ESRF	**Experiment title: Temperature dependent powder diffraction studies of magnetic vanadates.**	**Experiment number**: HS3316
Beamline: ID31	**Date of experiment**: from: 31/01/2007 to: 06/02/2007	**Date of report**:
Shifts: 18	**Local contact(s)**: A. N. Fitch	*Received at ESRF:*

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Report:

The mixed valence vanadates $MV^{3+}V_3^{4+}O_8$ (M=Yb, Y, Lu) are structurally related to $CaFe_2O_4$. They are built of a three-dimensional framework of VO_6-octahedra. Within the framework, tunnels parallel to [001] are formed in which the trivalent cations are incorporated [1,2]. Two different phases, denominated α and β, are known. The vanadate framework is basically identical in both phases and they only differ in the arrangement of the Yb/Y ions. They build a pseudocentered orthorhombic net, which in the β-phase is stacked with a pseudotranslation of (b+c)/4 or (b-c)/4 , while in the α-phase the stacking sequences (b+c)/4 and (b-c)/4 are alternating.

Due to the different arrangement of the trivalent cations, the *b* lattice parameter of the β-phase is doubled with respect to the α-phase (YbV_4O_8: α-phase: a=9.0648(3), b=10.6215(4), c=5.7607(1) and β =90.148(3) with space group $P12_1/n1$; β-phase: a=9.030(5), b= 21.44(3), c=5.752(2) and α = 89.911(3) with space group $A2_1/d11$). The similarity of the two phases favours the occurrence of polytypism and one-dimensional disorder is frequent in these compounds. Crystals showing systematic intergrowths of the two modifications have been described and treated [2,3]. The structures at ambient conditions have generally been refined in the superspace assuming a commensurate composite model, where the vanadate framework forms one subsystem and the Y/Yb atoms represent the second subsystem [4].

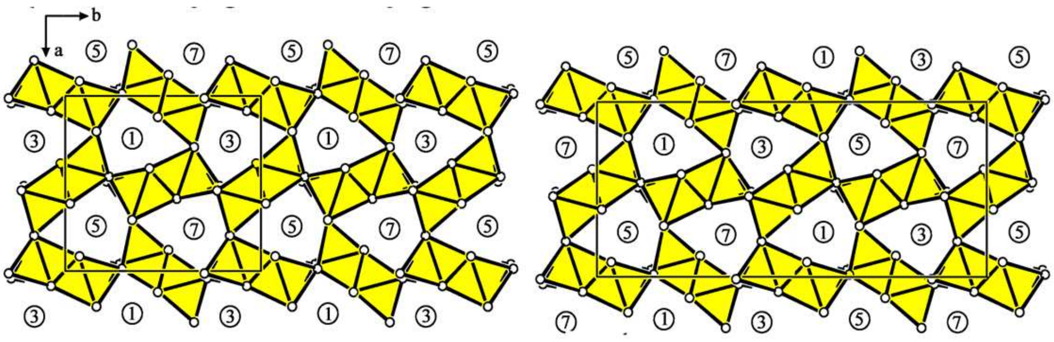

Figure 1: Structures of the α- (left) and β- (right) phases of YbV$_4$O$_8$. Vanadate octahedra are shown in yellow. The height of the Yb ions is indicated in fractions of 8.

The two polytypic modifications show different magnetic behaviours. For the β-phases, the magnetic susceptibility shows pronounced anomalies at approximately 185 K (YbV$_4$O$_8$, [5]) and 190 K (YV$_4$O$_8$, [2]), respectively. For the α-phases, on the other hand, no anomalies are observed in this high temperature region, but instead anomalies occurr below 100 K. The anomalies are accompanied by the corresponding ones in the thermodynamic data, which suggest structural instabilities, especially for the higher temperature anomaly of the β-phases.

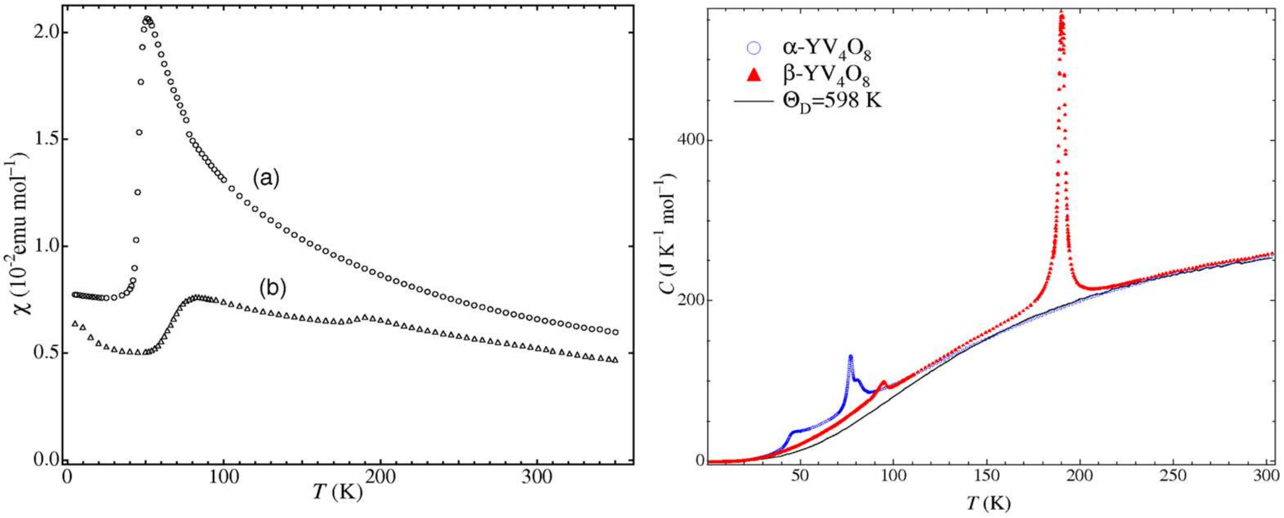

Figure 2 left: Temperature dependence of the magnetic susceptibility χ of (a) α-YV$_4$O$_8$ and (b) β-YV$_4$O$_8$ (right). Specific heat measurement of YV$_4$O$_8$ (left).

We carried out powder diffraction studies at beamline ID31 in the temperature range from 290 to 10 K on samples of YbV$_4$O$_8$, YV$_4$O$_8$ and LuV$_4$O$_8$. For each compound three different samples were studied:

- **pure α:** a sample containing exclusively the α -phases of the compounds;
- **β-I** : a sample containing approximately 99 % β- phase, ≤ 1% α –phase and a small amount of a pyrochlore impurity; domain sizes for of the α-phases estimated on the basis of the Scherrer formula are ≥ 90Å;
- **β-II**: sample containing 99 % β- phase, ≤ 1% α –phase and a small amount of a pyrochlore impurity; domain sizes for of the α-phase are ≤ 40Å.

For all samples, the data confirm the existances of structural phase transitions at temperatures corresponding to the anomalies in the magnetic susceptibility and specific heat described above. In all the samples the diffraction diagrams can be indexed assuming identical symmetry of the high and low temperature phases, i.e., we do not observe new reflections or a broadening of the existing ones. The two phases, designated α/α' and β/β'in the following, coexist within a temperature range of approximately 10 K (see Figure 3) and the phase transitions are fully reversible. Changes in the diffraction pattern and in lattice parameters are discontinuous (Figure 4), indicating the first order character of the phase transitions. Complementary single crystal diffraction experiments on α- and β-YbV_4O_8 confirm the existance of isosymmetrical phase transitions, which are related to a complete charge ordering. While above the phase transition the bond valence sums indicate no clear charge separation of the tri- and tetravalent V-ions over the four symmetrically independent octahedral sites, below the transition temperature a complete charge ordering is observed.

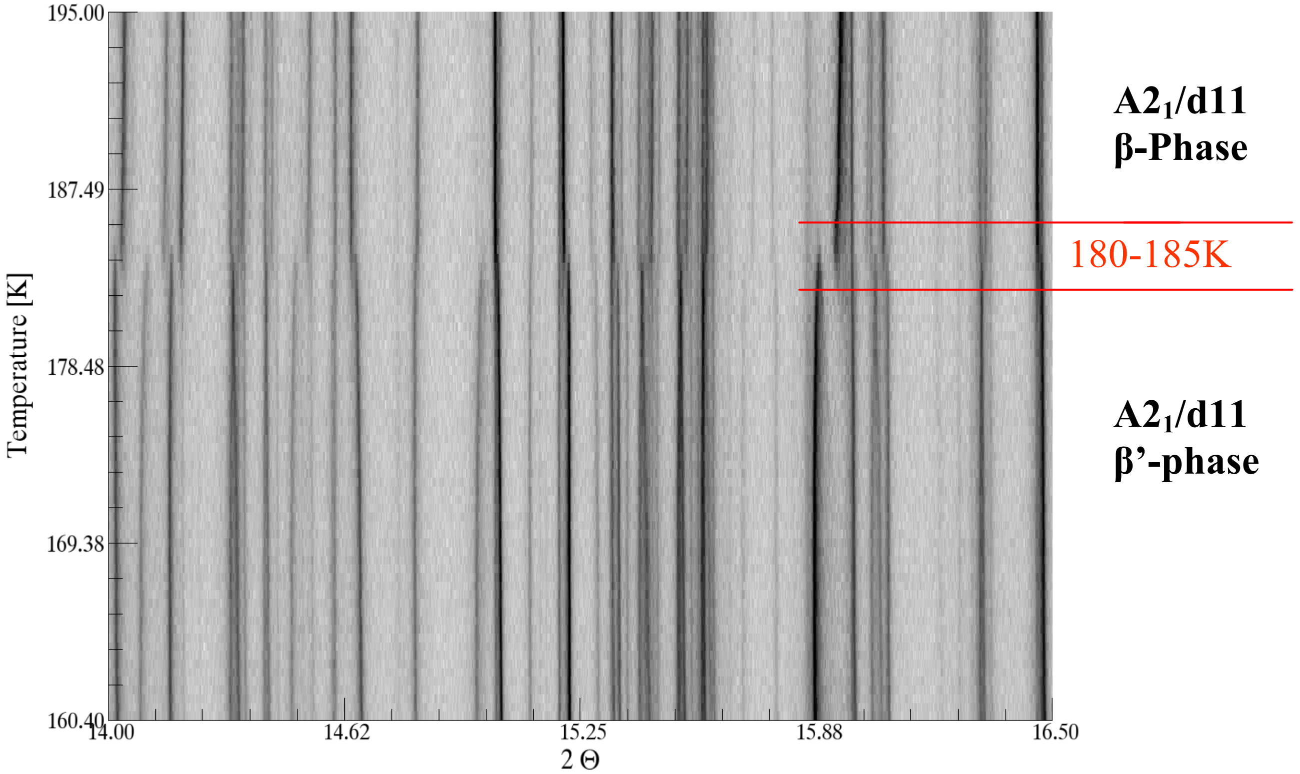

Figure 3: Guinier Simulation for β-YbV_4O_8 in the temperature range around the isosymmetrical phase transition β→ β' (reconstructed with Powder3D [7] based on data measured at beamline ID31).

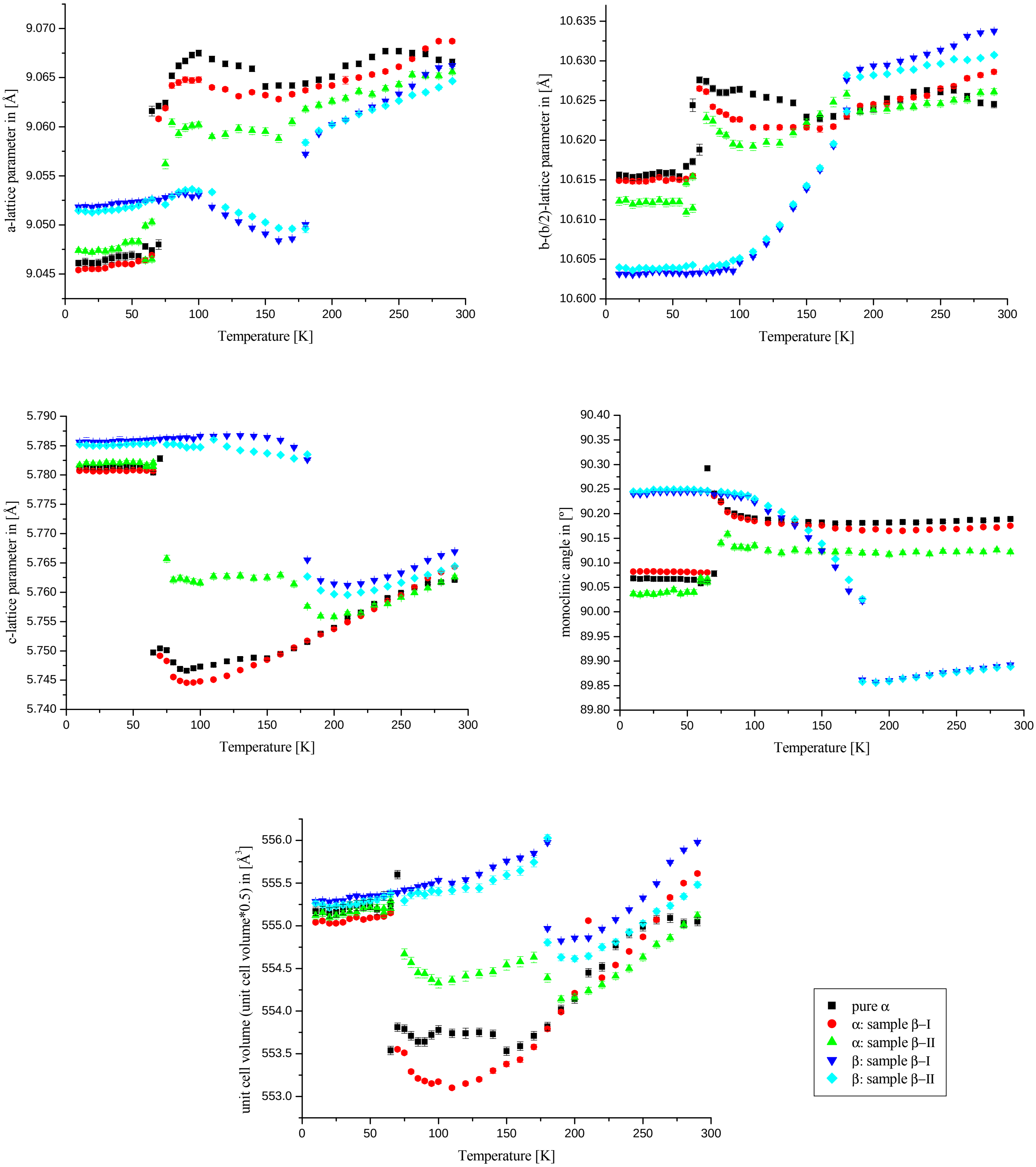

Figure 4: Lattice parameters and unit-cell volumes of YbV_4O_8 *as a function of temperature.*

The transitions are accompanied by paramagnetic-paramagnetic transitions. These anomalies can be understood assuming that the Curie-Weiss type d-electrons of the vanadium cations in the high temperature phases separate at the phase transition into d electrons, which maintain their Curie-Weiss character and others, which lose their spin moment with decreasing temperature. The unusual complete charge ordering can thus be attributed not only to Coulomb repulsion between the V and Yb cations, but also to spin annihilation [5,6].

Figure 4 shows the lattice parameters and unit-cell volumes of YbV_4O_8 obtained by a LeBail fit [8] of the powder diffraction data with the program Jana2000 [9]. Five different sets of lattice parameter are given. Two of them correspond to the β-phases of sample β-I and β-II (0.5*b and 0.5*V is portrayed to keep data comparable to the α-phase lattice parameter). The three sets corresponding to the α-phases have been extraced from the samples pure α, β-I and β-II. Lattice parameters for the two β-phase samples are practically identical. The same is not true for the three α –phase samples, where a domain size effect is clearly detectable. While the lattice parameters of the α -phase samples with large domain sizes (pure-α and β-I) show a relatively smooth behaviour down to the phase transition temperature (65 K), the lattice parameters of the α -phase sample with domain sizes ≤ 40 Å (β-II) are influenced by the phase transiton in the β-phase (180 K). Furthermore, it is evident, that the smaller the domain size of the α -phase the more the lattice parameters seem to adapt to the ones of the β-phase.

These results are understandable on the basis of the observed polytypic disorder observed in these compounds. According to single crystal results, the β-phase is always twinned and the structure of the twin boundary corresponds to the structure of the α-phase [2,3]. For the sample β–II this region cannot be larger than 40 Å, which explains why the lattice parameters of the α-phase in this sample are so strongly distorted with respect to the lattice parameters of the pure α-phase sample. It is also evident that the α to α ’ transtion strongly relieves the strain on the α-phase domains, as the lattice parameter of the two polytypic modifications α and β get more comparable.

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