Charge order and spin-singlet pairs formation in Ti$_4$O$_7$

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Charge ordering in the low-temperature triclinic structure of titanium oxide (Ti$_4$O$_7$) 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. 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 disproportion 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 Ti(1) and 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$_3$O$_4$), in which a first-order metal-insulator transition occurs at $\sim$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$_2$O$_4$.\(^3,4\) Recently, a local spin density approximation (LSDA)+U study of the low-temperature phase of Fe$_3$O$_4$ 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$_2$OBO$_2$), which shows a broad semiconductor-to-semiconductor transition at $\sim$317 K associated (as in Fe$_3$O$_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 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 (Ti$^{3+}$Ti$^{4+}$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$_4$O$_7$ (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,
calls for a fivefold supercell. Diatomic phase pairing also persists but its long-range order nonmagnetic metal-metal bonds, whereas in the intermetallic phase, whereas a rather isotropic occupation of the $t_{2g}$ states has been found at room-temperature. 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 3$d$ 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. 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 Ti(1)$^{3+}$/Ti(3)$^{3+}$ and Ti(2)$^{4+}$/Ti(4)$^{4+}$ cations, respectively. This order parameter is found to be quite large, although the total 3$d$ 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 interpair coupling is only of $\approx 40$ K. This is in a good agreement with small and temperature independent magnetic susceptibility in the low-temperature phase of Ti$_4$O$_7$.

II. COMPUTATIONAL DETAILS

The present band-structure calculations have been performed for the low-temperature triclinic structure of Ti$_4$O$_7$. The $P1$ 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, $c = 20.2068$ 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 $R_{Ti1-4} = 2.27$ a.u., $R_{O1,3(O3,4)} = 1.78$ a.u., and $R_{O2,6} = 1.66$ 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.

![FIG. 1: (color online) The low-temperature crystal structure of Ti$_4$O$_7$. 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.](image)
III. LSDA BAND STRUCTURE

Our LSDA band structure calculations for the low-temperature P1 structure confirmed the results of the previous work. 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 -3eV 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. However, the LSDA calculations fail to reproduce an insulating spin-singlet ground state of the low-temperature phase of Ti_2O_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_2O_7 in the low-temperature P1 structure. In our calculations we use Coulomb interaction parameter \( U = 3.0 \text{ eV} \) and exchange coupling \( J = 0.8 \text{ eV} \) taken in agreement with previous constrained LDA calculations. 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 \( U = 4.5 \text{ eV} \). This remarkable increase of the gap value is accompanied by the enhancement of the spin magnetic moment from 0.56 up to 0.8 \( \mu_B \) 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_2O_7. In particular for \( U \) of 2.5 eV a metallic self-consistent solution with substantial 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 \( \mu_B \), respectively, and Ti(2)/Ti(4) with 0.04/-0.02 \( \mu_B \). 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)^3+ cations (d') 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_2O_7.
FIG. 3: The partial DOS for Ti(1)$^{3+}$ and 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.

FIG. 4: (color online) Structure of Ti$_4$O$_7$ showing the angular distribution of the majority and minority spin 3$d$ 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 3$d$ 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 3$d$ electron density of Ti cations, marked by red and cyan color (or light and dark on the black and white image), respectively. Since Ti(1)$^{3+}$ and 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 Ti(1) and 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 $d_{xy}$ orbital. As shown in Table II the average Ti(1)-O distance (2.061 Å) in the plane of $d_{xy}$ orbital is considerably larger than average distances in the other $yz$ and $zx$ planes (2.032 and 2.045 Å, respectively). The same is also true for the Ti(3) cation but in this case the variation of the average 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. Remarkably, for the low-temperature phase the Ti(1)-Ti(3) intra-pair

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 $P1$ phase of Ti$_4$O$_7$.

<table>
<thead>
<tr>
<th>Ti ion</th>
<th>$q$</th>
<th>$q_s$</th>
<th>$q_p$</th>
<th>$q_d$</th>
<th>$M$ ($\mu_B$)</th>
<th>$t_{2g}$ orbital</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(1)$^{3+}$</td>
<td>2.27</td>
<td>0.18</td>
<td>0.27</td>
<td>1.83</td>
<td>0.66</td>
<td>$d_{xy}$</td>
<td>0.74</td>
</tr>
<tr>
<td>Ti(2)$^{4+}$</td>
<td>2.22</td>
<td>0.22</td>
<td>0.33</td>
<td>1.68</td>
<td>0.04</td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>Ti(3)$^{3+}$</td>
<td>2.16</td>
<td>0.18</td>
<td>0.25</td>
<td>1.74</td>
<td>-0.07</td>
<td>$d_{xy}$</td>
<td>0.73</td>
</tr>
<tr>
<td>Ti(4)$^{4+}$</td>
<td>2.16</td>
<td>0.21</td>
<td>0.33</td>
<td>1.62</td>
<td>-0.02</td>
<td></td>
<td>0.07</td>
</tr>
</tbody>
</table>

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 $\sigma$ bonds with O $2p$ states, which results in appreciable contribution of the former to the occupied part of the valence band. Ti 4$s$ and 4$p$ 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.
TABLE II: The averaged Ti-O distances in the plane of $t_{2g}$ orbitals ($d_{abh}$) and in the oxygen octahedra ($d_{av}$) for $P1$ structure of Ti$_4$O$_7$. $d_{xy}$ approximates to the occupied orbital of the 3d $^3$ Ti(1) and Ti(3) 3+ states.

<table>
<thead>
<tr>
<th>Ti atom</th>
<th>orbital</th>
<th>$d_{abh}$ (Å)</th>
<th>$d_{av}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(1)</td>
<td>$d_{xy}$</td>
<td>2.061</td>
<td>2.046</td>
</tr>
<tr>
<td></td>
<td>$d_{yz}$</td>
<td>2.032</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{zx}$</td>
<td>2.045</td>
<td></td>
</tr>
<tr>
<td>Ti(2)</td>
<td>$d_{xy}$</td>
<td>2.012</td>
<td>2.000</td>
</tr>
<tr>
<td></td>
<td>$d_{yz}$</td>
<td>1.976</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{zx}$</td>
<td>2.013</td>
<td></td>
</tr>
<tr>
<td>Ti(3)</td>
<td>$d_{xy}$</td>
<td>2.047</td>
<td>2.043</td>
</tr>
<tr>
<td></td>
<td>$d_{yz}$</td>
<td>2.041</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{zx}$</td>
<td>2.042</td>
<td></td>
</tr>
<tr>
<td>Ti(4)</td>
<td>$d_{xy}$</td>
<td>1.973</td>
<td>1.977</td>
</tr>
<tr>
<td></td>
<td>$d_{yz}$</td>
<td>1.976</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{zx}$</td>
<td>1.981</td>
<td></td>
</tr>
</tbody>
</table>

$d_{xy}$-$d_{xy}$ 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 $P1$ phase of Ti$_4$O$_7$ 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 Ti$^{3+}$ and Ti$^{4+}$ 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$_3$O$_4$ and Fe$_3$OBO$_3$. The occupied $t_{2g}$ states of Ti$^{3+}$ 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$_4$O$_7$.

VI. ACKNOWLEDGEMENTS

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2. Several reviews of research on the Verwey transition up to 1980 are contained in the special issue of Philos. Mag. B 42 (1980).
7. Here and in the following we assume a redistribution of charge between Ti $t_{2g}$ and other states using term screening.
12. To our knowledge of all the $V_xO_{2n-1}$ compounds only $V_7O_{13}$ does not exhibit a metal-insulator transition.
The distribution is calculated according to $\rho(\theta, \phi) = \sum_{m,m'} n_{m,m'} Y_m(\theta, \phi) Y_{m'}^*(\theta, \phi)$, where $n_{m,m'}$ is the occupation matrix of 3d majority states of Ti(1) and 3d minority states of Ti(3) cations. The occupation matrices were calculated by the LDA+U with $U = 3.0$ eV, $J = 0.8$ eV for the low-temperature $P\bar{1}$ phase of Ti$_4$O$_7$. $Y_m(\theta, \phi)$ denotes corresponding spherical harmonics.