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Isosymmetrical Phase Transition and Charge Ordering in the Mixed Valence Vanadate *β*-YbV_4O_8

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The mixed valence vanadate β-YbV_4O_8 crystallizes in a structure related to $CaFe_2O_4$. The structure is built of a three-dimensional framework of VO_6 octahedra in which the Yb ions are incorporated. At 185 K the compound undergoes an isosymmetrical phase transition which is accompanied by discontinuous changes in the lattice parameter, as well as in the interatomic distances and angles. 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. The structural transition is accompanied by an anomaly in the magnetic susceptibility data, which corresponds to a paramagnetic-paramagnetic transition. This anomaly can be understood assuming that the Curie-Weiss type d electrons of the vanadium cations separate at 185 K into d electrons, which maintain their Curie-Weiss character, and others, which lose their spin moment with decreasing temperature. Thus, the unusual complete charge ordering can be attributed not only to Coulomb repulsion between the V and Yb cations but also to the spin annihilation of the vanadium cations.

Introduction

Charge ordering generally gives rise to abrupt changes in transport or magnetic properties of a solid. It involves the ordering of metal ions in different oxidation states over specific lattice sites in a crystal structure. During a charge order phase transition, the symmetry is generally lowered as the ordering process tends to convert equivalent sites in the disordered phase to distinct ones in the ordered phase. However, the structural changes related to the rearrangement of the ions with different valences, and therefore different ionic radii, are generally very subtle.[1] A good example is the case of mixed-valence manganates $Ln_{1-x}A_xMnO_3$[2] (Ln = rare earth, A = alkaline earth) exhibiting the colossal magnetoresistance effect.[3] Models based on charge ordering of Mn^{3+}/Mn^{4+} were able to explain the magnetic structure,[2] yet the bond valence sums derived from interatomic Mn−O distances (as determined by X-ray diffraction experiments) were very close to 3.5 v.u. for the two symmetrically independent Mn sites. This stands in clear contrast to the values of 3 and 4 v.u. expected for a completely ordered arrangement of the two ions. Examples of other systems where the charge separation was found to be only partial are $CaFeO_3$,[4] $YBaCo_2O_5$,[5] or $YNiO_3$.[6] Even the classical Verwey transition in Fe_3O_4[7] results only in a partial charge separation.

Recently, vanadium oxides have been of wide interest because of charge, spin, and orbital ordering. Most of the studies are focused on the compounds with vanadium in one single oxidation state liable to undergo both magnetic and/or structural phase transitions, e.g., $SmVO_3$,[8] vanadium spinels,[9] and vanadium perovskites.[10] Investigations on mixed-valence vanadates show that these materials follow the trend observed for other mixed valence transition metal oxides. In AlV_2O_4, which has a charge order transition at 700 K, the number of electrons at each V site after the transition is still fractional.[11] The metal-insulator transition in the quasi one-dimensional conductor β-$Na_{0.33}V_2O_5$ is

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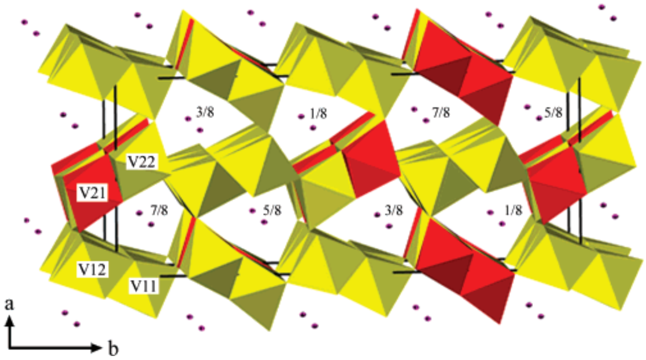

Figure 1. Perspective view of the structure of β-YbV_4O_8. $V(11)O_6$, $V(12)O_6$, and $V(22)O_6$ octahedra are shown in yellow and $V(21)O_6$ octahedra in red. Yb atoms are shown in blue. Approximate heights of the Yb atoms in fractional coordinates of z are given.

accompanied by the charge disproportion of V^{4+} and V^{5+} rather than by charge ordering.[12]

The compounds MV_4O_8[13,14] (M = Y, Yb) crystallize in structures related to the $CaFe_2O_4$ type. The structures are built of a three-dimensional framework of VO_6 octahedra. Within the framework, tunnels parallel to [001] are formed in which the Y or Yb ions are incorporated (Figure 1). Both for YV_4O_8 and YbV_4O_8 two different phases, denominated α and β, are known. The vanadate framework is basically identical in both modifications and they differ only in the arrangement of the Yb (or Y) cations.[13−15]

The average valence for V in YV_4O_8 and YbV_4O_8 is 3.25 v.u.; this value corresponds to three V^{3+} and one V^{4+} per formula unit. Although the structures allow for ordering of the four cations over the four symmetrically independent octahedral sites, earlier investigations based on single-crystal diffraction experiments showed no indication for charge ordering at room temperature.[14,16]

Our present studies are centered on the low temperature behavior of β-YbV_4O_8, which undergoes a structural phase transition at approximately 185 K, coinciding with an anomaly in magnetic susceptibility. The last observation suggests that charge ordering of the V^{3+} and V^{4+} ions could be involved in the mechanism of the phase transition. Thus, the aim of this study has been (1) to characterize the structural changes occurring at 185 K, (2) to relate them to the magnetic properties of the material, and (3) to compare this behavior to what is observed in other transition metal oxides.

Experimental Section

The single crystal of β-YbV_4O_8 investigated here is identical to the one used for the earlier structure determination.[16] Powder samples have been prepared in a separate synthesis using $YbVO_3$, $YbVO_4$, and V_2O_3 as starting materials. A detailed description of the procedures has been published earlier.[13]

The magnetic susceptibility data were collected on the powder samples (63.25 mg) with a Magnetic Property Measurement System from Quantum Design in the temperature range from 300 to 2 K.

Differential scanning calorimetry was carried out with the systems Pyris 1 and 7 (Perkin-Elmer) in the temperature range from 290 to 100 K.

High-resolution X-ray powder diffraction experiments were performed at the beamline ID31 of the European Synchrotron Radiation Facility, Grenoble, France.[17] Lattice parameters were extracted from the powder diffraction diagrams using the LeBail method[18] with the program Jana2000.[19]

Single-crystal diffraction intensities were collected using a Stoe IPDS II diffractometer at the "Single Crystal Diffraction" beamline at the Institute for Synchrotron Radiation (ANKA, Karlsruhe Research Center, Germany). A N_2 cryostat from Oxford Cryosystems was used and the datasets were collected at temperatures of 290, 250, 200, 175, 150, 125, and 100 K at a wavelength of 0.8 Å.[20]

Single-crystal structure refinements were carried out using a commensurate composite crystal approach in four-dimensional space with the program Jana2000.[19] The model corresponded to the four-dimensional twin model used previously to describe the structure of β-YbV_4O_8[16] at room temperature. More detailed information about the higher dimensional treatment is given in the Supporting Information. The final result in the four-dimensional setting in superspace group $P2_1/n(0\beta\gamma)0s$ was transformed to a three-dimensional model in space group $A2_1/d11$,[21] a nonstandard setting of $P2_1/n$, which is used to have a direct comparison of the α- and β-phases of YbV_4O_8.

Results

The magnetic susceptibility data (Figure 2) are obtained with external fields of 0.1 T (both zero field cooled and field cooled) and 5.0 T (zero field cooled). The data show two anomalies at approximately 185 and 70 K, and a minute anomaly at about 25 K. The latter two anomalies may be attributed to the pyrochlore impurity, $Yb_2V_2O_7$, which shows the ferromagnetic ordering of the V^{4+} sublattice at 73 K and the ferromagnetic ordering of the Yb^{3+} sublattice at about 30 K.[22] Assuming that the difference in the susceptibility between 0.1 and 5.0 T is caused exclusively by the

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(17) Two different types of scan were carried out. For the precise determination of lattice parameters in Figure 5, a continuous scan with a speed of 2.5°/min was used; scan limits in 2θ were $-5° < \theta < 20°$. (The beamline is equipped with nine detectors, which have an offset of 2° in 2θ with respect to each other. The limits given refer to the middle detector.) In addition, we continuously performed a scan from 8 to 14° in 2θ with a speed of 3°/min, while raising the temperature slowly with a rate of approximately 10 K/h from 160 to 195 K (Figure 4; altogether 82 scans were acquired). For cooling a He flow cryostat from Janis Inc., United States, was used.

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(21) Symmetry operations for $A2_1/d11$: (i) x, y, z; (ii) $^1/_2 + x, {}^3/_4 - y, {}^1/_4 - z$; (iii) $-x, {}^1/_2 - y, -z$; (iv) $^1/_2 - x, {}^1/_4 + y, {}^1/_4 + z$; (v) $x, {}^1/_2 + y, {}^1/_2 + z$; (vi) $^1/_2 + x, {}^1/_4 - y, {}^3/_4 - z$; (vii) $-x, -y, {}^1/_2 - z$; (viii) $^1/_2 - x, {}^3/_4 + y, {}^3/_4 + z$. (Note the origin shift with respect to ref 13.)

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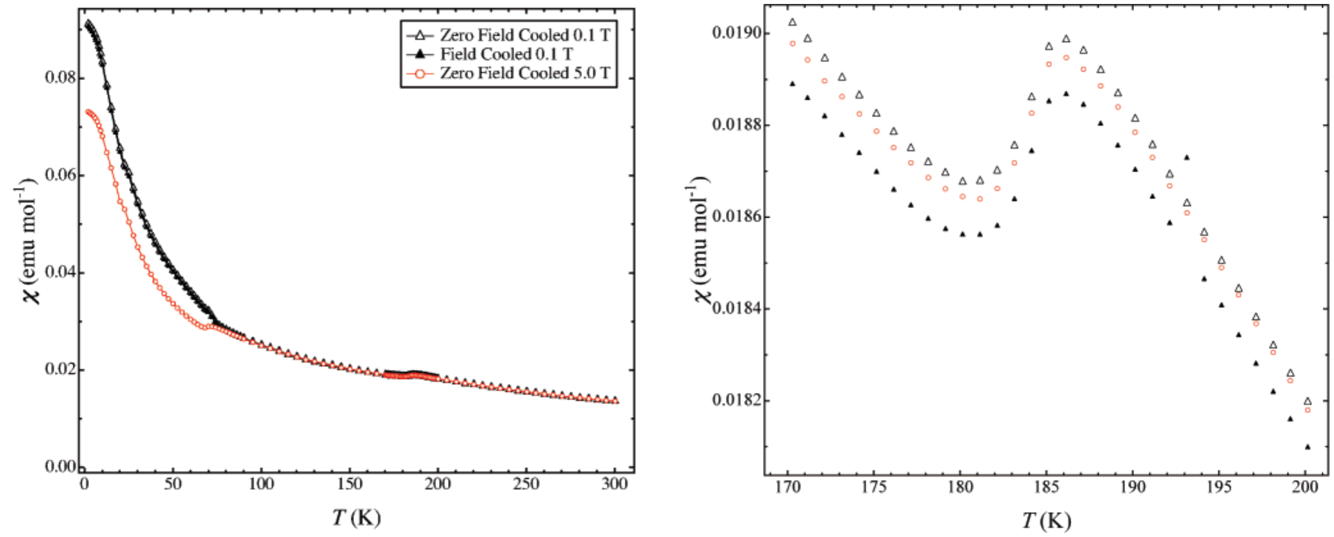

Figure 2. Magnetic susceptibility versus temperature of β-YbV$_4$O$_8$.

Table 1. Curie Constant C, Weiss Temperature θ, and Temperature-Independent Susceptibility χ_0 of β-YbV$_4$O$_8$[a]

C (e.m.u./K/mol)	θ (K)	χ_0 (e.m.u./mol)	temperature range analyzed
4.51(14)	−66.4(4.7)	0.0013(2)	195 K ≤ T ≤ 300 K
2.18(14)	−27.4(4.7)	0.0079(5)	90 K ≤ T ≤ 170 K

[a] The parameters are obtained from the data at 5.0 T.

pyrochlore impurity with the saturation moment of 2 μ_B per formula unit, and that its moment saturates at 0.1 T or below, the amount of the pyrochlore impurity is estimated to 0.23 mg. This corresponds to 0.36% of the total sample amount of 63.25 mg (a quantity in good agreement with results from powder diffraction data, see below).

The pair of 0.1 T data, zero field cooled and field cooled, does not show any significant difference throughout the measured temperature range, indicating that β-YbV$_4$O$_8$ is free from any magnetic order. The anomaly at 185 K indicates a paramagnetic-paramagnetic transition. Above 185 K, the magnetic susceptibility obeys the Curie-Weiss law (Table 1). The obtained Curie constant, 4.51(14) emu K^{-1} mol^{-1}, is in between the calculated values, 4.70 emu K^{-1}mol^{-1} for one Yb^{3+} (^{2}F$_{7/2}$, $p_{\mathrm{eff}} = 4.54$), one V^{3+} ($S = 1$, $p_{\mathrm{eff}} = 2.83$), and three V^{4+} ($S = {}^1/_2$, $p_{\mathrm{eff}} = 1.73$) per unit formula, and 4.07 emu K^{-1} mol^{-1} for one Yb^{3+} (^{2}F$_{7/2}$) and four V^{4+} ($S = {}^1/_2$) per unit formula. As will be explained later, the bond valence sums indicate that the four V sites exhibit an essentially uniform charge distribution above 185 K. One possible explanation for the spin state above 185 K is as follows. At least three of the four V sites show $S = {}^1/_2$ local moment. The remaining V site exhibits either $S = {}^1/_2$ or $S = 1$ local moment. The $S = 1$ moment, if any, is randomly distributed among the four V sites. Negative Weiss temperature (Table 1) indicates antiferromagnetic interaction among the local moments. The remaining three or two 3d electrons per unit formula are itinerant among the four V sites. β-YV$_4$O$_8$ shows similar behavior with corresponding anomaly at 190 K and Curie constant of 1.44(13) emu K^{-1} mol^{-1}, which is almost equivalent to four V^{4+} ($S = {}^1/_2$) per unit formula.[14]

Below 185 K, the magnetic susceptibility decreases slightly but abruptly, and seemingly obeys the Curie-Weiss law (Table 1) down to the anomaly at 70 K. However, the obtained Curie constant, 2.18(14) emu K^{-1} mol^{-1}, is even smaller than the calculated value, 2.57 emu K^{-1} mol^{-1}, for one Yb^{3+} (^{2}F$_{7/2}$) per unit formula. Preliminary studies on the related compound β-YV$_4$O$_8$ showed that its magnetic susceptibility below the transition at about 190 K depends on the individual specimen. While one specimen shows a negative slope in the magnetic susceptibility versus temperature as shown in reference 14, another specimen shows a positive corresponding slope.

A possible explanation for this behavior is that below 185 K in β-YbV$_4$O$_8$ (or 190 K in β-YV$_4$O$_8$), the Curie-Weiss type d-electrons of the vanadium cations separate into two different types, Curie-Weiss type and spin gap type. The former maintain their Curie-Weiss character, though their Curie constants and Weiss temperatures probably change. The magnetic susceptibility corresponding to this type increases with decreasing temperature, obeying $\chi = C/(T - \theta)$, where C = Curie constant and θ = Weiss temperature. The latter lose their spin moment with decreasing temperature, for example, obeying $\chi = A \exp(-\Delta/T)$, where A and Δ are constant. Then the magnetic susceptibility, χ, increases with decreasing temperature if the former type of vanadium cation is dominant and decreases with decreasing temperature if the latter is dominant.

We believe that the ratio of the Curie-Weiss type or spin gap type d-electrons depend on the individual sample. As demonstrated earlier,[14] the β-YV$_4$O$_8$ phase consists of both α- and β-domains. Their domain sizes, especially the size of the α-domains (about 40 Å), should be small enough to influence the magnetic susceptibility. The domain sizes and the α/β ratio in β -YV$_4$O$_8$, on the other hand, depend on the individual specimen. In analogy to the Y-compound, we expect a similar effect for β-YbV$_4$O$_8$ below 185 K and believe that its magnetic susceptibility might also depend on the domain sizes of the α- and β-domains, as well as on the α/β ratio.

Below 70 K, the 5.0 T data decrease slightly and then turn to increase. This decrease is not attributable to the ferromagnetic impurity. This anomaly is considered to be

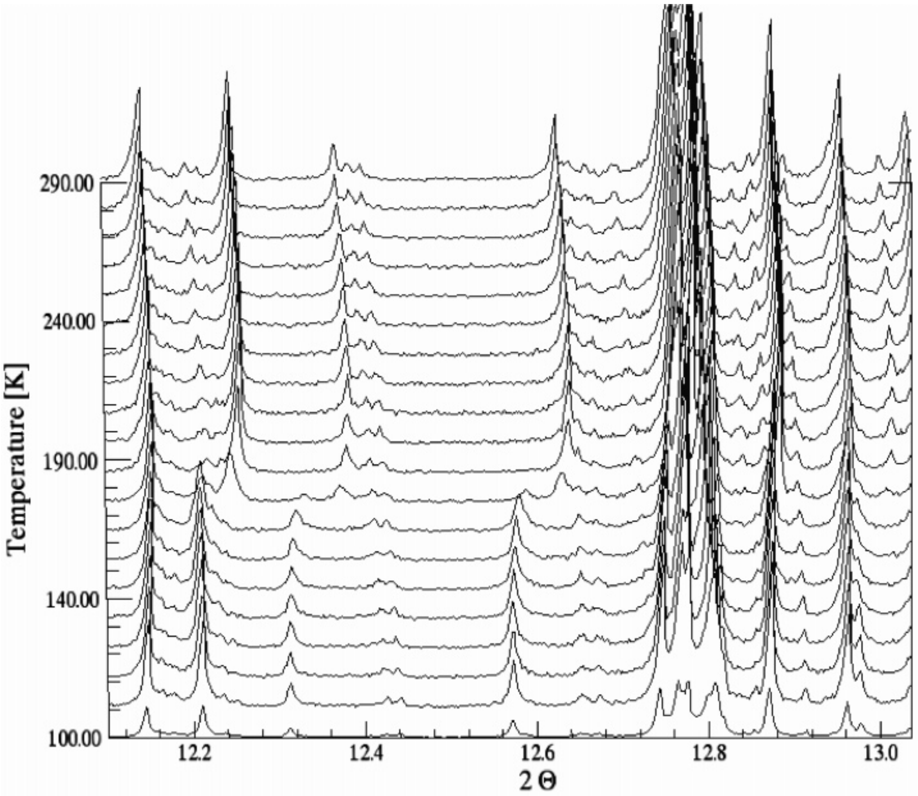

Figure 3. Excerpt of the powder diffraction diagrams of β-YbV$_4$O$_8$ as a function of temperature. Data were measured at beamline ID31, European Synchrotron Radiation Facility, Grenoble, France. The shift of reflections at the phase transition can be clearly observed. At 180 K reflections of both phases β and β' can be observed simultaneously. For the graphic representation the program Powder 3D[24] was used.

intrinsic to either β-YbV$_4$O$_8$ or α-YbV$_4$O$_8$. A similar decrease has been observed in β-YV$_4$O$_8$ at 83 K.[14]

The powder diffraction diagrams can be interpreted assuming a mixture of three phases: the dominant phase β-YbV$_4$O$_8$ (≈75%), the minor admixture α-YbV$_4$O$_8$,[23] (≈24.4%) and a very small volume fraction of an Yb$_2$V$_2$O$_7$-pyrochlore impurity (≈0.6%). The diagrams (Figure 3) reveal that the magnetic transition at approximately 185 K is accompanied by a structural phase transition manifested by the appearance of new reflections between 180 and 185 K. More detailed powder diffraction scans[17] from 160 to 195 K demonstrate that the additional reflections can be attributed to the coexistence of two phases in the temperature range 180−185 K (Figure 4).

The structure refinement based on the single-crystal data show that neither the monoclinic metrics nor the space group symmetry is changed at the phase transition. Hence, we have encountered an isosymmetrical phase transition between two monoclinic phases (in the following designated β and β') with the same monoclinic symmetry $A2_1/d11$.

It has been demonstrated earlier that an isosymmetrical phase transition[25] is necessarily of first order. Discontinuous changes of lattice parameters, resulting in an abrupt change of the unit cell volume (Figure 5), are indeed evidence for this type of phase transition in β-YbV$_4$O$_8$. Relative changes in the lattice parameters at the phase transition are not bigger than 0.4%. In particular, the monoclinic angle α for the β-phase is slightly smaller than 90° and decreases while the transition temperature is approached. At the onset of the phase transition, the "new" monoclinic angle (now of the phase β') is only very slightly smaller than 90° and immediately changes to values larger than 90°. The unit cell volume clearly increases at the phase transition but the relative change is very small (<0.2%). The first-order character of this transformation was also confirmed by differential scanning calorimetry. Although the enthalpy of 2.11 cal/g is fairly small, it is significantly out of the range expected for a second-order transition.

The change in the lattice parameters can be correlated with selected geometrical criteria obtained from the refinements on the basis of the single-crystal data (Figure 6, see Supporting Information). The abrupt decrease of the *a*-lattice parameter can be mainly attributed to the shortening of the V(21)−O(11) distance (approximately 7%) which at the phase transition changes its value from 1.964(9) Å (200 K) to 1.872(8) Å (175 K). The change in the *b*-lattice parameter is basically due to a decrease of the interoctahedral angles. The substantial increase in the *c*-direction can be ascribed to an increase of the V(11)−O and V(12)−O distances which are oriented approximately parallel to this direction.

The most important change in the structure at the phase transition is related to the V(21)O$_6$ octahedra (shown in red in Figure 1) and in particular to the interatomic distance

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(23) It is not possible to synthesize the β-phase pure, as the crystals always show twinning and the twinning boundaries correspond to the structure of α-YbV$_4$O$_8$.

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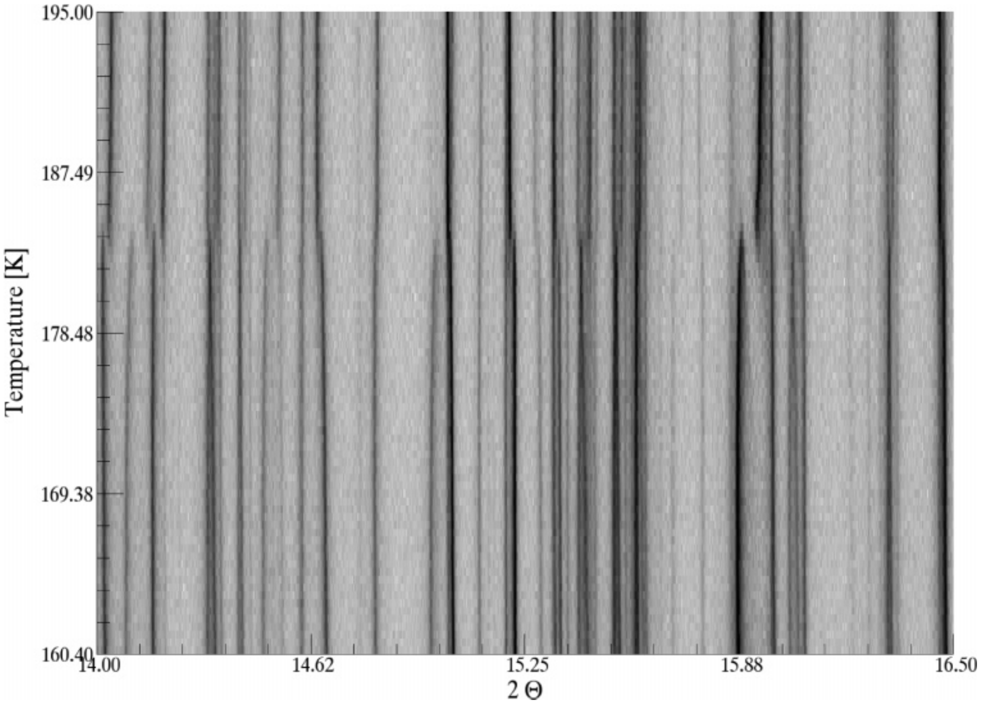

Figure 4. Excerpt of a Guinier simulation (made with the program Powder3D[24]) of the powder diffraction diagrams of β-YbV_4O_8 as a function of temperature. Data were measured at the beamline ID31 of the European Synchrotron Radiation Facility, Grenoble, France. The shift of reflections at the phase transition can be clearly observed. In the temperature range 180−185 K both monoclinic phases β and β' coexist.

V(21)−O11.[26] Altogether this distance shrinks 7% in the temperature range from 290 to 100 K. As a consequence, the average V−O distances in the octahedra decrease (Figure 6). On the other hand, the average distances for the other three octahedral show a small increase. The changes in average distances are reflected in the bond valence sums[27] for the vanadium ions (Figure 6, right). At temperatures above the phase transition, the bond valence sums (calculated on the basis of the empirical parameter for V^{3+}) indicate that there is no clear charge separation of the tri- and tetravalent ions, although a partial separation can possibly be postulated. At the phase transition, the bond valence sum for V21 abruptly increases. When we carry out the calculation for this atom using the empirical parameter for V^{4+}, it becomes evident that a clear charge ordering of V^{3+} and V^{4+} occurs during the phase transition. Despite the fact that the empirical values for bond valence calculations are determined for room temperature, we can safely say that the charge ordering in this compound is complete. The V^{3+} ions are incorporated into the V11, V12, and V22 octahedra, while the V^{4+} ions occupy the V21 octahedra.

One possible origin of the charge ordering might be the Coulomb repulsion between the cations. Each of the four symmetry-independent V atoms has approximately the same coordination by other V-atoms, all of them having eight nearest V neighbors in the shape of a bicapped trigonal prism. Yet the coordination by Yb differs for the four sites (see also Supporting Information). V11, V12, and V22 have four nearest Yb neighbors (at distances between 3 and 4.2 Å) in a coordination which can alternatively be described as a strongly distorted tetrahedron or a monocapped planar triangle. The V21 site, on the other hand, has only three nearest Yb neighbors (at distances between 3.1 and 3.35 Å). This difference in the coordination might imply a lower Coulomb repulsion between the cations and could explain the preference of the higher charged V^{4+} for this site.

Since the transition temperature is as high as 185 K, it would be reasonable to consider that Yb^{3+} maintains its Curie-Weiss paramagnetic character with $^2F_{7/2}$ state. This assumption is also supported by the fact that the coordination sphere around the Yb cation hardly changes at the transition.

We thus attribute the magnetic anomaly exclusively to the magnetic character of the vanadium cations. The small but abrupt change in the magnetic susceptibility at 185 K would then be directly related to the charge ordering of the four vanadium cations. Several Curie-Weiss spins of these four vanadium cations gradually vanish with decreasing the temperature from 185 K. As most of the V−V distances are elongated or nearly unchanged after the transition and only part of the V11−V12 and V12−V12 distances shorten (Figure 7), we expect the annihilation of the spins to take place in the V11−V12 zigzag chain. The V11 and V12 cations would thus assume spin gap type behavior, while the V21 and V22 cations would maintain their Curie-Weiss-type character. In this context, one should also take into account that to relax the Coulomb repulsion, partial charge ordering would be sufficient, but that the spin annihilation could require the unusual complete charge ordering observed in this compound. We believe that (like in β-YV_4O_8) the ratio of vanishing spin/surviving spin depends on the structural disorder, the ratio of the α and β' domains, and

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(26) Additional figures showing important interatomic distances and angles as a function of temperature are included in the Supporting Information.

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(28) Symmetry code: (i) $-x, -y, ^1/_2 - z$; (ii) $x, -^1/_2 + y, -^1/_2 + z$; (iii) $x, -^1/_2 + y, ^1/_2 + z$; (iv) $-x, ^1/_2 - y, -z$; (v) $-x, 1 - y, ^1/_2 - z$. (Note the origin shift with respect to ref 13.)

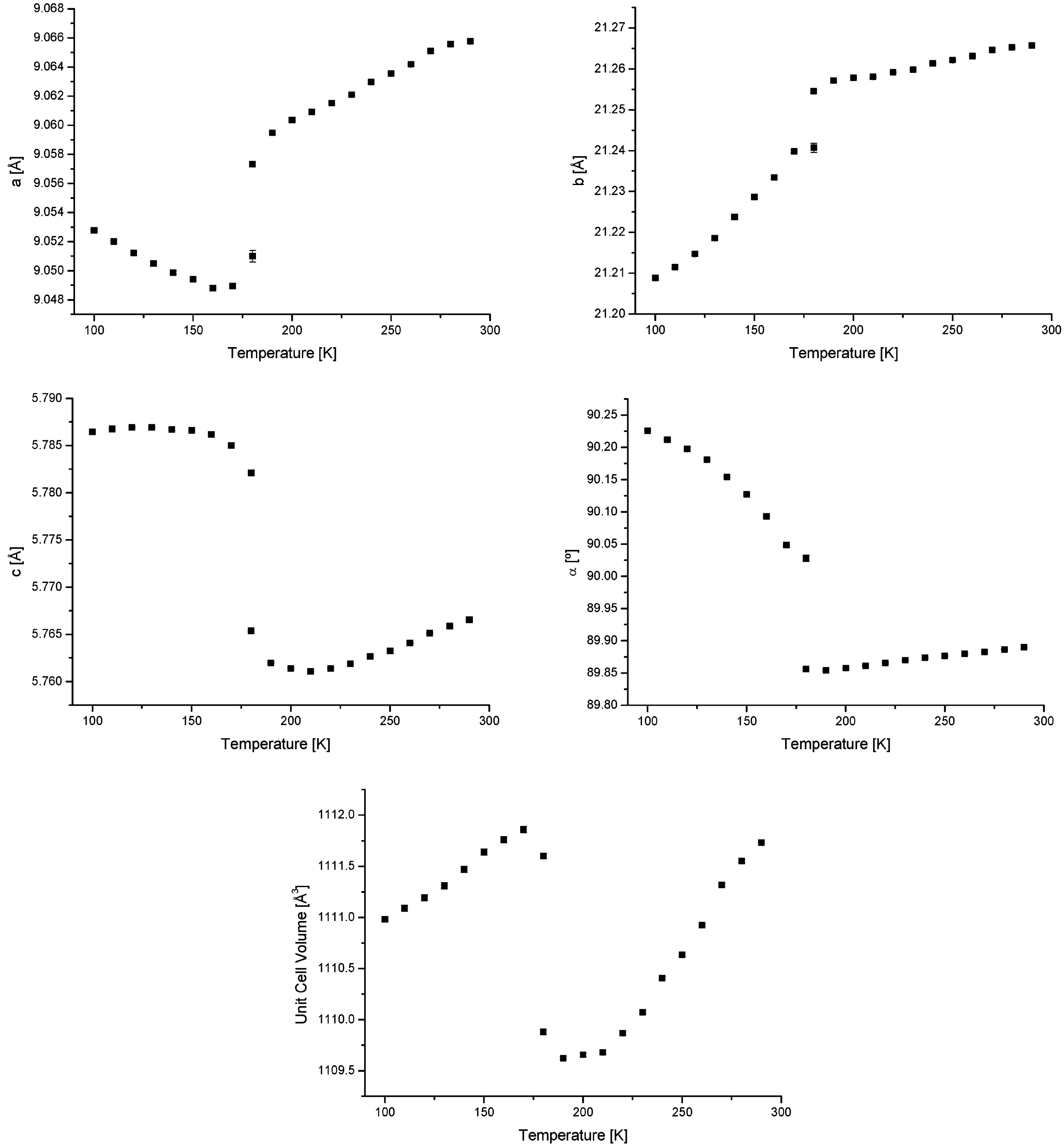

Figure 5. Temperature dependence of lattice parameters and unit cell volume of β-YbV$_4$O$_8$.

their corresponding domain sizes, yet more detailed experimental evidence is necessary to elucidate these mechanisms further.

Discussion

As has already been pointed out in the Introduction, charge ordering in transition metal oxides involves usually a partial charge separation. The complete ordering of V^{3+} and V^{4+} observed here is therefore a unique case.

It is also noteworthy that isosymmetrical phase transitions are not frequently observed. They are often induced by pressure and are usually associated with a collapse of the unit cell volume. Several mechanisms have been observed or suggested. The phase transitions in Na_3MnF_6[29] and cerium[30] have been attributed to changes in the electron configurations. Mechanisms of a more geometrical nature have also been postulated. The transformation in potassium titanyl phosphate is characterized by a tilting of the PO_4 tetrahedra with respect to the TiO_6 octahedra.[31] On the other hand, the cation coordination number is changed at the transition in orthorhombic PbF_2.[32] The transition in $EuCoP_2$ has been associated with a change of the valence state of

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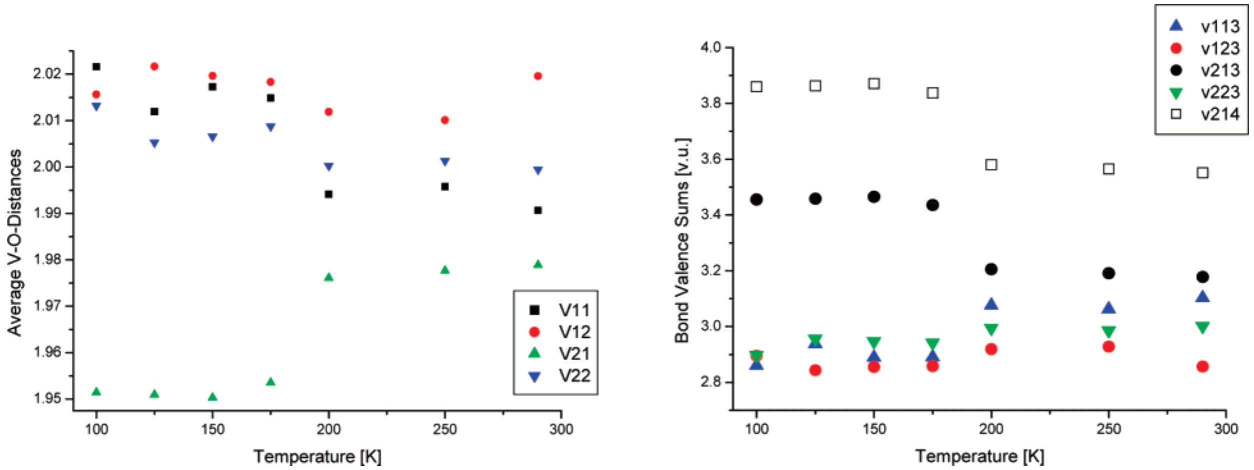

Figure 6. Left: Average V−O distances in the VO_6 octahedra of β-YbV_4O_8 as a function of temperature. Right: Bond valence sums according to Brese & O'Keeffe[27] for the V-cations as a function of temperature. Full symbols represent BVS calculated on the basis of the bond valence parameter for V^{3+}; open symbols represent values calculated on the basis of the empirical parameters for V^{4+}.

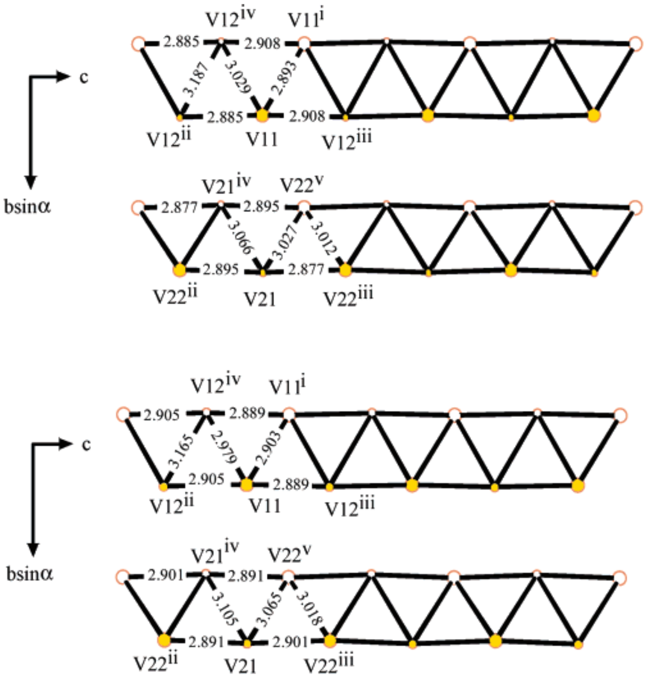

Figure 7. V−V distances in Å in β-YbV_4O_8 (top, 290 K) and β'-YbV_4O_8 (bottom, 100 K).[26,28]

europium (Eu^{2+} changes to nonmagnetic Eu^{3+}) accompanied by a simultaneous appearance of magnetism related to the Co(3d) sublattice.[33]

As far as temperature-induced isosymmetrical phase transitions are concerned, the number of well-characterized examples is very limited. Isostructural transitions in the intermetallic compounds TbPdAl and GdPdAl have been attributed mainly to changes in the electronic structure of Pd.[34] A nearly continuous isosymmetric phase transition induced by temperature has been observed in ammonium hexafluorophosphate NH_4PF_6[35] due to small coordination changes of the NH_4^+ ion. A high spin-low spin transition in Fe(II) has been found responsible for the isosymmetrical transition induced by X-ray illumination in the Prussian blue analogue cesium iron hexacyanochromate.[36] One of the best examples of isosymmetrical phase transitions related to valence changes is the "heavy fermion system" $YbInCu_4$.[37] Above the transition temperature this compound is a Curie-Weiss paramagnet, while at low temperatures Yb assumes a mixed valence state and the compound is a Pauli paramagnet.

No cases of an isosymmetrical phase transition associated to charge ordering exist in the literature. This is obviously due to the fact that in general charge ordering is a symmetry-breaking process. In β-YbV_4O_8 the situation is rather special as there are four symmetrically independent positions in the nonordered structure and the ordering is possible without lowering the space group symmetry.

Similar studies on other related compounds of the family are in progress and should provide additional evidence which might help to understand the underlying mechanism for the observed paramagnetic-paramagnetic transition and clarify its relation to the charge ordering.

Conclusion

The mixed valence vanadate β-YbV_4O_8, which crystallizes in a structure related to $CaFe_2O_4$, undergoes a structural phase transition of first order at approximately 185 K. The phase

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transition is accompanied by a paramagnetic-paramagnetic anomaly. The transition is remarkable in two respects:

(1) It is the first isosymmetrical phase transition observed attributed to charge ordering.

(2) In contrast to charge ordering transitions in other transition metal oxides, where the charge separation is only partial, the bond valence sums for β-YbV$_4$O$_8$ indicate that the charge ordering in this compound is complete.

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Supporting Information Available: Explanatory note concerning the higher dimensional refinement (PDF); additional information concerning the single-crystal refinements for both the three- and four-dimensional models (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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