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Exploring the entropy change in barocaloric ammonium sulfate using QENS and INS

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Ammonium sulfate, a common garden fertiliser, displays a ferroelectric phase transition with a large entropy change whose origins have proved controversial. Understanding this will provide an important insight in to its barocaloric properties, and how these might be developed into future environmentally friendly cooling applications. Here we approach this question using quasielastic, inelastic, and total neutron scattering, as functions of both temperature and pressure, and DFT simulation.

Our QENS results reveal a geometry of hydrogen motion that is inconsistent with the usual simple order-disorder model of configurational entropy. In addition, pressure is unusually found to decrease the barrier to rotation in the low temperature phase, due to the stiff hydrogen bond network being destabilised, increasing the possibility for hydrogen atoms to buckle sideways, which relates to the observed inverse barocaloric effect. Conversely, in the high temperature phase, pressure has little effect, as the denser hydrogen bond network prevents the buckling.

Instead our INS and DFT results indicate that the entropy arises from large-amplitude, anharmonic librations in the high temperature phase. In the low temperature phase the ammonium librational modes, partially identified by their negative mode Gruneisen parameters, are separate from the the other low frequency collective modes, suggesting that the hydrogen bonding holds these ions relatively firmly in place. In addition the librational ammonium motions are able to drag the neighbouring sulfate ions along with them causing the lattice to contract with temperature, giving rise to a region of negative thermal expansion. In the high temperature phase the ammonium ions sit on a new mirror-plane and are more loosely held in place, leading to lower vibrational frequencies that exert less influence over the shape and size of the lattice.

Our combined study suggests that, in the search for molecular materials with large entropy changes, vibrational entropy arising from broad, anharmonic energy minima is likely to be just as important as configurational entropy arising from crystallographic disorder.

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