Personal Statement for the PANalytical Thesis Prize for Physical Crystallography 2012

David Royse, University of Oxford – "High Density Ammonia Storage Materials"

My Thesis, entitled "High Density Ammonia Storage Materials," is a study of the structure and reactivity of metal ammines, and is presented here for consideration in the Physical Crystallography Prize. This work uses of a wide variety of characterisation techniques, including X-ray, single crystal and neutron diffraction, neutron spectroscopy and density functional theory (DFT) modelling, to demonstrate how crystallography, when combined with these complementary techniques, permits us to develop a holistic understanding of the structure and atomic motions of a solid.

The Thesis studies solid-state metal ammines of $LiBH_4$, $MgCl_2$, $MgBr_2$, MgI_2 and $Mg(BH_4)_2$ with reference to their properties as ammonia storage materials. The structures of lithium borohydride ammines, $Li(NH_3)_{1\text{-}4}BH_4$, are solved for the first time using a combination of X-ray and neutron diffraction, vibrational spectroscopy, nuclear magnetic resonance, and first-principles calculations. The bonding of the ammonia molecule and its uptake and release by $LiBH_4$ are investigated by thermogravimetric analysis and vibrational spectroscopy. The ammines of magnesium halides are investigated using X-ray and neutron powder diffraction, thermogravimetric analysis, nuclear magnetic resonance, first-principles calculations and vibrational spectroscopy. The origin of their disordered structures, bonding, and temperatures of decomposition are discussed, and the trends in their properties are used to form a wider understanding of the properties of other ammines. The ammines of magnesium borohydride are investigated by X-ray and neutron powder diffraction, thermogravimetric analysis, first-principles calculations and vibrational spectroscopy. The structure, ammonia uptake and evolution properties of $Mg(NH_3)_6(BH_4)_2$ are determined for the first time.

The use of diffraction techniques is the central theme of this work: the structures of $Li(NH_3)BH_4$ and $Li(NH_3)_2BH_4$ were solved using a combination of high resolution synchrotron X-ray powder and single crystal diffraction data. The higher ammines, $Li(NH_3)_3BH_4$ and $Li(NH_3)_4BH_4$, were synthesised in-situ on the HPRD diffractometer at the ISIS facility, and a combination of simultaneous thermogravimetric and neutron diffraction techniques was used to solve their structures. The molecular dynamics of these materials were identified from inelastic neutron scattering experiments, combined with density functional theory energy minimisations, which themselves were based on electronic structure obtained from the crystallographic structure determined by my previous neutron diffraction experiments. The structure solution and modelling of these disordered systems using Rietveld refinement, followed by geometry optimisation and molecular dynamics calculations, correlated to and by inelastic neutron scattering experiments, provides the answer to the crucial questions of ammine material: how does ammonia reversibly intercalate into the host structure? What are the origins of the barriers to ammonia absorption and desorption? Why does $Li(NH_3)_2BH_4$ have the lowest melting point of the family? How do different numbers of ammonia molecules interact with the host ions? What determines decomposition or reversible ammonia evolution?

This work develops the understanding of these materials and publications arising from it have led to a worldwide increase in the study of lithium borohydride ammines as potential ammonia and hydrogen storage materials. Furthermore, it demonstrates how the combination of physical scattering techniques with computational methods can be used to develop an unparalleled understanding of structure, molecular dynamics and functional properties.