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## TiOCl, an orbital-ordered system?

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**Abstract.** – We present first-principles density-functional calculations and downfolding studies of the electronic and magnetic properties of the layered quantum spin system TiOCl. We discuss explicitly the nature of the exchange paths and the concept of *orbital ordering* in this material. An analysis of the electronic structure of slightly distorted structures according to various phonon modes allowed in this material suggests that this system may be subject to orbital fluctuations driven by the electron-phonon coupling.

Spin = 1/2 quantum spin systems involving early transition metal ions with a  $3d^1$  configuration are being lately intensively studied since they present a large variety of interesting novel phenomena. Examples of these materials are those containing  $V^{4+}$  or  $Ti^{3+}$  ions where one  $d$  electron occupies one of the three  $t_{2g}$  orbitals and competing spin, charge, and orbital degrees of freedom determine their properties. For instance,  $NaV_2O_5$  is a mixed-valence system with  $V^{4.5+}$  which undergoes at  $T = 34$  K a phase transition to a charge-ordered state ( $V^{4+}/V^{5+}$ ) accompanied by the opening of a spin gap and a lattice distortion. The origin of this phase transition is not yet completely settled [1]. Another interesting system is  $LaTiO_3$ , where an unusual many-body state with antiferromagnetic (AFM) long-range order and orbital fluctuations has been observed [2] and discussed at length in relation to a possible quantum orbital liquid phase [3]. This interpretation though, is still unclear in view of recent X-ray and neutron diffraction data [4] as well as the dynamical mean-field theory (DMFT) coupled with local density approximation (LDA) calculations [5,6] which support the existence of non-degenerate  $t_{2g}$  orbitals in  $LaTiO_3$ .

Here we want to focus our attention on the layered system TiOCl which has recently raised a lot of discussion. Theoretical considerations as well as susceptibility studies [7], NMR [8], ESR [9] and infrared and Raman spectroscopy [10] have been reported. Susceptibility measurements show a kink at  $T_{c2} = 94$  K and an exponential drop at  $T_{c1} = 66$  K indicating the opening of a spin gap [7]. This feature which seems to be accompanied by a doubling of the unit cell along the  $b$ -axis [8] (see fig. 1) has been originally described as a spin-Peierls transition. However, the observation of large phonon anomalies [10] as well as temperature-dependent  $g$ -factors and linewidths in ESR [9] indicate that this is not a conventional spin-Peierls transition but rather a transition driven by competing lattice, spin, and orbital degrees of freedom with possible orbital fluctuations.

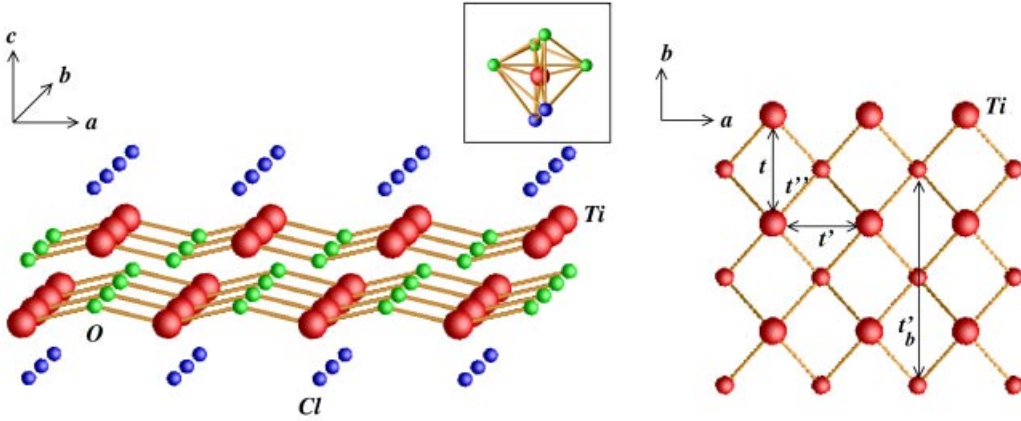


Fig. 1 – Crystal structure of TiOCl. Left panel: layered structure of the compound and the distorted octahedral Ti environment (see inset). Right panel: network of Ti atoms projected onto the  $ab$  plane with the various hopping paths. Seen in the figure are two layers of Ti atoms. The two different sizes of the Ti atoms correspond to atoms belonging to two different layers.

LDA+U calculations for a ferromagnetic (FM) ground state using the full-potential LMTO method [11] suggest that the equilibrium state above  $T_{c2}$  is described by one-dimensional spin-(1/2) chains running along the  $b$ -axis where the spins are localized in Ti  $d_{xy}$  orbitals [7]. Since the three  $t_{2g}$  orbitals are close in energy, a scenario with possible orbital ordering in this material has also been suggested [7, 8]. We shall investigate this proposal hereafter.

The purposes of our study in this letter are the following: i) to supplement Seidel *et al.*'s [7] work on TiOCl for the crystal structure measured at high temperatures  $T > T_{c2}$  by performing a detailed study of the ground state of the system in terms of various probable magnetic structures; ii) to calculate explicitly hopping parameters between Ti ions and the nature of the exchange paths with the downfolding procedure [12]; iii) finally and importantly, motivated by the signature of strong coupling between lattice and spin degrees of freedom [9, 10], to perform a frozen phonon study in order to understand the influence of the ion displacements on the electronic ground state. Our results suggest that though the high-temperature phase above  $T > T_{c2}$  is certainly not an orbital ordered state, during the vibration of certain phonon modes, occupation of various  $t_{2g}$  orbitals can change drastically and hence this system may be subject to orbital fluctuations driven by the electron-phonon coupling. No such theoretical calculations have been attempted before and may provide a useful guide in understanding this interesting material.

*Crystal structure and ligand field.* – The high-temperature phase of TiOCl crystallizes in the  $Pmmn$  space group and consists of bilayers of  $\text{Ti}^{3+}$  and  $\text{O}^{2-}$  parallel to the  $ab$  plane separated by layers of  $\text{Cl}^-$  (see fig. 1). The basic unit in this structure, *i.e.* the  $\text{TiCl}_2\text{O}_4$  octahedron (shown as inset in fig. 1), is distorted with distances  $d(\text{Ti-O}_{\text{apical}}) = 1.95 \text{ \AA}$ ,  $d(\text{Ti-O}_{\text{equatorial}}) = 2.25 \text{ \AA}$ ,  $d(\text{Ti-Cl}) = 2.32 \text{ \AA}$  and the angle  $\alpha(\text{O}_{\text{apical}}\text{-Ti-O}_{\text{apical}}) \approx 153^\circ$ . In a perfect octahedral environment the crystal field splits the five degenerate  $d$  orbitals into (in the local reference frame) the low-energy triplet  $t_{2g} = (d_{xy}, d_{xz}, d_{yz})$  and the higher-energy doublet  $e_g = (d_{z^2}, d_{x^2-y^2})$ . In the case of TiOCl, a further splitting of the  $t_{2g}$  orbitals into a lower  $d_{xy}$  and higher energy  $d_{xz}$ ,  $d_{yz}$  occurs [13]. These considerations suggest that the ground state for TiOCl at  $T > T_{c2}$  should be described by the Ti  $3d_{xy}$  orbitals.

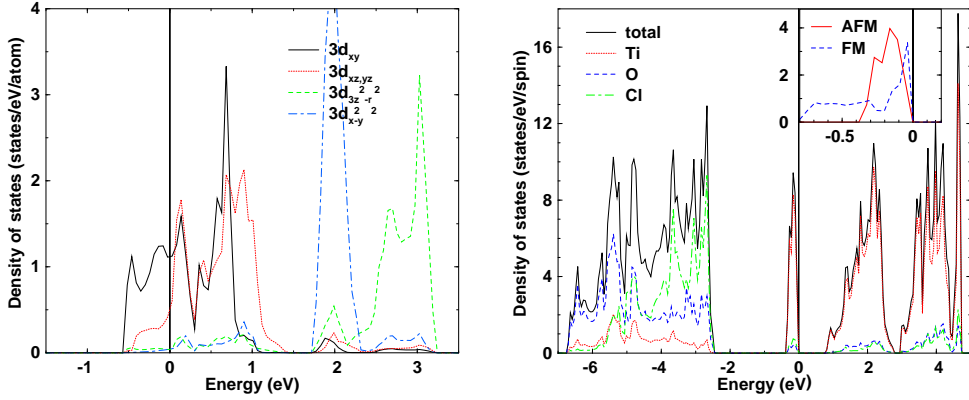


Fig. 2 – FPLO-LDA density of states for TiOCl. Left panel: orbital-resolved Ti-3d states for the non-spin-polarized case. The  $3d_{xy}$  orbital lies at lower energy than the  $3d_{xz,yz}$  states. The  $t_{2g}$ - $e_g$  split is about 2 eV. Right panel: LDA + U results for AFM Ti spin arrangement along  $b$ . The O-2p and Cl-3p states are mainly occupied but show sizable hybridization with the Ti 3d states. The narrow peak close to the Fermi level is predominantly Ti- $3d_{xy}$ . In the inset the Ti  $3d_{xy}$  states for the AFM and FM configurations are compared.

*Ab initio calculations.* – We have performed density-functional calculations in the LDA, generalized gradient approximation (GGA) [14] and in the LDA + U [15] approximation for this system using the linearized muffin tin orbital (LMTO) method based on the Stuttgart TBLMTO-47 code [11] and the full potential minimum basis local orbital code (FPLO) [16]. We checked convergence of the band structure results obtained with the LMTO scheme—where the downfolding procedure is implemented—*vs.* the results from the full potential scheme [17].

In fig. 2 we present the orbital-resolved density of states (DOS) obtained in the FPLO scheme. The coordinate system has been chosen as  $\hat{z} = a$ , and  $\hat{x}$  and  $\hat{y}$  axes rotated  $45^\circ$  with respect to  $b$  and  $c$ . We observe that the degeneracy between the  $t_{2g}$  orbitals is already lifted by the ligand field into  $d_{xy}$  and the slightly higher in energy  $d_{yz}$ ,  $d_{xz}$  [18] (see fig. 2, left panel). TiOCl is an insulator although the LDA and GGA calculations suggest metallic behavior due to the inadequate treatment of the Coulomb term in those approximations. A better description of the electronic correlation is obtained by the LDA+U approach which takes into account the orbital dependence of the Coulomb and exchange interactions [15]. Such a calculation is carried out on a spin-polarized state. The earlier study by Seidel *et al.* [7] considered only the FM arrangement of the Ti spins. In order to investigate whether the nature of the magnetic configuration has any influence on the orbital structure and in view of the possible antiferromagnetic (AFM) coupling of Ti ions along the  $b$ -direction—as suggested by the AFM Heisenberg chain model fitting the susceptibility data [7]—we have carried out further calculations where the Ti ions are AFM aligned along  $b$  and FM aligned along  $a$  and  $c$ . This calculation requires the doubling of the unit cell along  $b$  transforming the unit cell from orthorhombic to monoclinic. In the LDA + U an appropriate value for  $U$  and the onsite exchange  $J_o$  has to be taken. Previous first-principles studies [7] considered a FM spin-polarized state with  $U = 3.3$  eV and  $J_o = 1$  eV. We have chosen here the same  $J_o$  and we did not observe significant changes in the results by considering a lower  $J_o$  value (0.3 and 0.4 eV) which may be more appropriate for early transition metals like Ti.  $U$  was taken to vary in the range 2–7 eV. The results for both FM and AFM structures show a gap opening between occupied  $d_{xy}$  orbitals and unoccupied  $d_{xz}$  and  $d_{yz}$  orbitals, as seen in the LDA + U DOS shown in the right panel of

TABLE I – *Predominant hopping integrals (in eV) for TiOCl at various levels of downfolding.  $t_{xy}$ : all except the Ti- $xy$  channel have been integrated out.  $t_{xy} + Op + Clp$ : all except Ti- $xy$ , O- $p$  and Cl- $p$  have been integrated out.  $t_{xy} + Op$ : all except Ti- $xy$  and O- $p$  have been integrated out.  $t_{xy} + Clp$ : all except Ti- $xy$  and Cl- $p$  have been integrated out. The hopping paths are as shown in fig. 1.*

	$t_{xy}$	$t_{xy} + Op + Clp$	$t_{xy} + Op$	$t_{xy} + Clp$
$t$	-0.21	-0.26	-0.16	-0.31
$t''$	0.03	0.08	0.04	0.20
$t'$	0.04	-0.01	0.06	-0.02
$t'_b$	-0.03	-0.05	-0.03	-0.04

fig. 2. We observe that the choice of a FM or AFM state influences the total energy and the shape of the bands but not the orbital nature of the ground state. Independent of the choice of the  $U$  value (see below), the AFM spin configuration was found to be lower in total energy compared to the FM state. We have also considered a third possibility, namely Ti AFM aligned along  $a$  and FM along  $b$  and along  $c$ . The LDA +  $U$  calculations show again a band structure with a gap opening between occupied  $d_{xy}$  orbitals and unoccupied  $d_{xz}$  and  $d_{yz}$  orbitals.

Our study corroborates the fact that the ground state is indeed described by chains of Ti ions along the  $b$ -direction occupying the  $d_{xy}$  orbitals as also observed in the interpretation of ESR [9] and infrared spectroscopy [10] results. Consideration of other probable magnetic structures as well as the study of the role played by  $U$  and  $J_o$  in the LDA +  $U$  calculations along with the ligand field calculation of an isolated octahedron prompts us more definitely to conclude that at  $T > T_{c2}$  TiOCl cannot be described as an *orbital ordered* state, thereby leaving no room for discussion on the possibility of the ground state being described by a *zigzag* chain along  $a$  formed by alternating approximately degenerate  $d_{xz}$  and  $d_{yz}$  as was initially suggested as a possible scenario for TiOCl in refs. [7, 8].

We obtained the exchange constant  $J$  between neighboring Ti along the  $b$ -direction by subtracting the LDA +  $U$  total energy in the FPLO scheme between the AFM-coupled Ti spins along  $b$  and the totally FM spin configurations as a function of  $U$ . We found an almost linear dependency of  $J$  with respect to  $1/U$  for  $U$  values between 2 and 7 eV. For  $U \sim 3.3$  eV the computed AFM  $J$  is about 750 K, in good agreement with the estimate for an AFM superexchange  $J = 4t^2/U$  and with susceptibility measurements [7]. This good agreement suggests that FM contributions to the exchange play a minor role in this system. For an analysis of these results we proceed in the next section with a study of the various interaction paths in this material.

*Downfolding: effective Hamiltonians.* – In order to provide an understanding of the interaction paths in TiOCl, we have applied the tight-binding-downfolding procedure implemented within the framework of the improved version of the LMTO method, namely the NMTO method [12]. The method can be used to derive a few-orbital effective Hamiltonian  $H_k$  starting from the full LDA or GGA Hamiltonian by folding down the inactive orbitals. The Fourier transform of this few-orbital downfolded Hamiltonian provides *ab initio* estimates of the hopping matrix elements of the corresponding tight-binding (TB) Hamiltonian defined in the effective orbital basis, while the effective orbitals themselves provide the Wannier-like functions of the corresponding bands.

In table I we present the hopping parameters (see fig. 1, right panel) obtained from downfolding the GGA bands in TiOCl in order to define an effective Ti  $d_{xy}$ -only Hamiltonian. We observe that the predominant hopping ( $t$ ) is between nearest neighbors Ti  $d_{xy}$  along  $b$ , while the hopping parameters between next-nearest neighbors along  $b$  and along  $a$  and  $c$  directions are small. The system therefore virtually behaves as one-dimensional. An important point here is to investigate the nature of the (Ti  $d_{xy}$ )-(Ti  $d_{xy}$ ) interaction path. The effective (Ti

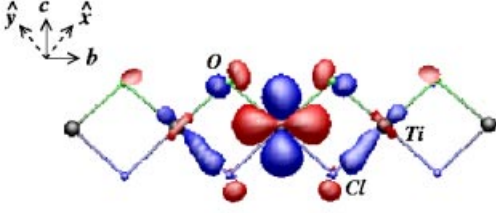


Fig. 3

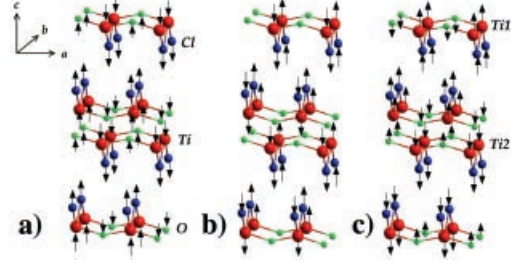


Fig. 4

Fig. 3 – Effective  $\text{Ti-}d_{xy}$  orbital (Wannier orbital) plotted in the  $bc$  plane in the downfolded representation where all the channels other than  $\text{Ti-}d_{xy}$  have been integrated out.

Fig. 4 – Ti-Cl in-phase distorted structures according to various allowed phonon modes in TiOCl. a) Distortion with no doubling of the unit cell. Here two different cases can be possible, one in which the Ti atoms belonging to two different layers within a given bilayer are pulled apart as shown in the figure, and another in which the Ti atoms are pushed towards each other (obtained by reversing the direction of arrows). b) Distortion with the unit cell doubled along  $b$ . c) Distortion with the unit cell doubled along  $c$ . Here the Ti belonging to two different layers within the bilayers are alternately pulled apart in one bilayer (Ti2 atoms) and pushed towards each other in the next bilayer (Ti1 atoms).

$d_{xy}$ )-(Ti  $d_{xy}$ ) hopping obtained by downfolding all the channels except Ti  $d_{xy}$  (shown in the first column of table I), involves the direct (Ti  $d_{xy}$ )-(Ti  $d_{xy}$ ) hopping renormalized by the contributions of the out-integrated O- $p$  and Cl- $p$  channels. In order to quantify the contribution of O and Cl to the various (Ti  $d_{xy}$ )-(Ti  $d_{xy}$ ) interaction paths, we considered the downfolding procedure by keeping active, in addition to two Ti- $d_{xy}$  in the basis set, i) O- $p$  and Cl- $p$  orbitals (Ti $xy$ +Op+Clp), ii) O- $p$  orbitals (Ti $xy$ +Op) and iii) Cl- $p$  orbitals (Ti $xy$ +Clp). This method has been proven to be very useful for determining the nature of the interaction paths in the frustrated  $\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2$  and  $\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2$  systems [19].

The TB parameters corresponding to the (Ti $xy$ +Op+Clp) set give an idea of the magnitude of the direct (Ti  $d_{xy}$ )-(Ti  $d_{xy}$ ) overlap. On the other hand, downfolding to (Ti $xy$  + Op) and (Ti $xy$  + Clp) accounts for the (Ti  $d_{xy}$ )-(Ti  $d_{xy}$ ) overlaps via Cl- $p$  and O- $p$ , respectively, in addition to direct overlap. Comparing the numerical values of the (Ti  $d_{xy}$ )-(Ti  $d_{xy}$ ) hopping integral,  $t$ , at various levels of downfolding we observe that, while already the direct overlap is considerable (in the range of energies that we are dealing here), the contribution of O- $p$  and Cl- $p$  is not negligible. This can be more easily seen in fig. 3, which shows the effective Ti  $d_{xy}$  orbital in the downfolding calculation where the channels other than Ti  $d_{xy}$ , namely Cl- $p$  and the O- $p$ , as well as the other Ti- $d$  characters, have been integrated out. The contribution of the integrated-out orbitals appears as a *tail* of the effective orbital with the *central* character having the same symmetry as the bare, unrenormalized orbital. Examining fig. 3, we see that the central Ti site shows the expected  $d_{xy}$  character, while the *tail* of the orbital sitting at the O and Cl sites has appreciable weight shaped to O- $p_x$ ,  $p_y$  and Cl- $p_x$ ,  $p_y$  symmetries which indicates appreciable renormalization effect coming from O- $p_x$ ,  $p_y$  and Cl- $p_x$ ,  $p_y$ . This analysis leads us to conclude that the equilibrium state of TiOCl at  $T > T_{c2}$  is given by the Ti  $d_{xy}$ -Ti  $d_{xy}$  direct coupling with *sizable* interaction via the surrounding O and Cl.

*Distorted structures.* – A fascinating feature about this system is its anomalous behavior [9, 10] near the phase transition at  $T_{c2}$  which has been attributed to competing lattice, spin and orbital degrees of freedom. As described above, *ab initio* calculations on the crystal structure measured at high temperatures  $T > T_{c2}$  predict unambiguously an electronic

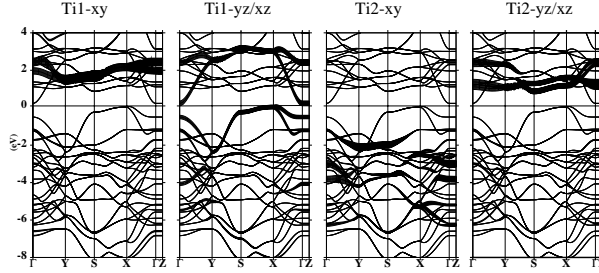


Fig. 5 – LMTO-LDA + U band structure in FM configuration for the distorted structure shown in fig. 4c). Only the band structure corresponding to the majority spin bands is shown, since for the minority spin the  $d$ -bands are completely unoccupied. The fatness of the bands in each panel corresponds to the weight of the indicated orbital in the wave function. The first and second panels show that the occupied orbitals for Ti1 are the near-doublet  $d_{yz}$ ,  $d_{xz}$ , while  $d_{xy}$  is higher in energy. The third and fourth panels show that, for Ti2,  $d_{xy}$  remains the lowest-energy, occupied orbital.

ground state formed of non-degenerate Ti  $3d_{xy}$  orbitals while  $d_{yz}$  and  $d_{xz}$  are higher in energy. However, displacements of the Ti sites due to phonon modes are expected to influence the electronic state and it remains to be seen whether during vibration occupation of certain  $d$  orbitals changes drastically. This would indicate that orbital fluctuations are important in this system since small atomic displacements can induce a change in the electronic occupation.

In order to investigate this scenario, we have performed a frozen phonon study where we calculated the ground-state properties for distorted structures according to the various Raman active  $A_g$  phonon modes expected for the  $Pmmn$  space group. These modes were calculated by considering a shell model [20,21] for TiOCl. The displacements considered in the *ab initio* calculation were chosen according to the eigenvector components of the  $A_g$  modes obtained from the shell calculation. The  $A_g$  phonon modes define ion displacements along the  $c$ -axis. Raman observations [10] suggest that the Ti-Cl in-phase zone boundary  $A_g$  mode plays an important role above the transition at  $T_{c2}$ . From those observations it is not conclusive [22] whether it corresponds to a phonon for a unit cell doubled along  $c$ ,  $b$  or  $a$ . The doubling of the unit cell along  $b$  reported by NMR [8] happens in the gapped region well below  $T_{c2}$ . In view of the above, we calculated the ground-state properties of various cases where the ions were displaced from their equilibrium position by considering displacements in magnitude smaller than 4% of the lattice constant according to various  $A_g$  phonon modes [10, 20]. We have considered three types of Ti-Cl in-phase distortions, as shown in fig. 4. Case (a): No doubling of the unit cell. Case (b): The unit cell doubled along  $b$ . In this case, the distorted structure is monoclinic with two crystallographically inequivalent Ti atoms. Case (c): The unit cell doubled along  $c$ . Here the unit cell remains orthorhombic with two inequivalent Ti ions, Ti1 and Ti2. We have carried out LDA(GGA) and LDA+U calculations in FM spin configurations for each of these cases [23]. In case (a), as drawn in fig. 4a), the ground state remains the same as for the undistorted case with  $d_{xy}$  as the lowest-energy, occupied orbital. However in the distorted structure with the atoms displaced in the opposite sense to fig. 4a), we observe a change in the orbital occupancies. The ground state is described by the  $d_{yz}$  and  $d_{xz}$  orbitals instead of  $d_{xy}$ . In case (b) the distortion enlarges the splitting between  $d_{yz}$  and  $d_{xz}$  while the ground state remains described by the  $d_{xy}$  orbital. In case (c) we observe a change in the orbital occupancies for Ti1 atoms as is evident from the LDA + U band structure results shown in fig. 5. This may be compared with the change of orbital occupancies for case (a) with atoms moved in opposite direction than drawn in fig. 4a). The ground state in case (c) is described by the  $d_{yz}$  and  $d_{xz}$  orbitals at Ti1, while  $d_{xy}$  remains as the lowest-energy, occupied

orbital at Ti2. These results support therefore the concept of possible orbital fluctuations in this system induced by strong electron-phonon interactions.

Although we have considered only a few chosen cases of distorted structures, and have certainly not explored all the possible allowed distortions in this material, the change of ground state in some of the above distorted calculations undoubtedly suggests that lattice, charge and orbital degrees of freedom are intimately related in this system. One may argue about the size of the distortion considered. Further analysis with smaller distortions shows that this effect may be still observed [24]. In conclusion, this system is not orbital ordered but may be subject to orbital fluctuations at high temperatures. We hope that our study will stimulate further investigations in the direction of understanding this fascinating compound.

\* \* \*

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