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High-quality single crystals for neutron experiments

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Abstract. To make headway on any problem in physics, high-quality single crystals are required. In this talk, special emphasis will be placed on the crystal growth of various oxides (superconductors and magnetic materials), borides and carbides using the image furnaces at Warwick. The floating zone method of crystal growth used in these furnaces produces crystals of superior quality, circumventing many of the problems associated with, for example, flux growth from the melt. This method enables the growth of large volumes of crystal, a prerequisite especially for experiments using neutron beams. Some examples of experimental results from crystals grown at Warwick, selected from numerous in-house studies and our collaborative research projects with other UK and international groups will be discussed.

Keywords. Crystal growth; floating zone method; neutron scattering.

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1. Introduction

For studying the problems that arise in magnetism or superconductivity, high-quality single crystals are essential. This is because most of the materials of interest tend to exhibit anisotropic behaviour, either as a result of their crystal structure and interactions or as a consequence of the application of magnetic fields or pressure. The underlying physics of such materials can only be unravelled by investigating high-quality crystals. Recent examples of interesting physics where single crystals have been absolutely essential are the high temperature superconductors (HiT$_c$), the colossal magnetoresistant (CMR) oxides and most recently in the discovery of superconductivity in the hydrated sodium cobaltate system.

The production of single crystals of new materials is a highly competitive business and invariably the best crystals produced in a few laboratories around the world are those that are in demand for the crucial and definitive experiments. It is not uncommon for leading international laboratories to have their own crystal growth programmes to support their needs. This gives these laboratories an advantage over groups who are reliant on others for the supply of crystals.

2. Crystal growth using optical image furnaces

The optical furnaces work by focussing light from the halogen/xenon lamps which are placed at the focal point of a semi-ellipsoidal mirror cavity, on to a joint focal point, where the sample is placed. The growth region is isolated from the mirror regions by a quartz tube thus allowing different growth atmospheres and pressures. The actual crystal growth is carried out by melting a rod (feed) of the material and fusing it to a seed rod (or crystal) at the bottom and establishing a freely floating molten zone. This floating zone is then scanned by lowering it at a set, slow speed through the hot zone. In a variation of this method called the travelling solvent floating zone technique, a flux or solvent material is introduced into the molten zone, which is then scanned up the 'feed' rod, while the crystal deposits itself out of the flux on to the seed rod. The floating zone method of crystal growth has definite advantages over more conventional methods of growth: (a) the method is crucible-free and hence the crystals produced are uncontaminated, (b) large crystals can be obtained, (c) uniform levels of substitution and doping can be achieved, (d) refractory materials and dielectrics can be melted with ease.

At Warwick, three optical furnaces are used for crystal growth. The first of these was acquired to grow single crystals of the high-temperature superconductors soon after they were discovered. Then a more sophisticated four-mirror furnace was acquired equipped with halogen lamps, from CSI, Japan. This furnace has the advantage of providing a more uniform temperature definition in the molten zone and has therefore proved valuable for use in incongruently melting multi-component systems. The third, a high-power xenon arc lamp furnace allows us to reach temperatures up to 2800°C. This is the first and only one of its kind in the UK and is used for the crystal growth of refractory materials – borides and carbides – which have high melting points not accessible using a halogen lamp system (maximum 2150°C). With this equipment and expertise, we are in a position to grow crystals and investigate the physics of a whole variety of oxides, borides and borocarbides. These materials range from magnets (antiferromagnetic, ferromagnetic, low dimensional, frustrated, etc.) to superconductors (high T_{c}, low T_{c}, conventional and exotic) and heavy fermions. Where crystals cannot be grown using the optical furnaces, other more conventional techniques are employed. Our laboratories are also well equipped for crystal growth by flux techniques and chemical vapour transport.

3. Large crystals

In general, the volume of the crystals that can be obtained by the floating zone method is large enough for most regular laboratory-based experiments. For inelastic neutron scattering measurements, where large volumes of samples are a prerequisite, this method is ideal. Large diameter crystals are also required for certain laboratory experiments where crystals of defined orientations along specific crystallographic axes have to be cut from the grown boule. The crystals that are normally produced are typically about 1.5 cc in volume. With the high power xenon arc lamp furnace in operation, we are now able to melt larger diameter starting rods which result in crystals which have larger volumes (>4 cc). Where previously it was necessary to use an array of several crystals for a neutron experiment, it is now possible

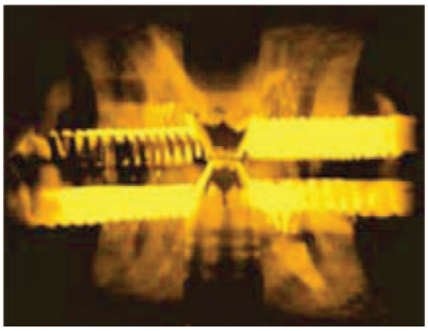


Figure 1. The floating molten zone used for crystal growth using the optical furnaces.

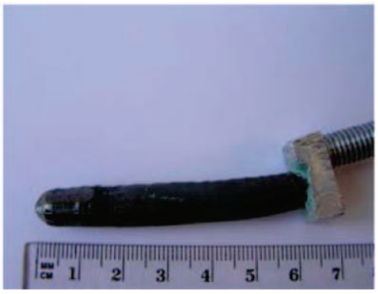


Figure 2. Large single crystal of magnetite (∼4.5 cc) used in a neutron scattering experiment at ISIS.

to use just one or two of these large diameter crystals. For example, in a recent experiment on a single crystal of magnetite using the PRISMA spectrometer at ISIS, one large crystal of volume ∼4.5 cc, grown at Warwick, was used successfully for the experiment (figure 2).

4. Oxides

Oxide physics has been one of the main scientific themes in condensed matter physics and has been important since the discovery of high-temperature superconductivity. Given the two-dimensional character of many of these oxide structures and their highly anisotropic physical properties, it has been absolutely necessary to obtain high-quality single crystals of the oxides in order to fully explore their properties. The floating zone and travelling solvent floating zone methods are ideally suited for the crystal growth of oxides. In the following, we outline some of our current activities in the area of oxide physics that we envisage will definitely continue into the next three- to four-year period.

4.1 $Na_xCoO_2{\cdot}yH_2O$

The discovery of superconductivity in the layered cobalt oxide ($\mathrm{Na}_x\mathrm{CoO}_2{\cdot}y\mathrm{H}_2\mathrm{O}$) [1] and its many apparent similarities to both the high T_c and the $\mathrm{Sr}_2\mathrm{RuO}_4$ systems has led to an explosion of interest in this material. It is the first layered, cobalt-based oxide superconductor, and the first superconductor where the presence of water is

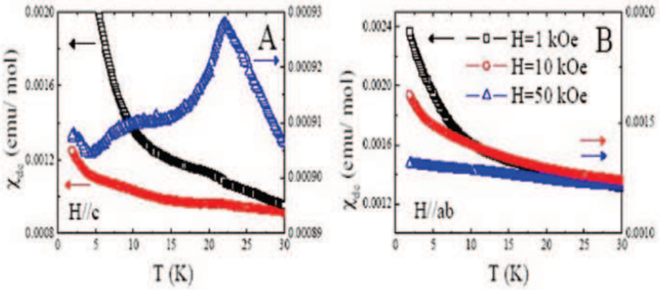


Figure 3. Magnetic susceptibility measurement showing the spin density wave in a crystal of $Na_{0.7}CoO_2$ observed for $H\|c$.

critical to the onset of superconductivity. Previous work on both the superconducting and non-superconducting phases of $Na_xCoO_2{\cdot}yH_2O$ has underlined the need to carry out investigations on well-characterized, high-quality samples. The difficulties in preparing homogeneous material with well-defined sodium and water levels mean that some of the published data on this system may not be representative of the true behaviour of this material. In addition, given the anisotropic layered structure, measurements on single crystals are necessary in order to reveal the true nature of both the normal and superconducting properties of this system. We have demonstrated that good quality single crystals of a range of compositions x can be grown by the floating zone method [2]. We have concentrated our studies around the $x = 0.7$ composition studying the magnetic properties (spin density wave) seen at this doping level (figure 3).

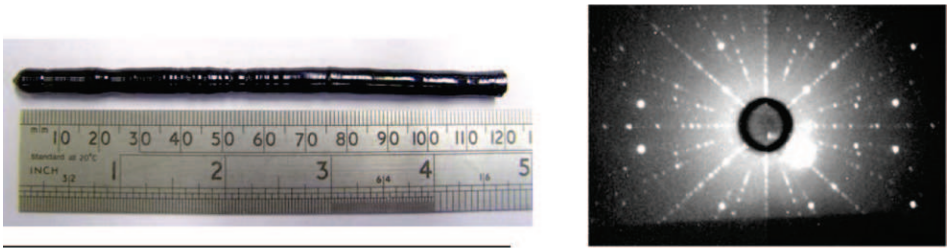
4.2 *Multiferroics*

There is a surge of interest in materials that exhibit interplay between lattice distortions and electrical and magnetic orderings. The group of materials known as multiferroics in which magnetism and ferroelectricity coexist are being investigated. The RMnO$_3$ and RMn$_2$O$_5$ ($R =$ rare earth) family of compounds are examples of materials that exhibit these properties. In these materials, it is possible to control the electric polarization by the application of a magnetic field. Large crystals of the RMnO$_3$ type compounds can be grown by the floating zone technique.

Figure 4a shows a typical boule of a manganite crystal grown at Warwick by the floating zone technique using the optical mirror furnaces available there. Figure 4b shows the X-ray Laue back reflection photograph taken along the crystallographic c-axis of a crystal of $TbMnO_3$, showing the quality of the crystals grown.

4.3 *Frustrated magnets*

The study of frustrated magnets has been one of the major areas of interest within the group and has spawned several collaborations with scientists from outside Warwick. Our collaborative work on the so-called ‘spin ice’ pyrochlore systems



(a) (b)

Figure 4. (**a**) An as-grown boule of a single crystal of a manganite grown using the floating zone technique at Warwick, using a four-mirror optical furnace. (**b**) X-ray Laue photograph of a single crystal of $TbMnO_3$ taken along the *c*-axis of the crystal.

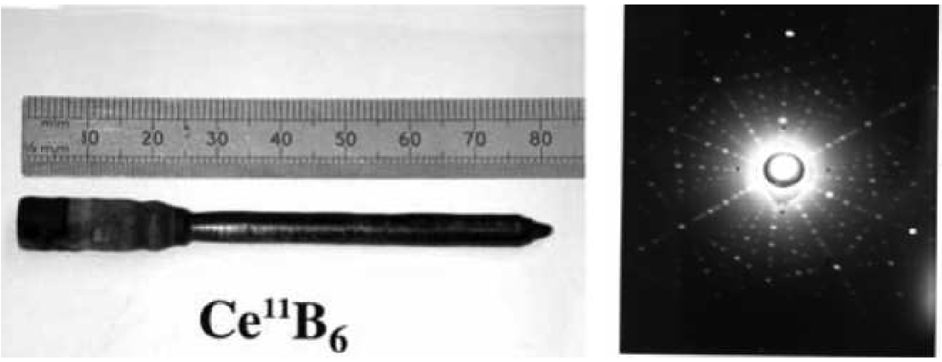
$Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ has attracted a lot of interest and we have carried out several studies on single crystal samples of these materials [3]. While our interest has been in the production of high-quality crystals for the investigation of the physics of the frustrated magnets, we have successfully collaborated with the Pacific National Laboratory, USA, for radiation damage studies on $Gd_2/Sm_2Ti_2O_7$ and $(Gd,Zr)_2Ti_2O_7$. These studies are driven by the suitability of the pyrochlore structures for encapsulating radioactive waste. We foresee that the interest in the titanate pyrochlores will continue, mainly to support the needs of other users. We have investigated the Kagomé-type structures described below.

4.3.1 *Kagomé-type structures.* One of the most interesting frustrated systems is the Kagomé lattice which has a two-dimensional depleted triangular structure that creates macroscopic degeneracy. Good examples of these are the compounds $A_3V_2O_8$ where A = Ni or Co. The compounds $Ni_3V_2O_8$ and $Co_3V_2O_8$ adopt a buckled version of the Kagomé lattice called the Kagomé staircase. Such distortions relieve the frustration and provide the mechanism for lifting the degeneracy, thereby establishing long-range magnetic order. Initial investigations on these crystals have shown that the samples have complex magnetic field–temperature phase diagrams. Multiple phase transitions are observed at low temperatures. Large high-quality crystals are required for inelastic neutron scattering experiments to investigate in detail the low temperature dynamics of the magnetic excitations. We have already established that these crystals can be grown by the floating zone technique [4]. Figure 5 shows a boule of one of the Kagomé staircase compounds grown by the floating zone technique. We have demonstrated that it is possible to produce crystals suitable for neutron scattering experiments.

5. Borides and silicides

Borides of transition metals and rare earths have been extensively studied especially with regard to their hardness and their highly refractory properties. A number of these borides have also been investigated for their extensive range of magnetic

Figure 5. As grown crystal boule of $Ni_3V_2O_8$.



(a) (b)

Figure 6. (**a**) Crystal of CeB_6 grown using ^{11}B isotope for neutron scattering studies and (**b**) X-ray Laue pattern obtained from the crystal.

properties they exhibit. Borides in general have very high melting points (∼2800°C) and so crystal growth by conventional techniques poses a problem. Small crystals can be obtained using Al flux, but large volume samples are invariably necessary for the study of their magnetic properties using neutrons. During the course of the last three years, we have demonstrated that it is possible to grow large high-quality crystals of several borides using our high-temperature xenon arc lamp image furnace. Crystals of the rare earth hexaborides, RB_6 (R = La, Ce, Pr, Nd) have been grown with ease, as they all have congruent melting points [5]. Several crystals with ^{11}B isotope have been produced especially for investigations using neutron scattering techniques (see figure 6). Borides of transition metals are also extremely interesting. For example, we have also been able to grow crystals of CrB_2, which exhibit helical magnetism at $T = 80$ K [6]. This crystal has been studied in an inelastic neutron scattering experiment using the PRISMA spectrometer at ISIS.

6. Summary

Crystals of a wide range of materials can be produced by the floating zone technique using optical mirror furnaces. At Warwick, high-quality crystals of several oxides, borides and borocarbides are produced by the use of a range of optical furnaces. These crystals are ideal for a variety of experiments and are especially suited for neutron scattering experiments where large volumes of sample are required for inelastic measurements.

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