Two Pressure-Induced Transitions in TiOCl: Mott Insulator to Anisotropic Metal

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Using Car-Parrinello molecular dynamics we investigate the behavior of the low-dimensional multi-orbital Mott insulator TiOCl under pressure. We show that the system undergoes *two* consecutive phase transitions, first at P_c from a Mott-insulator to a metallic phase in the *ab* plane with a strong Ti-Ti dimerization along *b*. At a pressure $P_c' > P_c$ the dimerization disappears and the system behaves as a uniform metal. This second transition has not yet been reported experimentally. We show that the insulator-to-metal transition at P_c is driven by the widening of the bandwidth rather than structural changes or reduction of crystal field splittings and it shows a redistribution of the electronic occupation within the t_{2g} bands. Our computed pressure-dependent lattice parameters are consistent with experimental observations and the existing controversy on the change of crystal symmetry at high pressures is discussed.

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Understanding the Mott-insulator-to-metal transition in strongly correlated systems is a central issue in condensed matter physics due to the striking phenomena, like unconventional superconductivity, emerging at the vicinity of the transition [1,2]. Application of chemical [3,4] or hydrostatic pressure [5] to a Mott insulator is an ideal way to trigger the Mott transition, as the one-electron bandwidth (W) is directly controlled by pressure, leading to the change of electron correlation strength (U/W) with U the effective on-site Coulomb interaction. However, pressure-induced structural changes, as present in FeO [6] or MnO [7], and orbital repopulation in multiorbital systems increase the degree of complexity of the transition and make it difficult to identify as a Mott transition.

Recently, TiOCl, a layered Mott insulator at room temperature, has attracted considerable interest [8–12] due to its unconventional transitions to a spin-Peierls state through a zero-field structural incommensurate phase. This phase has been ascribed to competing large magnetoelastic couplings with ferromagnetic interchain frustration [13]. The idea of inducing a metallic state or even superconductivity by application of pressure has recently been tried out by some experimental groups [14–17]. Kuntscher *et al.* [14,17] report from optical measurements and x-ray diffraction analysis the observation of an insulator-to-metal transition at 16 GPa accompanied by a structural symmetry change. Forthaus *et al.* [15], on the contrary, neither observe any indication of a metallic state up to pressures of 24 GPa from transport measurements nor do they identify from x-ray diffraction analysis changes on the crystal symmetry at 16 GPa. Recently, Blanco-Canosa *et al.* [16] found a dimerized insulating state at high pressure by x-ray diffraction and magnetization measurements combined with *ab initio* calculations.

In view of the existing controversy, we present *ab initio* Car-Parrinello molecular dynamics results for TiOCl under pressure, where both lattice dynamics and electronic properties are treated on the same footing. Correlation effects are considered within the generalized gradient approximation GGA + U functional. We find, in agreement with Refs. [14,17], that TiOCl undergoes an insulator-to-metal transition at a critical pressure $P = P_c$ and the transition is accompanied by a lattice dimerization along b with a change from orthorhombic *Pmmn* to monoclinic $P2_1/m$ symmetry. This structural change is consistent with Ref. [16]. Moreover, our results show that the system undergoes a second phase transition from a dimerized ($P2_1/m$ symmetry) to a uniform (undimerized) metal (*Pmmn* symmetry) at a pressure $P = P_c' > P_c$. This transition has not yet been reported experimentally.

The microscopic analysis of the insulator-to-metal transition at $P = P_c$ reveals that this transition happens in the *ab* bilayers with closure of the gap at the Fermi level, while the conductivity along c may be hindered by the large van der Waals gap between different bilayers, reminiscent of the anisotropic conductivity in cuprates upon doping [18]. The transition is driven by the widening of the Ti $3d$ bands rather than a reduction of the crystal field splittings and we find orbital repopulation of the electronic density in the t_{2g} orbitals. The concomitant dimerization along b is attributed to the pressure-enhanced hybridization. We show that both phase transitions at P_c and P_c' are of first order. The calculated pressure-induced changes of lattice parameters are in good agreement with the experimental results [15,17] and we can explain their strong anisotropic properties as well as their abrupt jump behavior (contraction-expansion) at the transitions.

For our calculations, we employed the Car-Parrinello [19] projector-augmented wave (CP-PAW) method [20] and studied the pressure effects on the electronic and lattice variables with the Parrinello-Rahman fictive Lagrangian approach [21]. The great advantage of this procedure is the ability to deal with crystals with anisotropic compressibilities along different directions as is the case for TiOCl. In order to have the correct insulating behavior at ambient pressure, we employed the GGA + U functional. It has already been shown [13,22] that strong correlations are also important for the correct description of the lattice structure. In fact, the lattice parameters and the distances and angles between atoms obtained from CP-PAW with GGA + U at ambient pressure are more consistent with the experimental results than GGA or local density approximation (LDA) determined structures. We performed carefully converged calculations with high energy cutoffs of 45 and 180 Ry for the wave functions and charge density expansion, respectively. A value of $U = 1.65$ eV with which correct spin exchange along b is reproduced [13] was used for the GGA + U calculations. The relation between the U value used in different codes is discussed in Ref. [13].

In Fig. 1 we present the calculated change of lattice parameters as a function of applied external pressure. The lattice parameters at each pressure are obtained by fully relaxing the lattice structure without any symmetry constraints. Although a spin ordered state has to be imposed within the GGA + U functional, the results are completely consistent with the experiments [15,17]. We observe that the largest compression happens along c since the interaction between neighboring bilayers is of van der Waals type. Along b, which is the direction of the Ti chains with strong antiferromagnetic (AF) interaction J_b [8], a noticeable shrinkage is observed as pressure increases. The magnitude of the shrinkage depends on the choice of the spin configuration set in the GGA + U calculation. The experimental results are reproduced when we set AF order along b while this direction becomes incompressible if the spin configuration is set to be ferromagnetic (FM). This is due to the fact that the Pauli principle prevents two electrons with the same spin to occupy the same bonding state with low energy. Therefore, if the volume along b is reduced in a FM spin configuration, the total energy will increase rapidly due to occupation of an antibonding state as two Ti ions come closer. For an AF configuration along b, the Pauli principle does not affect the energy and the system becomes compressible along b as observed [15].

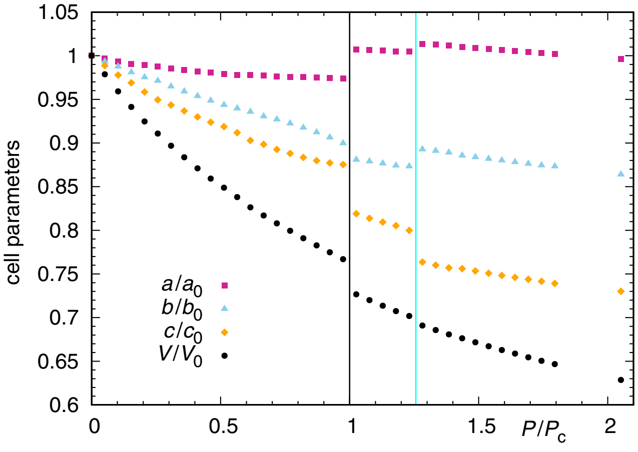

FIG. 1 (color online). Pressure dependence of lattice parameters and volume. Pressure is normalized to the critical pressure for the insulator-to-metal transition and lattice parameters are normalized to their values at ambient pressure. The compressibility along a, b and c is strongly anisotropic. The existence of two phase transitions is recognizable by jumps in all quantities.

In contrast, TiOCl remains almost incompressible along a regardless of the spin configurations we chose along this direction. This is due to the fact that the Ti-Ti interaction along a is of Ti$d_{x^2-y^2}$-Op-Ti$d_{x^2-y^2}$ superexchange nature, and not direct exchange as along b. In this case spin order is irrelevant for compressibility. Throughout this work, we adopted AF order along b and FM along a and c [13].

At $P = P_c$ (black vertical line in Fig. 1) all lattice parameters show an abrupt jump. While b and c contract, the a direction expands, as experimental observations seem to indicate [23]. We find a second jump of the lattice parameters at $P = P_c' > P_c$ (blue vertical line in Fig. 1) that defines a second phase transition. At this pressure, both a and b directions show an abrupt expansion. In order to understand the nature of these phase transitions, we now analyze the density of states (DOS) and change of symmetry.

In Fig. 2 we show the Ti d partial DOS in the range of energies between -2 and 6 eV at pressures in the vicinity of P_c and P_c'. We chose the local coordinate system as $x \parallel b$, $y \parallel c$, and $z \parallel a$, which diagonalizes the Hamiltonian with $d_{x^2-y^2}$, d_{xz}, d_{yz} forming the t_{2g} bands and d_{xy}, d_{z^2} the e_g bands. In the insulating phase at $P/P_c = 0.51$ [see Figs. 2(a) and 2(b)], a gap is present in the DOS, separating the occupied $d_{x^2-y^2}$ state from the unoccupied d_{yz} and d_{xz} states. The whole character of the DOS and structure is similar to that at ambient pressure for temperatures above the spin-Peierls transition [8,12] except for a reduction of the gap and the width of the d bands. At $P/P_c = 1.03$, right above the transition [see Figs. 2(c) and 2(d)], the gap disappears and the d states are suddenly rearranged. The Fermi level crosses the d_{yz} and d_{xz} states while a gap within $d_{x^2-y^2}$ (orbital in the bc plane) still remains. These results indicate an insulator-to-metal transition at P_c. Moreover, the abrupt expansion along a can be explained by the occupation of the d_{yz} and d_{xz} orbitals which strongly overlap between neighboring Ti ions along a. Direct repulsive interactions between same-spin electrons in these orbitals based on the Pauli principle lead to a sudden expansion. We also observe a sudden contraction of the structure along b and a dimerized pattern, as shown in Fig. 2(d), which is due to the occurrence of tighter Ti-Ti dimer states between neighboring sites along b and explains the gap in the $d_{x^2-y^2}$ partial DOS. The obtained insulator-to-metal transition is in agreement with optical experiments [14] but contradicts electrical resistivity measurements [15]. TiOCl is a strongly anisotropic crystal with a large van der Waals

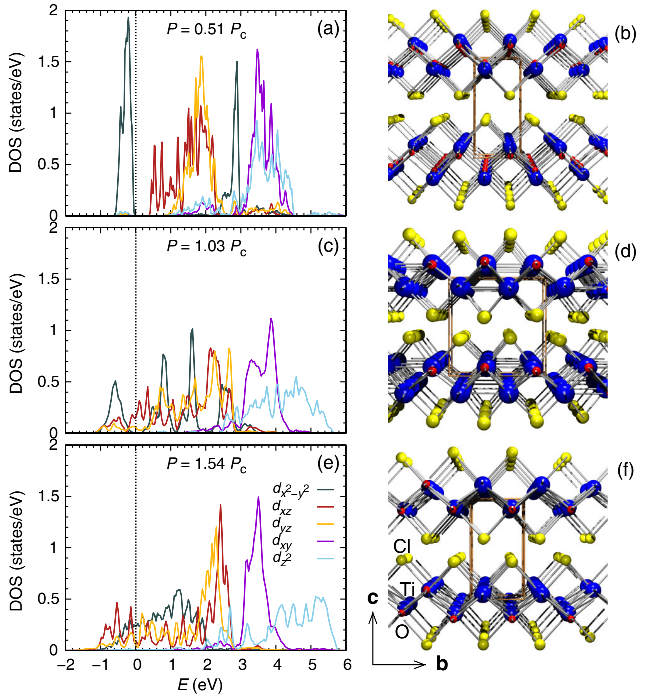

FIG. 2 (color online). (a),(c), and (e) are the partial density of states at three different values of pressure in different phases. In the insulating state, only $d_{x^2-y^2}$ orbital is occupied while all the t_{2g} bands are occupied in the metallic regions. In the dimerized metallic phase, a gap still opens in $d_{x^2-y^2}$ orbital. (b),(d), and (f) is the structure at these three different values of pressure. The structure in the dimerized metal is quite different from the other two. In the metallic phase, all the O atoms behind Ti atoms are invisible due to the flatness of the Ti-O-Ti angle.

gap along c. If the resistivity measurements have been done along c, the predominance of this gap is to be expected. We observe from our calculations that the metalicity is in the ab bilayers [14].

In Fig. 2(e) we show the DOS at $P = 1.54P_c$ above the transition at $P = P_c'$. The gap in $d_{x^2-y^2}$ as well as the structural dimerization along b disappear [Fig. 2(d)]. The system shows a uniform metallic phase which has not yet been established experimentally. The abrupt increase of occupation numbers in d_{yz} and d_{xz} orbitals at $P = P_c'$ accounts for another sudden expansion in a, and the disappearance of the dimer states along b for the abrupt expansion of b.

In Fig. 3 we present the pressure-induced changes of the d-state bandwidths as well as the crystal field splittings between the lowest d band ($d_{x^2-y^2}$) and all other t_{2g} and e_g bands. We observe within the three phases that the bandwidths of all d states widen monotonically with pressure [Fig. 3(a)], while the crystal field splittings show two different trends [Fig. 3(b)]. The orbital excitations from $d_{x^2-y^2}$ to the e_g orbitals increase monotonically with pressure, in agreement with experiment (for the optically allowed excitation $d_{x^2-y^2}$ to d_{xy}) [14]. Meanwhile, the

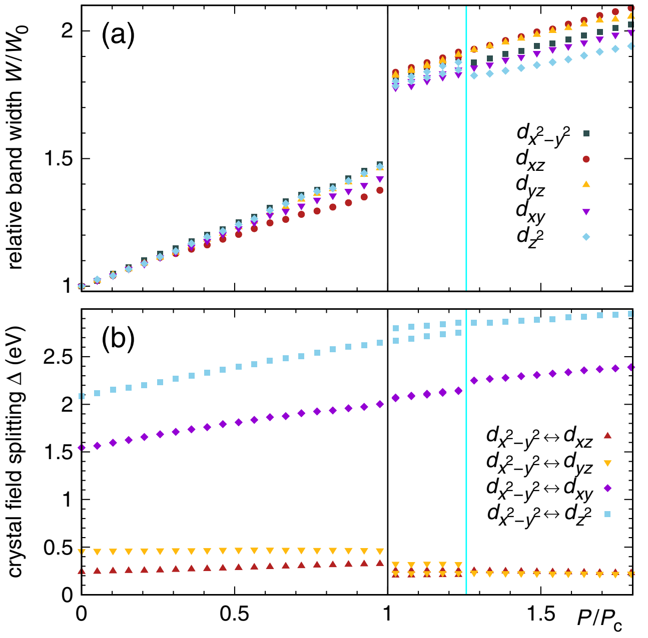

FIG. 3 (color online). (a) Bandwidth of all five d states as a function of applied pressure. Pressure is normalized to the critical pressure, bandwidth to the value at ambient pressure. (b) Crystal field splittings from $d_{x^2-y^2}$ to the other d orbitals as a function of pressure. Lower symmetry in the dimerized metallic phase produces two values instead of one for both quantities.

excitations to the t_{2g} orbitals depend very little on pressure. From these results we conclude that the insulator-to-metal transition is mainly controlled by an increase of bandwidths rather than by crystal field splitting. However, the phase transition is characterized by a redistribution of electronic occupation among all three t_{2g} bands. Thus, it is not a typical one-band Mott transition where electron transfer occurs only within one band. Moreover, in agreement with the sudden changes of lattice parameters at pressures $P = P_c$ and $P = P_c'$, bandwidths and crystal field splittings also show abrupt jumps at the phase transitions. The cooperative effect between variations of electronic bandwidths and changes of crystal field splittings by lattice distortions may be the mechanism responsible for the first order phase transitions.

The analysis of Ti-O, Ti-Cl distances as well as Ti-O-Ti angles as a function of pressure shows that, as expected, the distances between atoms in the insulating phase decrease monotonically with increasing pressure. Nonetheless, the distances between Ti-O along a increase suddenly at pressures P_c and P_c' due to the expansion along this direction at the phase transitions. The strongly distorted octahedron [TiO_4Cl_2] at ambient pressure is modified towards a regular octahedron by a flattening of the Ti-O-Ti angle with increasing pressure (Fig. 4). At $P > P_c'$, the angles become slightly larger than 180°.

A subject of controversy has been the crystal symmetry for pressures above P_c [14,15,17]. We have identified the

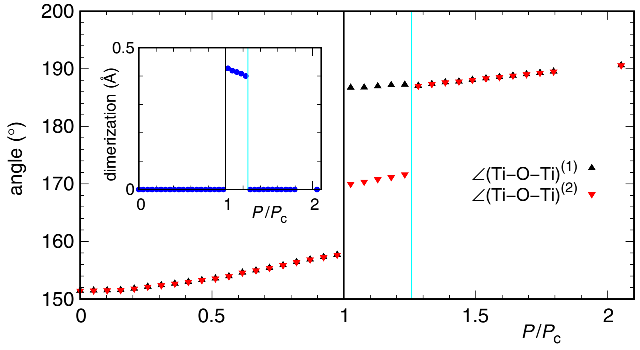

FIG. 4 (color online). Angle between Ti-O-Ti as a function of pressure normalized by the critical pressure. The inset shows the difference between long and short Ti-Ti bonds along b.

calculated structure as orthorhombic space group *Pmmn* (59) for pressures $P < P_c$ and $P > P_c'$ and monoclinic space group $P2_1/m$ (11) for pressures $P_c < P < P_c'$. In order to confirm that the restoration of the high symmetry *Pmmn* at pressures $P > P_c'$ is independent of the choice of unit cell and spin order, we also performed calculations with different spin configurations (AF/FM) for different supercells and artificially disordered structures at pressures $P > P_c'$. The high symmetry *Pmmn* is recovered in all cases. These investigations indicate that the lattice first undergoes a transition from orthorhombic to monoclinic structure as dimerization sets in, which is consistent with Ref. [16], and under further pressure increase a transition back to the orthorhombic symmetry occurs as the dimerization vanishes due to nonlinearities in the elastic response. The abrupt onset and disappearance of dimerization shown in the inset of Fig. 4 indicates that both phase transitions are of first order. Such complicated structural phase transitions and high lattice anisotropy could be the origin of the difficulties in determining the lattice structure from x-ray diffraction data, leading to different conclusions from experiments [14–17].

Finally, we note that the phase transitions in the CP-PAW calculations with the GGA + U functional occur at higher pressures (39 ± 1 GPa) than the experimental pressures (≈16 GPa). Such deviations are attributed to the artificial long-range AF order along b we imposed, which is used to mimic the strong correlation in the GGA + U approach. However, as is well-known, only short-range AF fluctuations exist in a Mott insulator. The situation can be clearer if we resort to the phase diagram shown in Ref. [24]. It is found that one has to apply much higher pressure to drive an AF insulator to a Fermi liquid than to drive a Mott insulator to a metal. To remedy this shift in the transition pressure, relaxation with a yet to be developed constant pressure *ab initio* molecular dynamics LDA + DMFT method would be required.

In conclusion, our *ab initio* molecular dynamics study of TiOCl under pressure shows that this system undergoes two phase transitions, the first one from an insulator to an anisotropic metal accompanied with a strong structural Ti-Ti dimerization along b, and a second one from the dimerized to a uniform metallic state. Our results indicate that the Mott-insulator-to-metal transition is mainly driven by bandwidth widening leading to an abrupt change of the electronic structure and orbital population and inducing a structural change. We propose resistivity experiments contacting the *ab* planes in order to settle the question of insulator or metal as well as analysis at higher pressures to confirm our prediction of a second phase transition. Because of the orbital repopulation and the structural change, which leads to a dimensional crossover from quasi-one-dimensional to quasi-two-dimensional system at $P > P_c'$, the question of possible superconductivity is still open.

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