

Charge order and spin-singlet pairs formation in Ti_4O_7

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Charge ordering in the low-temperature triclinic structure of titanium oxide (Ti_4O_7) is investigated using the local density approximation (LDA)+ U method. Although the total $3d$ charge separation is rather small, an orbital order parameter defined as the difference between t_{2g} occupancies of Ti^{3+} and Ti^{4+} cations is large and gives direct evidence for charge ordering. $\text{Ti } 4s$ and $4p$ states make a large contribution to the static “screening” of the total $3d$ charge difference. This effective charge screening leads to complete loss of the disproportionation between the charges at $3+$ and $4+$ Ti sites. The occupied t_{2g} states of Ti^{3+} cations are predominantly of d_{xy} character and form a spin-singlet molecular orbital via strong direct antiferromagnetic exchange coupling between neighboring $\text{Ti}(1)$ and $\text{Ti}(3)$ sites, whereas the role of superexchange is found to be negligible.

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I. INTRODUCTION

The mixed valent transition metal oxides, that simultaneously contain metal atoms in two (or more) different valence states, are of strong current interest.¹ One of the classical examples of such a system is magnetite (Fe_3O_4), in which a first-order metal-insulator transition occurs at ~ 120 K.² According to Verwey, this transition is caused by the spatial ordering of $2+$ and $3+$ Fe cations on the octahedral B -sublattice of the inverted spinel structure AB_2O_4 .^{3,4} Recently, a local spin density approximation (LSDA)+ U study of the low-temperature phase of Fe_3O_4 resulted in a charge and orbitally ordered insulating ground state with a well pronounced orbital order.^{5,6} However, the strong difference in t_{2g} occupancies of $2+$ and $3+$ Fe was found to be drastically reduced by effective “static” screening.⁷ A similar result (see Ref. 8) has been obtained for another iron oxide, containing both $2+$ and $3+$ Fe cations, iron oxoborate (Fe_2OBO_3), which shows a broad semiconductor-to-semiconductor transition at ~ 317 K associated (as in Fe_3O_4) with a spatial order-disorder transformation of $2+$ and $3+$ Fe cations on quasi-one-dimensional Fe chains.^{9–11}

The aforementioned phenomena of sharp metal-insulator transitions associated with pronounced charge and/or orbital ordering are characteristic for the *Magnéli* phases $\text{M}_n\text{O}_{2n-1}$ ($\text{M} = \text{Ti}, \text{V}$).¹² These compounds form a homologous series and have been studied recently to understand the differences in crystal structures and electronic properties between the end members MO_2 ($n \rightarrow \infty$) and M_2O_3 ($n = 2$).¹³ In particular, the metal-insulator transition of VO_2 discovered some fifty years ago still is the subject of ongoing controversy and is another “hot topic” in solid state physics. LDA calculations have revealed strong influence of the structural degrees of freedom on the electronic properties of VO_2 and

neighbouring rutile-type dioxides.^{14–18} In this scenario the characteristic dimerization and antiferroelectric displacement of the metal atoms translate into orbital ordering within the t_{2g} states and a Peierls-like singlet formation between neighbouring sites. Recently, this was confirmed by LDA+DMFT calculations, which suggested to regard the transition of VO_2 as a correlation-assisted Peierls-transition.¹⁹

Ti_4O_7 titanium oxide is another remarkable member of the *Magnéli* phases with $n=4$ which shows metal-insulator transitions associated with the spatial charge ordering. It is a mixed valent compound which has an even mixture of $3+$ and $4+$ Ti cations ($\text{Ti}_2^{3+}\text{Ti}_2^{4+}\text{O}_7$), corresponding to an average $3d$ occupation of $1/2$ electron per Ti site. Electrical resistivity, specific heat, magnetic susceptibility, and x-ray diffraction data reveal two first-order transitions in the temperature range of 130 – 150 K.^{20–22} At 150 K a metal-semiconductor transition occurs without measurable hysteresis in resistivity and specific heat. It is followed by a semiconductor-semiconductor transition at 130 – 140 K, which again is characterized by an almost two orders of magnitude abrupt increase in electrical resistivity and has a hysteresis of several degrees.^{20,21} The magnetic susceptibility shows a sharp enhancement when heating through 150 K. However, it is small and temperature independent below this temperature and does not show any anomaly at 140 K.

The crystal structure of Ti_4O_7 (see Fig. 1) can be viewed as rutile-type slabs of infinite extension and four Ti sites thickness, separated by shear planes with a corundum-like atomic arrangement. Below 130 K it crystallizes in a triclinic crystal structure with two formula units per primitive unit cell.^{23–25} Four crystallographically inequivalent Ti sites are found at the centers of distorted oxygen octahedra. They form two types of chains,

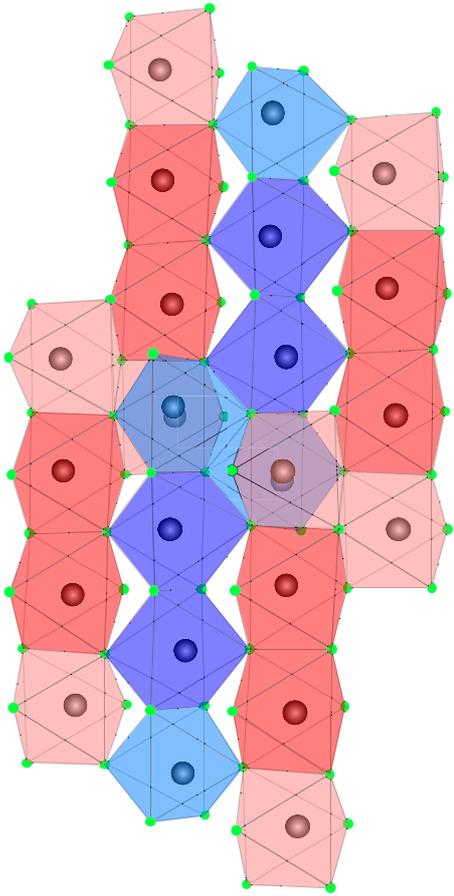


FIG. 1: (color online) The low-temperature crystal structure of Ti_4O_7 . Chains of four Ti sites run parallel to the pseudo-rutile c -axis. Red and blue (light and dark on the black and white image) chains of four Ti atoms correspond to the (a) and (b) chains Ti atoms, respectively. Further gradation of red and blue on light and dark subsets indicates inequivalent Ti sites in (a) and (b) chains.

namely, (a) 1-3-3-1 and (b) 2-4-4-2, which run parallel to the pseudo-rutile c -axis and are separated by the crystallographic shear planes. Although interatomic distances in the (b)-chain are almost uniform (3.01 and 3.07 Å between 4-4 and 2-4 Ti sites, respectively) they are remarkably different for the (a)-chain (3.11 and 2.79 Å between 3-3 and 1-3 Ti sites).

Accurate determination of the crystal structure allowed to elucidate the nature of the three phases distinguished by the two first-order transitions.^{22–25} In particular, in the metallic phase the average Ti-O bond lengths for crystallographically inequivalent TiO_6 octahedra are very similar which results in the average valence state of 3.5+ per each Ti cation. Below 130 K charge has been transferred from the (b) to the (a)-chains. In addition, Ti^{3+} cations in alternate (a)-chains are paired to form nonmagnetic metal-metal bonds, whereas in the intermediate phase pairing also persists but its long-range order calls for a fivefold supercell.²¹ Thus, the 130-140 K tran-

sition is associated with a transition to the phase with a long-range order of Ti^{3+} - Ti^{3+} pairs, whereas above 150 K 3+ and 4+ Ti cations are disordered. The presence of the Ti^{3+} - Ti^{3+} pairs strongly differentiates Ti_4O_7 from Fe_3O_4 and results in two steep first-order transitions found in the electrical resistivity.

Recent LDA band structure calculations of both high- and low-temperature phase of Ti_4O_7 results in significant t_{2g} charge separation between crystallographically independent 3+ and 4+ Ti sites in the low-temperature phase, whereas a rather isotropic occupation of the t_{2g} states has been found at room-temperature.²⁶ While, in addition, an orbital order at the Ti d^1 chains originating from metal-metal dimerization was found, the LDA gave only metallic solution with semimetallic-like band overlap instead of the semiconducting gap. This problem is overcome in our work taking into account strong electronic correlations in Ti $3d$ shell using the LDA+ U method.

In the present paper we investigate the electronic structure of the low-temperature phase using the LDA+ U approach in the tight-binding linear muffin-tin orbital (TB-LMTO) calculation scheme.^{27–29} The LDA+ U calculations result in a charge and orbitally ordered insulator with an energy gap of 0.29 eV, which is in a good agreement with an experimental gap value of 0.25 eV. From our results, we propose an orbital order parameter, defined as the difference between t_{2g} majority/minority spin occupancies of $\text{Ti}(1)^{3+}/\text{Ti}(3)^{3+}$ and $\text{Ti}(2)^{4+}/\text{Ti}(4)^{4+}$ cations, respectively. This order parameter is found to be quite large, although the total $3d$ charge difference between 3+ and 4+ cations, remains small. Also it is interesting to note that the total charge separation between 3+ and 4+ Ti cations completely loss due to efficient screening by the rearrangement of the other Ti electrons. In addition, we find a strong antiferromagnetic coupling of $J \approx 1700$ K of the local moments within the dimerized Ti^{3+} - Ti^{3+} pairs, whereas an inter-pair coupling is only of ≈ 40 K. This is in a good agreement with small and temperature independent magnetic susceptibility in the low-temperature phase of Ti_4O_7 .

II. COMPUTATIONAL DETAILS

The present band-structure calculations have been performed for the low-temperature triclinic structure of Ti_4O_7 .²⁵ The $P\bar{1}$ unit cell used in the calculations was constructed from the translation vectors of the original $I\bar{1}$ cell with $a = 5.626$ Å, $b = 7.202$ Å, $c = 20.2608$ Å, $\alpha = 67.90^\circ$, $\beta = 57.69^\circ$, and $\gamma = 109.68^\circ$ found at 115 K. The radii of muffin-tin spheres were taken as $R_{\text{Ti}1-4} = 2.27$ a.u., $R_{\text{O}1,\text{O}3,\text{O}4-6} = 1.78$ a.u., and $R_{\text{O}2,\text{O}7} = 1.66$ a.u. Fifteen kinds of empty spheres were introduced to fill up the inter-atomic space. For simplicity we neglect small spin-orbit coupling and consider only a collinear spin case.

III. LSDA BAND STRUCTURE

Our LSDA band structure calculations for the low-temperature $P\bar{1}$ structure confirmed the results of the previous work.²⁶ The LSDA gives a nonmagnetic metallic solution with substantial charge separation between crystallographically independent Ti(1)/Ti(3) and Ti(2)/Ti(4) cations. The lower part of the valence band below -3 eV is predominantly formed by O $2p$ states with a bonding hybridization with Ti $3d$ states. Crystal field splitting of the latter is roughly of 2.5 eV. Ti t_{2g} states form the group of bands at and up to 2 eV above the Fermi energy whereas Ti e_g states give a predominant contribution to the bands between 2.5 and 4.5 eV. Within the t_{2g} group of bands the symmetry inequivalence of Ti(1)/Ti(3) and Ti(2)/Ti(4) sites leads to substantial t_{2g} charge separation between these two groups of Ti atoms. In addition, an analysis of the partial density of states reveals significant bonding-antibonding splitting of d_{xy} (in local cubic frame) states of about 1.5 eV for Ti(1)/Ti(3) cations, whereas Ti(2)/Ti(4) cations show a relatively weak substructure. This substantial bonding-antibonding splitting of Ti(1)/Ti(3) t_{2g} states agrees well with the concept of formation of $Ti^{3+}-Ti^{3+}$ spin-singlet pairs proposed earlier by Marezio.^{21,30} However, the LSDA calculations fail to reproduce an insulating spin-singlet ground state of the low-temperature phase of Ti_4O_7 . Apparently, the electron-electron correlations, mainly in the $3d$ shell of Ti cations, play a significant role.

IV. LDA+ U RESULTS AND CHARGE ORDERING

In order to take into account strong electronic correlations in Ti $3d$ shell we perform LDA+ U calculations for Ti_4O_7 in the low-temperature $P\bar{1}$ structure. In our calculations we use Coulomb interaction parameter $U = 3.0$ eV and exchange coupling $J = 0.8$ eV taken in agreement with previous constrained LDA calculations.³¹ The LDA+ U calculations result in a charge and orbitally ordered insulator with an energy gap of 0.29 eV (see Fig. 2). This is in a strong contrast to the metallic solution with a substantial charge disproportionation between crystallographically inequivalent Ti(1)/Ti(3) and Ti(2)/Ti(4) cations obtained by LSDA and in a reasonably good agreement with an experimental gap value of 0.25 eV. Note, however, that the charge and orbital order pattern remains exactly the same for U in the range 2.5-4.5 eV, whereas the energy gap increases considerably up to 1.12 eV for $U=4.5$ eV. This remarkable increase of the gap value is accompanied by the enhancement of the spin magnetic moment from 0.56 up to 0.8 μ_B per $3+$ Ti(1)/Ti(3) cation as U is increased from 2.5 to 4.5 eV.

In addition, we perform LDA+ U calculations for high-temperature metallic phase of Ti_4O_7 . In particular for U of 2.5 eV a metallic self-consistent solution with substan-

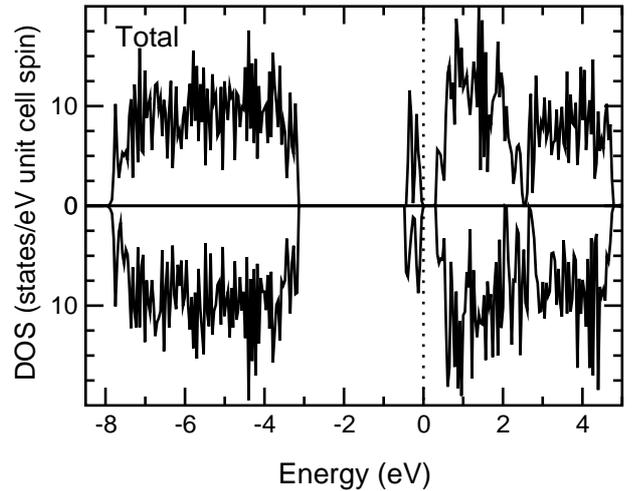


FIG. 2: The total DOS obtained from LDA+ U calculations with $U=3.0$ eV and $J=0.8$ eV for the low-temperature $P\bar{1}$ phase of Ti_4O_7 . The top of the valence band is shown by dotted lines.

tial density of states (76 states/Ry) at the Fermi level has been found, whereas for U of 3 eV the LDA+ U solution becomes unstable but remains metallic. With further increase of the U value the metallic solution collapses into insulating one.

After self-consistency four crystallographically independent Ti atoms are split out in two subgroups in respect to the spin magnetic moment per Ti site: Ti(1)/Ti(3) with a moment of 0.66/-0.67 μ_B , respectively, and Ti(2)/Ti(4) with 0.04/-0.02 μ_B . Thus, one of t_{2g} majority/minority spin states of Ti(1)/Ti(3) becomes occupied (d^1), whereas all other t_{2g} states are pushed by strong Coulomb interaction above the Fermi level. In contrast, all t_{2g} states of Ti(2) and Ti(4) are almost depopulated (d^0) and form bands up to 2.5 eV above the Fermi level. The occupied Ti(1)/Ti(3) states are strongly localized and form a prominent structure with a band width of 0.25 eV just below the Fermi level (see Fig. 3). The strong Coulomb interaction does not affect much the empty Ti e_g states, which give predominant contribution between 2.5 and 4.5 eV. The obtained magnetic structure is almost antiferromagnetic with the spin magnetic moments within $Ti(1)^{3+}-Ti(3)^{3+}$ as well as $Ti(2)^{4+}-Ti(4)^{4+}$ pairs being of the same magnitude with opposite sign.

An analysis of occupation matrices of $Ti(1)^{3+}/Ti(3)^{3+}$ majority/minority $3d$ spin states confirms substantial charge disproportionation within the Ti $3d$ shell. As shown in Table I, one of the t_{2g} states of Ti^{3+} cations (d^1) is occupied with the occupation number of 0.74, whereas the remaining two t_{2g} orbitals have a significantly smaller population of about 0.08. Thus, according to Ref. 5 we define an orbital order parameter as the largest difference between $3+$ and $4+$ Ti t_{2g} populations which amounts to 66% of ideal ionic charge ordering model. The orbital order parameter clearly shows the existence of substantial charge disproportionation in the Ti $3d$ shell of Ti_4O_7

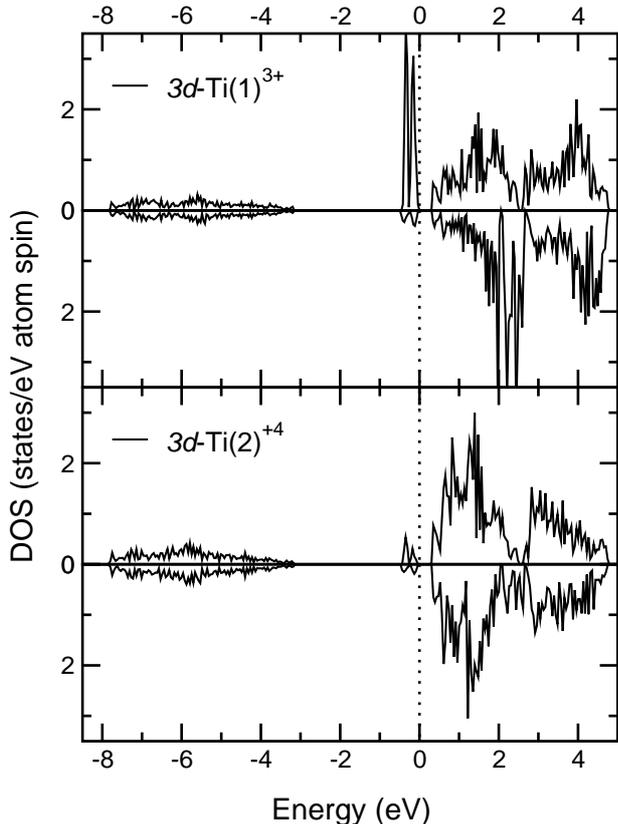


FIG. 3: The partial DOS for $\text{Ti}(1)^{3+}$ and $\text{Ti}(2)^{4+}$ cations are shown. The gap value of 0.29 eV was obtained by LDA+ U with $U=3.0$ eV and $J=0.8$ eV. The Fermi level is shown by dotted line.

TABLE I: Total (q) and l -projected ($q_{s,p,d}$) charges, magnetic moments (M), and occupation of the most populated t_{2g} orbitals (n) calculated for inequivalent Ti atoms in the low-temperature $P\bar{1}$ phase of Ti_4O_7 .

Ti ion	q	q_s	q_p	q_d	M (μ_B)	t_{2g} orbital	n
$\text{Ti}(1)^{3+}$	2.27	0.18	0.27	1.83	0.66	$d_{xy\uparrow}$	0.74
$\text{Ti}(2)^{4+}$	2.22	0.22	0.33	1.68	0.04		0.08
$\text{Ti}(3)^{3+}$	2.16	0.18	0.25	1.74	-0.67	$d_{xy\downarrow}$	0.73
$\text{Ti}(4)^{4+}$	2.16	0.21	0.33	1.62	-0.02		0.07

which is remarkable because of the complete lack of the total charge separation (see column q in Table I) between 3+ and 4+ Ti cations. The occupation matrices analysis shows that the change of the t_{2g} occupations is very efficiently screened by the rearrangement of the other Ti electrons. A significant portion of the screening charge is provided by Ti e_g states due to formation of relatively strong σ bonds with O $2p$ states, which results in appreciable contribution of the former to the occupied part of the valence band. Ti $4s$ and $4p$ states give additional contributions to the screening of the difference in t_{2g} occupations which leads to complete loss of the disproportionation between the charges at 3+ and 4+ Ti sites.

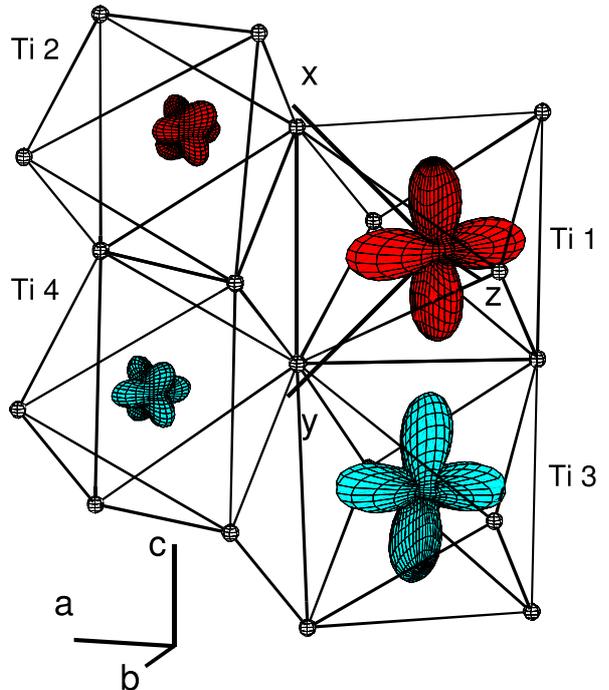


FIG. 4: (color online) Structure of Ti_4O_7 showing the angular distribution of the majority and minority spin $3d$ electron density of Ti cations. Red and cyan (light and dark, respectively, on the black and white image) orbitals correspond to the majority and minority $3d$ spin states, respectively. Oxygen atoms are shown by small spheres. The size of orbital corresponds to its occupancy. X-Y-Z coordinate system corresponds to the local cubic frame.

The occupied t_{2g} Ti^{3+} states are predominantly of d_{xy} character in the local cubic frame (according to that we later mark the orbital as d_{xy} orbital). This is illustrated in Fig. 4, which shows the angular distribution of the majority and minority spin $3d$ electron density of Ti cations, marked by red and cyan color (or light and dark on the black and white image), respectively.³² Since $\text{Ti}(1)^{3+}$ and $\text{Ti}(3)^{3+}$ cations are antiferromagnetically coupled, the obtained ferro-orbital order is consistent with the formation of a bonding spin-singlet state from the d_{xy} orbitals of two neighboring $\text{Ti}(1)$ and $\text{Ti}(3)$ sites. The orientation of occupied Ti^{3+} t_{2g} orbitals is consistent with the largest average Ti-O distance in the plane of t_{2g} orbitals. As shown in Table II the average $\text{Ti}(1)$ -O distance (2.061 Å) in the plane of d_{xy} orbital is considerably larger than average distances in the other two yz and zx planes (2.032 and 2.045 Å, respectively). The same is also true for the $\text{Ti}(3)$ cation but in this case the variation of the average $\text{Ti}(3)$ -O distances is much smaller (2.047 vs 2.041 and 2.042 Å) and, as a consequence, the out-of-plane rotation of the occupied t_{2g} minority spin orbital is stronger.

In addition, hopping matrix elements were evaluated via Fourier transformation from reciprocal to real space of the Ti t_{2g} LDA Wannier Hamiltonian.³³ Remarkably, for the low-temperature phase the $\text{Ti}(1)$ - $\text{Ti}(3)$ intra-pair

TABLE II: The averaged Ti-O distances in the plane of t_{2g} orbitals ($d_{\text{orb.}}$) and in the oxygen octahedra ($d_{\text{av.}}$) for $P\bar{1}$ structure of Ti_4O_7 . d_{xy} approximates to the occupied orbital of the $3d^1$ Ti(1) and Ti(3) $3+$ states.

Ti atom	orbital	$d_{\text{orb.}}$ (Å)	$d_{\text{av.}}$ (Å)
Ti(1)	d_{xy}	2.061	2.046
	d_{yz}	2.032	
	d_{zx}	2.045	
Ti(2)	d_{xy}	2.012	2.000
	d_{yz}	1.976	
	d_{zx}	2.013	
Ti(3)	d_{xy}	2.047	2.043
	d_{yz}	2.041	
	d_{zx}	2.042	
Ti(4)	d_{xy}	1.973	1.977
	d_{yz}	1.976	
	d_{zx}	1.981	

d_{xy} - d_{xy} hopping matrix element is found to be of 0.61 eV, whereas all other hoppings are 3-4 times smaller. This strong inhomogeneity of the hopping matrix elements disappears in the high-temperature phase. Thus, according to our calculations hopping elements in the high-temperature phase are 0.23, 0.21, 0.39, and 0.33 eV between 1-3, 2-4, 3-3, and 4-4 Ti sites, respectively.

Estimation of exchange interaction parameters via the variation of the ground state energy with respect to the magnetic moment rotation angle^{29,34} results in a strong antiferromagnetic coupling of -1696 K between Ti(1)³⁺ and Ti(3)³⁺ cations.³⁵ All other couplings are two orders of magnitudes smaller. This indicates a possible formation of the spin-singlet pairs via direct antiferromagnetic exchange between neighboring Ti(1) and Ti(3) sites. The contribution of the superexchange via O p orbitals to the Ti(1)-Ti(3) exchange coupling is found to be negligible. This was verified by calculating the exchange coupling constants with the sub-blocks of the LMTO Hamiltonian responsible for the Ti-O hybridization being set to zero.

This calculation gave qualitatively same results for the exchange constants although the possibility for the superexchange via O p orbitals was eliminated.

V. SUMMARY AND CONCLUSIONS

In summary, in the present LDA+ U study of the low-temperature $P\bar{1}$ phase of Ti_4O_7 we found a charge ordered insulating solution with an energy gap of 0.29 eV. The total $3d$ charge separation is small (less than 0.14), whereas the orbital order parameter defined as the difference between t_{2g} occupancies of Ti³⁺ and Ti⁴⁺ cations is large and gives direct evidence for charge ordering. Ti $4s$ and $4p$ states give a strong contribution to the static “screening” of the total $3d$ charge separation. This effective charge screening leads to complete loss of the disproportionation between the charges at $3+$ and $4+$ Ti sites which is in remarkable contrast to one finding in Fe_3O_4 and Fe_2OBO_3 .^{5,8} The occupied t_{2g} states of Ti³⁺ cations are predominantly of d_{xy} character (in the local cubic frame) and form a spin-singlet molecular orbital via strong direct antiferromagnetic exchange coupling between neighboring Ti(1) and Ti(3) sites of $J \approx 1700$ K, whereas the role of superexchange is found to be negligible. This is in a good agreement with small and temperature independent magnetic susceptibility in the low-temperature phase of Ti_4O_7 .

VI. ACKNOWLEDGEMENTS

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