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Structural order parameters of the $\text{RbPO}_3\text{-HT-RbPO}_3\text{-H}$ transition—a soft-Ising-system

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Received 26 March 1998

Abstract. Order parameter and spontaneous strain of the coelastic Brillouin zone boundary transition $\text{RbPO}_3\text{-HT (Bbmm)} \rightarrow \text{RbPO}_3\text{-H (Pbnm)}$ at $T_c = 915$ K were obtained from Rietveld refinement of high-resolution neutron powder diffraction data. The main aspect of the transition is that of zone boundary ordering of an Ising pseudo-spin variable, describing two distinct distorted states $\pm\Phi$, where the absolute value $|\Phi|$ has some displaced character and is also temperature dependent. For Rietveld refinement the system was thus described by an Ising-like occupational parameter Q_{OD} and displaced atomic shifts from the aristotype structure, which were derived from a constrained split model. The thermodynamic order parameter, representing the average state of order in the system, is the product of the occupational and displaced variables. An empirical power law $Q \sim (T - T_c)^\beta$ leads to a scaling exponent $\beta = 0.17$, whereas the total symmetric spontaneous strain ε of the unit cell follows a critical scaling $\varepsilon \sim (T - T_c)^{2\beta}$. Due to a small hysteresis derived from thermo-analytical measurements Landau first-order behaviour could be verified with a discontinuous shift of the polyphosphate chains in [010] of $\Delta y \approx 10 \pm 0.5$ pm. Below about 840 K deviations of the order parameter behaviour to a less pronounced temperature dependence indicate a change in local dynamics.

1. Introduction

Rubidiumpolyphosphate, RbPO_3 shows a series of structural phase transitions from a disordered high-temperature prototype, $\text{RbPO}_3\text{-HT}$, to various structurally related or derivative, ordered phases (Holst *et al* 1994). The general architecture of all phases is two-dimensional packing of polyphosphate tetrahedral zweier-einfach chains running along the crystallographic b -axis with Rb^+ cations in-between. The phase transitions are topotactic and do not change the direction of the chains. The sequential transitions are driven by conformational ordering of the chain composing phosphate tetrahedra through collective dynamic tilting. The space group symmetry Bbmm of the high-temperature prototype phase, $\text{RbPO}_3\text{-HT}$, arises from a statistical superposition of distorted chains. On cooling below $T_c = 915$ K, collective ordering of one particular conformational degree of freedom sets in at the Brillouin-zone boundary. The order parameter of the resulting phase, $\text{RbPO}_3\text{-H}$, belongs to the irreducible representation Y_2^+ according to the labelling of Stokes and Hatch (1988), and leads to space group Pbnm. At lower temperatures further conformational degrees of freedom order at different points of the Brillouin-zone

surface. The nomenclature of the phases and the non-standard space-group settings used in this paper follow the suggestions of Jost and Schulze (1971) who investigated the crystallography of the isostructural high-temperature phases of KPO_3 by single-crystal x-ray diffraction.

The order parameter Q of the $\text{RbPO}_3\text{-HT} \rightarrow \text{H}$ transition shows quasi-continuous behaviour with an empirical power law $Q \sim (T - T_c)^\beta$ with $\beta \sim 0.2$ as derived from the temperature dependence of x-ray powder diffraction intensities of superlattice reflections (Holst *et al* 1994). Due to the limited data resolution, however, this power law may indicate tri-critical to slightly first-order behaviour. As the main aspect this zone boundary ordering of an Ising pseudo-spin variable, describing two distinct distortional states $\pm\Phi$, also involves a displaced distortion of the absolute value of $|\Phi|$. This distortion possesses identical symmetry characteristics, such that it increases with increasing degree of order as the temperature is reduced. Soft-Ising systems have been considered by Schneider and Stoll (1971), Bruce (1980), Giddy *et al* (1989), Normand *et al* (1990) and others from a theoretical point of view. To investigate the $\text{RbPO}_3\text{-HT} \rightarrow \text{RbPO}_3\text{-H}$ transition mechanism in more detail, in particular the coupling between displaced and the order/disorder aspect, high-resolution neutron time-of-flight powder diffraction spectra were taken and analysed by the Rietveld method.

2. Experimental details

2.1. Thermal analysis, differential scanning calorimetry (DSC)

Thermal analytical measurements of rubidium polyphosphate, prepared after Holst *et al* (1994) by thermal dehydration of RbH_2PO_4 , were performed in platinum crucibles by a SETARAM DSC 121 in an argon atmosphere with a heating rate of 1 K min^{-1} in the range from 300 K to 1025 K. The detection limit is 14.65 mJ s^{-1} with a temperature error of about 0.05 K.

2.2. Time-of-flight neutron scattering

The measurements were performed on the high-resolution powder diffractometer (HRPD) at the Rutherford Appleton laboratory (RAL, ISIS) in Didcot (UK) equipped with a furnace. The vanadium sample-can holds approximately 1 cm^3 . Backscattering geometry ($160^\circ \geq 2\theta \geq 176^\circ$) and using ^6Li doped glass-scintillators lead to a resolution of $\Delta d/d \approx 8 \times 10^{-4}$ of the spectra. They were taken between 30 000 and 130 000 μs flight time at 739 K, 789 K, 839 K, 879 K, 889 K, 909 K and between 40 000 and 140 000 μs at 864 K, 929 K, 949 K and 959 K, where the error in temperature was estimated to be $\pm 0.2 \text{ K}$. The spectra were summed for 6 h and corrected for the incident flux distribution by division of each spectrum by a suitable monitor spectrum. Furthermore, the data were corrected for detector efficiency by normalization with a flux normalized vanadium spectrum. Rietveld refinement was carried out using the code of David *et al* (1992).

From figures 4–10 error bars do not exceed the datapoint area, if not otherwise stated or shown.

3. Results and discussion

3.1. Differential scanning calorimetry

The RbPO₃-HT → H phase transition is associated with a λ -shaped excess heat capacity without any discernible latent heat. However, the transition exhibits a small hysteresis loop at $\Delta T = 0.7$ K. On heating, the transformation to RbPO₃-HT takes place at $T_c = 915.1$ K, while the retransformation-peak to the low-symmetry phase occurs at $T_c = 914.4$ K (figure 1). Thus, the transition is not totally continuous and, therefore, of first order. In the light of this result, the non-classical power-law behaviour described by Holst *et al* (1994) can be understood as an empirical approximation to quasi-continuous first-order behaviour.

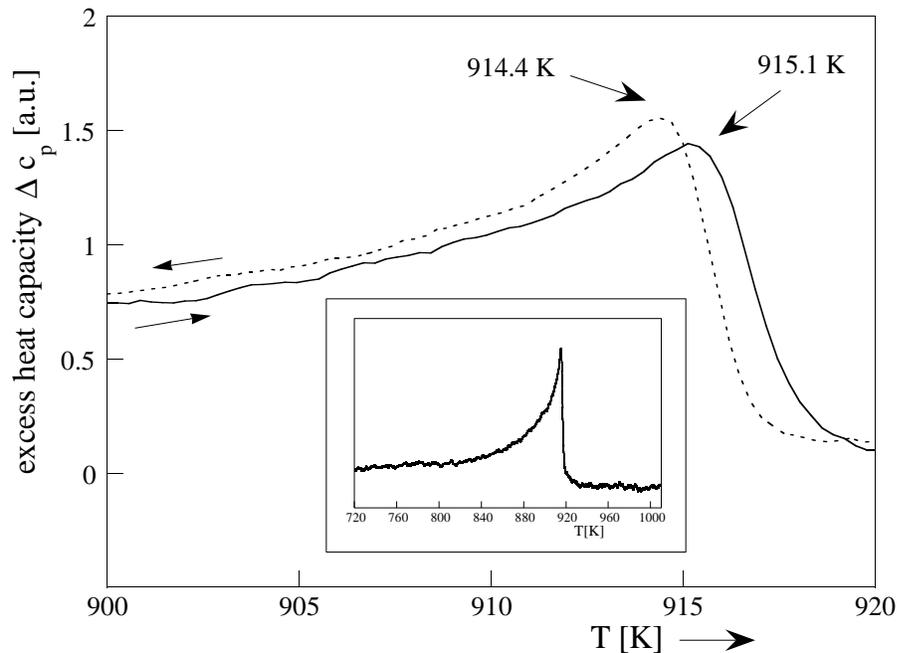


Figure 1. DSC-trace of the RbPO₃-H \leftrightarrow RbPO₃-HT transition, measured with a heating rate of 1 K min⁻¹. Given are the heating and cooling curves very close to the transition point $T_c \approx 915$ K showing a small hysteresis effect at $\Delta T = 0.7$ K. The small picture illustrates λ -shape.

3.2. Neutron diffraction Rietveld results

Table 1 indicates the free positional variables necessary for the description of the RbPO₃-HT (Bbmm) and RbPO₃-H (Pbnm) structures. For reference the corresponding ideally symmetric state of untilted chains is also given; this aristotype is also of Bbmm symmetry, with all atoms in special positions. In the refinement of RbPO₃-HT, the tilting disorder is accounted for by ‘split-positions’: a small displacement from the special position leads to a probability density distribution splitting into two slightly displaced symmetry-related maxima. This distribution function arises from superposition of two equally occupied

Table 1. Refinable positional parameters for RbPO₃-H, RbPO₃-HT and the hypothetical aristotype structure, the ideal *zweier-einfach* chain. For *H*-modification the constraints of the two superimposed polyphosphate chains are given, distinct by a lower index of (+) or (−), the free variables x , y , z or Δx , Δy , respectively are identical for the corresponding sites, whose sum of occupation is constrained to one. In RbPO₃-HT and the aristotype symmetry, breaking positions according to Pbnm-spacegroup symmetry are marked in bold.

	x	y	z	Occ.
RbPO ₃ -H (Pbnm)				
Rb	x	$0.25 + \Delta y$	0.25	1.0
P ₍₊₎	x	$0.75 + \Delta y$	0.75	p
O(1) ₍₊₎	x	$0.75 + \Delta y$	z	p
O(2) ₍₊₎	$0.25 + \Delta x$	y	0.75	p
P _(−)	x	$0.75 - \Delta y$	0.75	$1 - p$
O(1) _(−)	x	$0.75 - \Delta y$	z	$1 - p$
O(2) _(−)	$0.25 - \Delta x$	$-y$	0.75	$1 - p$
RbPO ₃ -HT (Bbmm)				
Rb	x	0.25	0.25	
P	x	0.75	0.75	
O(1)	x	x	z	
O(2)	x	y	0.75	
aristotype (Bbmm)				
Rb	x	0.25	0.25	
P	x	0.75	0.75	
O(1)	x	0.75	z	
O(2)	0.25	0	0.75	

ϕ -tilt-states of the polyphosphate chains. The short value of the b_0 -lattice parameter of 4.54 Å compared to the length of an edge of a phosphate group (~ 2.4 Å) also indicates clearly, that in the high-temperature modification the chains are tilted rather than straight (figure 2, Holst *et al* 1994), albeit with no lateral long correlation between the chains. This kind of conformational disorder has been found by Jost and Schulze (1971) in the isotopic modification KPO₃-HT. Note that in the Pbnm-modification another mode of dynamic tilting disorder in [001] is present already according to the RbPO₃-H \rightarrow RbPO₃-Z transition, which we choose to account for by refining anisotropic temperature factors. However, their values predominantly increase in the direction of the chain movement with increasing temperature and exhibit relatively small error. Moreover, the phosphate-tetrahedron geometry is much less distorted than in isotropic refinement.

The symmetry will be Pbnm if the two split positions or tilt-states are no longer equally occupied. Accordingly, an occupational probability variable has to be introduced for RbPO₃-H, which describes the difference in occupation of two superimposed symmetry-constrained phosphate chains of opposite tilting as indicated in figure 2. A fractional occupancy for the Rb-site is expected as well, but this could not be resolved with the present data-set. However, any small displacement is covered by the anisotropic refinement.

The anisotropic refinement of the data of the HT-phase converged to satisfactory difference plots (figure 3). In this modification displacement-splitting for the P-position is expected in the y -direction, but could not be resolved in the scope of this work; any attempt to refine these parameters lead to severe numerical problems due to correlations with the mean-square displacement parameters u_{22} of these positions. The values obtained always fall within the estimated standard deviation. However, the obtainable split for both was

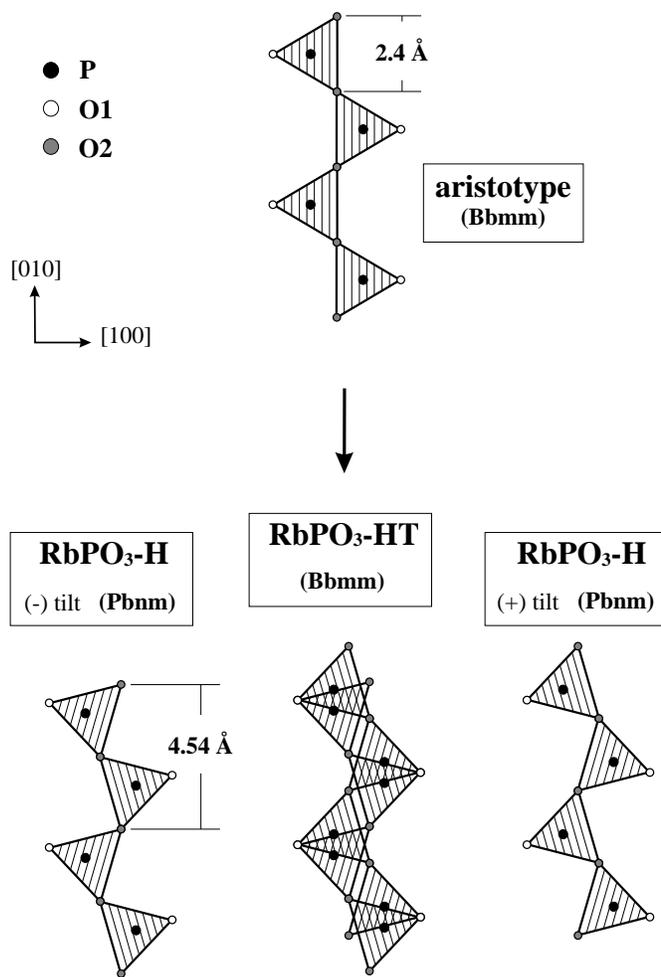


Figure 2. Schematic visualization of the superposition of two oppositely oriented polyphosphate chains in RbPO₃-HT. The ideal hypothetical aristotype configuration is also shown for reference.

marginal and covered by the estimated standard deviations. Accordingly, the y -coordinates were fixed on the mirror plane at $y = 0.25$ and $y = 0.75$, respectively. Split positions for the oxygen atoms, however, were well resolved. Atomic positions, mean-square displacement data and bond distances and angles for three representative temperatures (789 K, 909 K and 959 K) are given in table 2. Data for the other temperatures can be obtained from the authors on request.

For the refinement of the H-phase the positional and occupancy parameters as outlined in table 1 were used. For temperatures below 840 K the occupancy parameter refined to 1.0 within limits of error, i.e. the disorder in chain-tilting as indicated in figure 2 is practically absent, while the displaced distortion is still increasing with decreasing temperature (figure 4). When the temperature approaches T_c however, the occupancy of the opposite tilt state becomes appreciable. Note that this ‘two-chain’ refinement results in a well resolved split position of the phosphorous site. Attempts to refine the structure without

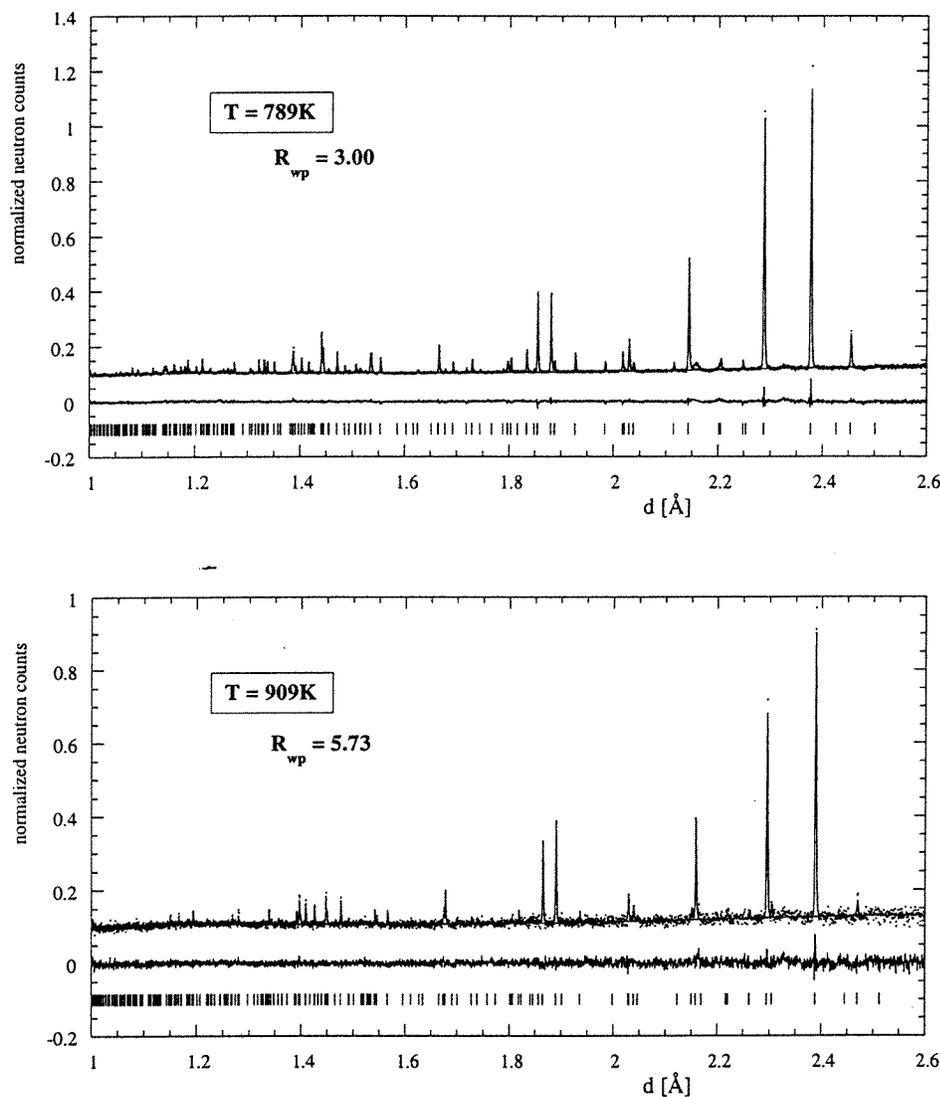


Figure 3. Neutron diffraction Rietveld refinement results for RbPO₃-HT at 959 K and RbPO₃-H at 789 K and 909 K.

split positions in this temperature range result in a considerable distortion of the phosphate tetrahedra and is discarded. The structural data of the final results are given in table 2, a representative Rietveld difference plot is given in figure 3.

3.3. Symmetry considerations—order parameter

The sign of the [100]-tilt of each individual chain may be considered as an Ising-like variable, $\pm\Phi$. Equal probability of $+\Phi$ and $-\Phi$ leads to Bbmm symmetry; preferential anti-phase ordering with wavevector $q_0 = 1/2(a^* + C^*)$ leads to Pbnm symmetry, for which the probability of finding either ‘+’ or ‘-’ at a particular chain position becomes

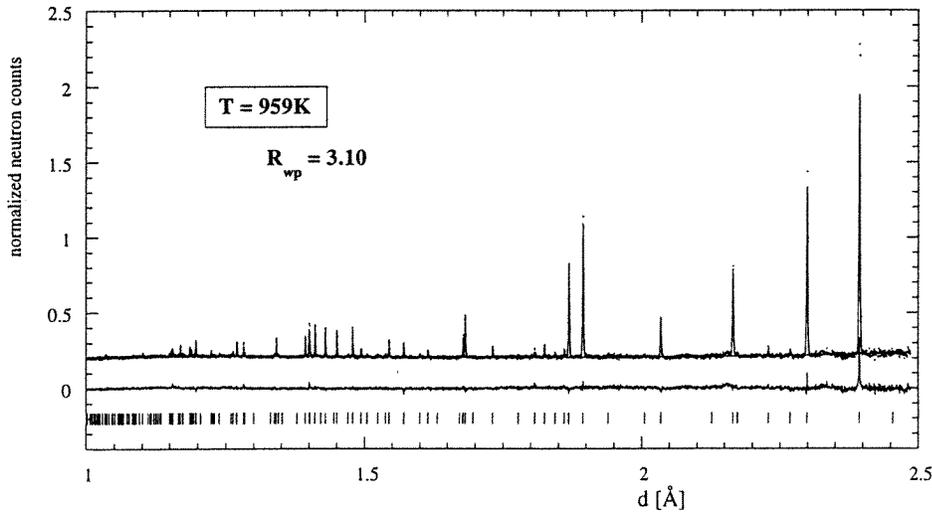


Figure 3. (Continued)

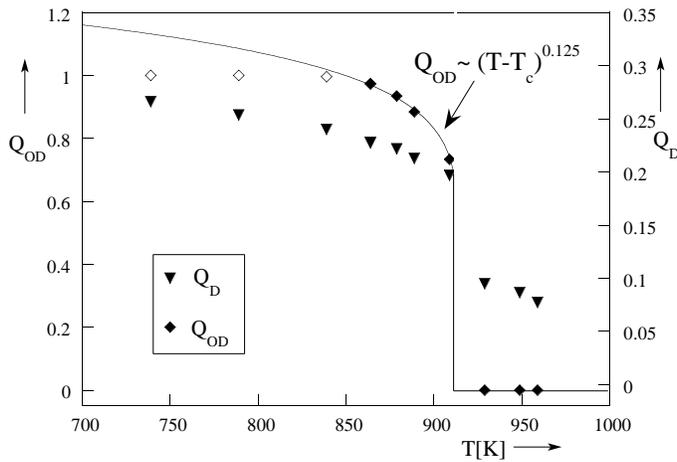


Figure 4. Thermal behaviour of Q_{OD} and the chain displacement Q_D . The latter exhibits a discontinuity at $T_c = 915$ K. In the region $840 \text{ K} < T < T_c$ the critical scaling of Q_{OD} can be described by an empirical power law $Q_{OD} \sim (T - T_c)$. Error bars in this and figure 5 do not exceed the data-point area.

different from $1/2$. An ordering variable Q_{OD} may thus be defined from the difference in occupational probability p for the two states as

$$Q_{OD} = p_+ - p_- = 2p_+ - 1 \quad (1)$$

with $p_+ + p_- = 1$. Note that with this definition Q_{OD} is independent of the magnitude of the tilt angle. The thermal behaviour of Q_{OD} is displayed in figure 4 (if not otherwise stated or shown error bars do not exceed the size of the datapoint). This refinement parameter rises steeply with decreasing temperature below T_c and the ‘ordered’ state $Q_{OD} = 1$ is reached at rather high temperature, $\sim 840 \text{ K} \approx 0.9 T_c$. For the region 840 K to T_c an empirical

Table 2. Rietveld refinement results from high-resolution neutron diffraction. Structural parameters for three representative temperatures, 789 K (< 840 K), 909 K (840 K $< T < T_c$) and 959 K ($> T_c$) are given. (Data of all temperatures may be obtained from the authors.)

RbPO ₃ -H (789 K), Pbnm (No 62), Z = 4										
$a = 13.21034(8)$ Å, $b = 4.57385(1)$ Å, $c = 6.13441(2)$ Å										
Atomic coordinates										
Atom	x	y	z	Occ.	B ₁₁	B ₂₂	B ₃₃	B ₂₃	B ₁₃	B ₁₂
Rb	0.1031(3)	0.2778(6)	0.25	1.0	8.6(2)	3.8(1)	5.2(2)			-0.1(1)
P ₍₊₎	0.1782(3)	0.8060(6)	0.75	1.0	5.2(2)	1.2(1)	4.5(2)			-0.7(1)
O(1) ₍₊₎	0.1229(4)	0.7571(7)	0.5473(6)	1.0	16.0(3)	5.6(2)	10.0(3)	-1.9(2)	-7.5(2)	0.6(1)
O(2) ₍₊₎	0.2184(3)	0.1310(6)	0.75	1.0	4.0(2)	1.3(1)	16.3(4)			-1.0(1)
P ₍₋₎	0.6782(3)	0.8060(6)	0.25	0.0	5.2(2)	1.2(1)	4.5(2)			-0.7(1)
O(1) ₍₋₎	0.6229(4)	0.7571(7)	0.0473(6)	0.0	16.0(3)	5.6(2)	10.0(3)	-1.9(2)	-7.5(2)	0.6(1)
O(2) ₍₋₎	0.7184(3)	0.1310(6)	0.25	0.0	4.0(2)	1.3(1)	16.3(4)			-1.0(1)
RbPO ₃ -H (909 K), Pbnm (No 62), Z = 4										
$a = 13.3209(3)$ Å, $b = 4.58934(5)$ Å, $c = 6.16223(9)$ Å										
Atomic coordinates										
Atom	x	y	z	Occ.	B ₁₁	B ₂₂	B ₃₃	B ₂₃	B ₁₃	B ₁₂
Rb	0.1035(7)	0.265(2)	0.25	1.0	8.5(6)	5.6(4)	6.1(6)			-0.1(4)
P ₍₊₎	0.176(1)	0.792(3)	0.75	0.87(2)	8.2(7)	1.1(5)	6.0(7)			-0.8(5)
O(1) ₍₊₎	0.122(1)	0.755(4)	0.549(2)	0.87(2)	17.9(8)	9.6(6)	11.0(8)	-4.0(9)	-8.4(7)	1.4(8)
O(2) ₍₊₎	0.221(1)	0.107(2)	0.75	0.87(2)	7.3(10)	2.6(8)	21.0(9)			-3.4(4)
P ₍₋₎	0.676(1)	0.792(3)	0.25	0.13(2)	8.2(7)	1.1(5)	6.0(7)			-0.8(5)
O(1) ₍₋₎	0.622(1)	0.755(4)	0.049(2)	0.13(2)	17.9(8)	9.6(6)	11.0(8)	-4.0(9)	-8.4(7)	1.4(8)
O(2) ₍₋₎	0.721(1)	0.107(2)	0.25	0.13(2)	7.3(10)	2.6(8)	21.0(9)			-3.4(4)
RbPO ₃ -HT (959 K), Bbmm (No 62), Z = 4										
$a = 13.3695(1)$ Å, $b = 4.59648(2)$ Å, $c = 6.17481(4)$ Å										
Atomic coordinates										
Atom	x	y	z	Occ.	B ₁₁	B ₂₂	B ₃₃	B ₂₃	B ₁₃	B ₁₂
Rb	0.1037(3)	0.25	0.25	1.0	9.3(3)	6.3(2)	6.0(2)			
P	0.1786(4)	0.75	0.75	1.0	7.8(3)	2.6(2)	5.5(3)			
O(1)	0.1220(6)	0.695(3)	0.552(1)	1.0	18.8(5)	4.9(10)	11.7(4)	-1.7(4)	-8.5(4)	0.8(3)
O(2)	0.2211(6)	0.070(2)	0.75	1.0	3.8(8)	4.4(5)	24.2(8)			-3.4(3)

power law $Q_{OD} \sim (T - T_c)^\beta$ with $\beta = 1/8$ can be fitted to the data (figure 4). However, it is evident that this system does not show any kind of classical two-dimensional (2D) Ising-like behaviour, because complete ordering, $Q_{OD} = 1$, is already reached at $0.9 T_c$ and therefore, the fitted power law curve deviates considerably to higher values at lower temperatures.

In addition to the chain disorder as described by Q_{OD} , the magnitude of the tilt becomes smaller with increasing temperature and the chain conformation tends towards an ideal zweier-einfach chain. The tilt angle is a measure of symmetry breaking atomic shifts away from the aristotype conformation indicated in figure 2 and table 1. The rigid-unit tilting system requires that the y-coordinates of all positions in the Pbnm-phase locally deviate from the mirror planes perpendicular to the chain which are present in the Bbmm symmetry. Further, the tilting shifts the bridging oxygen (O2) away from the diad in [100] in the aristotype. All these shifts belong to the same irreducible representation as

the variable Q_{OD} : they all break the same symmetry elements and lead to space group Pbnm. Therefore, we defined a displaced amplitude of ordering, Q_D as the sum of the Bbmm-symmetry breaking positional shifts according to the atomic parameters $y(\text{Rb})-0.25$, $y(\text{P})-0.75$, $y(\text{O1})-0.75$, $x(\text{O2})-0.25$ and $y(\text{O2})$ (see also table 1).

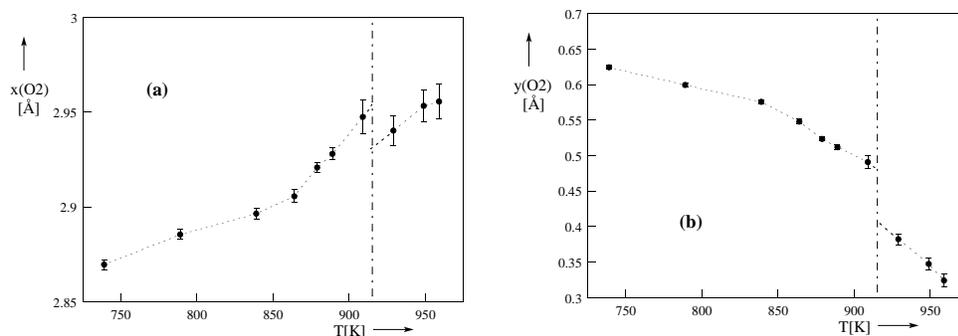


Figure 5. Atomic positional parameter (a) $x(\text{O2})$ and (b) $y(\text{O2})$ against temperature. In addition to the discontinuous jump occurring at $T_c = 915$ K a change in thermal regime is observed at about 840 K ($T/T_c \approx 0.92$).

As expected, the value of Q_D decreases with increasing temperature, exhibits a discontinuity at the transition point and remains non-zero in the high-temperature phase (figure 4). These facts do not allow us to fit a power law to the thermal behaviour of Q_D . The temperature dependence of the bridging oxygen (O2) x - and y -fractional coordinates are given in figure 5. Note that the onset of the chain disorder at about 840 K is connected to a change in the slope of that temperature dependence displaced parameters, indicating a change in thermal regime.

3.4. Unit cell strain

At the RbPO₃-HT \rightarrow RbPO₃-H transition only translational symmetry is broken, and point group symmetry is conserved. Accordingly, ordering is associated with a non-symmetry-breaking (co-elastic) strain of the unit cell. Co-elastic spontaneous strain ε only occurs in the [100]- and [010]-direction while within experimental error the c -axis ([001]) shows linear thermal expansion (figure 6).

The significant non-zero components of the strain tensor, $\varepsilon_{11} = (a_{HT}/a) - 1$ and $\varepsilon_{22} = (b_{HT}/b) - 1$, were obtained by reference to the extrapolated thermal behaviour of the lattice constants of the HT-phase a_{HT} and b_{HT} (figure 6). The scalar spontaneous strain $\varepsilon_s = (\sum \varepsilon_{ik}^2)^{1/2}$ (Aizu 1970) follows an empirical power law $\varepsilon_s \sim (T - T_c)^\beta$ with $\beta = 0.34$ and $T_c = 915$ K (figure 7). Again, below about 840 K the temperature dependence becomes much weaker.

As discussed, the parameters Q_{OD} and Q_D distort the symmetry in the same way and hence belong to the same irreducible representation. However, it is important to note that they do not represent thermodynamic order parameters. According to Landau theory, such parameters should show the same or at least a very similar temperature dependence unless they operate on very different time scales (Salje 1990). This however, is not the case for the present system. Further, neither for Q_{OD} nor Q_D can a linear-quadratic scaling relation with spontaneous strain be established (figure 8).

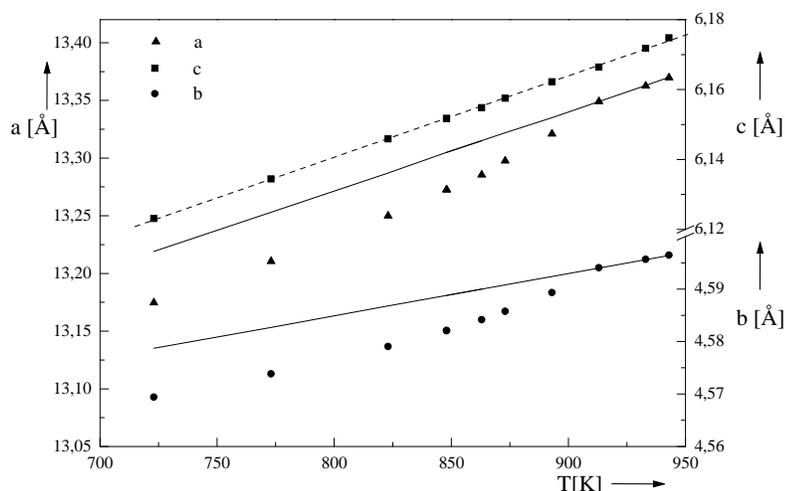


Figure 6. Lattice parameters a , b and c against temperature. The lines are the extrapolated values of $\text{RbPO}_3\text{-HT}$ to lower temperatures. According to symmetry a spontaneous strain ε only occurs in $[100]$ and $[010]$, while $[001]$ exhibits linear thermal expansion.

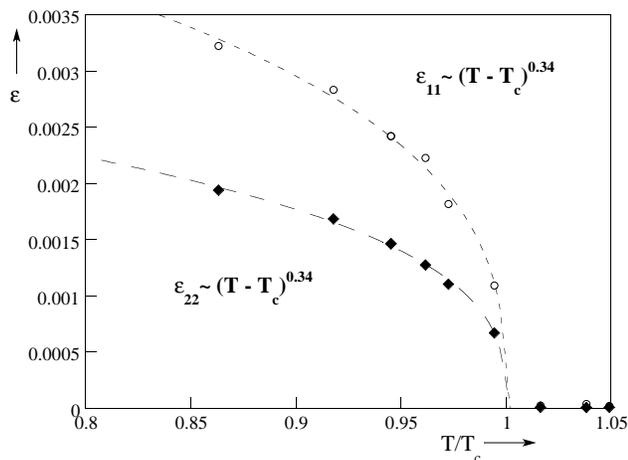


Figure 7. Critical scaling of the components ε_{11} and ε_{22} of the spontaneous strain. Power laws $\varepsilon_{ij} \sim (T - T_c)^\beta$ with $\beta = 0.34$ and $T_c = 915$ K can be fitted.

3.5. Thermodynamic order parameter

The observations can be explained by considering the thermodynamic order parameter as a soft-Ising variable. The local ordering variable, the tilt angle of an individual chain, resides locally in a shallow local double well potential, and it is coupled to its neighbour by some coupling constant j . The deep well limit is associated to the classical Ising model (Bruce, 1980). Such models have frequently been employed in molecular dynamics simulations of phase transitions (Schneider and Stoll 1971, Giddy *et al* 1989, Padlewski *et al* 1992). The local behaviour of every polyphosphate chain site can hence be expressed by the previous mentioned double well potential (figure 9). The intersite coupling j mediates the

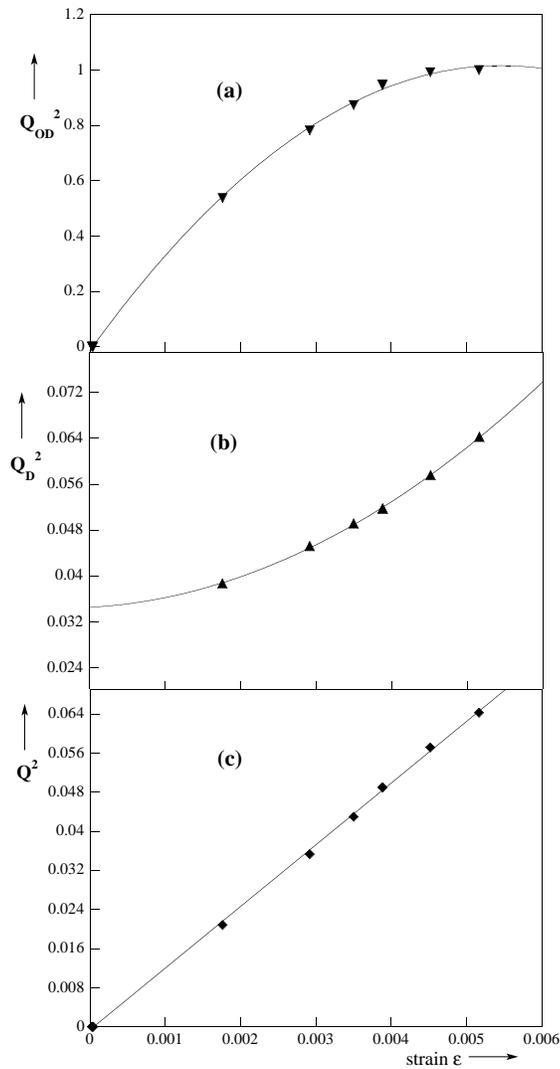


Figure 8. Scaling of the square of the parameters Q_{OD} ((a) top), Q_D ((b) centre) and $Q = Q_{OD} * Q_D$ ((c) bottom) in terms of the strain ϵ . Only for the product $Q = Q_{OD} * Q_D$ is a linear-quadratic scaling relation valid and therefore, identified to be the thermodynamic order parameter.

macroscopic transition, the breakdown of the long range intersite correlation at T_c .

It is now straightforward to assign our obtained values Q_{OD} and Q_D to the corresponding parameters of this model. Each minimum of the double well potential is associated with the maximum value of either positive or negative chain distortions, respectively. Due to the anharmonicity, the increasing thermal excitation shifts the average values in each minimum towards the centre of the well with increasing temperature. Finally, the antiferro correlation between neighbouring chains is destroyed and the chain is able to oscillate locally across the whole well. Let the local order parameter x_j at a chain site at

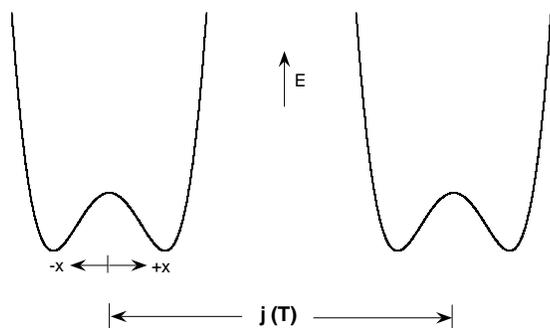


Figure 9. Visualization of the interaction of local double well potentials. According to the shape of the minimum the increasing thermal excitation shifts the average position of a dynamically tilting single polyphosphate chain in the direction of the centre of the well. Above a certain crossover-temperature the chain is able to oscillate locally across the whole well. The macroscopic transition at T_c is mediated by the intersite coupling j .

r_j be defined as

$$x \propto \Phi_j [\exp(-2\pi q_0 r_j)] \quad (2)$$

where Φ_j is the tilt angle and q_0 is the critical wavevector of ordering $q_0 = 1/2(a^* + c^*)$, such that the phase factor in square brackets takes values of $+1$ or -1 . The average tilt angles for ‘positive’ and ‘negative’ ordering states can be written as

$$\langle x^+ \rangle = \frac{1}{n^+} \sum_{i=1}^{n^+} |x_i^+| \quad \text{and} \quad \langle x^- \rangle = \frac{1}{n^-} \sum_{i=1}^{n^-} |x_i^-| \quad (3)$$

where n is the number of entities and the upper indices $+$ or $-$ denote positive or negative tilt, respectively. The value of Q_D obtained by diffraction corresponds to the mean value of the modulus of the displacement $\langle |x| \rangle$. The thermodynamic order parameter of the system is the mean value of the local order parameter averaged over space and time and, neglecting the time dependence we may write

$$\langle x \rangle = \langle Q \rangle = \frac{1}{N} \sum_{i=1}^N x_i \quad (4)$$

with $N = n^+ + n^-$. It can be separated into two sums taken over all sites with positive and negative values of the order parameter, respectively

$$\langle x \rangle = \langle Q \rangle = \frac{1}{N} \left(\sum_{i=1}^{n^+} |x_i^+| - \sum_{i=1}^{n^-} |x_i^-| \right) \quad (5)$$

using equation (3) the order parameter becomes

$$\langle Q \rangle = \frac{1}{N} (n^+ \langle x^+ \rangle - n^- \langle x^- \rangle) \quad (6)$$

while

$$Q_D = \langle |x| \rangle = \frac{1}{N} (n^+ \langle x^+ \rangle + n^- \langle x^- \rangle). \quad (7)$$

Using $Q_{OD} \equiv (n^+ - n^-)/N$ equation (6) can be rewritten as

$$\langle Q \rangle = Q_{OD} \langle x^+ \rangle + \left\{ \frac{1}{2} (1 - Q_{OD}) (\langle x^+ \rangle - \langle x^- \rangle) \right\}. \quad (8)$$

In the symmetric phase we have $\langle |x| \rangle = \langle x^+ \rangle = \langle x^- \rangle = Q_D$, which will also be valid in good approximation in the ordered phase for $Q_{OD} \rightarrow 0$. On the other hand, in the well ordered state, say for $Q_{OD} \rightarrow +1$ and $n^- \rightarrow 0$, we also have $Q_{OD} \rightarrow \langle x^+ \rangle$, and we thus, can finally expect that the thermodynamic order parameter is neither Q_{OD} nor Q_D but is given by

$$\begin{aligned} \langle Q \rangle &= \frac{(n^+ - n^-)}{N} \langle |x| \rangle \\ &= Q_{OD} * Q_D \end{aligned} \tag{9}$$

in fair approximation.

Hence this mean average chain displacement $\langle x \rangle$ across the crystal is in good approximation expressed by the product of both parameters, $Q = Q_{OD} * Q_D$, and follows an empirical power law $Q \sim (T - T_c)^\beta$ with $\beta \approx 0.17$. The experimental validation is given in figure 8; while neither Q_{OD} nor Q_D shows a linear-quadratic relation to the spontaneous strain ε , it is the case for the product of both $Q = Q_{OD} * Q_D$.

3.6. First-order Landau model

As thermo-analytic and diffraction experiments indicate a slightly first-order behaviour of the system, a symmetric Landau free-energy expansion of the thermodynamic potential up to sixth-order must be considered (Landau, 1937)

$$g = g_0 + \frac{1}{2}\alpha(T - T_0)Q^2 + \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6. \tag{10}$$

In the ordered phase below the transition temperature $T_c = 915$ K the thermal evolution of the thermodynamic order parameter is described by the equation

$$Q^2 = \frac{2}{3}\Delta Q^2 \left[1 + \sqrt{1 - \frac{3(T - T_0)}{4(T_c - T_0)}} \right] \tag{11}$$

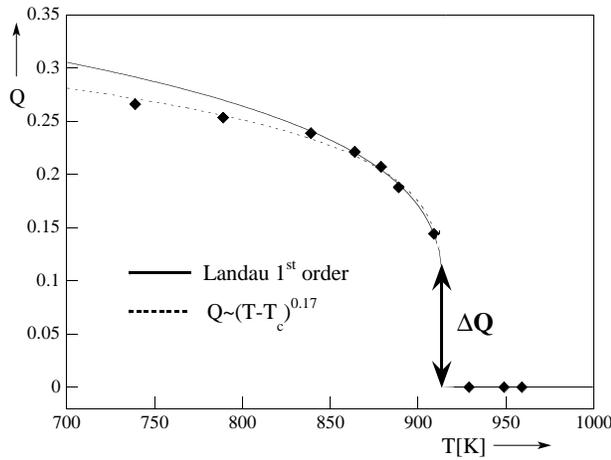


Figure 10. Thermal behaviour of the order parameter Q . The scaling follows an empirical power law $Q \sim (T - T_c)^\beta$ with $\beta = 0.17$ (broken curve). A fit (full curve) of the Landau model in equation (9) in the region $840 \text{ K} < T < T_c$ yields the discontinuous jump ΔQ as well as $T_0 \approx 913.3$ K, the metastability limit of the high-symmetry modification in the region of the low-symmetry phase.

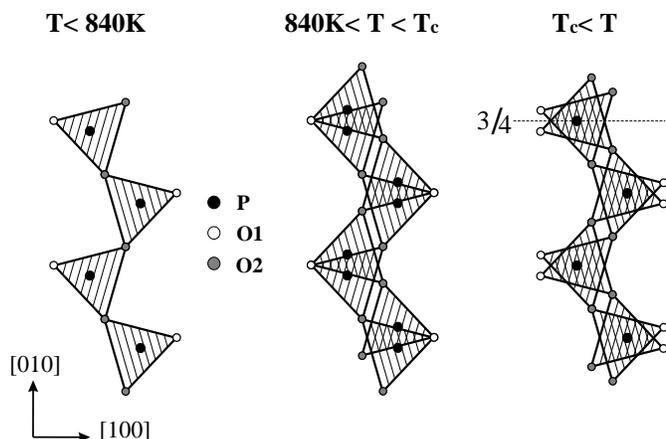


Figure 11. Distinction of three thermal regimes. At $T < 840$ K no chain-disorder exists. Between 840 K and T_c the chains are partly disordered, whereas total disorder occurs above T_c . At T_c the chains are shifted discontinuously so that the tetrahedra (phosphorous site) are centred on $x, 3/4, 3/4$.

where

$$\Delta Q = \sqrt{-\frac{3b}{4c}} \quad (12)$$

is the magnitude of the order parameter jump at T_c . This dependency is easily derived from the Landau functional for first-order phase transitions (e.g. Gebhard, Krey, 1980). Fitting this equation to the observed order parameter $Q = Q_{OD} * Q_D$ results directly in the discontinuous jump ΔQ of the order parameter at T_c as well as in the metastability limit $T_0 \approx 913.3(3)$ K of the high-symmetry modification in the region of the low-symmetry phase (figure 10).

The thermal behaviour of the chain conformation is sketched in figure 11, outlining the different thermal regions. The jump of the chains Δy is derived from ΔQ to be 10 ± 0.5 pm, which is in good agreement with the observed discontinuity in the atomic positions (e.g. $y(O2)$ in figure 5). As a consequence this fit is only valid above 840 K, indicating the change in thermal regime too.

To reflect further upon this unsolved crossover behaviour at about 840 K we estimate a change in local dynamics to occur. The change of the local chain behaviour from librating in the left or right minimum to oscillating across the whole well determines the crossover from order/disorder mechanism to the displaced case in the so-called ϕ^4 model (Padlewski *et al* 1992). At the $\text{RbPO}_3\text{-H}$ to $\text{RbPO}_3\text{-HT}$ transition this effect seems to be responsible for the obtained change of thermal regime at about $0.9T_c \approx 840$ K as indicated earlier. This places the transition in the softmode regime, but very close to the crossover itself and therefore, makes it a very interesting case. Not yet fully evaluated investigations indicate a change in local dynamics behaviour at about 800–850 K. Further measurements are underway to confirm this assumption, involving IR- and NMR-spectroscopy as a local probe.

4. Concluding summary

1. The thermodynamic order parameter Q is identified as the mean value of the tilt angle averaged over polyphosphate chains. It is the product of a crystallographic occupational parameter and the local average displacement of an individual chain, $Q = Q_{OD} * Q_D$ and couples linear-quadratically to the spontaneous strain ε .

2. The system can be described by a soft-Ising-like variable. A change in the dynamics of the ordering variable at 840 K indicates a crossover from softmode regime to an order/disorder mechanism.

3. The transition is discontinuous and follows first-order Landau behaviour.

4. Care must be taken on assigning crystallographic refinement parameters to thermodynamic order parameters.

Acknowledgment

We wish to thank the Bundesminister für Bildung und Forschung (BMBF) for financial support of this work.

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