ESRF	**Experiment title:** Mechanism of spin-singlet formation in Tl2Ru2O7	**Experiment number**: HS2471
Beamline: ID31	**Date of experiment**: from: 10/3/04 to: 12/3/04	**Date of report**: 31/8/05
Shifts: 6	**Local contact(s)**: I. Margiolaki	*Received at ESRF:*

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Report:

The original aim of this experiment was to study the low-temperature crystal structure of $Tl_2Ru_2O_7$. However, a preliminary synchrotron X-ray diffraction experiment revealed significant problems with sample homogeneity that could not be detected by our laboratory X-ray diffractometer and that will require a whole new synthesis approach to overcome. Therefore, we were given permission to use the beamtime to study the low-temperature crystal structures of the multiferroic compounds $TbMn_2O_5$, $DyMn_2O_5$ and $HoMn_2O_5$. These three materials are all ferroelectric and antiferromagnetic below ~35 K; they display strong coupling of the electrical polarisation to external magnetic fields, manifested in phenomena such as field-induced polarisation reversals [1] and giant magnetocapacitance [2]. They all adopt orthorhombic, centrosymmetric Pbam structures at room temperature, but the crystal structures of the ferroelectric phases are unknown. We therefore used ID31 to look for evidence of structural phase transitions at low temperatures. An X-ray wavelength of 0.3364 Å was used; powder samples were packed into quartz capillaries and temperature control between 5 K and 295 K was achieved with a He-cooled cryostat.

We did not detect any change in symmetry (extra peaks appearing, peak splitting) for any of the three samples between 5 K and 295 K. The diffraction patterns could be refined in the space group Pbam at all temperatures. This is consistent with a previous structural study of YMn_2O_5, which failed to find evidence for the necessary lowering of

symmetry in the ferroelectric phase [3]. Furthermore, no obvious changes in the atomic coordinates or bond lengths occurred with temperature. However, the lattice parameters of $DyMn_2O_5$ suggest that a phase transition may occur at ~30 K, close to the ferroelectric transition temperature [2]. Although the *a* lattice parameter shows a steady decrease with temperature down to 5 K, the *b* and *c* parameters both show an upturn below ~30 K (Figure 1). This leads to a slight negative thermal expansion of the unit cell volume at low temperatures. Since we collected only short scans over a period of ~2 minutes each, the signal to noise ratio of our data was not sufficient to reveal the structural changes occurring at 30 K. It is possible that small shifts of oxygen atoms are involved, and thus neutron diffraction may be necessary to uncover the modes of distortion giving rise to the ferroelectricity. The spontaneous electrical polarisation in the RMn_2O_5 materials (*R* = rare earth, Y, Bi) is 2 or 3 orders of magnitude smaller than in typical ferroelectrics, and hence the atomic shifts giving rise to the net dipole moment are likely to be extremely small and difficult to identify.

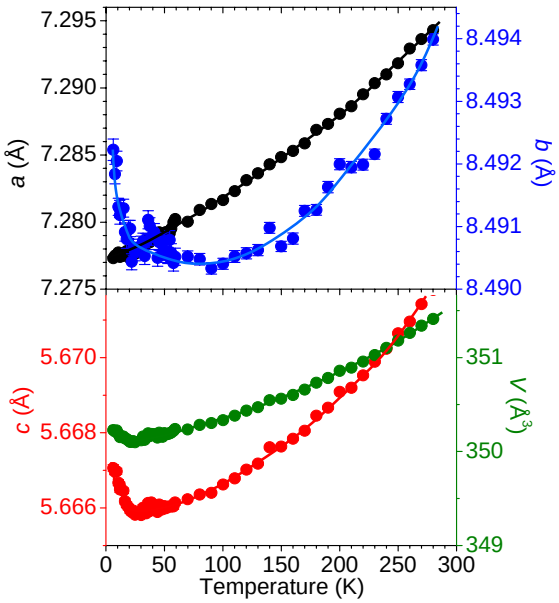

Figure 1: Refined lattice parameters of $DyMn_2O_5$

References

1. **N. Hur, S. Park, P.A. Sharma, J. S. Ahn, S. Guha, and S-W. Cheong, Nature 429, 392 (2004).**
2. **N. Hur, S. Park, P.A. Sharma, S. Guha, and S-W. Cheong, Phys. Rev. B 93, 107207 (2004).**
3. **I. Kagomiya, S. Matsumoto, K. Kohn, Y. Fukuda, T. Shoubu, H. Kimura, Y. Noda, and N. Ikeda, Ferroelectrics 286, 167 (2003).**