

Orbital-assisted Peierls state in $\text{NaTiSi}_2\text{O}_6$

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Abstract. – Does the quasi-one-dimensional titanium pyroxene $\text{NaTiSi}_2\text{O}_6$ exhibit the novel *orbital-assisted Peierls* state? We calculate its groundstate properties by three methods: Monte Carlo simulations, a spin-orbital decoupling scheme and a mapping onto a classical model. The results show univocally that for the spin and orbital ordering to occur at the same temperature—an experimental observation—the crystal field needs to be small and the orbitals are active. We also find that fluctuations in the spin-orbital sector drive the transition, explaining why bandstructure methods fail to find it. The conclusion that $\text{NaTiSi}_2\text{O}_6$ shows an orbital assisted Peierls transition is therefore inevitable.

Introduction. – Transition-metal compounds display a dazzling collection of physical properties, spanning the range from colossal magneto-resistance in manganites, the spin-Peierls effect in quasi-one-dimensional systems to high T_c superconductivity in cuprates [1,2]. In these materials the interactions between electrons can be so strong that they destroy the Fermi surface. A Mott insulator is the canonical example. In this situation electrons become localized and they regain their local spin, charge and orbital degrees of freedom. The orbital degrees of freedom play a special role here since they can couple both to the lattice, via the Jahn-Teller effect, and to the spins, via superexchange interactions [3]. Orbitals can even actively lower the dimension of a magnetic system [4]. The interplay between all these degrees of freedom is the apparent root of the observed wealth in different types of ordered, symmetry broken and disordered ground states [1–7] in, *e.g.*, doped manganites and even the driving force behind multiply ordered systems, such as, *e.g.*, multiferroics [8,9].

Recently different types of novel ground states, the *orbital-related Peierls states*, were proposed to exist in several compounds. Such states are expected to appear in one-dimensional systems where orbital degrees of freedom lead to the dimerization of the atoms that make up the chain, in analogy to the *spin-Peierls state*, where the dimerization is driven by the electron spins. As the orbital degrees of freedom couple to both the lattice and spin, the orbital-related Peierls states are expected to reveal themselves experimentally through orbital, spin and lattice anomalies. The search for these states, specifically in vanadates and titanates, motivated a number of experimental and theoretical studies [10–24] and the findings became the subject of intense debate. The first candidate with possibly an orbital Peierls ground state is the perovskite vanadate YVO_3 . In YVO_3 the proposed ordered state consists of true

orbital singlets. However, the evidence in favor [10–12] is opposed by extended band-structure calculations that indicate that the compound is electronically three-dimensional [13]. Recently, it was proposed that also the spinel structures of CuIr_2S_4 and MgTi_2O_4 show an orbitally induced Peierls state [25]. In this letter we focus on another possible compound with orbital-assisted dimerization, the pyroxene compound $\text{NaTiSi}_2\text{O}_6$. This material is different from YVO_3 because the formation of true orbital singlet states is not allowed by the crystallographic symmetry. Instead we find that the orbital fluctuations in the titanium pyroxene drive the formation of a spin-paired state, just as in the spinel structures studied by Khomskii and Mizokawa [25]. However, their analysis of an orbital-assisted Peierls distortion relies on the proximity of the electronic system to an itinerant state, whereas our approach is valid deep into the Mott insulating regime and relies on the presence of strong on-site Coulomb interactions.

A number of studies of the microscopic spin-orbital Hamiltonian of titanium pyroxene have shown that indeed this novel orbital-assisted Peierls state can form, but *ab initio* band structure and ionic crystal field calculations contradict this claim [17–24]. Here we present a unified picture and show that indeed it exhibits orbital-assisted Peierls ordering.

The titanium pyroxene. – The distinguishing feature of the pyroxene compound $\text{NaTiSi}_2\text{O}_6$ is the presence of quasi-one-dimensional arrays of edge-sharing TiO_6 octahedra. Besides its spin ($s = 1/2$), each Ti^{3+} ion has an additional orbital degree of freedom. The system shows a dramatic drop in the magnetic susceptibility below $T_{OO} = 210$ K [17], while at the same temperature a structural change is observed. Raman scattering reveals that this transition is accompanied by a phonon frequency shift and broadening [18, 21]. It was immediately suggested that this apparent connection between lattice and spin degrees of freedom is driven by the ordering of titanium t_{2g} orbitals. Starting from a tight-binding Hubbard model a microscopic spin-orbital model was derived in support of this picture and it was shown explicitly that the spin-orbital model can have an orbital-assisted Peierls ground state at low temperatures [18, 19].

However, also two pieces of evidence disputing this claim have appeared. Ionic crystal-field calculations suggest that the t_{2g} orbital splitting is substantial in this compound [23]. Since the microscopic models are based on the assumption that the orbitals are (nearly) degenerate, these results seem to strike a serious blow to the proposed orbital-assisted Peierls picture. A strong crystal field would lead to a fixed orbital ordering, but at the same time it would suppress all of the thermal orbital fluctuations which are necessary for the orbital-assisted Peierls scenario. Besides this, density functional calculations by Popović *et al.* indicate that a *Haldane spin-one chain* forms at low temperature, pre-empting the orbital-assisted Peierls transition [20]. Recently this result was challenged by LDA+U band structure calculations, in which electron correlation effects are partially incorporated on a mean-field level [24].

In this letter we will show that we can account for all of these results, by an analysis that is based on the microscopic model that was originally proposed in ref. [18]. In particular we will show that the orbital-assisted Peierls state can form in $\text{NaTiSi}_2\text{O}_6$, in spite of the presence of a sizeable crystal-field splitting. Both numerical Monte Carlo simulations and an analytical spin-orbital decoupling for the microscopic model show that even if the crystal-field splitting is comparable to the size of the inter-site exchange coupling, the orbital assisted Peierls transition still occurs. Thus for the spin and orbital ordering to occur at the same temperature — as it does experimentally — the crystal field should be smaller than or at most comparable to the inter-site exchange energy. This places a strict upper bound on the crystal-field splitting. Furthermore we find that fluctuations in the spin and orbital sector actually drive the orbital-assisted Peierls transition. Recently, the importance of composite spin-orbital fluctuations also came to the fore in other theoretical studies of Hamiltonians that model materials with

t_{2g} orbital degeneracy [26]. Precisely these kinds of fluctuations are not taken into account in band structure calculations. Neglecting them in our microscopic Hamiltonian actually reduces it to a solvable classical model. An exact transfer matrix computation shows that without the fluctuations indeed alternating ferromagnetic correlations between neighboring spins appear, as in band structure calculations. This explains the failure of these methods to find the orbital-assisted Peierls ground state. Judging from these results the conclusion that NaTiSi₂O₆ exhibits an orbital-assisted Peierls transition is inevitable.

Microscopic model. – Each Ti³⁺ ion in the edge-sharing TiO₆ octahedra has a single electron in one of the three t_{2g} orbitals denoted by $|xy\rangle$, $|yz\rangle$ and $|zx\rangle$. The $|zx\rangle$ orbital turns out to be inert, which renders it higher in energy and it is thus neglected. The Coulomb interaction between electrons on the same titanium atom is so large that the exchange interactions can be determined by a second-order perturbation expansion in the electron hopping parameter. The leading-order spin-orbital Hamiltonian is [18]

$$H_{ST} = 4J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \left[T_i^z T_j^z + \frac{(-1)^i}{2} (T_i^z + T_j^z) + \frac{1}{4} \right], \quad (1)$$

where we use spin operators \mathbf{S} and orbital operators T (where $T_z = \pm \frac{1}{2}$ and the plus (minus) sign correspond to an occupied $|xy\rangle$ ($|yz\rangle$) orbital). Here we only need Ising variables to describe the orbital operators, because the direct hopping from one titanium site to the next does not allow any other terms. For edge-sharing octahedra with t_{2g} orbitals, for instance titanium spinels [25], direct hopping is usually larger than indirect hopping via the oxygen orbitals. Indeed, for our titanium pyroxene band structure calculations indicate that direct hopping dominates [20, 23]. But as indirect hopping is allowed by symmetry, it is always present to some extent. It will induce additional orbital quantum fluctuations —as in the case of YVO₃. It is easy to see that on each Ti-Ti bond two orbitals are coupled to each other by direct hopping and the other four by indirect hopping: therefore these two hoppings involve complementary sets of orbitals. A very large indirect hopping might actually stabilize an orbital-singlet state, which has ferro spin correlations within the orbital-singlet and antiferro ones between them.

In the Hamiltonian above nearest-neighboring lattice sites are denoted by i and j and J denotes the exchange integral. Here we neglected Hund's rule exchange for simplicity. It has been shown by Hikihara *et al.* [19] that the introduction of a moderate Hund's rule coupling will not lead to a new ground state, nor alter the nature of the transition. We also include two orbital-only contributions to the Hamiltonian, the crystal-field splitting, lifting the degeneracy of the two t_{2g} orbitals, parameterized by J_{CF} , and a term due to the superexchange [19]:

$$H_T = J \sum_{\langle ij \rangle} T_i^z T_j^z + J_{CF} \sum_i T_i^z, \quad (2)$$

The symmetry of the crystal field term that we use here is the one found in LDA+U, GGA, and other theoretical calculations [19, 21, 23]. Notice that J_{CF} acts against the proposed mechanism of orbital-assisted spin singlet formation. An important outcome of the present study is that the orbital-assisted Peierls transition will be stable against a finite J_{CF} .

Methods. – We study the model given by eqs. (1) and (2) by three different methods. First we performed a Monte Carlo simulation of the Hamiltonian for a system of 100 sites. In this simulation we added an inter-chain coupling in a mean-field fashion, in order to account

for the three dimensionality of the system:

$$H = H_{ST} + H_T + J_{\text{inter}} T_{\text{tot}}^z \text{ and } J_{\text{inter}} = \frac{4zJ'}{N} \langle T_{\text{tot}}^z \rangle. \quad (3)$$

Here J_{inter} is the effective mean-field inter-chain coupling, z is the number of neighbor sites and J' the bare inter-chain coupling strength. We take $J' = J/10$ in the present calculations. As was shown by Hikihara *et al.* [19], J' must be much smaller than J , and its exact size cannot qualitatively affect the ordering mechanism. It is worthwhile to note that one can simulate the full quantum Hamiltonian (3) with a classical Monte Carlo algorithm. This is justified by a particular symmetry in the spin-orbital model: the staircase structure of the titanium chains combined with the orientation of the t_{2g} orbitals does not allow any spin states other than single spins or dimers.

Within the Monte Carlo simulation we determine the magnetic (spin) and orbital susceptibilities, χ^S and χ^O , as well as the nearest-neighbor correlators for spins and orbitals: C^S and C^O , respectively. From the temperature dependence of the spin/orbital susceptibility we then obtain the transition temperatures below which spins and orbitals order (T^S and T^O). These quantities we studied as a function of both J and J_{CF} .

In the second method we employ a decoupling of the spin and orbital degrees of freedom of the Hamiltonian (1). We decouple H_{ST} by introducing static orbital and spin fields:

$$s + (-1)^i \delta s \equiv \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \quad \text{and} \quad t + (-1)^i \delta t \equiv \left\langle \frac{1}{4} + T_i^z T_j^z + \frac{(-1)^i}{2} (T_i^z + T_j^z) \right\rangle, \quad (4)$$

so that the decoupled part of $H_{ST} \simeq H_{\text{de}}^S + H_{\text{de}}^O$ with

$$\begin{aligned} H_{\text{de}}^S &= 4J \sum_{\langle i,j \rangle} (t + (-1)^i \delta t) \mathbf{S}_i \cdot \mathbf{S}_j, \\ H_{\text{de}}^O &= \sum_{\langle i,j \rangle} [4J (s + (-1)^i \delta s) + J] T_i^z T_j^z + \sum_i (4J \delta s + J_{\text{CF}}) T_i^z. \end{aligned} \quad (5)$$

We focus first on the orbital part of this decoupled Hamiltonian. Since the only operator appearing in H_{de}^O is T^z , it is effectively a classical Hamiltonian, closely related to the Ising model. This makes it possible to construct a transfer matrix that allows us to obtain an exact expression for the partition function. From there we can obtain any other thermodynamic quantity related to the orbital physics of H_{de}^O . The spin part of the decoupled Hamiltonian (5) cannot be diagonalized exactly as it stands. Therefore, following a canonical approach to the spin-Peierls Hamiltonian [27], we consider only the XY part of the spins. Then we can use the Jordan-Wigner transformations to diagonalize the remaining part of H_{de}^S , and find all spin-related thermodynamic quantities.

Finally, we have considered the full Hamiltonian (3) without quantum spin fluctuations, *i.e.* taking into account only the z components of the spin operators. The motivation for considering this limit is that in band structure calculations quantum fluctuations of this kind are effectively discarded. Since this Hamiltonian is classical, we can construct the transfer matrix that will allow us to find the partition function and thus all thermodynamic quantities of this system.

Results. – In fig. 1 the spin and orbital ordering temperatures are shown as a function of the crystal-field splitting J_{CF} , as deduced from their respective susceptibilities in the Monte Carlo calculations. The transition temperatures for magnetic ordering coincide with the ones

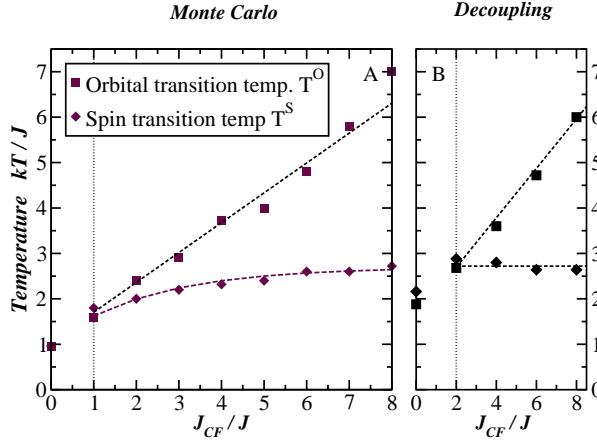


Fig. 1 – Left: orbital and spin transition temperatures *vs.* crystal-field splitting determined from the Monte Carlo calculations. On the left of the dotted line the spin and ordering temperature coincide. Right: transition temperatures determined by spin-orbital decoupling calculations.

for orbital ordering, as long as the crystal-field splitting is not too large, *i.e.*, when $J_{CF}/J < 1$. The calculations show that the orbital and magnetic ordering occur at different temperatures only for a crystal-field that is larger than the exchange coupling, *i.e.* when $J_{CF}/J > 1$. In that case T^O is proportional to J_{CF} , whereas T^S tends to a constant. The same conclusion we find from decoupling calculations, shown in the right panel of fig. 1.

We now invert the argument above. Experimentally the drop in spin susceptibility and

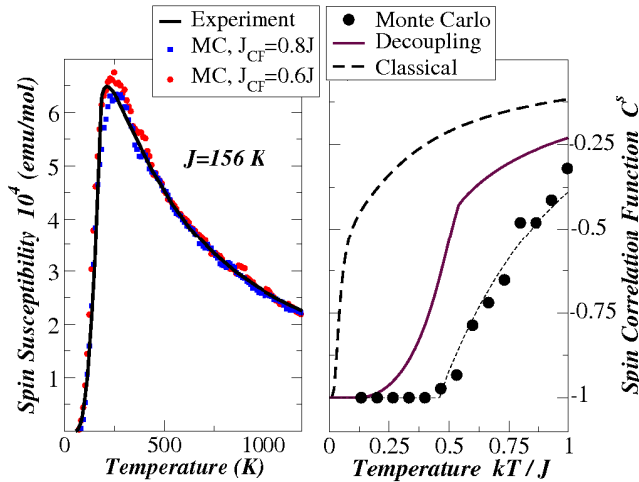


Fig. 2 – Left: fit of the Monte Carlo results to the experimental spin susceptibility. Right: nearest-neighbor spin correlation function $C^S = \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$, as calculated from the Monte Carlo simulation, the spin-orbital decoupling scheme, and the classical model. The correlation functions are normalized to their zero-temperature values ($-3/8$, $-1/4$ and $-1/8$. These values follow directly from our considering Heisenberg (with one singlet on every second Ti-Ti bond), XY and Ising spins, respectively). In the first two cases spin valence bonds are formed; in the last case small residual interactions due to Hund’s rule coupling will cause the formation of a chain of alternating ferro and antiferro bonds, see fig. 3.



Fig. 3 – A sketch of the zero-temperature states. The lobes of the orbitals that lie in the plane of the titanium chain are depicted. The dark lobes are occupied orbitals. (A) Orbital-assisted Peierls state with spin valence bonds. (B) Alternating ferro and antiferro spin bonds as found in the classical spin model and density functional studies.

the structural changes that are indicative of orbital ordering occur both at $T_{OO} = 210$ K. As experiment shows that these temperatures coincide, the splitting of t_{2g} levels can thus not be larger than the superexchange coupling of neighboring spins: evidently titanium pyroxene is in the regime where $J_{CF}/J < 1$. This conclusion can be further quantified. In fig. 2, left panel, we compare the intrinsic experimental spin susceptibility from ref. [17] and our Monte Carlo results. From fitting the experimental susceptibility we find $J_{CF}/J = 0.7 \pm 0.1$, $J = 156$ K and a gyromagnetic moment $g = 1.85$.

We also calculated the nearest-neighbor spin and orbital correlation function C^S/C^O as a function of temperature with all three methods. The results for the spin correlator are shown in fig. 2, right panel. The corresponding orbital correlators C^O indicate that in all cases there is a uniform and parallel ordering of the orbitals at low temperatures and these are not shown. The correlators in fig. 2 are, for clarity, normalized to their zero-temperature value. Clearly spins tend to align antiparallel on neighboring bonds and form a valence bond solid, as shown in fig. 3A. The Monte Carlo results show that this tendency is very strong and that even above the ordering temperature spin dimer correlations are substantial. It is interesting to note that when the spin and orbital fluctuations are decoupled, the spin correlation function C^S is appreciably reduced at finite temperatures. Thus the simultaneous fluctuations of spin and orbital degrees of freedom actually strengthen the spin valence bond solid. This seems counterintuitive, but has a straightforward physical cause. A spin flip in the valence bond state transforms a singlet dimer into a triplet, which is a strong ferromagnetic bond that causes a large reduction of the average antiferromagnetic spin correlations. Suppose, however, that the flipped spin can at the same time change orbital. After such a combined spin-orbital excitation, the spins that originally formed a firm singlet valence bond, are effectively not interacting anymore. They have a vanishing contribution to the nearest-neighbor spin correlation function because of their respective orbital configurations and thus are less damaging to the magnetic ordering than fluctuations that exclusively involve the spin degree of freedom.

The importance of fluctuations becomes even more striking when we compare the classical to the quantum results. When we keep in the Hamiltonian H_{ST} only the z projection of the spin operators, as is the case in the density functional calculations, the spin correlation function C^S is drastically reduced at any finite temperature, see fig. 2. Only at the lowest temperatures long-range spin/orbital ordering sets in, which indicates that the system is strongly fluctuating due to the presence of many low-energy states that are quasi degenerate. In this case we expect that the system is very susceptible to any residual spin interaction. Indeed, we find that if we include a finite Hund's rule coupling, which leads to a very small ferromagnetic interaction between neighboring spins that are in different orbitals, the spins immediately order ferromagnetically along the π -like bonds, whereas the spins on the σ -like bonds, with orbitals pointing towards each other, order antiferromagnetically, see fig. 3B. In this case the nearest neighbor correlation function C^S , which is now the sum of antiferro and ferro correlations, goes to zero at $T = 0$. The resulting ground-state spin and orbital configuration (fig. 3B) exactly matches the one found by Popović *et al.* in ref. [20] on the

basis of band structure calculations. We find, however, that the ferro bonds are weak and the antiferro ones are strong, in accordance with recent LDA+U calculations [24]. Therefore even in this classical limit the system cannot be regarded to be a spin-one chain.

Conclusions. – Results from Monte Carlo simulations, from a spin-orbital decoupling and a classical approximation scheme of a microscopic Hamiltonian which incorporates both spins and orbitals of the titanium chains in NaTiSi₂O₆ place a firm upper bound on the size of the crystal-field splitting. This proves that in this system the orbital degrees of freedom are active at low energies and temperatures. The interacting spin-orbital Hamiltonian describes the experimental magnetic susceptibility very well. The calculated correlation functions show that the orbital-assisted Peierls state is realized below $T_{OO} = 210$ K. The so-formed orbital-assisted Peierls state differs from the orbital Peierls state found, for example, in YVO₃ [10–12] in that the orbitals themselves do not form singlet pairs, but the spins do. Therefore fluctuations in both the spin and orbital sectors of titanium pyroxene are essential for the stabilization of this type of spin-orbital solid.

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REFERENCES

- [1] TOKURA Y. and NAGAOSA N., *Science*, **288** (2000) 462.
- [2] IMADA M., FUJIMORI A. and TOKURA Y., *Rev. Mod. Phys.*, **70** (1998) 1039.
- [3] KUGEL K. I. and KHOMSKII D. I., *Sov. Phys. Usp.*, **25** (1982) 232; VAN DEN BRINK J., KHALIULLIN G. and KHOMSKII D. I., in *Colossal Magnetoresistive Manganites*, edited by CHATTERJI T. (Kluwer Academic Publishers, Dordrecht) 2004.
- [4] LEE S. *et al.*, *Nature Mater.*, **5** (2006) 471.
- [5] VAN DEN BRINK J., *Nature Mater.*, **5** (2006) 427.
- [6] VAN DEN BRINK J., *New J. Phys.*, **6** (2004) 201.
- [7] NUSSINOV Z. *et al.*, *Europhys. Lett.*, **67** (2004) 990.
- [8] KIMURA T. *et al.*, *Nature*, **426** (2003) 55.
- [9] EFREMOV D. V., VAN DEN BRINK J. and KHOMSKII D. I., *Nature Mater.*, **3** (2004) 853.
- [10] SIRKER J. and KHALIULLIN G., *Phys. Rev. B*, **67** (2003) 100408(R).
- [11] ULRICH C. *et al.*, *Phys. Rev. Lett.*, **91** (2003) 257202.
- [12] HORSCH P., KHALIULLIN G. and OLEŚ A. M., *Phys. Rev. Lett.*, **91** (2003) 257203.
- [13] FANG Z. and NAGAOSA N., *Phys. Rev. Lett.*, **93** (2004) 176404.
- [14] ISHIHARA S., *Phys. Rev. Lett.*, **94** (2005) 156408.
- [15] PEN H. F. *et al.*, *Phys. Rev. Lett.*, **78** (1997) 1323.
- [16] VAN DEN BRINK J. *et al.*, *Phys. Rev. B*, **58** (1998) 10276.
- [17] ISOBE M. *et al.*, *J. Phys. Soc. Jpn.*, **71** (2002) 1423.
- [18] KONSTANTINOVIC M. J. *et al.*, *Phys. Rev. B*, **69** (2004) 020409.
- [19] HIKIHARA T. and MOTOME Y., *Phys. Rev. B*, **70** (2004) 214404.
- [20] POPOVIĆ Z. S., SLJIVANCANIN Z. V. and VUKAJLOVIC F. R., *Phys. Rev. Lett.*, **93** (2004) 036401.
- [21] POPOVIĆ Z. V. *et al.*, *Phys. Rev. B*, **71** (2005) 224302.
- [22] VAN WEZEL J. and VAN DEN BRINK J., *J. Magn. & Magn. Mater.*, **290-291** (2005) 318.
- [23] BERSIER S. and KONSTANTINOVIC M. J., private communications, to be published.
- [24] STRELTSOV S. V., POPOVA O. A. and KHOMSKII D. I., preprint cond-mat/0512195.
- [25] KHOMSKII D. I. and MIZOKAWA T., *Phys. Rev. Lett.*, **94** (2005) 156402.
- [26] OLEŚ A. M. *et al.*, *Phys. Rev. Lett.*, **96** (2006) 147205.
- [27] CROSS M. C. and FISCHER D. S., *Phys. Rev. B*, **19** (1979) 402.