

Solid State Chemistry of Oxides and Nitrides

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Super D2b has been used to investigate the structural chemistry and magnetic behaviour of a number of new compounds that have been synthesised during the course of our research program in solid state chemistry. The modifications made to the instrument have enabled us to record data in less than half the time that would have been required before the upgrade, and have therefore resulted in a greater throughput of samples.

The interplay between nearest-neighbour (NN) and next-nearest-neighbour (NNN) magnetic superexchange interactions in Ruddlesden-Popper (RP) phases has been the focus of much attention recently. The relative strengths of these interactions determines whether the compound shows long-range magnetic order or spin-glass behaviour. In order to study the NNN interaction in isolation we have prepared compounds in which the NN sites around a magnetic cation are occupied by a diamagnetic cation. More specifically, we have prepared RP phases based on a 1:1 ordered arrangement of Ru^{5+} and Li^+ , for example $n = 1$ $\text{La}_2\text{Sr}_2\text{LiRuO}_8$ and $n = 2$ $\text{A}_2\text{BaLiRuO}_7$ ($\text{A} = \text{Nd}, \text{Pr}$). These compounds have been studied by magnetometry, neutron diffraction and electron microscopy in order to elucidate the details of both the cation ordering and the magnetic ordering.

Transition-metal nitrides constitute an interesting area of solid state chemistry and yet, in comparison to mixed-metal oxides, relatively little is known about them. In recent years interstitial *d*-block nitrides have become a focus for our attention. Although a variety of methods may be used to synthesise interstitial nitrides, many require complex precursor materials. The preparation of these precursors is time consuming and, more significantly, the composition of the eventual nitride product is limited by the stoichiometry of the precursor. Our reductive-nitridation method is a facile synthetic route which simply requires the reduction of stoichiometric mixtures of commercially available binary oxides under a nitrogen-containing atmosphere. The method provides an effective route to a wide variety of quaternary Fe-containing nitrides with, for example, the filled β -manganese structure. These compounds have the general formula $\text{M}_2\text{T}_3\text{X}$. Their cubic structure consists of a (10,3)-a network of M atoms interlaced with corner sharing T_6X octahedra. X is commonly boron, carbon or nitrogen. The β -phase of elemental manganese would be written as M_2T_3 in this notation with $\text{M} = \text{T} = \text{Mn}$; atoms of element X are thus considered to be filling an interstitial site in a metal framework. We have investigated the filled β -Mn phases $\text{Fe}_{2-x}\text{M}_x\text{Mo}_3\text{N}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}, \text{Rh}; 0.5 < x < 2$). All the compositions synthesised displayed ferromagnetism and a range of electrical properties was observed across the series. This magnetic behaviour contrasts sharply with that of β -Mn itself, which is the only form of the element not to order magnetically on cooling. This behaviour can in part be attributed to frustration in the crystal structure. No other ferromagnetic β -Mn phases are known. Our intention was to gain further insight into the behaviour of these phases by varying the number of valence electrons associated with the substituent metal, with the ultimate aim of establishing control over the electronic properties of these phases.