Spin-Peierls distortions in TiPO$_4$


$^1$Laboratory of Crystallography, University of Bayreuth, 95440 Bayreuth, Germany
$^2$Institute of Inorganic Chemistry, University of Bonn, 53121 Bonn, Germany
$^3$Department of Chemistry and Research Institute for Basic Sciences, Kyung Hee University, 130-701 Seoul, Republic of Korea
$^4$Department of Chemistry, North Carolina State University, 27695 Raleigh, North Carolina, USA
$^5$Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany

The spin-Peierls (SP) distortion denotes a particular type of magneto-elastic coupling, which occurs in compounds containing quasi-one-dimensional antiferromagnetic spin chains [1]. The most recent inorganic SP system TiPO$_4$ was reported in 2011 [2]. Two successive phase transitions at remarkably high transition temperatures $T_{c2} = 111$ K and at $T_{c1} = 74$ K were studied by magnetic susceptibility, heat capacity, electron spin resonance and nuclear magnetic resonance measurements. However, in house x-ray diffraction couldn’t detect any noticeable differences between room-temperature and low-temperature structures, while the structural distortions are expected for the SP transitions.

We have carried out single-crystal x-ray diffraction experiments at beam line D3 of Hasylab using the Huber four-circle diffractometer and a closed-cycle helium cryostat. Synchrotron radiation provides an excellent opportunity to detect weak satellite reflections, which appear as a consequence of slight structural distortions, and to perform a data collection for an accurate structure refinement. Furthermore, in order to assign a correct symmetry, possible small monoclinic lattice distortions must be studied. Such lattice distortions would result in splitting of Bragg reflections, therefore, in order to test the hypothesis of a monoclinic lattice we have measured $\omega - 2\theta$ maps centered on the reflections (-3 3 0), (0 -4 -2) and (4 0 -4) between 10 K and 145 K with narrow detector slits in $2\theta$ direction. These scans revealed no peak splitting at all temperatures, therefore manifesting the preservation of orthorhombic symmetry in both low-temperature phases (Fig. 1).

In order to detect superlattice reflections, we have performed the $q$ scans along all principal reciprocal lattice axes and diagonals. Weak satellite reflections were observed at positions $(h + \sigma_1, k, l)$. Below 74 K $\sigma_1$ amounts to $\frac{1}{2}$, and indicates a formation of the superstructure with a doubling of the room-temperature unit cell along a. The crystal structure of the intermediate phase appeared to be incommensurately modulated with temperature-dependent $q$-vector $(\sigma_1(0))$. Both low-temperature structures can be described by the same orthorhombic superspace group $Cmcm(\sigma_1(0))0s0$.

The most remarkable feature of the $2a \times b \times c$ superstructure below $T_{c2}$ is a dimerization of the Ti chains with a Ti-Ti distance alternation along c (Fig. 2(a),(b)), that is a structural evidence of the SP state in TiPO$_4$. In the incommensurate phase at intermediate temperatures the Ti chains along c remain dimerized, but all the chains possess different degrees of dimerization (Fig. 2(c)). Density functional calculations suggest that the incommensurate phase results from a competition of three energetically almost degenerate crystal structures and elastic coupling of the Ti chains via the rigid PO$_4$ units.

In conclusion, synchrotron-based x-ray diffraction studies of TiPO$_4$ at low temperatures allowed to obtain the structural proof of the SP transition, to characterize the structures of low-temperature phases and to uncover the origin of the incommensurate phase. The results of the project are reported in Ref. [3].

References

Figure 1: Diffracted intensity as a function of the scattering angle $2\theta$ and the crystal orientation $\omega$ for three reflections at selected temperatures corresponding to three different phases of TiPO$_4$.

Figure 2: (a) Single TiO$_2$ chain from the crystal structure of TiPO$_4$. Arrows indicate the atomic displacements corresponding to the $Pbnm$ structure model for the spin-Peierls phase at 10 K. (b) Projection of the crystal structure at 10K along [010]. (c) Incommensurate phase at 82 K represented by $4a \times b \times c$ basic-structure unit cells. Only Ti atoms are shown. Basic-structure coordinates are $x = 0$ or $1/2$ and $z = 0$ or $1/2$. For clarity all atomic displacements have been multiplied by 30. The figure is adapted from Ref. [3].
