Magnetism of 2D Thiocyanates

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Molecular framework materials can combine the functional properties typical of the traditional inorganic solid state, such as magnetism, with the remarkable tunability and flexibility that arises from the incorporation of molecular components. They therefore offer the opportunity to discover unusual behaviour that arises from the coupling of these properties.

We have recently shown that thiocyanate (NCS–) based frameworks are a fruitful ground for the study of these novel properties, as thiocyanate can both facilitate strong magnetic coupling (TCW>100K, [1]) and create intense optically absorption in the visible region [2]. Despite this, the rich chemistry of metal thiocyanates remains unexplored compared to the equivalent metal formates, azides or hypophosphites.

Our investigations of the functional properties of metal thiocyanate frameworks began with the simplest examples: the layered binary thiocyanates, M(NCS)2. We demonstrated, through powder neutron diffraction studies, that this M(NCS)2 family possesses a wide variety of interesting magnetic phases. As part of this investigation we synthesised three new binary materials, M = Cu, Mn, Fe; and demonstrated that their magnetic interactions are significantly stronger than the previously studied exemplars (M=Co,Ni) increasing |TCW| by a factor of four.[1] Our results also uncovered that Cu(NCS)2 is a good example of a quasi-1D quantum Heisenberg antiferromagnet which a significantly reduced ordered moment in its ordered state.[3]

We have also investigated the family of CsM(NCS)3 materials which adopt the 'post-perovskite' structure.[4] The post-perovskite structure type is so-called as it occurs at pressures beyond the stability field of conventional perovskites (e.g. MgSiO3, CaIrO3, NaMnF3), but these molecular post-perovskites readily form in standard solution chemistry. We find that this family of materials shows significantly reduced ordering temperatures and adopt non-collinear magnetic structures that give rise to considerable magnetic hysteresis.[5]

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