Orbital-spin order and the origin of structural distortion in MgTi$_2$O$_4$

S. Leoni$^1$, A.N. Yaresko$^2$, N. Perkins$^3$, H. Rosner$^1$, and L. Craco$^1$

$^1$Max-Planck-Institut für Chemische Physik fester Stoffe, D-01187 Dresden, Germany
$^2$Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany and
$^3$University of Wisconsin - Madison, 1150 University Avenue Madison, WI 53706-1390, USA

(Dated: January 29, 2009)

We analyze electronic, magnetic, and structural properties of the spinel compound MgTi$_2$O$_4$ using the local density approximation+U method. We show how MgTi$_2$O$_4$ undergoes to a canted orbital-spin ordered state, where charge, spin and orbital degrees of freedom are frozen in a geometrically frustrated network by electron interactions. In our picture orbital order stabilizes the magnetic ground state and controls the degree of structural distortions. The latter is dynamically derived from the cubic structure in the correlated LDA+U potential. Our ground-state theory provides a consistent picture for the dimerized phase of MgTi$_2$O$_4$, and might be applicable to frustrated materials in general.

PACS numbers: 71.30.+h, 72.80.Ga, 61.66.Fn, 71.15.Mb

I. INTRODUCTION

Over the last years, a lot of progress has been achieved in the study of transition metal oxides on frustrated lattices. Interest in these systems stems from the richness of their novel properties: the unexpected variety of ordered states and transitions between them, and the complexity of the underlying physics. Transition metal oxide (TMO) spinels AB$_2$O$_4$, with magnetic B ions forming a pyrochlore lattice, give the unique possibility to explore how the natural tendency of correlated systems to develop magnetic, orbital, and charge order is effectuated by geometrical frustration. The best studied example of TMO spinels, and historically the first one, is magnetite Fe$_3$O$_4$ which shows a high Curie temperature and undergoes the Verwey transition at $T_V \approx 120$ K.

Recently, B-spinel MgTi$_2$O$_4$, which is characterized by a pyrochlore lattice of Ti$^{3+}$ magnetic ions with one single electron in the $t_{2g}$-manifold, has attracted much attention due to a very peculiar phase transition from a metallic to a spin-singlet insulating phase near $T_C \approx 260$ K. The signature of the insulating state is the optical gap ($\approx 0.25$ eV at $T=10$ K) observed in optical conductivity spectra. Taken together, dc-resistivity and optical conductivity measurements consistently indicate that MgTi$_2$O$_4$ undergoes a sharp metal-insulator transition (MIT) with no sign of Drude weight at low frequencies below $T_C$. The MIT is accompanied by a structural transition from cubic to tetragonal symmetry, with a concomitant drop of the magnetic susceptibility and a resistivity jump below $T_C$. Neutron diffraction and X-ray measurements indicate spin-dimerization: Ti-Ti dimers are formed in a helical pattern in the spin-singlet state. Further structural refinements reveal that Ti-ions move away from the center of the TiO$_6$ octahedron. In the low-$T$ phase two out of six Ti-Ti bonds get closer, suggesting the formation of chemical dimers. These findings have suggested a removal of the pyrochlore degeneracy by a 1D helical dimerization of the spin pattern, with spin-singlets (dimers) located at short bonds.

There were several theoretical attempts to understand the nature of spin-dimerization and the origin of the MIT in MgTi$_2$O$_4$. Khomskii and Mizokawa assumed that the system is close to an itinerant state, and explained the formation of the nonmagnetic spin-singlet state by exploiting the concept of an orbitally driven Peierls state, leading to the formation of quasi 1D bands. In this case, the magnetic changes across the structural transition in MgTi$_2$O$_4$ can be understood with the help of 1D Peierls transition driven by the ordering of the $d_{xz}$ and $d_{yz}$ orbitals. This picture is consistent with B3LYP functional (GGA) calculations for the tetragonal phase of MgTi$_2$O$_4$, showing that the $xz$ and $yz$ or-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Orbital order in the tetragonal crystal structure of MgTi$_2$O$_4$ within the LDA+U framework ($U = 3$ eV). The electron density of the most populated $t_{2g}$ orbital is plotted. Lattice constants are taken from Ref.\textsuperscript{2}. The orange bonds represent the shortest bonds in the distorted structure, and the corresponding atoms are displayed in red (Ti), blue (O) and white (Mg).}
\end{figure}
orbitals are occupied while the $xy$ states are pushed to high energies.

Another approach is based on the assumption that the low-temperature tetragonal phase of MgTi$_2$O$_4$ is Mott insulator. In this case, the ground state of MgTi$_2$O$_4$ can be found by studying an effective low-energy spin-orbital super-exchange Hamiltonian. It was shown that the orbital degrees of freedom in MgTi$_2$O$_4$ modulates the spin exchange couplings, providing an explanation for the helical spin-singlet pattern observed in. It appears that the minimum energy configuration corresponds to such an orbital ordering for which the maximum number of spin-singlet dimers is formed. However, there are various dimer coverings of the pyrochlore lattice which have the same energy. As in spin-Peierls systems, the increase of magnetic energy gain can be achieved by the shortening of bonds, where dimers are situated. Therefore, each type of dimer coverings corresponding to a particular orbital ordering induces a different distortion of the lattice, which costs a different elastic energy. The ground state is chosen simply by finding a minimum energy state, which in case of MgTi$_2$O$_4$ corresponds to the minimal enlargement of the unit cell.

However, no theoretical studies have been yet performed in order to understand the origin of the MIT and the formation of the spin-singlet state. Is it the intrinsic lower dimensionality of MgTi$_2$O$_4$ that causes the formation of the spin-singlet state, or is the driving mechanism of different type?

In this work, in order to address these questions, we perform quantitative investigation of the band structure of MgTi$_2$O$_4$. Using local (spin) density approximation plus Hubbard U, L(S)DA+U, approach we show how an explicit incorporation of electronic correlations allows for a realistic description of the insulating ground state of MgTi$_2$O$_4$. Our results reveal that electronic correlations are fundamental in stabilizing the dimerized ground state of MgTi$_2$O$_4$. We show that MIT is driven by correlation (via LDA+U) induced orbital order (OO) rearrangement. Therein, U controls band splitting towards an orbital-insulating state without full orbital polarization (OP). In our picture OO stabilizes the spin-singlet ground state, which in turn controls the degree of structural distortions. This finding is consistent with the superexchange spin-orbital description. The opening of the electronic band gap is understood in terms of an orbital-selective MIT on a quasi 1D network.

II. RESULTS AND DISCUSSION

To elucidate the interplay between spin, orbital, and charge degrees of freedom in MgTi$_2$O$_4$ we perform correlated scalar-relativistic band-structure calculations using local (spin) density approximation plus Hubbard U, L(S)DA+U, approach. We employ the linear muffin-tin orbitals (LMTO) scheme in the atomic sphere approximation, with combined correction terms.

**FIG. 2:** LDA+U orbital resolved DOS for the tetragonal ($P4_12_12_1$) phase of MgTi$_2$O$_4$: $U = 0$ eV (top left), $U = 3$ eV (top right), $U = 5$ eV (bottom left), and $U = 6$ eV (bottom right). Notice the orbital selective nature of the correlation induced metal-insulator transition between 5 eV < $U$ < 6 eV solutions.
Self-consistency is reached by performing calculations on a 12×12×10 k-mesh for the Brillouin zone integration. Experimental atomic positions for the tetragonal (P4_122) low-T phase were used in the calculations. The radii of the atomic spheres were chosen as $r = 2.4789$ (Mg), $r = 2.0022$, 2.0106 (O1, O2), and $r = 2.5857$ (Ti) a.u. in order to minimize their overlap.

Our results for the paramagnetic (LDA+U) phase of MgTi$_2$O$_4$ are presented in Fig. 2. Therein the evolution of the 3$d^3$ correlated density of states (DOS) is shown. In cubic spinel oxides the $d$-electron orbital sector splits into the low-energy $t_{2g}$ and high-energy $e_g$ orbitals. Below we will denote the $t_{2g}$ orbitals in the tetragonal phase as $XZ$, $XY$, and $YZ$, which differ from the $d_{xy}$, $d_{yz}$ and $d_{zx}$ in the cubic phase (see details in). The corresponding DOS are plotted in red ($XY$), orange ($XZ$), and blue ($YZ$) in Fig. 2. The DOS with dominant $e_g$ contribution are shown by green and cyan curves. Due to partial oxygen relaxation, the crystal field has also a small trigonal component, which further splits the $t_{2g}$ manifold into $a_{1g}$ and $e_g$ sectors. We note that the $XZ$ orbitals directed along one of the short Ti–Ti bonds can only be formed as a linear combination of the $a_{1g}$ and $e_g$ orbitals. According to LDA results for cubic MgTi$_2$O$_4$ the occupation of the $e_g$ states is appreciably higher than that of the $a_{1g}$ one. Already in LDA calculations for the dimerized phase, the degeneracy of the $e_g$ orbitals is lifted as a consequence of the local distortion of TiO$_6$ octahedra and overall tetragonal symmetry. One of them (orange curve in Fig. 2) acquires $XZ$ character and becomes more populated than the $YZ$ one (blue). The $XY$ orbital (red), originating from the $a_{1g}$ state, forms a peak just above the Fermi level ($E_F$), its occupation being less than that of the other two. This picture does not change much in the weak correlation regime ($U \lesssim 3$ eV).

With increasing $U$ (3 eV ≤ $U$ ≤ 5 eV) transfer of spectral weight significantly modifies the weakly correlated scenario such that the $XZ$ orbital is now almost half filled ($n_{XZ} > 0.8$), whereas $YZ$ and $XY'$ states are pushed towards the $e_g$ bands, reducing the $t_{2g}$–$e_g$ charge transfer gap. In this large $U$ regime the overall electronic bandwidth is enhanced, accompanied by a reduction of the DOS near $E_F$ and selection of a single orbital channel to form the insulating state. We observe a clear tendency towards a pseudo-gap formation in the $XZ$ and $YZ$ channels ($U = 5$ eV), while the $XY'$ orbitals are pushed to higher energies. This indicates OP as the precursor of the MIT. By further increasing $U$ we obtain an insulating state at $U = 6$ eV. Our paramagnetic insulating solution is characterized by an almost half filled $XZ$ band, with appreciable splitting between occupied bonding and unoccupied antibonding states.

The bonding-antibonding splitting observed at large $U \geq 5$ eV (Fig. 2) aids the formation of the charge gap. The insulating state can be viewed as a consequence of strong hopping between the $XZ$ orbitals along the short Ti–Ti bonds, leading to robust singlet character of these bonds (see discussion below) along the $c$-axis. Thus, according to our results MgTi$_2$O$_4$ undergoes an orbital selective MIT, which is caused by correlation assisted orbital rehybridization.
The changes in OO and crystal structure are shown in Fig. 1. Consistent with ferro-orbital order (FOO) along the short Ti–Ti bonds, which stabilizes the molecular bond (orange) formation, starts to develop already for \( U \leq 3 \) eV. The spiralling of the dimer bonds along the \( c \)-axis is visible in Fig. 1. For \( U = 3 \) eV we obtain FOO, with the ground state orbital pointing through bond’s direction.

We now turn our attention to orbital, spin and charge responses in the magnetically ordered state. In Figs. 3 and 4 we display our LSDA+U (\( U = 3 \) eV) results for an idealized pseudocubic (upper panel) pyrochlore structure and the low-T tetragonal structure (lower panel).

In the idealized pseudocubic (PC) phase all atoms are arranged as in the high-T cubic structure supplemented by a reduced \( (P_{4}2_{1}2) \) tetragonal space group. This combination of atomic arrangements and crystal symmetries allows for the discovering of novel magnetic and orbital reorientations in the undistorted pyrochlore structure of MgTi\(_{2}\)O\(_{4}\), which are in principle allowed in the vicinity of the MIT point.

The orbital resolved DOS of the PC structure (Fig. 4) shows large OP and a small charge gap between the ground (XZ) and the first excited XY orbital. Notice the dramatic rearrangement of the minority states of the ground state orbital, which are shifted to energies above 3 eV.

Within the tetragonal metric of the low-T phase we find a similar evolution for the magnetically-ordered electronic DOS as for the pseudocubic regime.

In the lower panel of Fig. 3 we display the ground-state OO in the distorted phase of MgTi\(_{2}\)O\(_{4}\). The LSDA+U solution gives the same antiferromagnetic arrangement of spins along the short Ti–Ti bonds and in the \( a, b \) plane of the pyrochlore lattice, as found for the PC structure. The lower panel of Fig. 3 shows, however, that the canting of the XZ orbitals away from the Ti–Ti bond plane becomes significantly smaller when the low-T structural distortions are taken into account. Also, the average Ti–O distance in the XZ plane (2.068 Å) is appreciably larger than in the YZ (2.052 Å) and XY (2.041 Å) planes, which means that the occupation of the XZ state becomes energetically more favorable. This suggests a novel scenario for quasi 1D chains in the strongly frustrated network of MgTi\(_{2}\)O\(_{4}\), where the crystal-structure itself gets modified by the onset of OO. The small changes in the atomic positions of the Ti-ions shown in Fig. 3 additionally suggest that crystal structure transformations are coupled to the correlation-induced orbital re-orientation.
Another magnetically ordered LSDA+U solution (Fig. 5) with the same FOO but FM spin order in the $a, b$ plane and AFM one along the $c$ direction can also be obtained for both the PC and dimerized structures. The order along the short Ti–Ti bonds remains FOO with AFM spin order, however, the Ti spins at the ends of intermediate Ti-Ti bonds with AFOO ($XZ–YZ$) in the $c$ direction are antiparallel. As a consequence, the total energy of this solution is higher than the ground state solution shown in Fig. 3, in which the order along intermediate bonds is AFOO with FM spin order.

The dimerization of AFM spin chains and the formation of spin-singlets located on short bonds explains the crystal structure of MgTi$_2$O$_4$, which can be seen as a collection of helices running along the $c$ axis. This helix is formed by an alternation of short-long-short-long bonds as found in. As a consequence of the selective bond shortening superstructure features like tetrarners can be recognized (Fig. 6).

The static calculations have provided evidence on the role of electronic correlation in the formation of the spin-singlet state. To further unravel the coupling between structural rearrangement and correlation-assisted OO, we have performed full structure relaxation in the correlated LDA+U potential. Starting from the cubic structure with pyrochlore sublattice, Parrinello-Rahman (PR) structure relaxation$^{20}$ was performed. The Lagrangian formulation of PR allows for constant-pressure relaxation simulations, as variation of size and shape of the simulation box are allowed. This is typically used in connection with pressure-induced phase transitions. Here $U$ is acting as some sort of “pressure” on the orbital channels, whose rehybridization brings structural changes about. To properly capture this effect it is thus important to dispose of a molecular dynamics setup allowing for unbiased geometry changes. For $U = 3$ eV structural lock-in into the tetragonal dimerized phase is achieved with selective shortening of a subset of bonds (molecular dimers) as displayed in Fig. 6. The role of local Coulomb interaction $U$ as symmetry-reducing agent through selection of one orbital channel is apparent in the frame of the dynamic calculations. The found dimensional reduction selects thus a particular topological order among the various “degenerated valence bond configurations”, allowed in the quantum dimer framework of frustrated lattices.$^{21}$ in agreement with experiments.

III. CONCLUSION

In conclusion, we have studied the ground state orbital, charge and magnetic properties of MgTi$_2$O$_4$ using the LDA+U technique. Our results suggests an orbital selective$^{12}$ picture for the metal-insulator transition of MgTi$_2$O$_4$, which is driven by large spectral weight transfer due to correlations (via LDA+U). This in turn introduces a new type of bonding-antibonding splitting near the Fermi energy, which is characterized by large orbital polarization of excited orbitals. Using the LSDA+U results we have computed the orbital order pattern in both high-T pseudocubic and dimerized phase. The insulating low-T phase is shown to be driven by electron correlations in concert with spin and orbital order. The existence of short Ti-Ti distances along the $c$-axis follows as a consequence of spin dimerization on bonds (molecular dimers). Finally, consistent with x-ray diffraction experiments$^7$ the resulting superstructure features (tetrarners, spirals) are shown to be carried by correlation over orbital order, explaining magnetic and structural properties of MgTi$_2$O$_4$ in its low-T insulating phase.

Acknowledgments

S.L. thanks the Swiss National Foundation for financial support. L.C. and H.R. acknowledge support from the Emmy Noether-Programm of the DFG. Computational time provided by ZIH, Dresden is acknowledged.

---

1. Y. Taguchi, Y. Oohara, H. Yoshizawa, N. Nagaosa, and Y. Tokura, Science 291,2573 (2001); S. T. Bramwell and M. J. P. Gingras, Science 294,1495 (2001); P.G. Radaelli, Y. Horibe, M. J. Gutmann, H. Ishibashi, C. H. Chen, R.
M. Ibberson, Y. Koyama, Y.-S. Hor, V. Kiryukhin, S.-W. Cheong, Nature (London) 416, 155 (2002); T. Suzuki, M. Katsumura, K. Taniguchi, T. Arima, and T. Katsufuji, Phys. Rev. Lett. 98, 127203 (2007).

2 E. Verwey, Nature (London) 144, 327 (1939).

3 M. Isobe, and Y. Ueda, J. Phys. Soc. Jpn. 71, 1848 (2002).

4 J. Zhou, G. Li, J. L. Luo, Y. C. Ma, Dan Wu, B. P. Zhu, Z. Tang, J. Shi, and N. L. Wang Phys. Rev. B 74, 245102 (2006).

5 H. D. Zhou, and J. B. Goodenough, Phys. Rev. B 72, 045118 (2005).

6 Z. V. Popović, G. De Marzi, M. J. Konstantinović, A. Cantarero, Z. Dohčdević-Mitrović, M. Isobe, and Y. Ueda, Phys. Rev. B 68, 224302 (2003).

7 M. Schmidt, W. Ratcliff, II, P. G. Radaelli, K. Refson, N. M. Harrison, and S. W. Cheong, Phys. Rev. Lett. 92, 056402 (2004).

8 P. G. Radaelli, New Journ. Phys. 7, 53 (2005).

9 D. I. Khomskii and T. Mizokawa, Phys. Rev. Lett. 94, 156402 (2005).

10 S. Di Matteo, G. Jackeli, C. Lacroix, and N. B. Perkins, Phys. Rev. Lett. 93, 077208 (2004); S. Di Matteo, G. Jackeli, N.B. Perkins, Phys. Rev. B 72, 024431, (2005); G. Jackeli, J.Mol. Struct. 838, 220 (2007).

11 V.I. Anisimov, J. Zaanen, and O.K. Andersen, Phys. Rev. B 44, 943 (1991).

12 V.I. Anisimov, I. A. Nekrasov, D. E. Kondakov, T. M. Rice, M. Sigrist, European Physical Journal B 25, 191 (2002).

13 O. K. Andersen, Phys. Rev. B 12, 3060 (1975).

14 In the tetragonal frame $XY \sim d_{x^2-y^2}$, $XZ \sim (d_{zx} \pm d_{yz})/\sqrt{2}$, and $YZ \sim (d_{zx} \mp d_{yz})/\sqrt{2}$, where the sign reflects Ti–Ti bond orientation.

15 In the cubic frame $a_{1g}$ and $e'_g$ states can be written as:

\[ da_{1g} = (d_{xy} + d_{yz} + d_{zx})/\sqrt{3}, \]

\[ de'_{1g} = (2d_{xy} - d_{yz} - d_{zx})/\sqrt{6}, \]

\[ da_{2g} = (d_{yz} - d_{zx})/\sqrt{2}. \]

16 C.A. Marianetti, G. Kotliar, and G. Ceder, Phys. Rev. Lett. 92, 196405 (2004).

17 A.M. Oleś, P. Horsch, L.F. Feiner, and G. Khaliullin Phys. Rev. Lett. 96, 147205 (2006).

18 S.T. Bramwell, and M.J.P. Gingras, Science 294, 1495 (2001).

19 M. Parrinello and A. Rahman, Phys. Rev. Lett. 45, 1196 (1980).

20 S. Baroni, A. Dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Gallainio, S. Scandolo, G. Chiarotti, P. Focher, A. Pasquarello, K. Laasonen, A. Trave, R. Car, N. Marzari, A. Kolaj, [http://www.pwscf.org/].

21 M. Levin and T. Senthil, Phys. Rev. B 70, 220403 (2004).