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# High-pressure magnetic and structural properties of TiOX (X = Cl, Br)

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## ABSTRACT

We report high-pressure diffraction and magnetization measurements to demonstrate that the partial collapse of electronic gap at high-pressure insulator to metal transition reported in TiOCl (C. Kuntscher et al. Phys. Rev. B 74 184402 (2006).) corresponds to a  $\text{Ti}^{3+}$ – $\text{Ti}^{3+}$  dimerization at room temperature within the space group  $P2_1/m$ . The shortest Ti–Ti distance is comparable to that of the Ti metal, but a Peierls-like distortion prevents a metallic behaviour.

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## 1. Main text

Low dimensional spin systems are particularly susceptible to the effect of fluctuations, which normally suppress magnetic order but results in a very rich phase diagram. In recent years, much effort has been focused on understanding  $S = \frac{1}{2}$  spin systems due to its stability towards a structural transition driven by long range quantum fluctuations. Such instabilities, characterized by the gain of magnetic energy and a loss in the elastic energy, are known as spin–Peierls transitions [1]. The spin–Peierls transition is a magnetoelastic phase transition in which below  $T_{\text{SP}}$  the uniform distances between neighbouring spins, now alternate. In such situation, a dimerized singlet ground state is separated from the band of excited triplet states by an energy gap. Among the growing number of  $S = \frac{1}{2}$  spin systems, TiOX (X = Cl, Br) has attracted much interest due to its low temperature physics. Like  $\text{CuGeO}_3$  [2], TiOCl was discussed as a new class of low temperature spin–Peierls compound.

Temperature dependent X-ray diffraction [3], susceptibility [4], ESR [5], and NMR [6] show that at  $T_{\text{SP}} = 66$  K, TiOCl exhibits a first order transition with a doubling of the lattice constant  $b$  along the Ti chains to a monoclinic symmetry  $P2_1/m$ . At this transition, the spin lattice system dimerizes to a singlet ground state with a magnetic gap where two inequivalent Ti sites are observed [3], supporting a spin–Peierls scenario. The phase transition at  $T_{\text{SP}} = 91$  K is a second order in nature and it was suggested to correspond to a spontaneous transition to an onset of Ti site inequivalence. Between both transitions, an incommensurate

phase arises due to the frustration of the chains [4]. However, the occurrence of two transitions at  $T_{\text{SP}} = 68$  and 91 K are at odds with a canonical spin–Peierls system, where only a second order phase transition is expected to occur when the system dimerizes.

On the other hand, a possible insulator to metal transition at high pressures based on the drop of the optical gap was also reported [7] from spectroscopic measurements. Moreover, high pressure X-ray diffraction experiments have shown a structural transition at 14 GPa in the analogous TiOBr [8]. This structural transition was suggested as the possible origin of the collapse of the charge gap at high pressures. However, the high-pressure phase was not previously resolved to date and the issue of whether the system is truly metallic was not clarified.

The aim of this study is to determine the nature of the new phase that arises at 12 GPa and a complete study of the magnetic interactions with pressure in TiOCl and TiOBr. For an anisotropic structure like TiOCl, the application of pressure provides a way of modifying the exchange parameters along the  $b$ -axis together with the nearest neighbour interactions. For this, we have measured X-ray diffraction with pressure and magnetic susceptibility, monitoring both magnetic transitions observed at low temperatures.

Single crystal samples of TiOX (X = Cl, Br) were grown by chemical vapour transport technique [9] at temperatures of 650–700 °C under evacuated quartz tubes from stoichiometric amounts of Ti,  $\text{TiO}_2$ ,  $\text{TiCl}_3$  and  $\text{TiBr}_4$ . Magnetic susceptibility with pressure was measured in a SQUID magnetometer up to 10 kbar using a Be–Cu cell from EasyLaboratory X-ray synchrotron diffraction was performed up to 15 GPa with a diamond anvil cell at the 9.5HPT beamline of Daresbury Synchrotron Radiation Source.

TiOCl crystal structure consists of 2D Ti–O bilayers along the  $ab$  plane well separated by Cl ions along the  $c$  direction, crystallizing

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in an orthorhombic structure [3]. Structure refinements within the space group *Pmmn* show lattice parameters of  $a = 3.79 \text{ \AA}$ ,  $b = 3.38 \text{ \AA}$  and  $c = 8.03 \text{ \AA}$  for TiOCl and  $a = 3.785 \text{ \AA}$ ,  $b = 3.485 \text{ \AA}$  and  $c = 8.525 \text{ \AA}$  for TiOBr.  $\text{Ti}^{3+}$  electronic configuration makes the  $d^1$  electron to lay in the  $d_{z^2-y^2}$  orbital ground state. This configuration supports quasi-1D-chains along the  $b$  direction with a direct exchange interaction of  $J = 660 \text{ K}$ .

In Fig. 1 we plot the magnetic susceptibility of TiOCl and TiOBr. Two distinct phase transitions at the spin–Peierls temperature ( $T_{\text{SP}}$ ) and incommensurate spin–Peierls temperature ( $T_{\text{ISP}}$ ) are observed. Below  $T_{\text{SP}}$ , susceptibility is dominated by contributions of impurities and remains of organic solvents. The appearance of two transitions was attributed to the observation of two inequivalent Ti sites at low temperatures and to the presence of interchain interactions. From magnetization measurements under pressure, we observe an increase of the  $T_{\text{SP}}$  at a rate of  $1.91(2) \text{ K/kbar}$  for TiOCl and  $1.00(2) \text{ K/kbar}$  for TiOBr. As observed by X-ray diffraction, this temperature corresponds to the transition where the systems dimerize to a spin singlet phase. Taking into account the symmetry below  $T_{\text{SP}}$  is monoclinic  $P2_1/m$ , the enhancement of  $T_{\text{SP}}$  shows that the spin–Peierls transition strongly increases upon applying hydrostatic pressure. Susceptibility measurements under pressure have shown a similar behaviour of  $T_{\text{SP}}$  up to 6 kbar [10]. We were able to measure  $T_{\text{ISP}}$  in both TiOCl and TiOBr up to 10 kbar as well.  $T_{\text{ISP}}$  enhances at  $3.32(5) \text{ K/Kbar}$  for TiOCl and  $2.18(3)$  for TiOBr. The fact that the both transitions increase faster in TiOCl than in TiOBr suggests the exchange interaction along the  $b$  direction and the interchain frustration is stronger in the former case. This hypothesis is confirmed by the lower transition temperatures in TiOBr, with almost identical  $a$  parameter but with a  $\sim 5\%$  reduction of  $b$  (direct Ti–Ti distance) with respect to TiOCl.

If the increasing rate of  $T_{\text{SP}}$  of TiOCl is maintained at higher pressures, then the spin–Peierls transition should cross room temperature at about 12 GPa (Fig. 2).

Unfortunately we could not extend the magnetic measurements to such a high pressure. However, because the spin–Peierls transition involves a structural distortion, its pressure dependence can be traced through the analysis of the pressure dependence of the X-ray diffraction patterns. These lattice distortions are often small, such that any splitting of the overlapping Bragg reflections can only be measured in high-resolution diffraction experiments. Synchrotron radiation provides the required resolution. These measurements were performed at the 9.5HPT beam line

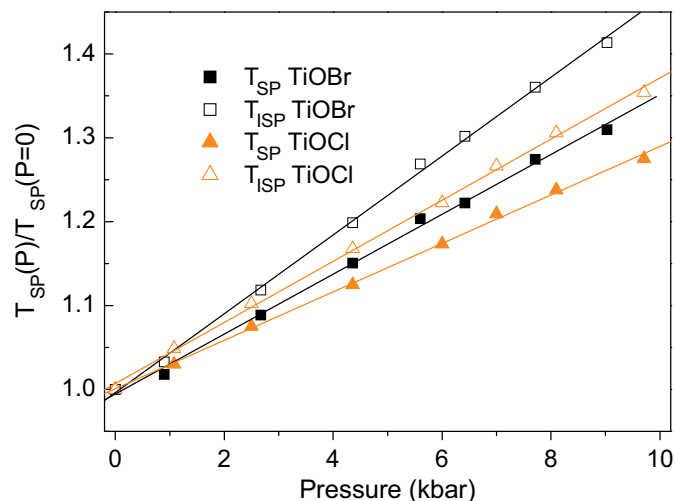


Fig. 2. Normalized pressure dependence of both  $T_{\text{SP}}$  and  $T_{\text{ISP}}$  in TiOCl and TiOBr.

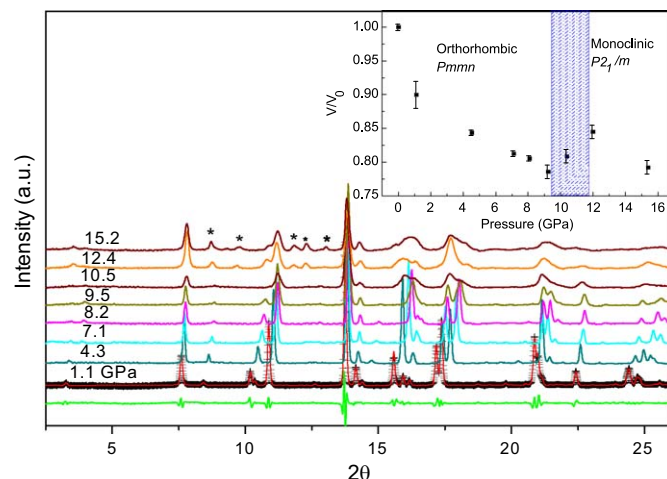


Fig. 3. Pressure dependence of the X-ray diffraction patterns in TiOCl up to 15 GPa. Asterisks denote the new peaks at high pressure. Inset, pressure dependence of the volume of the orthorhombic and monoclinic phases.

( $\lambda = 0.44397 \text{ \AA}$ ) of the Daresbury Synchrotron Radiation Source, using diamond anvil cells and a 4:1 methanol:ethanol as pressure media.

In Fig. 3 we present the X-ray diffraction patterns of TiOCl at different pressures between 2.5° and 26° and up to 9.5 GPa for TiOCl. Several issues are observed in the diffraction patterns. We can observe a displacement of the peaks to higher angles and broadening with pressure. Most likely, this broadening is due to nonhydrostatic effects at high pressures. We have fitted the lattice parameters within the *Pmmn* symmetry. Fitting the pressure dependence of the volume to the Birch–Murnaghan equation of state gave a bulk modulus of  $B = 67(4) \text{ GPa}$ , most of the compressibility coming from the  $c$ -axis. For the  $ab$  plane, where the relevant exchange interactions occur, we found that the  $b$ -axis is more compressible ( $B_b = 130 \pm 10 \text{ GPa}$ ) than the  $a$ -axis ( $B_a = 590 \pm 30 \text{ GPa}$ ).

At 12 GPa new peaks are seen in the range  $8\text{--}15^\circ$  confirming the structural transition. Kuntcher et al. [8] found a structural transition in the analogous TiOBr at 14 GPa using He as a pressure medium. However, they were not able to resolve the high-pressure structure. From our data the new phase above 12 GPa was successfully indexed within the monoclinic space group  $P2_1/m$  with lattice parameters at 15.2 GPa of  $a = 3.536(3) \text{ \AA}$ ,  $b =$

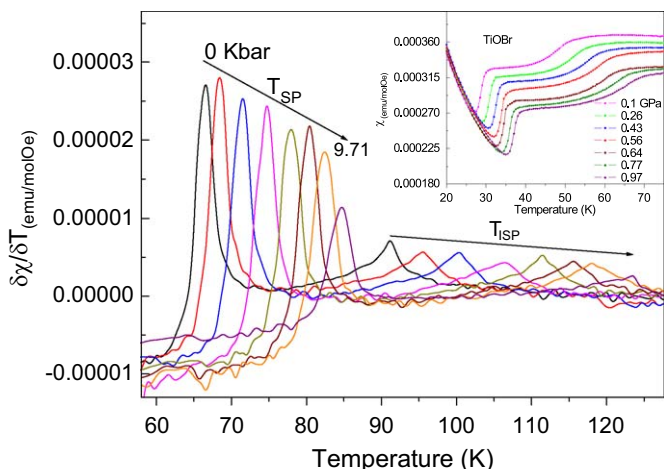
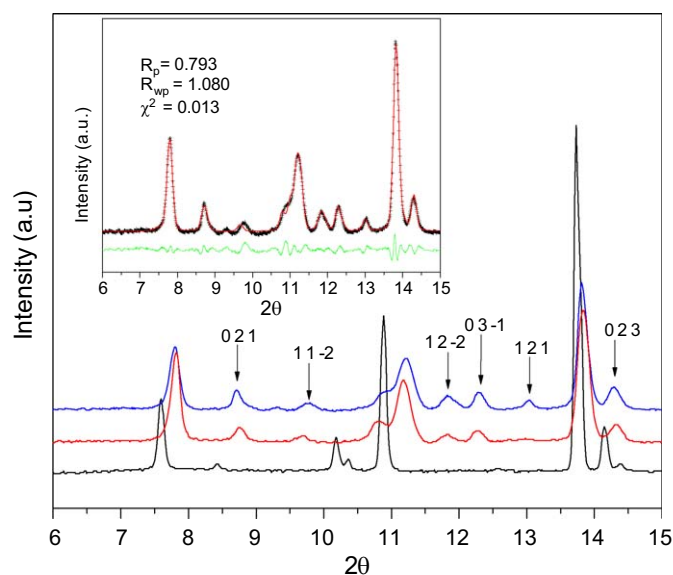
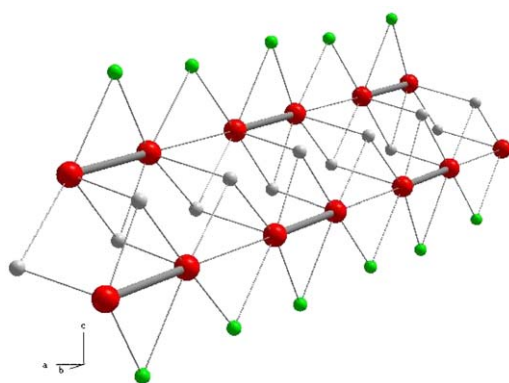


Fig. 1. Pressure dependence of the  $T_{\text{SP}}$  and  $T_{\text{ISP}}$  in TiOCl. We present the derivative in order to determine both  $T_{\text{SP}}$  and  $T_{\text{ISP}}$  accurately. Inset pressure dependence of the susceptibility in TiOBr.



**Fig. 4.** Comparison of low pressure orthorhombic X Ray with high pressure monoclinic phase with indexation of the new peaks. Inset, rietveld refinement of the 15.5 GPa phase.



**Fig. 5.** Dimerized structure proposed at 15 GPa. Red points represent Ti atoms, green, chlorine and grey, oxygen. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$6.631(3)\text{Å}$ ,  $c = 7.027(7)\text{Å}$ , and  $\beta = 98.89(8)^\circ$ . This means that the lattice parameter along the  $b$ -axis is doubled with respect to the low-pressure orthorhombic structure at room temperature. According to our structural data, the effect of pressure is to induce an alternating tilting of the  $\text{TiO}_4\text{Cl}_2$  octahedra resulting in a doubling of the unit cell along the  $b$  direction in the high-pressure monoclinic phase with respect to the low-pressure orthorhombic

structure. This results in two inequivalent  $\text{Ti}^{3+}$  sites along the  $b$ -axis with alternating  $\text{Ti}^{3+}$ – $\text{Ti}^{3+}$  distances of  $2.85(5)$  and  $3.55(5)\text{Å}$ .

We have to notice that the shortest distance is comparable to the close contact distance in Ti metal at room temperature ( $2.896\text{Å}$ ) and to the dimerized phase of the cubic spinel  $\text{MgTi}_2\text{O}_4$  ( $2.853(7)\text{Å}$ ). This result supports the formation of a metal–metal bond with partial electronic delocalization between the  $\text{Ti}^{3+}$  ions along the  $b$ -axis in  $\text{TiOCl}$  (Figs. 4 and 5).

Moreover, while in the low-temperature dimerized phase at ambient pressure the difference between the short–long bonds is roughly 5%, our X-ray data show that this difference increases dramatically up to  $\sim 20\%$  in the room-temperature high-pressure dimerized phase.

In summary, we have solved the symmetry of the high-pressure structure ( $> 12\text{ GPa}$ ) found at room temperature in  $\text{TiOCl}$ . With increasing pressure  $\text{TiOCl}$  apparently approaches an itinerant electronic state (as indicated by the strong dependence of the magnetic transitions with pressure), and at  $P \sim 12\text{ GPa}$  it would become a metal with  $U < t$  [11]. But the electron–lattice coupling in this case causes the instability of such 1D metal and leads to a Peierls-like dimerization. In the high-pressure phase,  $\text{Ti}^{3+}$ – $\text{Ti}^{3+}$  spin-dimers are formed; being the shortest  $\text{Ti}^{3+}$ – $\text{Ti}^{3+}$  metal–metal distance consistent with partial electronic delocalization along the pairs.

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