Dr Vincent Hardy: a Visiting Fellowship (GR/R94299/01)

1. Introduction

We received funding to support the visit of Dr. Vincent Hardy to the Physics Department here at the University of Warwick. Dr. Hardy worked in the Department for 12 months from September 2002. He was based in the laboratories of the Superconductivity and Magnetism Group and worked with the research staff in this group.

2. Dr Vincent Hardy

Dr. Vincent Hardy is a full time research scientist working for the Centre National de la Recherche Scientifique (CNRS), France's leading national research organisation. He has been employed by the CNRS since 1992 and is based in the CRISMAT laboratory in Caen, France.

Dr. Hardy is an experimentalist who has worked in many areas of oxide physics. He has studied the properties of several high T_C superconductors as well as various aspects of the manganese oxides including colossal magneto-resistance and magneto-electronic phase separation. He is also interested in the physical properties of materials containing 3d or 4f elements.

Before coming to Warwick, Dr Hardy had used a range of experimental techniques including measurements of magnetisation, ac susceptibility, magneto-transport and specific heat. His expertise and research interests overlapped considerably with ours and he was familiar with much of the equipment available within our group.

3. Warwick University: the host institution

3.1 The Superconductivity and Magnetism Group

The work supported by this grant was carried out within the Superconductivity and Magnetism Group of the Physics Department here at the University of Warwick. The group has four permanent members of staff. During Dr Hardy's stay, we also had 2 postdoctoral fellows and 1 Ph.D. student funded by the EPSRC. The group has a wide range of interests centred on the properties of strongly correlated systems. It has three core activities: (1) single crystal growth and sample preparation (2) neutron scattering studies and (3) measurements of magnetic, transport and thermodynamic properties.

3.2 Single crystal growth and sample preparation

We have an EPSRC funded single crystal growth programme **(GR/M33327)**. We grow high quality single crystals of many different types of materials including superconductors, frustrated and 1D magnets and the colossal magnetoresistance manganites. We have several types of systems available for sample preparation and single crystal growth; materials are prepared using a wide range of growth techniques. All the samples used in this work were prepared at Warwick or in Caen (see sections 4.2.2 and 4.3.2).

3.3 Neutron scattering

The Superconductivity and Magnetism Group uses a wide range of neutron techniques including elastic and inelastic scattering measurements at both continuous and pulsed neutron sources. Our neutron scattering work has included studies of frustrated and low dimensional magnetism and investigations of the structural and magnetic properties of 3d oxide systems. Although neutron scattering and μSR studies were not the main focus of this work, several proposals for beam time have been made as a result of these studies (see section 4.2.6).

3.4 Measurement Laboratories

Our laboratories are well equipped for the study of magnetic materials. We have a 12T vibrating sample magnetometer (VSM) which can operate between 1.5 and 1000K and a 5T SQUID magnetometer (1.8-400K).

We have recently acquired a Quantum Design **P**hysical **P**roperties **M**easurement **S**ystem (QD PPMS) that is capable of making heat capacity measurements between 350mK and 400K in magnetic fields of up to 9T. The machine was funded by the EPSRC through the 2000 JREI **(GR/R06540)** and was set up as multi-user facility for research workers based here at Warwick and at other HEI's within the UK. Dr. Hardy has considerable experience of using this commercial system. His insight into how best to operate this system has proved to be invaluable during the early phase of operation of this apparatus. His guidance with data manipulation and analysis has allowed us to maximise the effectiveness and productivity of this new piece of apparatus in all our research programmes and to ensure that the investment made by the EPSRC reaches its full potential.

4. Research Programme

4.1 Introduction

In the following we describe the research work carried out by Dr Hardy during his visit. The research programme was built around heat capacity measurements made using our PPMS system. Complementary measurements of the magnetic properties of samples were made using our SQUID and vibrating sample magnetometers.

The work was carried out in the laboratories of the Superconductivity and Magnetism Group here at Warwick University. Dr Hardy worked alongside the full time academics, postdocs. and students associated with this group including Dr Subham Majumdar (EPSRC funded post doc.) and Sonya Crowe (EPSRC funded Ph.D. student). His work fitted in well with our current research programmes. He also made a useful contribution to the final year projects of two undergraduate students.

Dr Hardy began his stay by investigating the properties of $Ca_3Co_2O_6$ and some related materials. In the second half of the year, we began a programme comparing the magnetic transitions in some manganite materials with those seen in Gd_4Ge_5 intermetallics.

4.2 $Ca_3Co_2O_6$: A peculiar 1D magnetic compound

4.2.1 Introduction and previous work

Cobalt oxides form a large family of compounds with fascinating structural and physical properties. The different possible oxidation states of cobalt, together with its various spin configurations are responsible for numerous original phenomena such as giant magnetoresistance in $La_{1-x}Sr_xCoO_3$ and the insulator-metal transition in the oxygen deficient perovskites $LnBaCo_2O_{5.5}$.

Among these cobalt oxides, the compound $Ca_3Co_2O_6$ presents two additional features well-known to generate exotic physical properties: low-dimensional magnetism and geometrical frustration. Recent studies carried out on this compound have revealed novel, complex magnetic behaviour. The rhombohedral structure of $Ca_3Co_2O_6$ consists of Co_2O_6 infinite chains running along the c axis of the corresponding hexagonal cell, and separated by calcium cations. Each chain is built of alternating CoO_6 trigonal prisms [site Co(1)] and CoO_6 octahedra [site Co(2)]. The one-dimensional magnetic character results from the large interchain separation which is about twice as large as the intrachain Co-Co distance. Each Co_2O_6 chain is surrounded by six chains forming a triangular lattice in the a-b plane.

Previous studies of $Ca_3Co_2O_6$ have established several basic features about the Co-Co interactions in this compound: (i) a strong Ising character, with the spins oriented along the chain axis; (ii) a ferromagnetic intrachain coupling; (iii) an antiferromagnetic (nearest-neighbour) interchain coupling. Such features, combined with the triangular arrangement of the chains on the ab plane, give rise to a prototypical situation of geometrical frustration.

On the other hand, many questions remain open. For example, the exact form of the magnetic phase diagram including the location and nature of the Partially Disordered Antiferromagnetic (PDA) or Frozen Spin (FS) states seen at low T is unclear. There is also unusual "multi-metamagnetic" behaviour found in M(H) at very low-T (between 2 and 5 K) accompanied by large hysteresis, and a sharp ferrimagnetic-to-ferromagnetic transition at intermediate temperatures around 10 K that are not well understood.

4.2.2 Sample preparation

Single crystals of $Ca_3Co_2O_6$ grown in Caen were available at the start of this project. Polycrystalline samples of Ca_3CoRhO_6 and $Ca_3Co_{1-x}Ir_xO_6$ were prepared at Warwick. Single crystal samples of the related material Sr_3CuPtO_6 were grown at Warwick using a flux method. As part of our continuing collaboration with Dr Hardy and CRISMAT, we are now attempting to grow larger single crystals of some of these Sr based materials in our IR image furnaces.

4.2.3 Specific heat study on single crystals of $Ca_3Co_2O_6$ [1]

The project began with the first combined specific heat/magnetisation study on single crystals of $Ca_3Co_2O_6$. Our work has revealed several features that complement previous magnetisation studies. We have shown that there is a peak at T_N~25 K in the magnetic component of the heat capacity, $C_M(T)$, under an applied field of 0 and 2T. This feature clearly demonstrates that the occurrence of a long-range ordering associated with the antiferromagnetic interchain coupling. In 5T, this peak is absent, as expected for a ferromagnetic transition in a large magnetic field. In an applied field of 2T, the ordered state is ferrimagnetic and the peak at T_N is found to be very pronounced. Under zero field, the peak at T_N is significantly reduced; the magnetic entropy displays a smooth, continuous evolution versus temperature below T_N, that is interrupted when entering the frozen spin state around T_{FS}~7K. One observes a pronounced crossover in the temperature dependence of $C_M(T)$ around T_{FS} . Below T_{FS}, the specific heat has a linear term (γT) that can be associated with frozen magnetic disorder. No additional peaks were detected in $C_M(T)$ below T_N, which appears to rule out a ferrimagnetic transition as proposed by some PDA scenarios. Our magnetisation measurements reveal a noticeable time dependence in the intermediate temperature range between T_{FS} and T_N. The combination of our specific heat and magnetisation results demonstrate that the magnetic state below T_N in zero field is still highly disordered and evolves continuously with both temperature and time. This feature probably derives from a combination of geometric frustration and the slow spin dynamics of ferromagnetic chains. The magnetic heat capacity exhibits a broad maximum at high T which can be related to one-dimensional short-range ordering along the ferromagnetic chains. The fact that only a small fraction (~0.18) of the total magnetic entropy [Rln(2S+1)] is released up to T_N is consistent with the expectations for a 1D system.

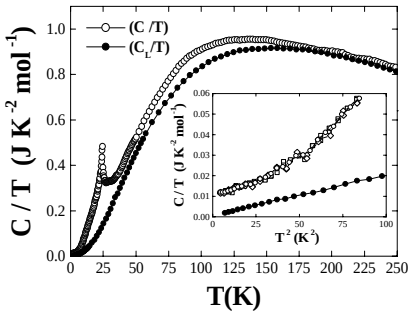

Figure 1. Total specific heat (C) and lattice contribution (C_L) in $Ca_3Co_2O_6$ under zero field. The inset shows the low-T C/T versus T^2 data.

4.2.4 Comparative study of the specific heat of $Ca_3Co_2O_6$ and Ca_3CoRhO_6 [2]

We extended this work by comparing the properties of $Ca_3Co_2O_6$ and Ca_3CoRhO_6. Previous magnetisation and neutron diffraction studies have shown that many of the properties of these compounds are similar, as expected from their related magnetic chain structure. We have shown that in contrast to $Ca_3Co_2O_6$, where a clear maximum in C(T) is seen at the onset of the interchain ordering, there is no such peak in the heat capacity data of Ca_3CoRhO_6. The crossover to the FS states, characterised by a linear term in C(T) of amplitude close to 10 $mJmol^{-1}K^{-2}$, is visible in the specific heat of both materials. In contrast to the situation for $Ca_3Co_2O_6$, the specific heat data for Ca_3CoRhO_6 is not consistent with a well defined ferrimagnetic-to-paramagnetic transition around T_N in intermediate fields (e.g. 2T). $Ca_3Co_2O_6$ and Ca_3CoRhO_6 have significantly different intrachain and interchain coupling constants, which take larger values in the latter compound. Our heat capacity studies have revealed that despite their structural similarity, there are several important differences in the behaviour of these two materials. Further work is required to understand the origin of these differences.

4.2.5 Quantum tunnelling in the magnetisation of $Ca_3Co_2O_6$ [3]

Very recently, we have completed a study of the low T magnetic properties of a single crystal of $Ca_3Co_2O_6$. We have observed a sequence of regularly spaced steps in the M(H) data of this material, reminiscent of quantum tunnelling of the magnetisation (QTM) observed in molecular magnets. Further evidence for QTM comes from studies of the spin dynamics of this system probed using variable frequency ac magnetic susceptibility measurements. The tunnelling mechanism appears to involve S=2 and S=6 spin units that arise as a result of the chain like structure of this material. More experiments and analysis are in progress. If our interpretation of the data is confirmed, this will be the first example of resonant tunnelling in a transition metal oxide.

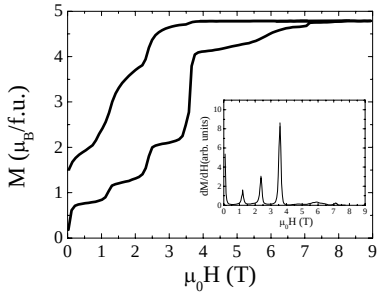

Figure 2. M(H) for $Ca_3Co_2O_6$ at 2K for H applied along the chain axis. There are a series of evenly spaced steps in the magnetisation. The inset shows dM/dH versus H.

4.2.6 Neutron and μSR studies of $Ca_3Co_2O_6$

In the following we give a brief overview of the neutron and μSR experimental work we have carried out on $Ca_3Co_2O_6$. Data analysis is underway and further experiments are planned.

- We have studied the temperature dependence of the crystal field excitations in $Ca_3Co_2O_6$ by inelastic neutron scattering (HET-ISIS). The q-dependence of these excitations suggests that the phonon modes may be coupled with the magnetic excitations in this system. These studies will shed more light on the spin state and spin-lattice interactions in this system.

- μSR investigations have been performed on $Ca_3Co_2O_6$ to study the temperature dependence of the magnetic order at low T and the short-range magnetic order along the chains at higher T.

- In November 2003 we will use PRISMA-ISIS to study the field dependence of the magnetic structure in a single crystal of $Ca_3Co_2O_6$ at low temperatures. The magnetisation versus field data for $Ca_3Co_2O_6$ contain a number of steps and plateaux of unknown origin. The proposed neutron diffraction experiment has the potential to establish unambiguously the magnetic structures of the different magnetic phases in this compound.

4.2.7 Specific heat studies in Sr_3CuPtO_6 [4]

We have extended our studies to isostructural compounds of the Sr_3MPtO_6 and Sr_3MIrO_6 families (M being a 3d transition element), which exhibit a great variety of magnetic behaviour including antiferromagnetism, ferromagnetism and random spin chain paramagnetism.

We have performed a detailed investigation of the magnetic susceptibility and the heat capacity behaviour of the compound Sr_3CuPtO_6. The use of a nonmagnetic iso-structural compound (Sr_3ZnPtO_6) has enabled us to extract the magnetic contribution to the heat capacity. Both the magnetic susceptibility and the heat capacity were found to be consistent with the Johnston and the Bonner-Fisher models for an S=1/2 AFM spin chain, with similar values of the intra-chain coupling parameters (J~25.5K). Based on the fact that there is no long range magnetic order observed in this system, at least down to 2 K, we estimate the ratio of the intra-chain and inter-chain coupling parameters to be ~130. In contrast to previous claims, these observations clearly identify Sr_3CuPtO_6 as

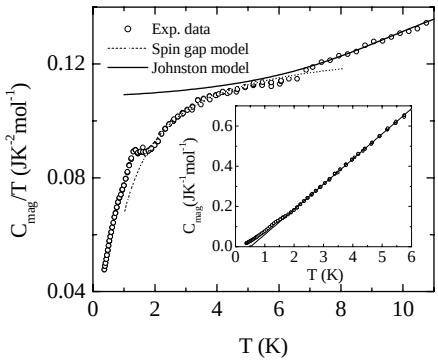

Figure 3. The low temperature magnetic heat capacity versus temperature data of Sr_3CuPtO_6 along with the curve (solid line) predicted by the Johnston model (down to 1 K) and the curve (dotted line) obtained by fitting to $C_{mag}=\gamma_{mag}T\exp(-\Delta/T)$ between 2 and 5K. The inset shows the quasi-linear behaviour of the C_{mag} versus T data below 6 K.

an S=1/2 spin chain compound with 1D magnetic character; deviations from the 1D uniform S=1/2 Heisenberg models observed at low T indicate the possible existence of a gap in the spin excitation spectrum of this material.

4.3 Investigation of phase separated states in manganites.

4.3.1 Introduction and previous work

Recently, a new and unusual behaviour has been found in some manganites with the general formula $Pr_{1-x}Ca_xMn_{1-y}M_yO_3$ (with x ~ 0.5, y ~ 0.05, and where M is a cation used to destabilise the Mn-sublattice). The virgin magnetisation curves at low-T display successive, abrupt steps as the field is increased. Related staircase-like behaviour were also observed in resistivity and specific heat measurements. The origins of these phenomena are still a matter of controversy. Very different kinds of interpretation have been proposed, ranging from field-dependent orbital ordering to a discontinuous growth of the ferromagnetic fraction within a phase-separation picture.

4.3.2 Sample preparation

Polycrystalline samples of $Pr_{1-x}Ca_xMn_{1-y}Ga_yO_3$ (x ~ 0.5, y ~ 0.05) synthesised in Caen were available at the start of this project. Polycrystalline samples of the intermetallic Gd_5Ge_4 were prepared at Warwick in our argon arc furnace.

4.3.3 Observation of spontaneous magnetisation jumps in manganites [5]

We have carried out a series of experiments on $Pr_{0.5}Ca_{0.5}Mn_{0.96}Ga_{0.04}O_3$ in order to investigate more directly the dynamics of the magnetisation jumps seen in this material. We have shown that for certain conditions of *fixed magnetic field* and *constant temperature*, large magnetisation steps can be observed in relaxation magnetisation data, i.e., in the evolution with time of the magnetisation. Changes of the order of one third of the full spin polarisation take place after a long incubation time (of the order of 1000 seconds). To the best of our knowledge, there have been no reports of such a step like magnetic relaxation in any other magnetic material. We have suggested that this jump in the magnetisation corresponds to a burst-like growth of the ferromagnetic fraction at the expense of the antiferromagnetic component within this intrinsically phase separated material. These changes are driven by the evolution of the strains at the interfaces between the two kinds of magnetic domains. These results bear a striking similarity with the phenomenon of an "incubation time" encountered in standard martensitic transformations and lend further support to the idea that there is a close analogy between the metamagnetic transition in Mn-site substituted manganites, and the isothermal martensitic transformation in metallic alloys.

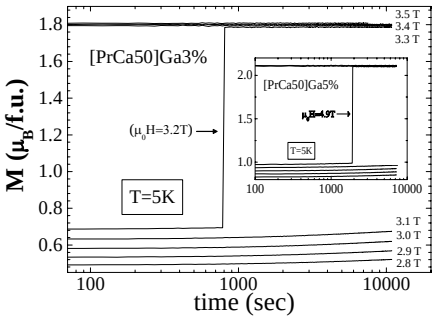

Figure 4. M v time recorded in different fields for $Pr_{0.5}Ca_{0.5}Mn_{1-x}Ga_xO_3$, x=0.03 (0.05) at T=5K. For data collected in 3.2T (4.9T) there is a spontaneous jump in the magnetisation data after a long incubation time

4.3.4 Field induced magnetisation steps in intermetallic compounds and manganites [6-7]

We have developed the idea that the properties of the phase separated manganites may be related to the martensic transition by directly comparing the behaviour of $Pr_{0.6}Ca_{0.4}Mn_{0.96}Ga_{0.04}O_3$ and Gd_5Ge_4. The $Gd_5(Si_xGe_{1-x})_4$ pseudobinary system has attracted a growing interest in recent years owing to the wealth of interesting physical properties it displays including a giant magnetocaloric effect and colossal magnetostriction. These striking phenomena are related to a strong interplay between the magnetic and the structural features in this system. These compounds have a layered structure made up of sub nanometric slabs connected via covalent-like bonds. The degree of interslab connectivity not only depends on x, but also on the magnetic state. For instance, with x=0, the slabs are completely interconnected in the ferromagnetic (FM) state, whereas all the bonds are broken in both the antiferromagnetic (AF) and paramagnetic (P) states. FM and AF domains can co-exist in Ge_5Ge_4 and the transformation between the two phases has a pronounced martensitic character. We have shown that for both $Pr_{0.6}Ca_{0.4}Mn_{0.96}Ga_{0.04}O_3$ and Gd_5Ge_4, isothermal, low T, M(H) data contain steps whose occurrence, size and position (in field) depend markedly on the magnetic field sweep rate. Such features are inconsistent with a standard

metamagnetic transition, whereas they can be qualitatively accounted for within a martensic scenario, in which there is a competition between the magnetic energy promoting the development of a FM phase, and the elastic energy associated with the AF/FM interfaces which tends to block the transformation.

4.3.5 Heat capacity study of the martensic transition in Gd_5Ge_4

We have investigated the heat capacity behaviour of the polycrystalline sample of Gd_5Ge_4 down to 2K. Our heat capacity versus magnetic field data shows a sharp step at an applied field slightly below 2T, which corresponds to the AFM-FM martensitic transition seen in the magnetisation data. We have also measured the zero field heat capacity of Gd_5Ge_4 as a function of temperature for the zero-field cooled virgin state and the field induced treated state (obtained after applying a 50 kOe field for 15 minutes at 2 K and then removing the field). The C(T) data for the virgin state and the field treated state deviate from one another at 25 K. Our investigation identified a zero-field ferromagnetic critical temperature at 25 K for the field induced state, where an order-order transition occurs between the high temperature AFM phase and the low temperature FM phase.

5 Benefits and outcomes of the visit

We believe that this grant represented excellent value for money. We have obtained the services of a leading research scientists for 12 months for ~50% of the cost of an RA1A for a similar period.

The science studied was exciting and topical. To date, the work funded by this grant has resulted in 7 published papers. Several others planned. All the staff and students in our group have benefited from the exchange of ideas with Dr. Hardy. His expertise in many areas of experimental solid state physics has made a valuable contribution to our work.

Dr Hardy's visit has helped us to establish strong links between two European laboratories with an interest in the physics of magnetic and superconducting materials. During the year two other scientists from Caen visited Warwick, while three research workers made visits to CRISMAT. We will continue to collaborate with Dr Hardy and his co-workers.

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