



	<b>Experiment title:</b> High-pressure single-crystal X-ray diffraction study of unconventional spin-Peierls compounds TiOCl and TiPO <sub>4</sub>	<b>Experiment number:</b> HC- 1064
<b>Beamline:</b> ID09A	<b>Date of experiment:</b> from: 04.11.2013 to: 07.11.2013	<b>Date of report:</b> 27.02.2015
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**Names and affiliations of applicants** (\* indicates experimentalists):

**Applicants:**

- \* Maxim Bykov. Laboratory of Crystallography, University of Bayreuth, Germany
- \* Prof. Dr. Sander van Smaalen. Laboratory of Crystallography, University of Bayreuth, Germany

**Participants:**

- \* Elena Bykova. Bayerisches Geoinstitut, University of Bayreuth, Germany
- \* Leonid Dubrovinsky. Bayerisches Geoinstitut, University of Bayreuth, Germany
- \* Kirill Yusenko. Department of Chemistry, University of Oslo, Norway

**Report:**

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]. Recently, the compounds TiOCl and TiPO<sub>4</sub> have been intensively investigated due to their unconventional low-temperature behavior [2, 3]. The SP transition temperature is related to the direct spin exchange interactions between Ti ions, which increase strongly with decreasing the distance between the Ti ions, and therefore is very sensitive to the applied hydrostatic pressure. Therefore, it is expected that at certain pressure, the temperature of the SP transition may even exceed room temperature. The goal of the proposed experiment was to study pressure-induced phase transitions of the SP compounds TiOCl and TiPO<sub>4</sub>. Since, the beam time has been allocated only for one of the compounds, we have chosen to study TiPO<sub>4</sub> for its better chemical stability towards moisture and oxygen in the air.

We have performed high-pressure single-crystal X-ray diffraction of TiPO<sub>4</sub> at the beamline ID09A (wavelength 0.4145 Å, MAR555 flat panel detector). In the range from ambient pressure up to 56 GPa we have detected four high-pressure phases (denoted as TiPO<sub>4</sub>-II through TiPO<sub>4</sub>-V), and solved their crystal structures. The compressional behavior of TiPO<sub>4</sub> is summarized in the Fig. 1. The two initial transitions resemble those at low temperatures [4]. A normal-to-incommensurate phase transition occurs close to 6 GPa and is followed by a lock-in transition at slightly higher pressure. So, we indeed have detected the spin-Peierls transition in TiPO<sub>4</sub> at room temperature. The evolution of the lock-in phase (TiPO<sub>4</sub>-III) with pressure up to 43 GPa doesn't reveal any anomalies. It is

characterized by a smooth decrease of the unit-cell volume, lattice parameters and average Ti–Ti distances. The diffraction pattern of  $\text{TiPO}_4$  considerably changes at 46 GPa. A thorough analysis of the diffraction data revealed that two polymorphs coexist. The formation of both polymorphs is accompanied by the pronounced volume drops of 3.6 % and 7.9 % for  $\text{TiPO}_4\text{-IV}$  and  $\text{TiPO}_4\text{-V}$  respectively. The volume drops are related to the changes in coordination numbers of Ti and P atoms. In  $\text{TiPO}_4\text{-IV}$ , the phosphorus atom remains four-coordinated, while the Ti atom is coordinated by 7 oxygen atoms. In  $\text{TiPO}_4\text{-V}$  Ti and P atoms are coordinated by 8 and 5 oxygen atoms respectively.

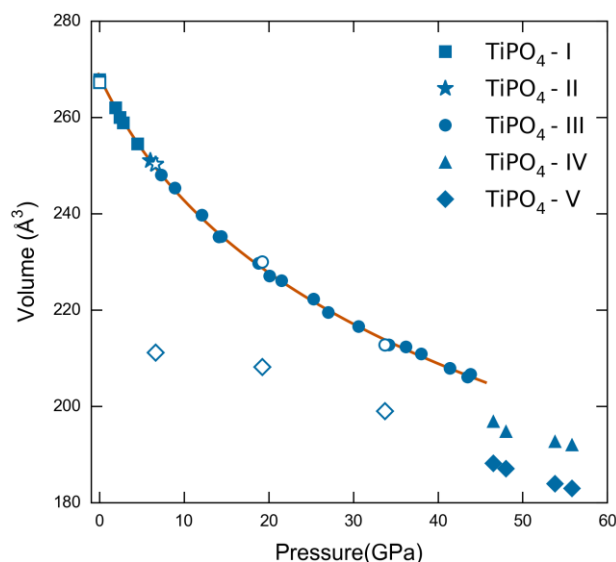


Figure 1. Pressure dependence of the unit cell volume. For  $\text{TiPO}_4\text{-II}$  and for  $\text{TiPO}_4\text{-III}$  given are the volumes of the average structures. Open symbols correspond to the decompression experiment. Solid curve represent the fit of the 3<sup>rd</sup> order Birch-Murnaghan equation of state to the experimental data.

In conclusion, synchrotron-based X-ray diffraction studies of  $\text{TiPO}_4$  at high pressure allowed to detect the SP transition at room temperature, to discover novel high-pressure polymorphs and to characterize the structures of all high-pressure phases. An analysis of chemical bonding at high pressures is in progress; a manuscript for publication in an international scientific journal is in preparation.

## References:

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