Spin singlet formation in MgTi$_2$O$_4$: evidence of a helical dimerization pattern

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The transition metal spinel MgTi$_2$O$_4$ undergoes a metal-insulator transition on cooling below $T_{M-I} = 260$ K. A sharp reduction of the magnetic susceptibility below $T_{M-I}$ suggests the onset of a magnetic singlet state. Using high-resolution synchrotron and neutron powder diffraction, we have solved the low-temperature crystal structure of MgTi$_2$O$_4$, which is found to contain dimers with short Ti-Ti distances (the locations of the spin singlets) alternating with long bonds to form helices. Band structure calculations based on hybrid exchange density functional theory show that, at low temperatures, MgTi$_2$O$_4$ is an orbitally ordered band insulator.

In addition to early transition metals, low-spin cations with higher $t_{2g}$ orbital occupancy can also form dimers. Recently, we have solved the low-temperature structure of the mixed-valent CuIr$_2$S$_4$ spinel, which displays simultaneous M-I, paramagnetic-diamagnetic and structural transitions at 230 K. In CuIr$_2$S$_4$, iridium has an average oxidation state of $3.5^+$, and half of the Ir ions were found to form short metal-metal bonds in the low-temperature insulating phase, giving rise to simultaneous charge ordering and dimerization. MgTi$_2$O$_4$ is another spinel with closely related phenomenology. In this compound, Ti is in the $3^+$ oxidation state with the 3$d^1$ electronic configuration and $S = 1/2$, which makes it a strong candidate for the observation of dimerization in a single-valence system. In fact, MgTi$_2$O$_4$ undergoes a M-I transition on cooling below $T_{M-I} = 260$ K, accompanied by a strong decrease of the magnetic susceptibility and a transition to a tetragonal structure. In this letter, we report the solution and refinement of the low-temperature crystal structure of MgTi$_2$O$_4$, as obtained from synchrotron x-ray and neutron powder diffraction data, and the results of electronic structure calculations based on the structural data. The structure was found to contain dimers with short Ti-Ti distances (2.85 Å), the locations of the spin singlets. The dimer ordering leads to the formation of helical chains of short and long bonds running along the tetragonal $c$ axis, a unique example of a chiral ordering of the spinel structure. The electronic structure is consistent with the opening of a 1 eV gap and the absence of magnetic moments, and enables one...
MgTi$_2$O$_4$ powder samples were prepared by solid-state reaction of MgO, TiO$_2$ and elemental Ti powder mixture sealed under vacuum in a silica tube. The reactants were sintered at 1080°C several times, followed by grinding in a glove box to increase homogeneity. Measurements of electrical resistivity and magnetic susceptibility of our sample produced results similar to those reported by Isobe and Ueda.[5] Synchrotron x-ray powder diffraction patterns of MgTi$_2$O$_4$ were collected on beamline ID31 at the European Synchrotron Radiation Facility in Grenoble, France, using a multi-analyzer, parallel beam geometry at a wavelength of 0.5Å. The sample was sealed in a 0.5mm glass capillary and cooled down to 275K (above the transition) and 200K (below the transition) using a He blower. Medium- and high-resolution neutron powder diffraction patterns were collected at the Rutherford Appleton Laboratory in Chilton, UK using the GEM and HRPD instruments respectively. High-resolution patterns were collected at 200K and 275K, while medium-resolution data were collected in the 20–275K temperature range in 20K steps. For the neutron experiments, MgTi$_2$O$_4$ was sealed in a 6mm vanadium can under Ar atmosphere and cooled by means of a closed cycle refrigerator. The neutron sample resulted from the second synthesis batch, and was purer than the x-ray sample.

Comparison of the 275K and 200K x-ray diffraction patterns confirmed the cubic-tetragonal phase transition and enabled us to identify most of the impurity peaks (mainly Ti$_2$O$_3$ and MgO) present in the pattern at the background level. A portion of the 200K x-ray diffraction pattern is presented in Fig. 1 (lower panel). Apart from the tetragonal splitting of the main Bragg peaks, a series of weak superlattice reflections also appear in the pattern (mainly Ti-O$_2$ octahedron, and the six nearest-neighbor Ti-Ti distances become inequivalent. Two out six Ti-Ti bonds (s = 2.849(7)Å and l = 3.152(7)Å) differ substantially from the Ti-Ti distances found in the cubic Mg$_2$Ti$_2$O$_4$ (3.00362(1)Å). The shortest distance is comparable to the close-contact distance in Ti metal (2.896Å at room temperature), suggesting the formation of a metal-metal bond. It should be noted that the intra-dimer distance in VO$_2$ is 2.654Å,[5] which is also comparable to the V-V distance in V metal (2.61Å). In the cubic spinel structure (Inset of Fig. 2), the TiO$_6$ octahedra form edge-sharing ‘ribbons’, so that the Ti-Ti bonds run in straight lines along six equivalent [110]$_c$ directions. In the tetragonal structure, both the short and the long bonds run along four: [011]$_c$, [011]$_c$, [101]$_c$, [101]$_c$, directions of the cubic structure ([112]$_d$ direction), alternating with one of the intermediate bonds ($i_1 = 3.002(5)$Å in the sequence ‘s-i$_3$-l-i$_1$’). Ti-Ti-bond lines running along the [100]$_c$ direction ([110]$_c$, [110]$_c$) are entirely made up of the other type of intermediate bonds ($i_2 = 3.0099(3)$Å). Neither of the Ti-Ti-bond lines is perfectly straight, the Ti-Ti bond angle being 174.7(2)$^\circ$ and 178.3(1)$^\circ$ along the [100]$_c$ and [112]$_c$ directions, respectively. Refinements of the temperature-dependent neutron data indicate that the phase transition is abrupt, with no coexistence region between the two phase (Fig. 1, upper panel). This is reflected in the splitting of the Ti-Ti bond lengths, which is about 80% of the full value at 250 K and is fully saturated below 200 K. The metal-insulator transition in MgTi$_2$O$_4$ is very sensitive to impurities. The magnetic susceptibility data for the Mg$_2$−xTi$_{1+x}$O$_4$ solid solution indicates that a partial replacement of the Ti$^{3+}$ with Ti$^{4+}$ (3d$^0$) and Mg$^{2+}$ breaks up the dimerization chains[8]. Ti$^{3+}$ undimerized due to impurities most likely contribute to the Curie point of the MgTi$_2$O$_4$ magnetic susceptibility.[8][9].

From the topological point of view, the most interesting aspect of the MgTi$_2$O$_4$ low-temperature structure is the dimerization pattern of the alternating short and long bonds. Here, the chiral nature of the space group is clearly revealed in the formation of ‘s-l-s-l’‘helices’ running along the c-axis (Fig. 2). With our choice of space group, the helices are left handed, but the right-handed space group $P4_1212$ is also an allowed solution. Several authors have pointed out the relevance of spin chirality for magnetism and transport on a pyrochlore lattice[12][13][14]. Otherwise, our observation of chirality in the structural sector of a pyrochlore lattice is extremely unusual, and immediately raises two issues. Firstly, it is interesting to consider whether the chiral dimerization pattern is in any way related to the geometrical frustra-
tion of the pyrochlore lattice. On this point, one should notice that, once the system ‘decides’ to dimerize, the topology of the problem changes drastically: the relevant lattice is no longer the pyrochlore lattice itself, but its ‘medial’ (or bond center) lattice at 1/6 filling (only one bond out of 6 is a dimer). Each Ti atom can only be involved in one dimer; therefore, one occupied dimer site precludes the occupancy of the 10 nearest-neighbor bonds. At such low filling, this rule clearly leads to a highly degenerate ground state, but, arguably, the system is no longer frustrated because the local degeneracy is absent. Secondly, the nature of the spin singlet state needs to be further investigated. To this effect, we have carried out band structure calculations using the CRYS-TAL code. All electron, triple valence basis sets were used in which three independent radial functions are included for all valence states. Electronic exchange and correlation are approximated using hybrid exchange density functional theory in which a component of the non-local Fock exchange is included with the local exchange and correlation approximated within the generalised gradient approximation (GGA) resulting in the B3LYP functional. This functional is currently very widely used in molecular studies as it yields ground state energetics significantly more reliably than GGA functionals. Here it is preferred to GGA as the component of the Fock exchange cancels in part the erroneous electronic self-interaction inherent in GGA functionals and thus the B3LYP approximation yields a reliable estimate of the band gap in a wide range of materials, including strongly interacting transition metal oxides. We note that initial calculations based on GGA description failed to reproduce the opening of the band gap in the tetragonal phase. The computed projected densities of states (DOS) are plotted in Fig. 3 for the cubic and tetragonal structures; the latter was found to have a lower total energy than the former, as observed experimentally. In the cubic phase, the states just below the Fermi energy $E_F$ form a highly dispersive, two-fold degenerate band. This band is a common feature of many early transition-metal spinels and originates mainly from $3d_{t_2g}$ titanium orbitals, with the $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ participating equally in each energy level. In MgTi$_2$O$_4$, the Fermi energy lies in a deep ‘trough’, where this band partially overlaps with more localized states at higher energy (also of $t_{2g}$ origin), which accounts well for the poor metallic properties at room temperature. In the tetragonal, low temperature phase the situation is radically different: four new bands with $3d_{xz}$ and $3d_{yz}$ contributions only are split off below the main $t_{2g}$ band. Complete filling of this bands with eight electrons in the double cell results in a gap of about 1 eV, in good agreement with the electrical conductivity, while the $3d_{xy}$ states are pushed to higher energy. These results are readily interpreted on the basis of the observed crystal structure, by noting that the short Ti-Ti bonds have the same orientation as the occupied $t_{2g}$ orbitals, alternating between the $3d_{xz}$ ($[011]_c$, $[011]_c$), and $3d_{zz}$ ($[101]_c$, $[101]_c$) directions on different sites. This is consistent with orbital ordering, and with the short bonds becoming the location of zero-spin Hund-Mulliken (molecular-orbital-like) singlets.

In summary, we have determined the crystal and electronic structures of the high- and low-temperature phases of MgTi$_2$O$_4$. At low temperatures, the Ti atoms dimerise forming an unusual chiral pattern. This results in orbital ordering, and in the opening of a gap between the fully occupied and unoccupied levels, in good agreement with the transport and magnetic properties of MgTi$_2$O$_4$.

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FIGURE CAPTIONS

Fig. 1 **Bottom:** The synchrotron x-ray diffraction pattern of MgTi$_2$O$_4$ at background level taken at 200K, $\lambda = 0.5\text{Å}$ (the strongest line has an amplitude of 32000 counts). The top to bottom rows of ticks mark the positions of MgTi$_2$O$_4$, Ti$_2$O$_3$ and MgO Bragg peaks respectively. The triangles mark the superlattice reflections, the circles mark an unidentified impurity. The inset shows a portion of the refined high-resolution neutron diffraction pattern of MgTi$_2$O$_4$ at 200K. The top and bottom rows of ticks mark the positions of MgTi$_2$O$_4$ and Ti$_2$O$_3$ Bragg reflections respectively. The splitting of the cubic peaks is apparent upon comparison to the spinel pattern taken at 275K. **Top:** The tetragonal lattice constants of MgTi$_2$O$_4$ and Ti-Ti bond lengths as functions of temperature. The solid lines are guides for eye.

Fig. 2 The Ti-Ti bond structure in tetragonal MgTi$_2$O$_4$ at 200K. The red and purple bonds represent the shortest (dimerized) and the longest bonds in the MgTi$_2$O$_4$ structure respectively. The dashed and solid blue bonds mark the intermediate $i_1 = 3.002(5)$Å and $i_2 = 3.0099(3)$Å Ti-Ti distances respectively. A portion of the Ti tetrahedral connectivity is also shown. The inset shows a fragment of the spinel structure in the same orientation, visualized using cation-anion polyhedra. One of the ‘helices’ is outlined in yellow.

Fig. 3 Electronic density of states (DOS) for cubic (top) and the tetragonal (bottom) MgTi$_2$O$_4$. The contribution of Ti and O is indicated with different line styles (the Mg contribution to DOS in negligible in this energy range). The vertical line marks the Fermi energy.
TABLE I: Lattice constants, fractional coordinates of atoms and bonds in MgTi$_2$O$_4$ at 200K ($P4_12_12$) and 275K ($Fd\bar{3}m$). The parameters originate from the Rietveld refinement of high- and medium-resolution neutron powder diffraction patterns.

| 200K | x     | y     | z     | $U_{iso}$ [Å$^2$] |
|------|-------|-------|-------|-------------------|
| Ti   | 8b    | -0.0089(5) | 0.2499(9) | -0.1332(4) | 0.0125(2) |
| Mg   | 4a    | 0.7448(3) | 0.7448(3) | 0   | 0.0073(2) |
| O(1) | 8b    | 0.4824(2) | 0.2468(3) | 0.1212(2) | 0.0064(2) |
| O(2) | 8b    | 0.2405(3) | 0.0257(2) | 0.8824(2) | 0.0035(2) |

$a = 6.01329(4)$Å, $c = 8.4703(1)$Å, $R_{wp} = 0.0467$, $R_p = 0.0637$

| 275K | x     | y     | z     | $U_{iso}$ [Å$^2$] |
|------|-------|-------|-------|-------------------|
| Ti   | 16d   | 1/2   | 1/2   | 1/2   | 0.0117(1) |
| Mg   | 8a    | 1/8   | 1/8   | 1/8   | 0.0069(1) |
| O    | 32e   | 0.25920(2) | 0.25920(2) | 0.25920(2) | 0.00522(5) |

$a = 8.49552(3)$Å, $R_{wp} = 0.0402$, $R_p = 0.0267$

| Bond [Å] | Cubic, 275 K | Tetragonal, 200 K |
|----------|--------------|-------------------|
| Ti-Ti    | 3.00362(1) $\times$ 6 | 2.849(7) $\times$1 3.002(5) $\times$2, 3.0099(3) $\times$2 3.152(7) $\times$1 |
| Ti-O     | 2.0487(2) $\times$6 | 2.028(5), 2.023(5), 2.021(5) 2.080(5), 2.135(4), 2.017(4) |