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Two pressure-induced structural phase transitions in TiOCl

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We studied the crystal structure of TiOCl up to pressures of $p=25$ GPa at room temperature by x-ray powder-diffraction measurements. Two pressure-induced structural phase transitions are observed: at $p_{c1} \approx 15$ GPa emerges an $2a \times 2b \times c$ superstructure with b -axis unique monoclinic symmetry (space group $P2_1/m$). At $p_{c2} \approx 22$ GPa, all lattice parameters of the monoclinic phase show a pronounced anomaly. A fraction of the sample persists in the ambient orthorhombic phase (space group $Pmmn$) over the whole pressure range.

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I. INTRODUCTION

Recently, high-pressure studies on the low-dimensional Mott-Hubbard insulators TiOCl and TiOBr have demonstrated the high sensitivity of their electronic and structural properties regarding the application of pressure. The first high-pressure experiments on TiOCl and TiOBr single crystals at room temperature revealed strong changes in the optical response in the infrared frequency range, with the suppression of the transmittance and increasing optical conductivity at high pressures.^{1–3} Based on these results, the possibility of a pressure-induced insulator-to-metal transition was suggested. However, subsequent electrical transport measurements on powder samples did not confirm a metallization of TiOCl at high pressure and found only an anomaly in the pressure-induced decrease in the charge gap at ≈ 15 GPa.⁴ A controversy regarding the high-pressure electronic properties of TiOCl also exists from the theoretical point of view. *Ab initio* calculations were carried out based on density-functional theory within the local-density approximation plus U approximation⁵ and using Car-Parrinello molecular dynamics.⁶ While the former claims an insulating phase up to at least 30 GPa, the latter predicts the metallic character of the high-pressure phases.

According to both experiment and theory, TiOCl exhibits structural phase transitions under pressure at room temperature. Signatures of a structural phase transition in TiOCl and TiOBr under pressure were observed in x-ray powder-diffraction studies.^{2,7} This structural phase transition coincides with an anomaly in the pressure-dependent electrical and optical properties at $p_{c1} \approx 15$ GPa.^{2,4,7} Blanco-Canosa *et al.*⁵ confirmed the occurrence of a structural phase transition but the corresponding critical pressure was considerably lower (≈ 10 GPa). The high-pressure phase was specified as b -axis unique monoclinic $P2_1/m$ phase with a strong dimerization of the one-dimensional spin chain along b .⁵ It was furthermore claimed⁵ that the dimerization is of pure electronic origin, i.e., resembles that of a conventional Peierls insulator, and that the magnetic interaction plays only a minor role at high pressure. It is noticed here that the reported

symmetry⁵ is not a subgroup of the ambient $Pmmn$ symmetry. The high-pressure phase thus is not a simple superstructure of the structure at ambient conditions but it requires major rearrangements affecting the connectivity between atoms. These might be provided by the observed monoclinic angle of $\beta \sim 99^\circ$ as compared to 90° in the orthorhombic phase. The reported atomic positions at $2e: (\frac{1}{4}, y, z)$ would require a mirror plane perpendicular to the a axis and thus are incompatible with the reported monoclinic b axis.⁵ Besides, several aspects of the high-pressure phases still need to be clarified, e.g., the values of the critical pressures and possible superstructures being induced at higher pressures.

Here we present x-ray diffraction data on TiOCl for an extended pressure range up to ~ 25 GPa. Our goal is to clarify the inconsistencies regarding the experimental findings for the high-pressure crystal structure of TiOCl. Besides a transition from the orthorhombic $Pmmn$ to the monoclinic $P2_1/m$ crystal structure with an $2a \times 2b \times c$ superstructure, we find a pressure-induced isostructural phase transition for the monoclinic phase with anomalies in the lattice parameters.

II. EXPERIMENT

Single crystals of TiOCl were synthesized by gas transport from TiCl_3 and TiO_2 .^{8,9} TiOCl crystallizes in the space group $Pmmn$ at ambient conditions and consists of distorted TiO_4Cl_2 octahedra. Pressure-dependent x-ray powder diffraction measurements at room temperature were carried out with monochromatic radiation ($\lambda = 0.4128$ Å) at beamline ID09A of the European Synchrotron Radiation Facility (ESRF) at Grenoble. Crystals were gently ground and placed into a diamond-anvil cell (DAC). The material of the gasket was stainless steel, and its initial thickness and hole diameter was 40 μm and 150 μm , respectively. The applied pressures p were determined with the ruby fluorescence method.¹⁰ Helium served as hydrostatic pressure-transmitting medium. Diffraction patterns were recorded with an image plate detector and then integrated with FIT2D (Ref. 11) to yield intensity vs 2θ diagrams. The DAC was rotated by $\pm 3^\circ$

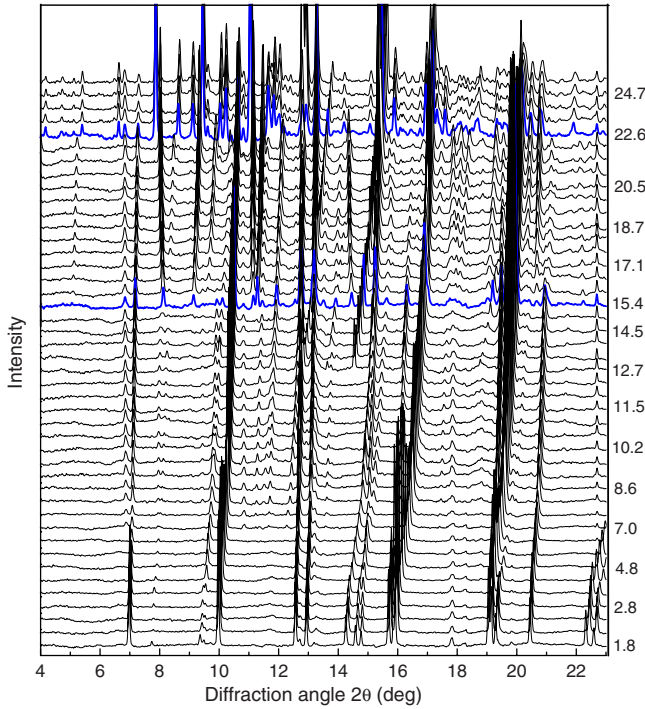


FIG. 1. (Color online) Room-temperature x-ray powder-diffraction diagrams of TiOCl at high pressures. The numbers on the right, vertical axis indicate the applied pressures in gigapascal. The diffraction diagrams at the critical pressures $p_{c1}=15.4$ GPa and $p_{c2}=22.6$ GPa are highlighted by bold, blue (black) lines.

during the exposure to improve the powder averaging. We carried out Le Bail fits of the diffraction data using the JANA2006 software,¹² in order to determine the lattice parameters as a function of pressure. Rietveld refinements of the diffraction data could not be carried out due to the preferred orientation of the crystallites inside the DAC, as described earlier.⁷

III. RESULTS AND DISCUSSION

Figure 1 shows the diffraction diagrams of TiOCl for all measured pressures. Fundamental changes in the diffraction diagrams are observed at 15.4 and 22.6 GPa, which define the critical pressures p_{c1} and p_{c2} for the two structural phase transitions. The x-ray powder-diffraction diagrams of TiOCl for selected pressures up to ~ 25 GPa are presented in Fig. 2. Up to the critical pressure $p_{c1} \approx 15$ GPa, the diffraction diagrams can be described by Le Bail fits applying symmetry and lattice parameters of the ambient pressure, orthorhombic crystal structure (space group $Pmmn$) and assuming contributions from the ruby chips added for the pressure determination. The lattice parameters and unit-cell volume of the orthorhombic crystal structure obtained by the Le Bail fits are shown in Fig. 3 and are in agreement with those reported in Refs. 7 and 14. We find a slightly nonlinear decrease in the lattice parameters with increasing pressure.

Above $p_{c1} \approx 15$ GPa, the diffraction diagrams can no longer be described by a single phase, but a good fit of the data can be achieved by assuming the coexistence of two

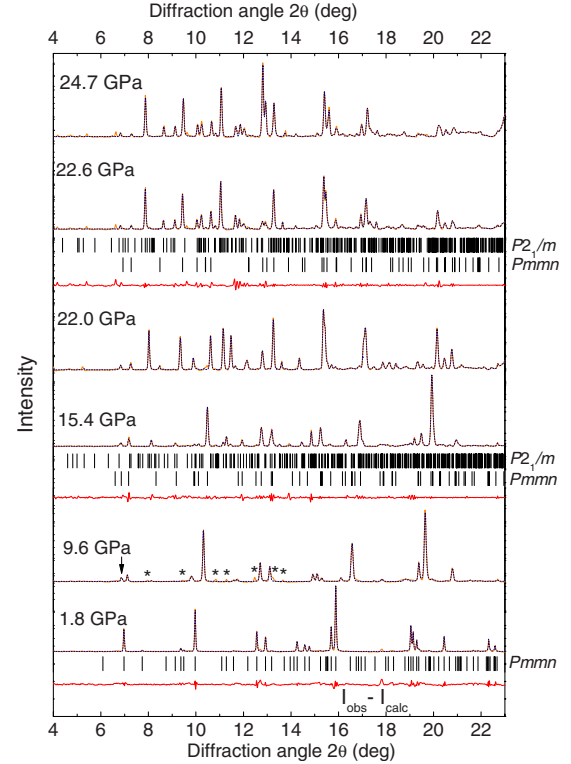


FIG. 2. (Color online) Room-temperature x-ray powder-diffraction diagrams (full, orange lines) of TiOCl at high pressures together with the Le Bail fits (dotted, blue lines). For the pressures 1.8, 15.4, and 22.6 GPa the difference curve ($I_{obs} - I_{calc}$) between the diffraction diagram and the Le Bail fit is shown. Markers show the calculated peak positions for the various phases. The arrow indicates the reflection from the ruby chip. The asterisks mark the reflections due to the monoclinic phase already present above ~ 7 GPa.

phases—namely, an orthorhombic phase (space group $Pmmn$) and a monoclinic phase (space group $P2_1/m$, b -axis unique) with double a and b axes. The lattice parameters and the angle β of the monoclinic unit cell hardly change up to ~ 22 GPa (see Figs. 3 and 4). The coexistence of two phases extends over a broad pressure range and signals the sluggish character of the phase transition. A large pressure range of phase coexistence, of 10 GPa or larger, has been observed for several first-order structural phase transitions^{15–17} and suggests that the two phases are almost energetically degenerate.¹⁸

It should be noted that already above ~ 7 GPa, several weak reflections occur, marked with asterisks in Fig. 2, which cannot be related to the orthorhombic phase¹⁹ but to the monoclinic phase, which fully develops at p_{c1} as described above. The appearance of diffraction peaks related to the monoclinic phase at pressures lower than p_{c1} might be due to nonhydrostatic conditions in the DAC, leading to locally higher pressures than indicated by the ruby fluorescence.

The appearance of additional reflections above p_{c1} due to a monoclinic phase *in addition* to those of the orthorhombic phase is also observed in the diffraction diagrams of Ref. 5. There, the additional reflections were attributed to a mono-

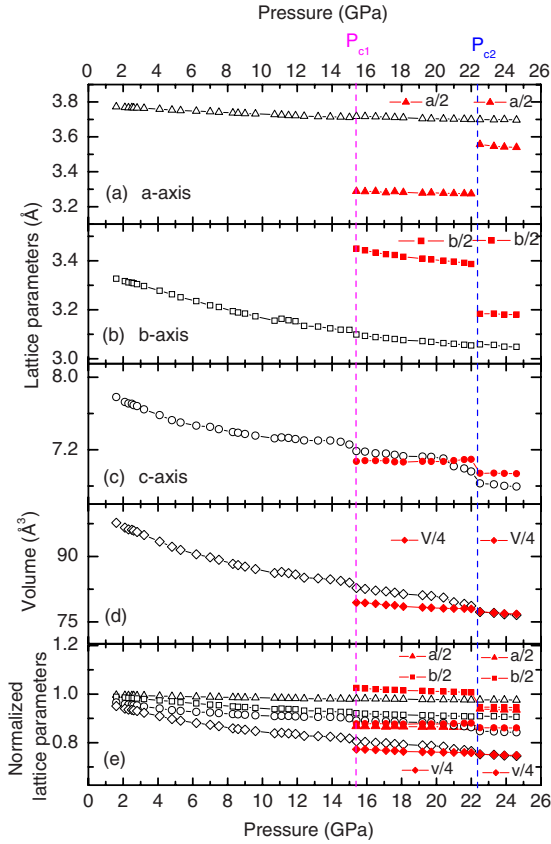


FIG. 3. (Color online) Results of the Le Bail fits of the room-temperature x-ray diffraction diagrams of TiOCl: lattice parameters and unit-cell volume as a function of pressure [$Pmmn$: black, open symbols; $P2_1/m$: red (gray), full symbols]. Lines are guides to the eyes. For the normalization of the lattice parameters and the unit-cell volume, the values of Ref. 13 were used.

clinic phase with a doubling of the unit cell along the b axis. Furthermore, it was claimed⁵ that the monoclinic phase above 10 GPa at room temperature resembles the monoclinic spin-Peierls phase occurring below the critical temperature T_{SP} at ambient pressure. This led to the conclusion that T_{SP} increases with increasing pressure, and it was proposed that

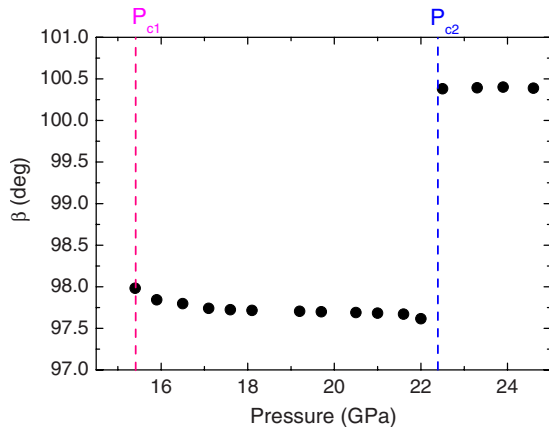


FIG. 4. (Color online) Angle β of the unit cell of the $P2_1/m$ monoclinic crystal structure at room temperature as a function of pressure.

T_{SP} reaches room temperature for pressures above 10 GPa.⁵ In contrast to the results of Blanco-Canosa *et al.*⁵ we find a doubling of the unit cell along both a and b axes in the monoclinic cell. This discrepancy could be explained by the fact that the results of Ref. 5 were restricted to the pressure range ≤ 15.2 GPa, where the monoclinic phase is not yet fully developed (which is the case only above $p_{c1} = 15.4$ GPa according to our data). Furthermore, it is important to stress the differences between the crystal structures of the ambient-pressure spin-Peierls phase at low temperatures and the high-pressure dimerized phase at room temperature. While the former shows an a -axis unique monoclinic symmetry with a monoclinic angle $\alpha \sim 90^\circ$,^{20–22} the latter has a b -axis unique monoclinic symmetry with monoclinic angle $\beta \sim 99^\circ$.⁵

It is interesting to note that an approximated doubling of the monoclinic unit cell along the a axis was recently observed in a high-pressure x-ray diffraction study on TiOCl at $T = 6$ K.²³ Starting from the ambient-pressure, low-temperature monoclinic spin-Peierls phase, Prodi *et al.* found a pressure-induced suppression of the dimerization along the b axis in the vicinity of a first-order structural phase transition at around 13 GPa.²³ The high-pressure phase shows an incommensurate superstructure of the type $(2a-\epsilon) \times b \times c$ and might be interpreted in terms of a conventional Peierls state.

At $p_{c2} \approx 22$ GPa again significant changes in the x-ray diffraction diagram are observed (see Figs. 1 and 2), indicating the occurrence of a second structural phase transition. All lattice parameters of the monoclinic phase show pronounced anomalies at p_{c2} , as seen in Figs. 3 and 4. Above p_{c2} , several weak reflections appear at diffraction angles below 10° , which can neither be related to the orthorhombic and monoclinic phase, nor explained in terms of reflections from the ruby chips, the diamond anvils or the gasket. In view of the complicated phase diagram of TiOCl under pressure, with a coexistence of multiple phases, we explain these weak reflections in terms of a third phase appearing above p_{c2} . In order to specify the structural details of this third phase, x-ray diffraction data at higher pressures are needed.

In the following, we speculate on the possible mechanism driving the structural phase transitions in TiOCl under pressure. We propose that their occurrence is closely linked to the tuning of the anisotropy or dimensionality of the system under pressure. For an illustration of the dimensionality, we plot and compare in Fig. 5 the lattice parameter ratios for the various phases. Here we assume that the average Ti-Ti distance scales with the lattice parameters. For the orthorhombic phase ($Pmmn$), the ratio b/a is shown for the whole pressure range studied. For the high-pressure phases we take into account the superstructures and thus plot the ratio b/a for the monoclinic phase ($P2_1/m$) in the pressure range $p > p_{c1}$.

For the orthorhombic phase, the ratio b/a monotonically decreases with increasing pressure for the whole pressure range studied, with the tendency to saturation at high pressures. This indicates a pressure-induced enhancement of the one-dimensional character of the system consistent with an earlier report.⁵ The enhanced one-dimensional character under pressure is due to the larger compressibility of the lattice

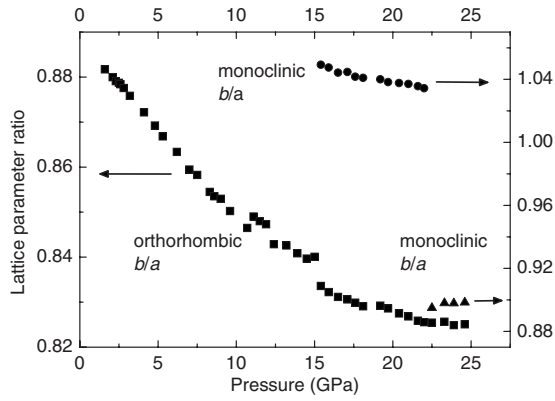


FIG. 5. Lattice parameter ratio as a function of pressure: Ratio b/a for the orthorhombic phase ($Pmmn$, squares) for the whole studied pressure range; ratio b/a for the monoclinic phase ($P2_1/m$, circles) in the pressure range $p_{c1} < p < p_{c2}$; ratio b/a for the monoclinic phase ($P2_1/m$, triangles) in the pressure range $p > p_{c2}$.

along the b direction.⁵ At p_{c1} , a monoclinic phase with doubled unit cell along a and b is energetically degenerate with the orthorhombic phase. For this monoclinic phase, we find a ratio b/a close to one, i.e., the system is *close to two-dimensional*, up to p_{c2} . This is due to the significant shrinkage of the unit cell along the a direction and its enlargement along the b direction, compared to the orthorhombic phase (Fig. 3). Accordingly, the interchain interaction is expected to play a major role in determining the electronic and magnetic properties of TiOCl in the monoclinic high-pressure phase. The importance of the interchain interaction in TiOCl at ambient pressure is commonly accepted.^{24–26} Our data suggest an enhanced interchain interaction, comparable to the intrachain interaction, for $p_{c1} < p < p_{c2}$. Above p_{c2} , the ratio b/a drops to ≈ 0.9 , i.e., similar to the ratio b/a of the orthorhombic phase at ambient conditions. Thus the material becomes more one-dimensional above p_{c2} .

The occurrence of two pressure-induced phase transitions in TiOCl was predicted by Zhang *et al.*⁶ At p_{c1} , a structural phase transition with a change from an orthorhombic ($Pmmn$) to a monoclinic crystal structure ($P2_1/m$) accompanied by a doubling of the unit cell along b is expected. The concomitant insulator-to-metal transition is proposed to be due to a broadening of the electronic bands and a redistribution of electronic occupation among the three t_{2g} bands.⁶ A

second first-order structural phase transition from the dimerized monoclinic $P2_1/m$ phase to a uniform (undimerized) metallic phase with orthorhombic $Pmmn$ symmetry is predicted at the critical pressure $p = p_{c2} \approx 1.26p_{c1}$.⁶ Because of the structural changes and the orbital repopulation a dimensional crossover of TiOCl from quasi-one-dimensional to quasi-two-dimensional was proposed to occur above p_{c2} .⁶ A tendency of the system at high pressures toward two-dimensionality is consistent with our experimental results. However, it occurs already above p_{c1} and is limited to the pressure range $p_{c1} < p < p_{c2}$ according to our data. Discrepancies also exist regarding the doubling of the unit cell along the a axis, and, furthermore, we do not find a pure undimerized, orthorhombic phase at high pressures, as theory⁶ predicts.

Interestingly, the pressure-induced structural instabilities seem to strongly depend on temperature. While at low temperature, the dimerization along the b axis becomes energetically unfavorable above ~ 13 GPa and a switching from the spin-Peierls phase to a phase with an incommensurate charge density wave along the a axis occurs,²³ at room temperature the dimerization along b for $p > p_{c1}$ persists at least up to 25 GPa according to our findings. Possible incommensurabilities of the superstructures at room temperature remain to be clarified.

IV. CONCLUSIONS

Pressure-dependent x-ray powder diffraction data show the occurrence of two structural phase transitions in TiOCl at room temperature. Above $p_{c1} \approx 15$ GPa, a monoclinic phase (space group $P2_1/m$, b -axis unique) with a dimerization along the a and b direction emerges. At $p_{c2} \approx 22$ GPa all lattice parameters of the monoclinic phase show pronounced anomalies. A fraction of the sample persists in the ambient orthorhombic phase (space group $Pmmn$) over the whole pressure range studied.

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