

## Orbitally Induced Peierls State in Spinel

D. I. Khomskii<sup>1,2</sup> and T. Mizokawa<sup>3</sup><sup>1</sup>*II Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*<sup>2</sup>*Groningen University, Nijenborgh 4, 9747 AG Groningen, The Netherlands*<sup>3</sup>*Department of Physics and Department of Complexity Science and Engineering, University of Tokyo, 5-1-5 Kashiwanoha, Chiba 277-8581, Japan*

(Received 17 May 2004; published 19 April 2005)

We consider the superstructures, which can be formed in spinels containing on  $B$  sites the transition-metal ions with partially filled  $t_{2g}$  levels. We show that, when such systems are close to the itinerant state (e.g., have an insulator-metal transition), there may appear in them an orbitally driven Peierls state. We explain by this mechanism the very unusual superstructures observed in  $\text{CuIr}_2\text{S}_4$  (octamers) and  $\text{MgTi}_2\text{O}_4$  (chiral superstructures) and suggest that a similar phenomenon should be observed in  $\text{NaTiO}_2$  and possibly in some other systems.

DOI: 10.1103/PhysRevLett.94.156402

PACS numbers: 71.30.+h, 71.28.+d, 75.25.+z

Systems with complicated lattices, such as a pyrochlore-type lattice of corner-sharing tetrahedra in spinels, often display complicated types of ordering. The best-known example is magnetite  $\text{Fe}_3\text{O}_4$ , which apparently has charge ordering below the Verwey transition at  $T_V = 120$  K; the details of the ordering are still a matter of hot debate [1]. Recently two other examples of exotic types of ordering were observed by Radaelli and co-workers: octamer ordering in  $\text{CuIr}_2\text{S}_4$  [2] and helical (or chiral) distortion in  $\text{MgTi}_2\text{O}_4$  [3]. In all three cases, superstructures appear in the insulating phase below metal-insulator transition; in  $\text{CuIr}_2\text{S}_4$  and  $\text{MgTi}_2\text{O}_4$  it is accompanied by the formation of a nonmagnetic state (spin singlet on a dimer). The origin of these strange and beautiful structures was not clarified in [2,3].

Below we suggest a very simple explanation of the superstructures in  $\text{CuIr}_2\text{S}_4$  and  $\text{MgTi}_2\text{O}_4$ , using the concept of the *orbitally driven Peierls state*. We show that the specific features of orbitals involved, on the pyrochlore lattice of  $B$  sites of spinels, lead to the formation of essentially one-dimensional bands and, with proper filling, lead to the Peierls-like effect, which in these particular cases has a form of tetramerization along certain directions. Viewed from a different perspective, the resulting states give just the octamer ordering of Ref. [2] and chiral ordering of Ref. [3]. Using the same concept, we predict also that a similar phenomenon should exist in some other materials, e.g., in  $\text{NaTiO}_2$  and possibly in some other systems.

In both  $\text{CuIr}_2\text{S}_4$  and  $\text{MgTi}_2\text{O}_4$ , the transition-metal (TM) ions Ir and Ti are located in almost regular  $S_6$  and  $O_6$  octahedra, so that the dominant crystal field (CF) splits the  $d$  levels into the  $t_{2g}$  triplet and  $e_g$  doublet. In both cases, only  $t_{2g}$  levels are occupied, by one electron in  $\text{Ti}^{3+}$  and by five or six electrons in  $\text{Ir}^{4+}$  and  $\text{Ir}^{3+}$ , respectively (average Ir valence is  $+3.5$ ). The shape of these orbitals is such that the strongest overlap in the elementary  $\text{Ir}_2\text{S}_4$  or  $\text{Ti}_4\text{O}_4$  cubes is between the same orbitals along the particular

direction, e.g.,  $xy$  with  $xy$  orbitals for the TM pair in the  $xy$  plane, or  $yz$  with  $yz$  orbitals for the pair in the  $yz$  plane; see Fig. 1. Thus the dominant hopping term  $t$  will be along the straight TM-TM chains, which would lead to the formation of one-dimensional bands with the dispersion  $E(k_\alpha) = -2t \cos k_\alpha$  where  $\alpha$  denotes the direction along the corresponding chain. This orbital-dependent hopping plays a crucial role in our explanation.

We start by discussing the case of  $\text{CuIr}_2\text{S}_4$ . In this system, below the metal-insulator transition temperature

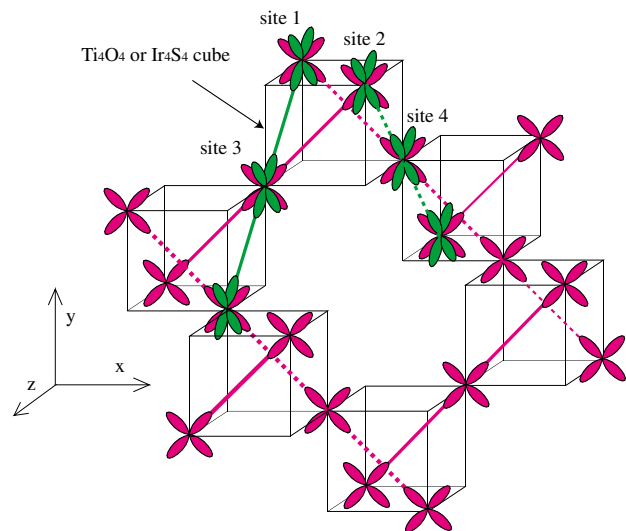


FIG. 1 (color). Orbital-dependent hopping in the pyrochlore lattice of spinels. For an electron in the  $xy$  orbital of site 1, the dominant hopping is along the  $[1, -1, 0]$  direction in the  $xy$  plane (to site 4). On the other hand, for an electron in the  $xy$  orbital of site 2, the dominant hopping is along the  $[1, 1, 0]$  direction in the  $xy$  plane (to site 3). The  $[1, 1, 0]$  chains shown by the red solid lines never cross the  $[1, -1, 0]$  chains shown by the red broken lines. For electrons with the  $yz$  orbitals of sites 1 and 2, the dominant hopping is along the  $[0, 1, -1]$  and  $[0, 1, 1]$  directions (to sites 3 and 4, respectively).

$T_{MI}$ , there appears the net tetragonal distortion (elongation,  $c/a = 1.03$  [4]), and, besides that, the complicated octamer structure appears [2]:  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  order in octamers, and the  $\text{Ir}^{4+}$  octamers have an alternation of short and long bonds; see Fig. 2 in [2]. This beautiful structure seems extremely unusual. However, the situation is much simpler if one looks at what happens in the *straight Ir chains*: one immediately notices that five out of six such chains have a tetramerization—an alternation of  $\text{Ir}^{3+}/\text{Ir}^{3+}/\text{Ir}^{4+}/\text{Ir}^{4+}/\dots$ —and one of them has a corresponding dimerization; see Fig. 2(a). The tetramerization in  $\text{CuIr}_2\text{S}_4$  was also noticed in [5].

One can naturally explain this tetramerization pattern if one looks at the electronic structure of this compound, schematically shown in Fig. 2(b). Because of the tetragonal elongation, the triply degenerate  $t_{2g}$  levels are split by a CF splitting, and, besides (which is probably more important), the  $xy$  band becomes broader. With the 5.5 electrons (or 0.5 hole) per Ir in these levels, the lowest two bands are fully occupied, and the upper  $xy$  one-dimensional band is 3/4 filled. Thus, we can expect a Peierls or charge density wave transition, accompanied by tetramerization in the  $xy$  chains (formation of superstructure with  $Q_\alpha = 2k_F = \pi/2$  along the  $[1, 1, 0]$  and  $[1, -1, 0]$  directions), with holes in the  $xy$  orbitals, as shown in Fig. 2(a). As is seen from this figure, the resulting state exactly corresponds to the one found in [2]:  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  form octamers. Besides, the  $\text{Ir}^{4+}$  pairs in the  $xy$  chains have orbitals directed towards one another; thus these pairs form spin singlets. When we release the lattice, corresponding bonds become shorter, again consistent with the structure of [2]. Thus the explanation of this apparently complicated structure becomes

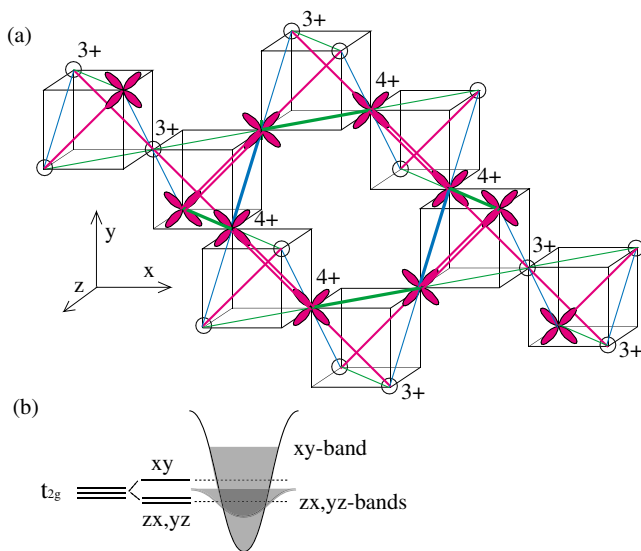


FIG. 2 (color). (a) Charge and orbital ordering in  $\text{CuIr}_2\text{S}_4$ . Octamer is shown by thick lines. Short singlet bonds are indicated by double lines. (b) Schematic electronic structure of  $\text{CuIr}_2\text{S}_4$ .

extremely simple and natural if we look at it from the viewpoint of straight Ir chains, which, for this orbital occupation, form natural building blocks in spinels.

The same idea explains also the chiral superstructures observed in  $\text{MgTi}_2\text{O}_4$  [3]. Below  $T_{MI}$  at 260 K, a tetragonal distortion (here compression) appears also in this system, together with the inequivalent bonds, so that, if one connects short and long bonds, they form spirals along the  $c$  or the  $z$  direction, which may be both left and right moving. Apparently, on the short bonds, Ti-Ti pairs form spin singlets which is rather typical for  $d^1$  configurations. This naturally explains the drop of magnetic susceptibility at  $T_{MI}$  [6]. This superstructure, the origin of which looks very puzzling, again can be explained very easily if one looks at the situation in the *straight Ti chains*. One immediately notices that in all chains running in the  $[0, 1, 1]$ ,  $[0, 1, -1]$ ,  $[1, 0, 1]$ , and  $[1, 0, -1]$  directions (lying in the  $zx$  and  $yz$  planes) one has the *tetramerization*: an alternation of short, intermediate, long, and intermediate bonds. This structure appears naturally if we look at the electronic structure of this system, Fig. 3(b). In the high temperature phase,  $\text{Ti}^{3+}$  ions have one electron in the triply degenerate  $t_{2g}$  level, which in the tight-binding scheme would give three one-dimensional degenerate bands (we neglect here small trigonal splitting). One can reduce the band energy by tetragonal distortion—the effect similar to the band Jahn-Teller effect invoked by Labbe and Friedel to explain the cubic-tetragonal transition in A15 compounds ( $\text{V}_3\text{Si}$ ,  $\text{Nb}_3\text{Sn}$ ) [7]. The tetragonal compression observed in  $\text{MgTi}_2\text{O}_4$  increases the bandwidths of the  $zx$  and  $yz$  bands

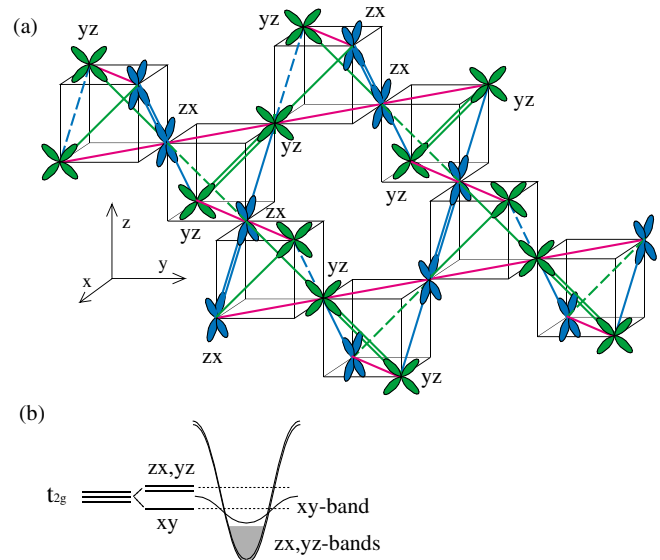


FIG. 3 (color). (a) Orbital ordering in  $\text{MgTi}_2\text{O}_4$ . Short singlet bonds are shown by double, intermediate–single, and long–dashed lines.  $yz$  orbitals are shown in green and  $zx$  orbitals in blue. (b) Schematic electronic structure of  $\text{MgTi}_2\text{O}_4$ . Note different orientation of coordinate axes as compared with Figs. 1 and 2.

and decreases that of the  $xy$  band, opposite to the case of  $\text{CuIr}_2\text{S}_4$ . With one electron per Ti, the lowest doubly degenerate  $zx$  and  $yz$  bands are  $1/4$  filled. This leads to the usual instability and to the formation of a superstructure with the wave vector  $Q_\alpha = 2k_F = \pi/2$ , i.e., to a tetramerization in the  $zx$  and  $yz$  directions, in accordance with the experiment. In contrast to the usual Peierls transition, we do not even have to move ions here: one can get a corresponding superstructure by changing the orbital occupation of respective ions [we call it an orbital density wave (ODW)].

Such an ODW may be stabilized by the electron repulsion. In the strong-coupling limit we get in each of these chains the orbital ordering of the type  $zx-zx-yz-yz-zx-zx\dots$ ; see Fig. 3 (this ordering satisfies the ‘‘Anderson rule’’ [8]: there will be two orbitals of each type in each Ti tetrahedron). Of course, the lattice then follows: a strong overlap of the orbitals in the pair with the lobes along the corresponding chains lead to the alternation of strong(short)-intermediate-weak(long)-intermediate bonds in each chain, with the spin-singlet states at short bonds. If now one connects short with long bonds, one gets the helical pattern stressed in [3]. Thus, one can visualize the structure observed in [3] both as a bond alternation and as a site-centered orbital ordering. Here we considered the tetragonal transition (band Jahn-Teller effect) and the orbitally driven Peierls transition separately, but in reality they occur simultaneously, so that it is the total energy gain that stabilizes this structure.

The situation in  $\text{MgTi}_2\text{O}_4$  is somewhat more complicated than that in  $\text{CuIr}_2\text{S}_4$ : whereas in the latter both the local CF splittings and the change of the bandwidths combine to make only the  $xy$  band partially occupied, in  $\text{MgTi}_2\text{O}_4$  these two effects oppose one another. Apparently the band Jahn-Teller effect dominates in  $\text{MgTi}_2\text{O}_4$ , leading to the tetragonal compression instead of elongation which would be more favorable for localized electrons. One can make a crude estimate, which shows that one gains much more kinetic energy with this filling (almost  $0.5t$ , where  $t$  is the nearest-neighbor hopping) when one occupies doubly degenerate  $zx$  and  $yz$  bands close to the bottom (which happens at a distortion with  $c/a < 1$ ) than if one would have an opposite distortion and would occupy a nondegenerate  $xy$  band. But the most direct confirmation of our picture comes from the band-structure calculations presented in Ref. [3]: according to them, below  $T_{\text{MI}}$  in  $\text{MgTi}_2\text{O}_4$ , only the  $zx$  and  $yz$  bands are occupied indeed. In the recent paper in [9] the superstructure in  $\text{MgTi}_2\text{O}_4$  was explained proceeding from the picture of the localized electrons and using the ‘‘Kugel-Khomskii’’ approach [10]. The resulting picture is rather similar to the one proposed in this Letter; this, in our opinion, confirms the correctness of our main idea and shows that the physical effect discussed above survives also in the case of strong electron correlations.

One can argue that a similar phenomenon should exist in other materials, e.g., in  $\text{NaTiO}_2$  with the triangular two-dimensional lattice of  $\text{Ti}^{3+}$  ions. This material also has a metal-insulator transition with a structural distortion at 250 K, which leads to a rather strong elongation of  $\text{TiO}_6$  octahedra along one of the local pseudocubic axes [11] (which, in combination with the original rhombohedral structure, makes the system monoclinic). The resulting situation may then become similar to that in  $\text{MgTi}_2\text{O}_4$ , and one can expect the formation of a similar superstructure with the alternation of  $zx-zx-yz-yz-zx-zx\dots$  orbitals along two sets of Ti chains running along the distortion axis, with the formation of corresponding spin-singlet states. The drop of susceptibility was, indeed, observed in  $\text{NaTiO}_2$  below  $T_{\text{MI}}$  [11], but the predicted superstructure was not yet seen.

The situation may also be similar in V spinels  $MV_2\text{O}_4$ ,  $M = \text{Mg, Zn, Cd}$  [12,13]. All of them have cubic-tetragonal transitions with  $c/a < 1$ , which lead to the splitting of  $t_{2g}$  levels with the low-lying  $xy$  singlet and higher  $zx, yz$  doublet. With two electrons per V ion, we have the situation resembling that of Ti: one electron occupies the  $xy$  orbital, but the second one is in the doubly degenerate ( $zx, yz$ ) orbitals or bands (note that this distortion with  $c/a < 1$  is again ‘‘anti-Jahn-Teller’’: the Jahn-Teller effect for localized electrons rather leads to the opposite distortion, with both electrons in the lower doublet). Consequently, one could have expected the formation of the superstructure similar to that discussed above. Recent results [13] confirm the presence of one-dimensional spin chains made by the  $xy$  electrons, and show some indirect evidences of superstructure in the  $c$  or  $z$  direction, which, however, the authors interpret as dimerization (alternation of planes with  $zx$  and  $yz$  orbitals); such a state was also obtained theoretically in an elegant work of Tsunetsugu and Motome [14] in the model of localized electrons. Corresponding distortion, however, was not yet observed experimentally. More detailed structural studies should clarify which structure is actually realized in these systems.

Finally, the same effect may be relevant in magnetite, at least partially. The most recent structure proposed for  $\text{Fe}_3\text{O}_4$  [15] (shown in Fig. 7 of [15]) has certain similarities with the structures discussed above: there is also a tetramerization in  $zx$  and  $yz$  chains, but of a somewhat different type than that in  $\text{CuIr}_2\text{S}_4$ : two out of four such chains have the same pattern,  $\text{Fe}^{2+}/\text{Fe}^{2+}/\text{Fe}^{3+}/\text{Fe}^{3+}/\dots$ , but two others have tetramerizations of a different type: in one  $2 + /2 + /2 + /3 + /2 + /2 + /2 + /3 + /\dots$  and in the other  $3 + /3 + /3 + /2 + /3 + /3 + /3 + /2 + /\dots$ . According to band-structure calculations [16],  $\text{Fe}_3\text{O}_4$  shows an orbital ordering in this structure, such that again only two types of orbitals  $zx$  and  $yz$  (or their combinations) are occupied by the extra  $t_{2g}$  electron of  $\text{Fe}^{2+}$ . It is not yet clear to us whether the effects studied above play a role in

this ordering in magnetite, but the analogy is rather suggestive.

Actually, the situation with an orbitally driven Peierls state leading to spin singlets is not unique for spinels or systems with triangular lattices as in  $\text{NaTiO}_2$  [17]. Such a phenomenon was also observed in pyroxene  $\text{NaTiSi}_2\text{O}_6$  [18]. One can argue that the same effect—orbitally driven singlet pair formation—occurs also in the recently synthesized  $\text{La}_4\text{Ru}_2\text{O}_{10}$  [19]. The explanation given in Ref. [19] (transition to a zero-spin  $\text{Ru}^{4+}$  state) seems rather unlikely, as it would require CF splitting of Ru  $t_{2g}$  levels exceeding the on-site Hund's rule energy, which seems rather improbable. Instead, one can suggest that the nonmagnetic ground state of  $\text{La}_4\text{Ru}_2\text{O}_{10}$  is also caused by the orbitally driven two-site spin singlets. Recent neutron scattering results on single crystalline  $\text{La}_4\text{Ru}_2\text{O}_{10}$  [20] may indeed agree with this interpretation. Thus, there appear more and more systems in which an orbital ordering leads to a singlet Peierls state.

To summarize, we argue that the complicated superstructures observed recently in some spinels ( $\text{CuIr}_2\text{S}_4$  and  $\text{MgTi}_2\text{O}_4$ ) are naturally explained as an orbitally driven Peierls distortion, caused by the proximity to an itinerant state. We predict similar phenomenon in  $\text{NaTiO}_2$ , and possibly in some other systems.

We are grateful to P. Radaelli, S.-H. Lee, and R. Osborn for useful discussions.

---

[1] M. Mizoguchi *et al.*, J. Phys. Soc. Jpn. **44**, 1501 (1978); M. Iizumi *et al.*, Acta Crystallogr. Sect. B **38**, 2121 (1982); J. P. Wright, J. P. Attfield, and P. G. Radaelli, Phys. Rev. Lett. **87**, 266401 (2001).

[2] P. G. Radaelli *et al.*, Nature (London) **416**, 155 (2002).  
 [3] M. Schmidt *et al.*, Phys. Rev. Lett. **92**, 056402 (2004).  
 [4] T. Furubayashi *et al.*, J. Phys. Soc. Jpn. **63**, 3333 (1994).  
 [5] M. Croft *et al.*, Phys. Rev. B **67**, 201102(R) (2003).  
 [6] Y. Ueda, N. Fujiwara, and H. Yasuoka, J. Phys. Soc. Jpn. **66**, 778 (1997).  
 [7] J. Labbe and J. Friedel, J. Phys. (Paris) **27**, 153 (1966).  
 [8] P. W. Anderson, Phys. Rev. **102**, 1008 (1956).  
 [9] S. Di Matteo, G. Jackeli, C. Lacroix, and N. B. Perkins, Phys. Rev. Lett. **93**, 077208 (2004).  
 [10] K. I. Kugel and D. I. Khomskii, Usp. Fiz. Nauk **136**, 621 (1982) [Sov. Phys. Usp. **231**, 25 (1982)]; Sov. Phys. Solid State **17**, 454 (1975).  
 [11] S. J. Clarke *et al.*, Chem. Mater. **10**, 372 (1998).  
 [12] H. Mamiya *et al.*, J. Appl. Phys. **81**, 5289 (1997); Y. Ueda, N. Fujiwara, and H. Yasuoka, J. Phys. Soc. Jpn. **66**, 778 (1997); N. Nishiguchi and M. Onoda, J. Phys. Condens. Matter **14**, 1551 (2002).  
 [13] S.-H. Lee *et al.*, Phys. Rev. Lett. **93**, 156407 (2004).  
 [14] H. Tsunetsugu and Y. Motome, Phys. Rev. B **68**, 060405(R) (2003); Y. Motome and H. Tsunetsugu, Phys. Rev. B **70**, 184427 (2004).  
 [15] J. P. Wright, J. P. Attfield, and P. G. Radaelli, Phys. Rev. B **66**, 214422 (2002).  
 [16] I. Leonov, A. N. Yaresko, V. N. Antonov, M. A. Korotin, and V. I. Anisimov, Phys. Rev. Lett. **93**, 146404 (2004).  
 [17] One should not mix these orbitally driven singlets with the recently proposed orbital dimers; see P. Horsch, G. Khaliullin, and A. Oles, Phys. Rev. Lett. **91**, 257203 (2003): in the latter case one speaks about a quantum orbital singlets, whereas we have a more traditional static orbital ordering, with spins forming singlets at certain bonds.  
 [18] M. Isobe *et al.*, J. Phys. Soc. Jpn. **71**, 1423 (2002).  
 [19] P. Khalifah *et al.*, Science **297**, 2237 (2002).  
 [20] R. Osborn *et al.* (unpublished).