

A6 - Neutron Diffraction - Applications**A6 - O1****IONIC DIFFUSION WITHIN SUPERIONIC Ag₃SI****S. Hull¹, D. A. Keen^{1,2}**¹*The ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, United Kingdom*²*Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, United Kingdom*

The structural properties of silver iodide (AgI) and silver sulphide (Ag₂S) have been extensively studied for many years because both compounds undergo superionic transitions at relatively modest temperatures (420K and 452K, respectively). At temperatures immediately above the superionic transition their high conductivity phases are both characterised by rapid jump diffusion of the Ag⁺, predominantly between the tetrahedrally co-ordinated interstices formed by an immobile body centred cubic (b.c.c.) sublattice of anions (I⁻ or S²⁻). The AgI-Ag₂S system contains only a single ternary compound of composition Ag₃SI. By varying the sample preparation procedure it is possible to synthesise this material in two forms, characterised by a disordered (* phase) or ordered (phase) ar-

range of the two cation species over the 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ positions which generate the b.c.c. array. Interestingly, the * phase possesses an ionic conductivity at ambient temperature over two orders of magnitude higher than the form. To understand the factors underlying this observation, powder neutron diffraction experiments (including analysis of the diffuse scattering) and molecular dynamics simulations have been used to probe the relationship between the long-range order within the anion sublattice and the dynamic cation disorder responsible for the macroscopic ionic conductivity. The results of these studies will be presented, together with a brief discussion of their implications for the wider question of ionic mobility within perovskite structured compounds.

A6 - O2**POSSIBILITIES OF NEUTRON POWDER DIFFRACTION FOR STUDY OF MAGNETIC FERROELECTRICS WITH PEROVSKITE STRUCTURE****S. A. Ivanov¹, S.- G. Eriksson², R. Tellgren³, H. Rundlöf³**¹*Karpov' Institute of Physical Chemistry, Moscow, Russia*²*Department of Inorganic Chemistry, University of Gothenburg, Sweden*³*Institute of Chemistry, Uppsala University, Uppsala, Sweden*

The interesting and frequently unexpected combination of physical properties of complex metal oxide with perovskite structure is very sensitive to even small structural changes and an understanding of the crystal chemistry of these compounds is crucial in the development of novel materials with an unusual combination of dielectric and magnetic properties. Although many perovskites have been investigated in recent years, structural information about A(B_{2/3}C_{1/3})O₃ materials remains scarce and from a structural point of view still many points remain unclear.

In this study, we have paid attention to 1:2 ordered perovskites, and will report the temperature evolution of their nuclear and magnetic structures. NPD studies have been carried out to study the magnetically ordered ferroelectric materials with perovskite-related structure A₃Fe₂BO₉ (A = Pb, Sr, Ca, Ba; B = W, Te), prepared by a solid state route. This class of so-called ferroelectric magnets exhibits both electric-dipole and magnetic ordering within a definite temperature range.

NPD patterns have been collected at the Swedish Research Reactor R2 (Studsvik) at different temperatures in the range 10 to 1000 K. The high-temperature data were used to determine the structure in the nonpolar and non-magnetic states, the exact stoichiometry and the cation site order. The data were analyzed with the FULLPROF software in order to characterize the temperature-induced phase transformations, and to determine the nuclear and magnetic structures. By replacing Pb by Sr, Ba or Ca the different types of lattice distortions of the initial cubic perovskite cell was found (tetragonal for Sr, hexagonal for Ba and monoclinic for Ca compounds). The size of the involved A-type cation is directly related to different types of structural distortions and B-site order/disorder. The structural peculiarities of distorted phases are discussed and possible mechanisms of phase transitions are presented.

It was found that for the Pb compound the Fe and W(Te) cations are randomly distributed over the B sites while in the case of Sr and Ca compounds a partial crystal-



lographic order was established. T_C values appear to depend mainly on the nature of the A-cation (ion size and electronic configuration) and degree of cation ordering of Fe/W(Te).

The ordering of magnetic moments of Fe in these systems are analyzed. And all the compounds show G-type magnetic structure. Magnetic properties would be more sensitive to the content of W cations in comparison with Te ones. The correlation between ferroic distortions and the magnetic ordering is also briefly discussed.

Effect of oxygen nonstoichiometry on structural and magnetic properties was studied in the Ba compound. It

was found that both the lattice distortion and physical properties are strongly influenced by the oxygen content.

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A6 - O3

CRYSTAL AND MAGNETIC STRUCTURES OF SELECTED STRONGLY CORRELATED ELECTRON SYSTEMS

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Recent advances in diffraction instrumentation at the ILL (construction of Super D2b) have allowed the collection of high-quality data even on small samples which adopt complex disordered structures. In this presentation, I will discuss some of our recent structural and magnetic work on strongly correlated electron systems, which include: (i) the structural and magnetic characterisation of switchable systems exhibiting multistability, e.g. the family of mixed valence transition metal cyanides (Prussian blue analogues), (ii) the structural characterisation of intermediate valence rare-earth systems exhibiting zero- or negative- thermal ex-

pansion, driven by electronic instabilities, and (iii) the origin of the anomalous magnetic behaviour of the antiferromagnetic insulators $(\text{NH}_3)\text{K}_{3-x}\text{Rb}_x\text{C}_{60}$ ($x = 0-3$) where TN first increases with lattice expansion and then swiftly decreases, in sharp contrast to what is expected for simple localised moment models (a smooth decrease in the exchange interaction, J and TN with increasing lattice constant). Complementary information obtained from synchrotron X-ray powder diffraction measurements are utilized throughout.

A6 - O4

FRUSTRATED ANTIFERROMAGNETIC INTERACTIONS IN THE NEW, -Mn RELATED, COMPOUNDS Mn_3IrGe AND Mn_3CoSi

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Two new compounds, Mn_3IrGe and Mn_3CoSi , have been synthesised. Both order magnetically at low temperatures, but although they are isostructural, the magnetic structures are completely different. The observation of magnetic order is very interesting, since the compounds have a crystal structure similar to that of -manganese [1]. The -Mn phase has been the focus of much attention, since it does not order magnetically. This is suggested to be an effect of geometric frustration of antiferromagnetic interactions on a triangular network of Mn atoms (a 3D analogue of the 2D kagomé net) [2]. However, the same triangular Mn network exists in Mn_3IrGe and Mn_3CoSi , and our results therefore shed new light on the understanding of -Mn.

The crystal structure of Mn_3IrGe and Mn_3CoSi is of the AlAu_4 -type [3], an ordered form of the -manganese structure. The compounds are thus isostructural with the re-

cently reported phase Mn_3IrSi [4]. Structure refinements by the Rietveld method, using the program FULLPROF [5], for neutron powder diffraction data collected at room temperature, gave the final agreement factors $R_{\text{profile}} = 4.23\%$, $R_{\text{Bragg}} = 4.04\%$ for Mn_3IrGe and $R_{\text{profile}} = 3.56\%$, $R_{\text{Bragg}} = 5.84\%$ for Mn_3CoSi .

Powder neutron diffraction results show noncollinear antiferromagnetic order for Mn_3IrGe at temperatures below 225 K, with a magnetic unit cell of the same size as the crystallographic cell. Structure refinements by the Rietveld method gave the final agreement factors $R_{\text{profile}} = 4.74\%$, $R_{\text{Bragg}} = 5.54\%$, $R_{\text{magnetic}} = 5.55\%$, for data collected at 10 K, with the magnetic moment $3.39(4) \mu_B$ on Mn. The magnetic structure is very similar to what was previously reported for Mn_3IrSi [4].

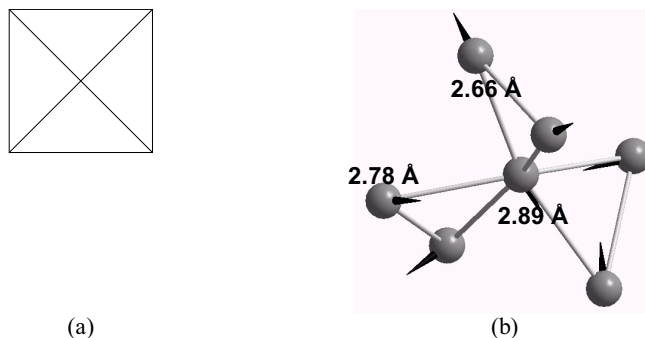


Fig. 1. (a) The crystal structure of Mn_3IrGe , with the network of corner linked triangles (shaded) of near neighbour Mn atoms. One Mn atom outside the unit cell (smaller) is added for clarity. (b) The orientations of the magnetic moments on a unit of three corner linked Mn triangles. Interatomic distances at 10 K are indicated.

In the crystal structure, the near neighbour Mn atoms are found on a network of corner linked triangles, where each corner (=Mn atom) is shared between three triangles, see Fig. 1a. The magnetic moments on Mn are oriented so that their projections onto the triangle planes have 120-degree angles between them, see Fig. 1b. In accord with the argument in Ref. 4, we suggest this to be the result of geometrically frustrated antiferromagnetic interactions.

A complete range of solid solubility exists for $\text{Mn}_3\text{IrSi}_{1-x}\text{Ge}_x$, as demonstrated by a linear variation of the unit cell parameter (obtained from powder x-ray diffraction films, recorded by a Guinier-Hägg camera). The magnetic susceptibility, measured by SQUID-magnetometry, is weakly temperature dependent, and the antiferromagnetic transition temperature, 225 ± 10 K, does not show any large variation with the silicon content for the solid solution $\text{Mn}_3\text{IrSi}_{1-x}\text{Ge}_x$, see Fig. 2. This could be explained by suppression of the transition temperature, caused by geometric frustration of strong antiferromagnetic interactions on the triangular network of Mn atoms.

Measurements of the magnetic susceptibility vs. temperature for Mn_3CoSi show a maximum at 110 K, indicating an antiferromagnetic transition. In contrast to the

magnetic structures of Mn_3IrGe and Mn_3IrSi , low temperature neutron powder diffraction patterns for the isostructural compound Mn_3CoSi show satellite peaks characteristic of an incommensurate magnetic structure. The transition from commensurate magnetic order in Mn_3IrSi to incommensurate order in Mn_3CoSi is currently under study for the solid solution $\text{Mn}_3\text{Ir}_{1-x}\text{Co}_x\text{Si}$. Interestingly, by a suitable choice of x , a compound with the same cell parameter as -Mn can be produced, which may provide some insight into the governing parameters behind the observed lack of magnetic order in -Mn .

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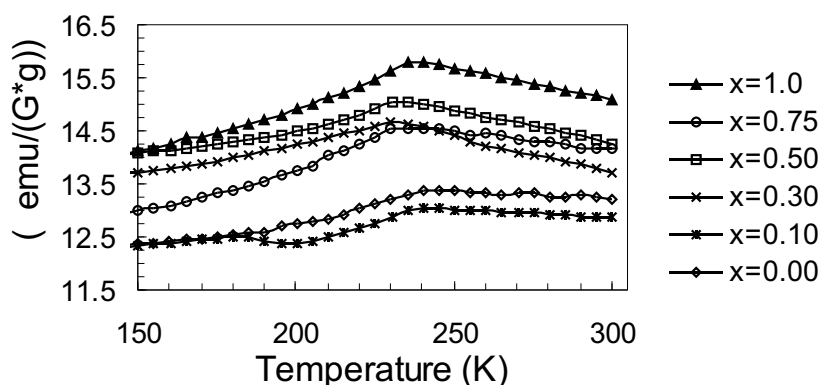


Fig. 2. Magnetic susceptibility (χ) vs. temperature for the substitution series $\text{Mn}_3\text{IrSi}_{1-x}\text{Ge}_x$ ($x = 0.00; 0.10; 0.30; 0.50; 0.75; 1.0$), measured in an applied field of 250 Oe.