ESRF	**Experiment title:** Phase Transitions in Single Crystal YVO_3	**Experiment number**: HS1278
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Report:

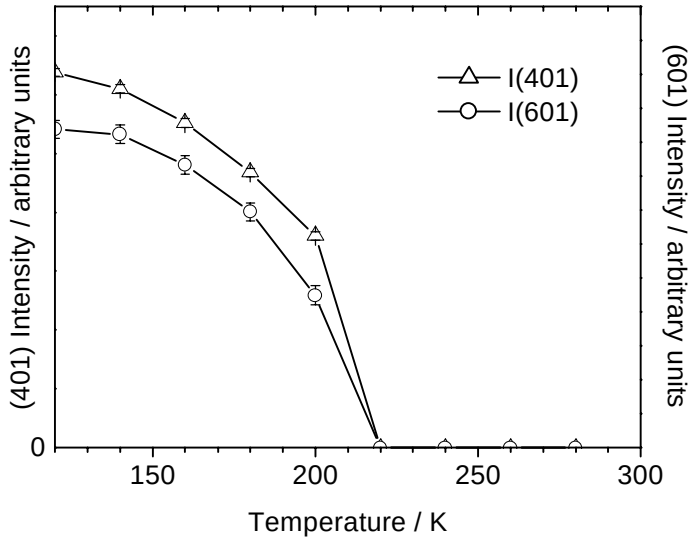
The aim of our experiment was to perform a full structural investigation of YVO_3. We have recently undertaken a detailed study of the unusual magnetic properties of YVO_3 single crystals [1], which display reversible changes in the sign of the magnetisation at 77K and ~95K. YVO_3 adopts the $GdFeO_3$-type distorted perovskite structure with the space group Pbnm at room temperature. The magnetisation reversal at 77K is connected with a change from G-type to C-type antiferromagnetic ordering of the unpaired vanadium spins on heating; below 77K a Jahn-Teller distortion indicates the presence of C-type ordering of the occupied vanadium d-orbitals. It has been predicted that the C-type magnetic ordering between 77K and 116K should coexist with G-type orbital ordering. Although G-type orbital ordering is incompatible with Pbnm symmetry, there has thus far been no crystallographic evidence for a space group other than Pbnm at any temperature. We therefore began by looking for a lowering of the space group symmetry, manifested by the appearance of weak "forbidden" reflections.

On cooling from room temperature, it soon became apparent that many weak reflections violating Pbnm symmetry appeared at approximately 200K. For example, the integrated intensities of the forbidden reflections (401) and (601) are plotted as a function of temperature in Figure 1. These reflections could not be detected at 220K and above but became easily visible at 200K; their intensities increased on cooling before levelling off at around 120K. These reflections provide definitive evidence for a phase transition with a lowering of the symmetry at approximately 200K. They are very weak compared to the "allowed" reflections, of the order of 10^{-4} times the intensity, and therefore it is unsurprising that they could not be detected using a laboratory X-ray source. The forbidden reflections disappeared again below 80K, as expected for a switch to C-type orbital ordering, which is compatible with Pbnm symmetry.

We collected full data sets at 295K, 225K and 50K, which were consistent with the space group Pbnm and did not contain any extra reflections. The structural refinements proceeded smoothly. A strong Jahn-Teller distortion corresponding to C-type orbital ordering was present in the 50K structure. However, the data sets collected at 80K, 100K, 125K, 150K and 175K all contained many extra, weak reflections; the systematic absences were consistent with the space group $P2_1/a$, although the monoclinic angle β remained close to 90°. The best refinements at these intermediate temperatures were obtained when a twinning model was included; it is known that monoclinic structures that are metrically orthorhombic (that is, with $\beta \approx 90°$) are often pseudo-merohedrally twinned on planes perpendicular to the *a* and *c* axes, where *b* is the unique axis. When the twinning model was included, the basal planes contained the expected alternating pattern of long and short V-O bond lengths characteristic of Jahn-Teller distortion and G-type orbital ordering.

The high flux on ID11 was essential in order to detect the weak reflections indicating a lowering of the symmetry at 200K from Pbnm to $P2_1/a$. Once the correct space group was used for the structural refinements, the expected orbital ordering schemes, as manifested by Jahn-Teller distortion, became apparent. In summary, YVO_3 is orthorhombic with Pbnm symmetry at room temperature. On cooling, a phase transition to monoclinic symmetry ($P2_1/a$) occurs at 200K, with the onset of G-type orbital ordering. C-type antiferromagnetic ordering occurs at 116K with no change in the crystal structure. On cooling through 77K, a first order phase transition takes place in both the magnetic and crystal structures; the configuration of the unpaired spins switches to G-type, with a concurrent change to C-type orbital ordering and a return to orthorhombic Pbnm symmetry.

Figure 1



[1] Y. Ren, T.T.M. Palstra, D.I. Khomskii, A.A. Nugroho, A.A. Menovsky and G.A. Sawatzky, *Phys. Rev. B*, **62**, 6577 (2000).