

## Enhanced Dimerization of TiOCl under Pressure: Spin-Peierls to Peierls Transition

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We report x-ray diffraction and magnetization measurements under pressure combined with *ab initio* calculations to show that high-pressure TiOCl corresponds to an enhanced  $\text{Ti}^{3+}$ - $\text{Ti}^{3+}$  dimerized phase existing already at room temperature. Our results demonstrate the formation of a metal-metal bond between  $\text{Ti}^{3+}$  ions along the *b* axis of TiOCl, accompanied by a strong reduction of the electronic gap. The evolution of the dimerization with pressure suggests a crossover from the spin-Peierls to a conventional Peierls situation at high pressures.

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1D electronic systems are particularly susceptible to different instabilities and to the effect of thermal or quantum fluctuations. In many cases this results in the low-lying gapless excitations that frustrate a long-range order and leads to a very rich phase diagram, with interesting phases like spin liquids or resonance valence bonded states [1,2]. Interaction among different degrees of freedom provides a way for opening up a gap for the collective excitations, and different types of long-range order become then possible. Among the latter, a magnetoelastic coupling in  $S = 1/2$  chains results in a spin-Peierls (SP) phase transition to a low temperature nonmagnetic dimerized structure [3,4], which is a localized counterpart of a conventional Peierls transition for itinerant electrons [5]. This effect was found in  $\text{CuGeO}_3$  [6], for a long time the only inorganic system with a pure SP distortion. Recently, the possibility that TiOCl shows a low temperature SP dimerization has been suggested, although the behavior of this material is probably more complex. Temperature dependent x-ray diffraction [7], susceptibility [8], ESR [9] and NMR [10] show that at  $T_{\text{SP}} = 66$  K TiOCl exhibits a first order transition with a doubling of the cell along the Ti chains (*b* axis) to a low temperature monoclinic  $P2_1/m$  phase. Below this temperature a spin singlet dimerization of the lattice opens up a magnetic gap, supporting a SP scenario. However, the ratio of the spin gap to the transition temperature is between 3 to 5 times larger than expected on the basis of a BCS-like mean-field model [11]. Moreover, there is a second-order phase transition at  $T_{\text{ISP}} = 91$  K corresponding to an incommensurate dimerized state due to frustrated interchain interactions [8].

On the other hand, Kuntscher *et al.* [12] observed a strong suppression of the transmittance and an abrupt increase of the near-infrared reflectance above  $\sim 10$  GPa in TiOCl. These effects were interpreted as a pressure-induced metallization of the 1D chain. Later on, a structural phase transition was observed in isostructural TiOBr,

coincident with the proposed pressure-induced metallization [13]. Recently, Forthaus *et al.* [14] measured the resistivity up to  $\sim 25$  GPa and reported an anomalous decrease of the electronic gap above  $\sim 12$  GPa in TiOCl, but ruled out the existence of a metallic phase at high-pressure. The reduction of the gap has been shown to be connected with an anomalous change of the lattice parameters with pressure. However, no evidence for structural phase transition in TiOCl has been reported within the accuracy of the energy dispersive x-ray data.

In this Letter, we report the strong enhancement of a dimerization of the 1D spin-chain of TiOCl under pressure, which for  $P > \sim 10$  GPa exists already at room temperature. *Ab initio* calculations confirm the dramatic decrease of the charge gap in the high-pressure dimerized phase, from  $\sim 1.5$  eV down to  $\sim 0.3$  eV, in very good agreement with both transport and optical experiments. Our results demonstrate the formation of direct  $\text{Ti}^{3+}$ - $\text{Ti}^{3+}$  bonds at room temperature and high pressure, with the shortest distance being consistent with partial electronic delocalization along this bond.

Single crystals of TiOCl were synthesized as in [15]. Magnetic susceptibility under pressure up to  $\sim 1$  GPa was measured in a SQUID magnetometer using a commercial Be-Cu cell from EasyLab. X-ray diffraction under pressure (up to 15 GPa) were done at Station 9.5HPT ( $\lambda = 0.44397$  Å) of the Daresbury Synchrotron Radiation Source [16], using diamond anvil cells and a 4:1  $\text{CH}_3\text{OH} : \text{C}_2\text{H}_5\text{OH}$  mixture as pressure media. The resulting 2D images were integrated using the software Fit2D, with Si as a standard to refine the instrumental parameters. All the experiments were performed at 293 (2) K. *Ab initio* calculations were performed based on the density functional theory, with the WIEN2K software [17] using a full-potential, all-electron scheme based on the APW + lo method [18]. Strong correlations were introduced by means of the LDA + *U* method [19]. The transition involves a structural

distortion, its pressure dependence can be traced through the analysis of the pressure dependence of the x-ray diffraction patterns.

Figure 1 shows the x-ray diffraction pattern up to  $\sim 15$  GPa. As evident from the figure, increasing pressure up to  $\sim 9.5$  GPa causes a progressive displacement of the peaks towards higher angles and a broadening, most likely due to a slight nonhydrostaticity at the higher pressures. The spectra at ambient pressure and up to 9.5 GPa are well fitted within the orthorhombic symmetry of the  $Pm\bar{m}n$  space group, giving  $a = 3.79(4)$  Å,  $b = 3.38(3)$  Å, and  $c = 8.03(7)$  Å, at room temperature. Fitting the pressure dependence of the volume below 9.5 GPa to the Birch-Murnaghan equation gives a bulk modulus  $B = 67(4)$  GPa. The orthorhombic crystal structure of TiOCl consists of 2D Ti-O bilayers along the  $ab$  plane well separated by Cl ions along the  $c$  direction [20]. Consistent with this structure, the variation of the lattice parameters is strongly anisotropic (see Fig. 2) and the bulk modulus is dominated by the highly compressible  $c$  axis. For the  $ab$  plane, where the relevant exchange interactions occur, we found that the  $b$  axis is much more compressible [ $B_b = 130(10)$  GPa] than the  $a$  axis [ $B_a = 590(30)$  GPa], in agreement with previous reports [14].

At pressures  $\sim 10$  GPa, where the optical [12] and transport [14] data have shown a strong change of behavior, with a rapid decrease of an energy gap, we find new diffraction peaks, indicating a structural phase transition.

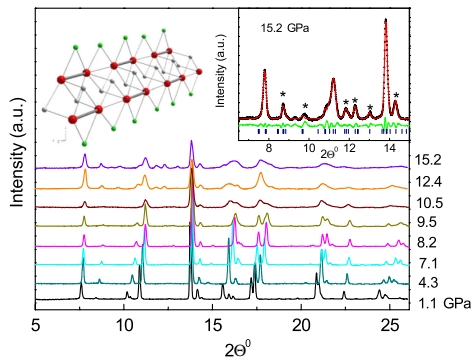


FIG. 1 (color online). Evolution of the x-ray diffraction pattern under pressure. Note the appearance of the new peaks of the monoclinic phase,  $P2_1/m$  above 10.5 GPa, with respect to the low pressure orthorhombic phase,  $Pm\bar{m}n$ . The coordinate  $z$  of the Wyckoff positions of Ti ( $2b: 0, \frac{1}{2}, z$ ), Cl ( $2a: 0, 0, z$ ), and O ( $2a: 0, 0, z$ ) in the  $Pm\bar{m}n$  phase at 0 GPa (7 GPa) are 0.113 (0.133), 0.320 (0.368), and 0.943 (0.929), respectively. In the  $P2_1/m$  phase there exist two inequivalent positions for each atom ( $2e: \frac{1}{4}, y, z$ ). The  $y, z$  at 15 GPa (20 GPa) are 0.415 (0.419) and 0.372 (0.353) for Ti1 and 0.905 (0.864) and 0.373 (0.350) for Ti2, respectively. Inset: Rietveld refinement of the high-pressure monoclinic phase (+ are the experimental points and the solid line is the fitting). Asterisks mark the new peaks of the high-pressure monoclinic phase. The left inset shows the structure generated from the refinement, highlighting the short Ti-Ti bonds along the  $b$  axis, which are displaced half a period between the chains.

These peaks of the high-pressure phase can be indexed within the monoclinic space group  $P2_1/m$ . Rietveld refinement of the high-pressure monoclinic phase (inset to Fig. 1) results in values of the lattice parameters at 15.2 GPa of  $a = 3.536(3)$  Å,  $b = 6.631(3)$  Å,  $c = 7.027(7)$  Å, and  $\beta = 98.89(8)^\circ$ . The small differences between the experimental and the calculated patterns are due to the difficulty in reproducing the broadening of the peaks. However, the structural transition is reproducible and reversible, ruling out any extrinsic origin. These results are also consistent with those reported for TiOBr [13].

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) Å and 3.55(5) Å (see the left inset to Fig. 2). The shortest distance is comparable to the close contact distance in Ti metal at room temperature (2.896 Å) and to the shortest distance in the dimerized phase of the cubic spinel  $\text{MgTi}_2\text{O}_4$  [2.853(7) Å] [21]. This result supports the formation of a metal-metal bond with partial electronic delocalization between  $\text{Ti}^{3+}$  ions along the  $b$  axis in TiOCl. Moreover, while in the low temperature dimerized phase at ambient pressure the difference between the short and long bonds is roughly 5%, our x-ray data show that this difference increases dramatically up to  $\approx 20\%$  in the room-temperature high-pressure dimerized phase. Such a huge difference is comparable to that obtained in the monoclinic phase of isoelectronic  $\text{VO}_2$ , where the lattice instability has been proposed to result from the trapping of itinerant electrons in homopolar bonds [22]. In the case of TiOCl, this large difference between the bonds in the dimerized state at high pressure points to a situation different both from the original SP state and from the weak-coupling Peierls state, as will be discussed below

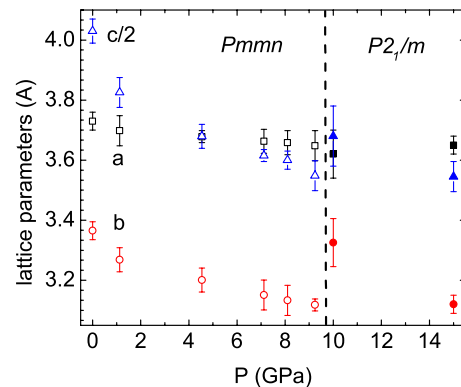


FIG. 2 (color online). Pressure dependence of the lattice parameters of TiOCl at room temperature as obtained from the Rietveld refinement in both the orthorhombic and monoclinic phase above 10 GPa. The open (closed),  $\circ$ ,  $\Delta$  symbols correspond to  $a$ ,  $b$  ( $b/2$ ) and  $c/2$ , in the orthorhombic (monoclinic) phase, respectively.

and in [23]. Our observation of a dimerized state in TiOCl under pressure at 300 K implies an unusual increase of the SP transition temperature  $T_{SP}$  with pressure. This is exactly what we obtain from the analysis of the pressure dependence of the magnetic susceptibility of TiOCl, shown in Fig. 3. This figure displays the magnetic susceptibility vs temperature and its pressure dependence up to  $\sim 1$  GPa. Two distinct phase transitions, at the incommensurate SP temperature [ $T_{ISP} \sim 91(1)$  K] and at the commensurate SP temperature [ $T_{SP} \sim 66(1)$  K], are observed. The pressure dependence of the magnetic transition temperature derived from these measurements are  $(\partial \ln T_{SP}/\partial P) = 2.88 \times 10^{-1} \text{ GPa}^{-1}$  and  $(\partial \ln T_{ISP}/\partial P) = 3.64 \times 10^{-1} \text{ GPa}^{-1}$ , the latter one decreasing its intensity with pressure. These values are slightly smaller than those reported for TiOBr ( $\partial \ln T_{SP}/\partial P) = 3.4 \times 10^{-1} \text{ GPa}^{-1}$  [24]. If this increasing rate is maintained at higher pressures, then the spin-Peierls transition should cross room temperature above 10 GPa, consistent with our high-pressure x-ray diffraction data.

We performed *ab initio* calculations at different pressures using the experimental lattice parameters and the atomic parameters optimized with GGA [25], minimizing the total energy of the system and reducing the forces on the atoms below 2 mRy/a.u. For the lattice parameters above 10 GPa, the structure optimization within a monoclinic structure leads to the formation of  $\text{Ti}^{3+}$ - $\text{Ti}^{3+}$  dimers along the  $b$  axis, confirming the experimental results. At  $P = 15$  GPa, the calculated alternating  $\text{Ti}^{3+}$ - $\text{Ti}^{3+}$  distances are 2.95(3) and 3.69(4) Å. Moreover, the structural transition produces changes in the electronic structure with the formation of molecular orbitals within the dimer. This modifies strongly the excitation spectra, leading to a dramatic reduction of the electronic gap with respect to the undimerized orthorhombic phase (Fig. 4). Within the orthorhombic structure the gap decreases with pressure by about 30%, to  $\sim 1$  eV (see the left inset to Fig. 4), in good agreement with the reduction observed experimentally [12,14]. In the dimerized monoclinic structure, stable at

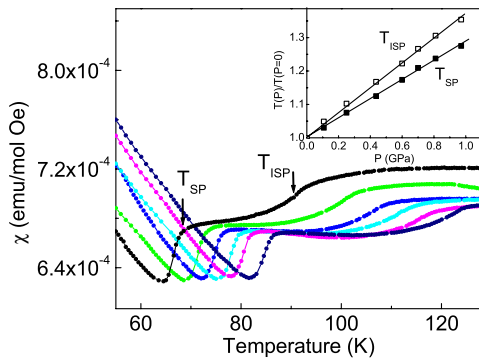


FIG. 3 (color online). Temperature dependence of the magnetic susceptibility at some representative pressures (from left to right: 0, 0.25, 0.43, 0.6, 0.7, and 0.97 GPa). The curves are slightly vertically displaced for clarity. The precise evolution of  $T_{ISP}$  and  $T_{SP}$  is shown in the inset.

room temperature beyond  $\sim 10$  GPa, the gap reduces drastically to  $\sim 0.3$  eV. This is again in very good agreement with the experimental observation of a sudden decrease of the charge gap at room temperature above  $\sim 10$  GPa [12]. Our calculations predict that more than 30 GPa would be necessary to obtain such a reduction of the electronic gap without considering a structural transition.

In both phases the electronic structure of TiOCl derived from our calculations is strongly anisotropic (quasi-one-dimensional). The occupied  $t_{2g}$  orbital ( $d_{yz}$ ) of the  $\text{Ti}^{3+}$  ( $d^1$ ) ions shows a large hopping integral along the  $b$  direction of the crystal. We have calculated total energies within the LDA +  $U$  approximation for various magnetic configurations and several pressures within the orthorhombic structure, and calculated from them different exchange constants and their pressure dependence.

Because of the structure of the material, we considered three different magnetic couplings and their pressure dependence:  $J_b$ , within the 1D chains along the  $b$  axis;  $J_s$ , between a Ti and its 4 closest neighbors; and  $J_a$ , the coupling along the  $a$  axis. At ambient pressure, the ratio  $|J_b/J_a| \sim 300$  and  $|J_b/J_s| \sim 25$ , and therefore the direct AF coupling along the  $b$ -axis is the dominant exchange interaction in TiOCl. On the other hand, the variation of  $J_b$  with pressure from our calculations is  $\sim 1.4$  times faster than that of  $J_a$ , and even faster with respect to the other directions. This corroborates that the pressure dependence of the transport in this system is dominated by the direct  $\text{Ti}^{3+}$ - $\text{Ti}^{3+}$  hopping, and more important, the 1D character of the compound increases with pressure. The calculated in-chain  $J$  is 600 K, in good agreement with fittings to a spin-1/2 Heisenberg chain model of the experimental susceptibility curves [26]. The pressure dependence of  $(\partial \ln T/\partial P) = 4.6 \times 10^{-1} \text{ GPa}^{-1}$ , would give  $J = 3300$  K at 9 GPa.

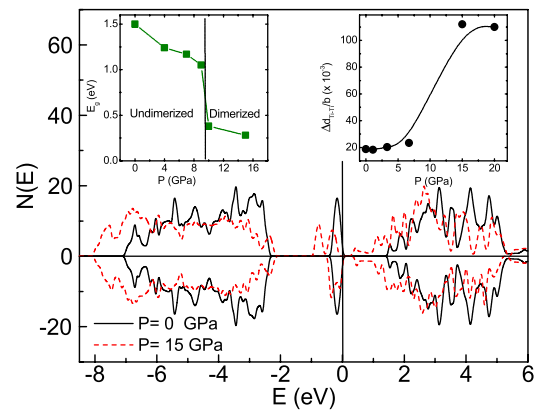


FIG. 4 (color online). Density of states for TiOCl at ambient pressure ( $Pmmn$ ) and at  $P = 15$  GPa ( $P2_1/m$ ). The vertical line marks the Fermi energy. The insets show the evolution of the band gap (left) and the difference between the short and long distances in the dimerized monoclinic phase (right) with pressure. Note that at low temperatures and ambient pressure TiOCl exhibits monoclinic structure and thereby the dimerized spin-Peierls state.



The pressure dependence measured for  $T_{SP}$  and  $T_{ISP}$  is much larger than expected on the basis of superexchange theory for a conventional antiferromagnetic transition. Partial electronic delocalization along the Ti-Ti bonds results in an effective screening of the Coulomb interaction and a decrease of  $U$ , which then increases the rate of variation of the exchange interaction with pressure as observed in other systems close to the itinerant boundary [27].

An important consequence follows also from the non-monotonic evolution of the degree of dimerization (difference of short-long distances) in the dimerized chain with pressure. As shown in the right inset to Fig. 4, this difference increases dramatically between 10 and 15 GPa. In this pressure range, the short Ti-Ti distance approaches the critical distance for metallic bonding. Our results support an enhanced shortening of the bond in order to form a molecular orbital, i.e., by a purely electronic mechanism. In this case the magnetic structure will play a secondary role, and hence the high pressure phase departs from the SP, and may be rather interpreted as a usual Peierls dimerization, proceeding from the itinerant limit. Thus, on the basis of the obtained experimental results and *ab initio* calculations we can propose the following scenario: At ambient pressure TiOCl is a Mott insulator with large energy gap  $E_g \sim 1.5$  eV caused by strong Coulomb (Hubbard) repulsion  $U$ , larger than the electron hopping  $t$ . Low-energy states in this case are determined by the effective antiferromagnetic Heisenberg model with the exchange constant  $J = 2t^2/U$ . In the 1D crystal structure of TiOCl there occurs a SP transition with corresponding dimerization. With increasing pressure TiOCl apparently approaches an itinerant state, and at  $P \sim 10$  GPa it would become a metal with  $U < t$ . But the electron-lattice coupling in this case again causes instability of such 1D metal and leads to the ordinary Peierls dimerization. Here, the corresponding critical temperature and dimerization are determined by the energy scale  $t$  (bandwidth), instead of  $J$  in a localized regime. As a result the dimerized SP phase of TiOCl at  $P < P_c$  exhibits above  $P_c$  a crossover to an insulating and dimerized Peierls phase with a smaller energy gap, but higher  $T_c$  and larger dimerization [23]. Such a nontrivial crossover from the Mott insulator with the SP dimerization to an essentially band insulator due to the usual Peierls distortion seems to be a unique feature of TiOCl, or rather TiOCl is the first system in which this phenomenon is observed: we think that there may be other examples of such interesting behavior in other quasi-one-dimensional inorganic and organic solids.

In summary, we have demonstrated the existence of a structural transition at high pressure in TiOCl, at which the  $Ti^{3+}$ - $Ti^{3+}$  dimerization is strongly enhanced as compared to that at ambient pressure. A dramatic reconstruction of the electronic crystal structure is driven by the proximity to the itinerant electron boundary in the short Ti-Ti bonds, suggesting a completely different mechanism for the high-

pressure dimerization, which should be treated not as a spin-Peierls, but rather as a Peierls transition.

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