering, EXAFS, and dielectric measurements.


Polymorphism, drugs and neutrons: Is making more stable phases really that simple?
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Controlling polymorphism in pharmaceutical drugs is a long-standing challenge in formulation science. A well-known example is paracetamol, C$_8$H$_9$NO$_2$, a representative of an active pharmaceutical ingredient composed of aromatic polyfunctional molecules with characteristic proton donor-receptor pairs.

The marketed phase I crystallises in the monoclinic space group P2$_1$/a with corrugated molecular layers that do not slip easily over each other. In contrast, the orthorhombic phase II, has planar layers that are compressible.

Despite the high compressibility and bioavailability of phase II, phase I is still the marketed form. For the first time INS measurements for the two crystalline polymorphs measured at 300K at pressures from ambient up to 1 GPa are presented. Under a pressure of ca 400 MPa the form II polymorph, exhibits an unexpected marked shift and dampening of the entire low energy libron manifold.

The results indicate an anisotropic strengthening of the potential surface around the form II backbone and are discussed in relation to the difference of the behaviour of the hydrogen bond environment in each polymorph.

Molecular motion in molecule-based magnetic materials: From molecular machines to multiferroics
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One of the main features of molecular compounds is the possibility of combining different properties giving a multifunctional material. The correct selection of ligands can permit the mobility of a specific part of the system either in the main framework or as guest molecules. Here we will discuss some examples where the motion of these components plays a key role in one of the properties that provide multifunctionality to the material, with neutron scattering being a fundamental tool in the study of both its structure and dynamics.

Spin-crossover compounds are particularly interesting to obtain the mentioned combinations of properties since their molecular bistability can be used to switch a second physical property. The compound Fe(pyrazine)[Pt(CN)$_4$] is one of the most successful examples in this quest for multifunctionality. We will focus in an exciting property of this system: the possibility of switching the rotation of a molecular fragment - the pyrazine rings - when switching the spin state [1].

Motion and order-disorder of molecules can also be used to address the electric behavior, opening new strategies for combining electric order with magnetic properties in the design of multiferroic materials. In this way, the disorder-order of the dimethylamine molecule in the Iron(II)-Iron(III) system [NH$_2$(CH$_3$)$_2$]$_n$[Fe$^{II}$Fe$^{III}$(HCOO)$_6$]$_n$ is in the
origin of the observed electric transition from paraelectric to antiferroelectric. This compound is a Néel N-Type ferrimagnet, thus combining the mentioned electric properties with magnetic order [2].


Fluid-like critical phenomenon on a solid-solid phase transition of β-pyrochlore oxide KOs$_2$O$_6$

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We have carried out the neutron powder diffraction (NPD) experiments on the beta-pyrochlore oxide KOs$_2$O$_6$ under ambient and elevated pressures [1]. This compound has a superconducting transition at $T_c = 9.6$ K and another novel transition at $T_p = 7.6$ K. A characteristic feature of this compound is that the K ions exhibit rattling vibrations in the cages formed by O atoms even at very low temperatures. The NPD data show no peak splitting nor extra peaks over the temperature range between 2 K and 295 K, suggesting that the $T_p$ transition is a rather unusual isomorphic transition. Rietveld analysis revealed an anomalous expansion of the lattice and a deformation of the O atom cage below 7.6 K. In the low-temperature phase, the distribution of scattering density corresponding to the K ions becomes broader whilst maintaining its maximum at the cage center. At elevated pressures, the transition temperature becomes lower and the shape of the transition broader with increasing pressure. Surprisingly, the transition almost disappeared at 80 MPa. The volume change around the transition is quite similar to those in liquid-gas transitions in pressure-temperature planes. We guess that the $T_p$ transition is due to the expansion of the cage volume and condensation of the K ions into the ground state of the rattling motion; the space for rattling motions could be associated with the order parameter of the transition.


Poling behaviour of technical ferroelectrics under electric field

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Neutron diffraction studies on technical ferroelectric ceramics under the influence of electric fields were performed to establish correlations between the macroscopic poling behaviour and corresponding structural changes. Bulk samples of lanthanum doped lead zirconate titanate (PLZT) with compositions around the morphotropic phase boundary were investigated at the high-resolution powder diffractometer SPODI (FRM II). Two set-ups were used with the electric field direction either perpendicular to the scattering plane or within the scattering plane. The first set-up is suitable for conventional Rietveld refinement of structure parameters while the latter configuration allows the analysis of texture and strain effects. Using the “vertical set-up”, systematic changes in the response to the electric field were observed for different compositions. Distributions of atomic displacements in the electric field were reflected by thermal displacement parameters. The data corresponding to the “horizontal set-up” could be analysed by Rietveld refinement using the MAUD software by a two-phase model (space groups P4mm + R3m) including parameters for structure, texture and strain. For a more detailed study of domain switching processes, a commercial actor, based on lead zirconate titanate with a tetragonal symmetry (space group P4mm) was investigated at the materials science diffractometer STRESS-SPEC (FRM II). A robot was used to orient the sample cell to obtain complete pole figures for (111), (002) and (200) reflections as a function of the electric field. A fibre texture could be deduced from the radial symmetries in the pole figures of (002) and (200) reflections.