



	Experiment title: Low temperature crystal structure of the ferromagnetic insulator Sr ₃ Ir ₂ O ₇	Experiment number: HS2386
Beamline: ID11	Date of experiment: from: 1/4/04 to: 3/4/04	Date of report: 31/8/05
Shifts: 6	Local contact(s): J.P. Wright	<i>Received at ESRF:</i>
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Report:

The role of local charge correlations and their competition with magnetic and electronic ground states has been widely studied in first-row transition metal oxides, but second- and third-row oxides have received relatively little attention. Although there is a tendency towards metallic character in these materials, strong electron-lattice coupling can still occur. For example, the 5d iridates are often non-metallic and can display unusual magnetic and transport properties that differ from their 3d counterparts [1-5]. One such material is the little-studied insulator Sr₃Ir₂O₇, a distorted Ruddlesden-Popper “ $n = 2$ ” compound in which double Ir-O perovskite layers are separated by a Sr-O layer. It has previously been reported that correlated rotations of the IrO₆ octahedra occur, resulting in a doubling of the unit cell volume and adoption of the orthorhombic *Bbca* space group at room temperature [6]. It is a canted antiferromagnet below $T_C=285$ K, and when single crystals are cooled in a magnetic field of less than 0.2 T a reversal of the net magnetisation in the basal plane takes place below 50 K. Magnetisation data also suggested that a magnetostrictive transition may occur at ~260 K. However, the nature of these possible transitions remain unclear since no low-temperature structural studies have been reported thus far.

The aim of our experiment on ID11 was to carry out an accurate structural determination of Sr₃Ir₂O₇ between 15 K and room temperature, and to determine whether any phase transitions occur in this range. A crystal of dimensions 80 × 40 × 20 μm was mounted on a quartz fibre and cooled using either a He or N₂ cryostream. Data were collected using a CCD camera at 15

K, 100 K, 220 K, and 295 K. A rough “field-cooled” measurement was also attempted by placing a magnet close to the crystal such that the field direction was parallel to the *ab* plane while cooling to 200 K. In addition, several crystals were crushed and the resulting powder packed into a capillary; powder diffraction patterns were collected using the kappa diffractometer and a N₂ cryostream at 5 K intervals between 120 K and 350 K.

The single crystal data at all temperatures contained weak Bragg reflections that violated the previously reported B-centering condition: (*hkl*), *h+l*=2*n*. The reflections observed were consistent with the primitive space group *Pban* at all temperatures. The unit cell is pseudo-tetragonal, with almost equal *a* and *b* lattice parameters; as expected for such a structure, the crystal was twinned by a 90° rotation around *c* with equal domain fractions. The main difference between this *Pban* structure and the previously reported *Bbcb* structure [6] is that the two perovskite-type bilayers in the unit cell become inequivalent in *Pban*. Octahedra in the two bilayers have significantly different rotation angles and bond lengths (Figure 1). That is, the octahedra in one bilayer are larger (both in the axial and equatorial direction) than in the other. The larger octahedron is more rotated around *c*, and the rotation angle increases on cooling from ~13° at 295 K to ~15° at 15 K. The rotation angle of the smaller octahedron remains ~8.5° throughout the temperature range. The reasons for the violation of B-centering are unclear; the two different Ir environments suggest that some kind of charge disproportionation might be present. No change in symmetry was detected between 15 K and 295 K, and cooling in the presence of a magnet had no effect on the structure. However, the *c* lattice parameter determined from the powder diffraction data suggested that a phase transition takes place at 220 K (Figure 2). The compression of the *c* axis between 100 K and 220 K is ~0.0045 Å, and about the same between 300 K and 220 K. Any corresponding change in bond lengths is likely to be half of this value or smaller, which is of the same order as the error bars in the bond lengths obtained from the single crystal refinements. Therefore, the reason for the compression of the *c* axis is unclear at present.

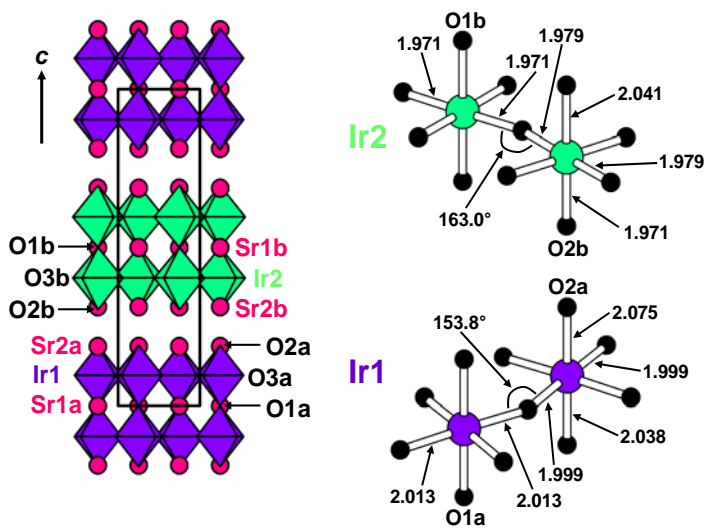


Figure 1: Crystal structure of Sr₃Ir₂O₇ at room temperature including bond lengths (Å) and angles.

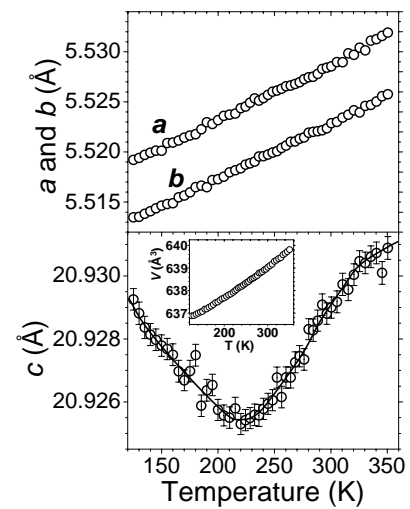


Figure 2: Lattice parameters and unit cell volume of Sr₃Ir₂O₇.

References

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