Magnetic Pathways – exploring the energy landscape

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Abstract

This study reports the use of computer modelling (particularly using density functional theory) to analyse magnetic interactions within a series of compounds structurally and chemically related to Schafarzikite ($FeSb_2O_4$). This technique has provided further understanding of the complex magnetic order observed in such structures, while also predicting a ferromagnetic derivative for the first time. This prediction has since been shown to be correct through a corresponding experimental study.

1   Introduction

Magnetism is important in many aspects of modern life, from loudspeakers and credit cards through to transformers and medical MRI machines. As such, magnetism is a highly active area of research across many disciplines, as in many cases the underlying physical properties are not entirely understood. The quest for new materials is necessary in order to improve existing technologies, and provide advanced materials for future applications. A prime example of this is computer hard-drives, where the limiting factor in magnetic storage density is the size of individual magnetic domains, and how small they can become without losing data integrity. This limit is gradually approaching, and so new devices must start to use other techniques. Low dimensional materials are one possible solution to the problem; these substances possess structures that give rise to highly directional properties. One
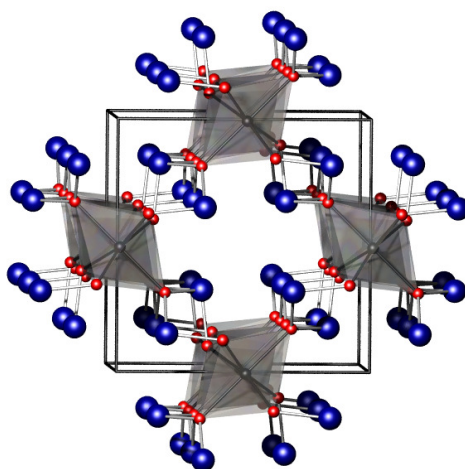

Figure 1: Schafarzikite crystal structure viewed along *c*-axis: Fe – grey octahedra, Sb – blue spheres, O – red spheres.

example would be a one-dimensional (1D) 'wire' for conducting electricity, which would ideally have high conductivity along one crystallographic direction, but low conductivity otherwise. Low dimensional magnetism could be one solution to the hard drive limit, as magnetic domains involving directionality may be able to overcome interference from surrounding magnetic fields, and thus more stable for data recording. Combining these novel magnetic properties with another capability (such as the electrical conductivity mentioned above) could lead to an easy way to control the magnetic ordering over even smaller length scales, and also improve device performance.

Schafarzikite (Figure 1) is a rare mineral with the chemical formula $FeSb_2O_4$. It possesses a crystal structure similar to rutile (TiO_2) of opposite edge-sharing FeO_6 octahedra, but here the dimensionality is reduced (to approximately 1D) due to antimony linkages between these octahedral 'chains'. It is of great chemical interest, however, due to the ability to dope and/or fully substitute some atoms in the structure with other cations such as Mn^{2+}, Co^{2+} and Pb^{4+} (de Laune *et al*, 2012). These dopants have been shown experimentally to lead to fundamental changes in the properties of the materials.

Many of the MSb_2O_4 compounds (M = Mn, Fe, Co, Ni) have been shown to order magnetically at low temperatures (approximately 60 K or -213 °C) but the exact nature of this ordering is critically dependant on the ions present in the structure. The ability to control the magnetic properties through doping is obviously desirable in order to develop specific device properties. In many cases, however, the exact cause of these changes in magnetic behaviour is not fully understood. This study has used density functional theory (DFT) modelling of the bulk electronic structure to evaluate the interactions present between magnetic cations, and further understand the properties. The study has also extended to prediction of the first example of a ferromagnetic Schafarzikite variant, $CuAs_2O_4$. This compound (found naturally as the mineral Trippkeite [Pertlik, 1975]) has since been shown to order ferromagnetically below 8 K, as predicted (Cumby *et al,* 2013).

2   Results

Schafarzikite and its derivatives can adopt a number of different magnetic structures, excluding arrangements involving a magnetic supercell. The differences relate to whether the magnetic moments (represented by green arrows) on a given cation (grey spheres) are aligned in the same direction as the adjacent cations, or opposed. By considering interactions both along a given octahedral chain and between adjacent chains, this gives rise to four possible structures, which are labelled A, C, G and F (Figure 2). For a given chemical composition, one of these magnetic structures (or possibly a combination) will be lowest in energy, and therefore favourable at low temperature. From neutron diffraction experiments, an A-type order is seen for M = Mn and Fe, while a C-type order is seen for M = Co and Ni.

Using DFT (as implemented using the CASTEP package [Clark *et al*, 2005]) we have been able to calculate the relative energies of each of the magnetic structures for a range of cation substitutions, the results of which have agreed well with the experimentally determined structures. Using these energies, it is then possible to compute the strength of the nearest-neighbour magnetic interactions, denoted *J*. These indicate which interaction is most influential for the resulting magnetic structure, and have revealed some surprising results. As expected due to the close proximity of magnetic ions along the chains, the 'direct' coupling (J_1) is most significant, promoting the change from A- to C-type order on varying the transition metals. The calculations reveal that the diagonal coupling between adjacent chains is stronger than expected, however, in some cases to a similar order of magnitude as J_1. This is surprising given the large length-scale over which the interaction occurs (ca. 12 Å, compared with 3 Å

along the chains) and indicates the effective exchange mechanism along the highly covalent $O-Sb-O$ linkages.

The previous result led to the investigation of $CuSb_2O_4$ and $CuAs_2O_4$ as a potential example where this inter-chain coupling was reduced, due to the electronic configuration of Cu^{2+}. Both of these materials show a strongly positive coupling along the chains, but negligible coupling between chains, as desired. The net result of this is that DFT indicates both copper-containing materials to exhibit ferromagnetic behaviour (type-F). Following this result, a synthetic sample of $CuAs_2O_4$ has been shown to be ferromagnetic below 8 K, consistent with the predictions. Currently, synthesis of $CuSb_2O_4$ has proved unsuccessful, and so the prediction cannot be confirmed.
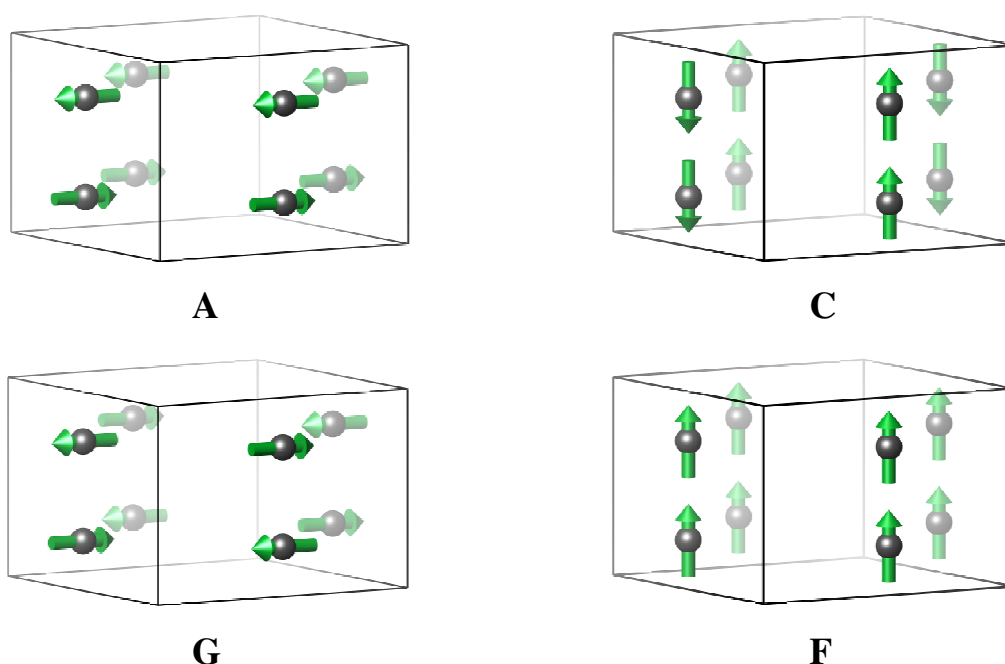

A **C**

G **F**

Figure 2: Magnetic ordering possibilities in Schafarzikite-related materials (only magnetic cations shown)

References

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