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Crystal Growth of Novel Oxides with a Light Furnace

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1 Background

The backdrop for this project was the growing demand in the UK for single crystal samples for experimental research into novel correlated-electron behaviour in oxides. This demand was primarily the result of the renewal of interest in the synthesis and characterization of different oxide systems following the discovery of the cuprate family of superconductors in 1986. By the mid-1990s a number of research groups in Oxford and elsewhere had become interested in studying the electronic properties of similar classes of oxide materials using different experimental techniques, especially neutron scattering, muon-spin rotation and magnetotransport. It became clear that a crystal-growth facility was needed to provide a reliable and plentiful supply of new materials for the experimental programmes.

At about the same time the EPSRC was investing heavily in central facilities at the Rutherford-Appleton Laboratory, and among the developments was the MAPS neutron spectrometer designed specifically for the study of magnetism in single crystals. Size and purity are essential parameters for crystals studied by many techniques, but for inelastic neutron scattering crystals with volumes of typically 1–5 cm^3 are essential if good results are to be achieved. Hence, a particular need for voluminous crystals arose.

In the case of oxides, by far the most successful technique for producing large, high-quality crystals is the floating-zone method using an optical (image) furnace. This technique was pioneered by the Japanese, who collectively operate more than 200 image furnaces and as a result lead the world in crystal growth of new materials

The present grant provided funding to install and operate an image furnace in the Clarendon Laboratory, and to use it to grow large, high quality single crystals of novel oxide materials, including colossal magnetoresistance (CMR) manganites, doped antiferromagnetic oxides, quantum magnets, and ferroelectrics.

2 Project overview

The success of the project, measured in terms of the number and quality of the crystals grown, has exceeded our most optimistic expectations, and owes much to the skill, dedication and hard work of Dr D. Prabhakaran, the RA employed on the grant. The project has delivered a large number of crystals, whose quality and size is as good as or better than available elsewhere, including materials not previously grown by the floating-zone method.

The coherence of the programme meant that efforts made to optimize the growth of a particular family of compounds served the needs of a large research community. By studying the same crystals by a variety of different techniques we were able to ensure consistency and comparability. The close connection between the sample preparation facilities and the research groups helped ensure that information on the quality of the crystals was fed back rapidly to improve the growth process.

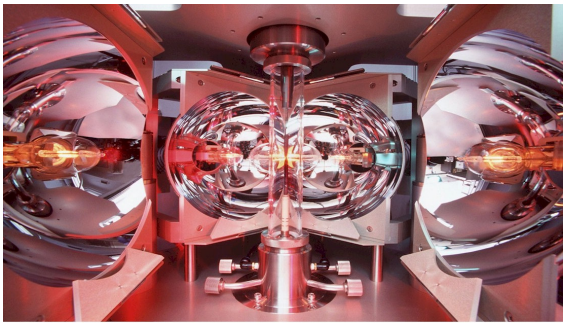

Fig. 1. View inside the Oxford image furnace showing the four ellipsoidal mirrors. A crystal rod is seen suspended vertically inside the quartz growth chamber.

As well as serving the needs of the Investigators we also regard it a high priority that the crystals should be made available to external groups. Information on the range of crystals grown has been disseminated via conferences, seminars and on a web site.[1] During the grant period crystals were supplied free-of-charge to several other UK and overseas institutions (see below), and a number of strong collaborations have been established this way.

3 The crystal growth equipment

The grant enabled us to purchase the four-mirror floating-zone furnace (fig. 1) from Crystal Systems Inc., two sintering/annealing furnaces (1500 ºC and 1800 ºC) used to prepare the polycrystalline starting material, a hydrostatic press for forming the powder into rods, a vertical furnace (1800 ºC) with sample rotation and translation to sinter the rods, a ball mill, and a diamond cutter. Additional sample preparation and characterization equipment was already available in the Clarendon Laboratory.

Most of the equipment was installed in Dec 1999, and after a short period of testing the first crystals were produced in Jan 2000.

4 Scientific highlights

A summary of the crystals grown during the grant period is given in Table 1. We concentrated our efforts on about a dozen transition-metal oxide systems. The growth condition for optimum size and quality varies strongly with composition and from one system to another. We paid particular attention to this optimization, and in many cases we have been able to improve on the best crystals previously available.

Fig. 2 Single crystal of $La_{0.7}Sr_{0.3}MnO_3$.

Table 1. Principal oxide families investigated during the grant period. The size given refers to the sections of the boules verified as being single-crystal grains. References are to papers we have written describing the crystal growth.

material	size	reference
$La_{1-x}Sr_xMnO_3$ (x = 0.0 to 0.5)	7–10 Ø × 50–80 mm^3	[2]
$La_{1-x}Sr_xGa_yMn_{1-y}O_3$	8–10 Ø × 50–80 mm^3	–
$La_{2-x}Sr_xNiO_4$ (x = 0.0 to 0.5)	7–10 Ø × 35–80 mm^3	[3]
Pr_2NiO_4 and Nd_2NiO_4	7–10 Ø × 35–80 mm^3	[4]
Pr_2CuO_4	6–8 Ø × 20–30 mm^3	–
$Bi_2Sr_2CaCu_2O_8$	3 × 5 × 1 mm^3	–
$Cu_{1-x}Zn_xO$ (x=0–0.1)	7–9 Ø × 20–30 mm^3	[5]
$La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x = 0.2 to 0.6)	5 × 10 × 2 mm^3 smaller for x > 0.45	[6]
TNb_2O_6 (T = Co, Mn, Ni, Fe, Mg, Zn)	8–10 Ø × 40–80 mm^3	[7]
$S_{2-x}La_xMnO_4$ (x = 1/3, 1/2)	8–10 Ø × 40–60 mm^3	–
$La_{3/2}Sr_{1/2}CoO_4$	9 Ø × 80 mm^3	–
$LaCoO_3$	9 Ø × 60 mm^3	–
$T_{1-x}Mg_xGeO_3$ (x<0.06 T = Co, Mn, Fe)	6–7 Ø × 60–70 mm^3	–
$LaTiO_3$, $YTiO_3$	8–10 Ø × 60–70 mm^3	–

For example, many groups have reported crystal growth of the prototypical CMR perovskites $La_{1-x}Sr_xMnO_3$, but frequent problems are cracking of the crystals and evaporation of Mn during melt growth. After many trials we discovered that a high-pressure Ar/O_2 growth atmosphere virtually eliminates these problems, and our best crystals are now stoichiometric, crack-free, and very large (8 mm dia. × 80 mm long) — see fig. 2. Our method has been published.[2]

Needless to say, the process of optimization is time-consuming, labour-intensive, and does not always have a successful outcome. Table 1 does not reflect cases where defeat had to be admitted.

Because our crystal growth programme was driven by physics its long-term success should be judged primarily on the quality of research performed on the crystals. However, the crystal growth optimizations include some innovations that are significant in their own right, and we consider it important that these findings be placed in the public domain for the benefit of other scientists. The methods we have developed have been presented at crystal growth conferences and in six publications to date.[2-7]

In the following sections we present a selection of the results obtained so far from experiments performed on the crystals. We also describe some experiments which will be performed in the near future at international facilities.

4.1 Coupled order parameters

We have made systematic studies by neutron and x-ray diffraction and by magnetometry of magnetic, charge and orbital order in the nickel, manganese and cobalt oxide families listed in Table 1. In the $La_{2-x}Sr_xNiO_4$ family we have examined the x = 1/3 and 1/2 compositions in detail. The stripe periodicity is commensurate with the lattice at one-third doping, but to our surprise we found that the charge ordering in the half-doped compound $La_{3/2}Sr_{1/2}NiO_4$ changes from commensurate to incommensurate at about the same temperature as the spins begin to order.[8] We also observed a spin reorientation transition peculiar to the x = 1/3 and 1/2 compositions.[8]

Magnetization measurements revealed irreversible behaviour in all $La_{2-x}Sr_xNiO_4$ compounds, and we have identified several distinct types of glassy magnetic effects associated with disorder of the charge stripes.

Synchrotron x-ray scattering has been used to study the interplay between charge, magnetic and orbital (Jahn-Teller) order in the bilayer manganate series $La_{2-2x}Sr_{1+2x}Mn_2O_7$ for x = 0.4 to 0.6 and in the layered nickelates. These studies provide insight into stripe melting phenomena and competing interactions that govern the magnetic and transport behaviour in these compounds.[9,10] The work has also revealed for the first time an enormous enhancement in the soft x-ray resonant magnetic scattering cross-section at the L_{II} and L_{III} edges of Mn.[11]

4.2 Spin and charge dynamics in stripe phases

The static properties of stripe phases are now quite well characterized, but much less is known about their dynamics. We have studied the spin dynamics in large single crystals of $La_{2-x}Sr_xNiO_4$ by inelastic neutron scattering at the ILL and ISIS neutron facilities. We have measured the spin excitation spectrum throughout the whole Brillouin zone in crystals with x = 0.275, 1/3 and 1/2. Fig. 3 displays the dispersion relation found in $La_{5/3}Sr_{1/3}NiO_4$. Fig. 4 shows the scattering from spin waves with energy 55 meV measured on the MAPS spectrometer at ISIS. By fitting a spin-wave model to these data we obtained values for the inter- and intra-stripe exchange interactions for the first time.[12]

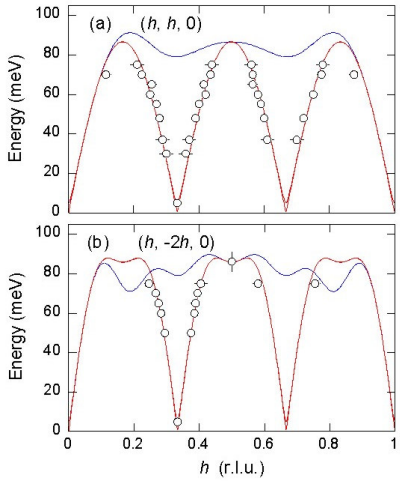

Fig. 3 Spin-wave dispersion in $La_{5/3}Sr_{1/3}NiO_4$ parallel to the (a) (h, h, 0) and (b) (h, $-2h$, 0) directions. The symbols are data from inelastic neutron scattering, and the lines are calculated from a spin-wave model with intra- and inter-stripe exchange parameters J = 15 meV and J' = 7.5 meV.[12]

At certain energies we observed deviations from spin-wave behaviour due, we conjecture, to coupling between spins and collective motions of the charge domain walls.[12] In a different set of measurements we observed diffuse scattering that we believe is evidence for dynamic correlations of spins in the stripe domain walls. These results are important because of what they tell us about the physics of stripe phases, and also because of the connection with phenomena observed in the copper-oxide superconductors.

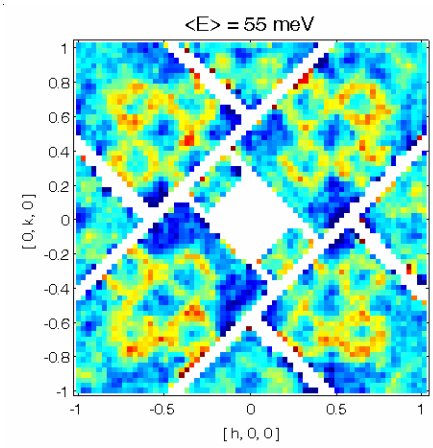

Fig. 4 Spin-wave scattering from $La_{5/3}Sr_{1/3}NiO_4$ measured on the MAPS neutron spectrometer. The picture is a constant-energy slice through the dispersion surface.

4.3 μSR studies of spin fluctuations in crystals

Single crystal samples of the bilayer manganates, layered nickelates and cobaltates have been studied using implanted muons at both the ISIS pulsed muon facility and the PSI continuous muon facility. These experiments have been motivated by our earlier muon studies on powder samples of both nickelates and manganates. Because the bilayered manganates are so anisotropic, measurements on powders yield somewhat limited information since the muon-spin relaxation is averaged over all directions.

For our latest experiments it has been possible to perform experiments with crystals grown in the light furnace which are subsequently cut in different ways, so that the muon-spin can be made to lie either in the bilayers or to be normal to them. The muon is sensitive to local magnetic fields perpendicular to the muon spin direction, so that in this way the anisotropic spin fluctuations and the direction of the ordered moment can be probed as a function of temperature.

Our initial measurements show a dramatic difference between the muon-spin relaxation in these different orientations. Hence we have demonstrated strongly anisotropic spin fluctuations in the bilayer manganates which are well within the muon time-window. This provides quantitative information concerning the anisotropy of the spin fluctuations and we are now studying these systematically in a number of single-crystal samples.

4.4 Spin excitations in a 1-d Ising chain

We succeeded in growing large single crystals of the $T\mathrm{Nb_2O_6}$ series (T = Co, Mn, Ni, Fe) for the first time by the floating-zone method. The structure of these compounds leads to highly one-dimensional magnetic properties which we have studied by magnetization and inelastic neutron scattering. $\mathrm{CoNb_2O_6}$ is as an Ising spin system, and we have observed a strong continuum in the excitation spectrum which splits into discrete bound states upon cooling below the 3D ordering temperature. This effect is identified with the formation of bound states of quantum solitons states in the presence of the effective confining potential from the 3D mean-field ordering. The measured energies and spectral weight of the excited states give direct information about how

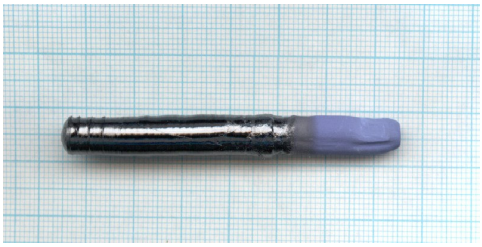

Fig. 4. Single crystal of $\mathrm{CoNb_2O_6}$.

multi-particle bound states form and what their wavefunction is, key ingredients of theoretical models of quantum magnets. Moreover, the relatively low energy scale of the excitations in $\mathrm{CoNb_2O_6}$ (~1 meV) indicate that moderate magnetic fields (~10 T) can be used to manipulate the many-particle states directly and to induce quantum phase transitions. Neutron scattering experiments to probe those effects have been scheduled at HMI in 2003.

4.5 Spin-state transitions in cobalt oxides

In some oxides containing $\mathrm{Co^{3+}}$ ions electronic configurations with different spin states can be close in energy due to a fine balance between intra-atomic Hund-Rule coupling, crystal-field and Jahn-Teller interactions. The most well-known example occurs in the compound $\mathrm{LaCoO_3}$, whose ground state is non-magnetic, but which transforms into a paramagnetic insulator above 100 K, and then undergoes a metal–insulator transition at around 500 K. It has been proposed that these features are associated with spin transitions of the $\mathrm{Co^{3+}}$ ions from a ground state with $S = 0$ to excited states with $S = 1$ and 2.

Surprisingly, these spin-state transitions have never been observed directly in the solid state, but we have successfully applied for beam time on the MAPS spectrometer at ISIS to study the excitation spectrum of $\mathrm{LaCoO_3}$ by neutron inelastic scattering. We will search for the proposed spin-state transitions and look for any collective excitations associated with them.

We have also obtained neutron beam time on ISIS (MAPS) and at the ILL to study the layered half-doped compound $\mathrm{La_{1.5}Sr_{0.5}CoO_4}$, which exhibits an ordered array of $\mathrm{Co^{2+}}$ and $\mathrm{Co^{3+}}$ ions in a regular ‘checkerboard’ pattern at temperatures below 750 K. Spin-state transitions are predicted to compete with other cooperative spin and

charge excitations in this compound, and we will examine the wavevector dependence of the energy spectrum to identify the important interactions.

4.6 Higher-order exchange processes

The dominant interaction in most transition-metal oxides is the Heisenberg superexchange, but higher-order interactions can show up in certain properties. If they can be measured then important information can be obtained. For example, cyclic exchange processes cause dispersion around the magnetic zone boundary which depends on the effective hopping t and the Coulomb energy U of the Hubbard model. Cyclic exchange has been measured in La_2CuO_4, and we have obtained neutron scattering time on the MAPS spectrometer at ISIS to search for similar effects in La_2NiO_4. The experiment will be performed early in 2003.

5 Methodology

The crystals used in the experiments described above were all grown by the floating-zone method in the new Oxford image furnace. Chemical and physical characterization was routinely performed on the grown crystals. X-ray powder diffraction was used to check phase purity before and after growth, and electron-probe microanalysis (EPMA) was used to determine cation ratios. Crystals having variable oxygen content were examined by thermogravimetric analysis in Zaragoza, Spain. X-ray and neutron Laue diffraction was used to assess crystalline quality and for alignment. Magnetic measurements performed with a SQUID magnetometer were extremely useful both for primary characterization as well as to identify different magnetic phases in the crystals.

The majority of the work performed with the crystals was centred around neutron, muon and x-ray scattering experiments. These were performed at the ISIS Facility, the Institut Laue-Langevin (Grenoble), the SINQ neutron and muon facilities in Switzerland, the ESRF (Grenoble), the SRS (Daresbury), and the HASYLAB (Hamburg).

6 Collaborations

Crystals have been supplied to the following groups in addition to those of the Investigators:

P. Hatton (Durham), D. Smith (Southampton), H. Fretwell (Swansea), R. Burriel (Zaragoza, Spain), H. Ronnow (CEA, Grenoble), J.B. Forsyth (RAL)

To help coordinate the different experimental programmes we held regular internal meetings with the co-Investigators on the project, and we also held a full collaboration meeting on 3 Sept 2001 at which all collaborators (internal and external) were invited to present their results on the crystals. This meeting helped us obtain feedback on crystal quality.

Among the groups of the Investigators, a number of graduate students on EPSRC Quota Studentships have carried out experiments on the crystals as part of their doctoral research: A.I. Coldea, P. Freeman, C. Steer, L. Helme.

7 Project plan review

The timetable for purchase, installation and commissioning of the equipment largely followed that anticipated in the proposal. The first usable crystals were grown approximately six months after the start of the grant.

The families of materials investigated were essentially the same as those described in the original proposal. The main omission was the work on critical phenomena in ferroelectrics. Efforts to grow some of the required crystals were not successful, and in the case of doped $SrTiO_3$ the melting point was right on maximum operating temperature of the furnace, and so extensive optimisation was not feasible.

Regarding finance, there were overspends of £11,400 on consumables and £3,270 on travel. These amounts are in excess of 20% relative to the budget. The overspend on consumables is accounted for by the cost of high-purity chemicals, spare parts for the image furnace, and liquid helium for characterization, all of which exceeded our initial estimates. The travel money was used for participation in conferences in Kyoto (Japan), Seattle (USA) and Liverpool (UK), and also for collaboration meetings. The allocated travel budget of £2106 was insufficient

to cover these events. Significant savings were made under the equipment heading through discounts negotiated with manufacturers of the main items of equipment.

8 Impact of the work

The project has so far resulted in 10 published or accepted papers with many more submitted and in preparation. These publications, together with several conference presentations not listed here, and collaborations with many groups in the UK and worldwide are evidence that the work is significant in an international context.

Of equal importance, however, is that in less than three years of operation the Oxford image furnace has produced a large reserve of high quality crystals, and created a fully functioning and highly productive resource for the crystal growth of new materials in the future. Experiments on existing crystals will continue for several more years, but continued operation of the facility (which is dependent on further funding) would be a cost-effective and efficient way to maintain the supply of crystals of new materials within the UK.

7 Conferences attended supported by grant

International Conference on Crystal Growth ICCG–13 (Kyoto 2001); American Conference on Crystal Growth and Epitaxy, ACCGE–14 (Seattle, 2002); British Association for Crystal Growth, BACG'02 (Liverpool, 2002).

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