

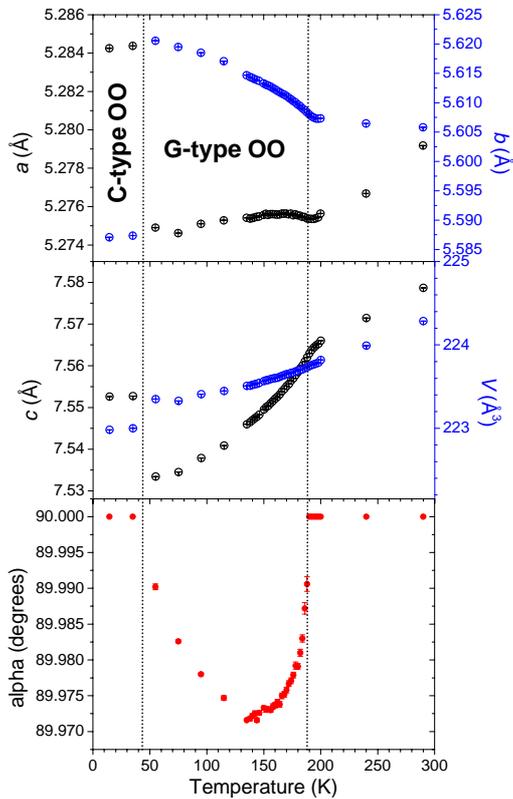


	<b>Experiment title:</b> Phase transitions in rare-earth orthovanadates	<b>Experiment number:</b> HS2164
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 10/3/03 to: 13/3/03	<b>Date of report:</b> 30/8/05
<b>Shifts:</b> 6	<b>Local contact(s):</b> M. Brunelli	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>*Graeme R. Blake, University of Groningen, Netherlands</b> <b>Paolo G. Radaelli, ISIS Facility, UK</b>		

## Report:

The  $RVO_3$  perovskites ( $R$  = rare earth,  $Y$ ) have recently attracted interest due to the complex interplay that they exhibit between spin, orbital and lattice degrees of freedom [1,2]. In particular, they are appealing systems for the study of  $t_{2g}$  orbital ordering (OO). Recent reports have suggested that orbital fluctuations play a significant role, giving rise to disorder in the orbital arrangement and hence to fluctuating magnetic superexchange interactions [3,4]. However, there is still a lack of accurate structural data for many members of the series. The magnitude of the structural distortions occurring in the OO phases of these  $d^2$  perovskites is rather small compared to those in  $e_g$  orbitally ordered systems. The so-called G-type OO that is expected to occur in all members of the series involves a subtle lowering of the crystal symmetry from orthorhombic to monoclinic, with minimal changes in the lattice parameters and little deviation of the monoclinic angle from  $90^\circ$ . This makes the OO phase difficult to detect using powder diffraction methods; the extremely high resolution of ID31 is essential.

We used ID31 with an X-ray energy of 25.01 keV to study the structures of  $HoVO_3$  and  $YbVO_3$  at temperatures between 15 K and 290 K. Crushed single crystals were packed into capillaries and temperature control was achieved using either a He-cooled cryostat or a  $N_2$  cryostream. Our aims were to investigate the types of OO in these materials, to determine the temperatures of the phase transitions, and to look for evidence of orbital fluctuations.



**Figure 1:** Lattice parameters and unit cell of  $\text{HoVO}_3$

and long values characteristic of C-type OO, with similar values to the low-temperature phase of  $\text{YVO}_3$ . The first-order nature of this transition was also evidenced by the presence of a small amount of the monoclinic phase in the 35 K pattern; the sample was fully transformed to the C-type phase at 15 K.

There was not enough time to collect as many data sets for  $\text{YbVO}_3$ , but its behaviour was similar to that of  $\text{HoVO}_3$ . The onset of G-type OO (perhaps incomplete or short-range) occurred at  $\sim 170$  K and the monoclinic angle  $\alpha$  reached a maximum value of  $89.982(1)^\circ$  at 100 K. Between 100 K and 80 K a sudden decrease in cell volume occurred and the structure was transformed to the C-type OO phase.

## References

1. G.R. Blake, T.T.M. Palstra, Y. Ren, A.A. Nugroho and A.A. Menovsky, *Phys. Rev. Lett.* 87, 245501 (2001).
2. G.R. Blake, T.T.M. Palstra, Y. Ren, A.A. Nugroho and A.A. Menovsky, *Phys. Rev. B* 65, 174112 (2002).
3. C. Ulrich, G. Khaliullin, J. Sirker, M. Reehuis, M. Ohl, S. Miyasaka, Y. Tokura and B. Keimer, *Phys. Rev. Lett.* 91, 257202 (2003).
4. P. Horsch, G. Khaliullin and A. Oleś, *Phys. Rev. Lett.* 91, 257203 (2003).

The structure of  $\text{HoVO}_3$  could be well refined at room temperature in the space group  $\text{Pbnm}$ . Between 188 K and 190 K a clear splitting of many diffraction peaks occurred and the profiles could be indexed in the monoclinic space group  $\text{P}2_1/\text{b}11$ , as expected for the G-type OO phase. The monoclinic angle  $\alpha$  rapidly decreased on further cooling to a minimum of  $89.972(1)^\circ$  at  $\sim 130$  K before increasing again towards  $90^\circ$  at lower temperatures. However, the pattern of alternating long and short V-O bond lengths in the  $ab$  plane that is expected for G-type OO was not present; all of the in-plane V-O bonds were roughly equivalent. The rather large errors in the refined oxygen coordinates in the monoclinic phase may have disguised the bonding pattern, or alternatively this may be evidence for a lack of long-range OO, supporting the proposed orbital fluctuations scenario. Between 55 K and 35 K the monoclinic peak splitting disappeared and the diffraction pattern could be refined in  $\text{Pbnm}$  once more; a sudden decrease in the unit cell volume occurred, indicating a first-order transition similar to that in  $\text{YVO}_3$  [2]. The V-O bonds in the  $ab$  plane were now clearly split into short