

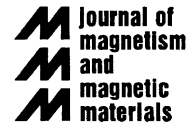


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# Orbital–Peierls transition in the spin chains of $\text{NaTiSi}_2\text{O}_6$

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## Abstract

The distinguishing feature of the pyroxene compound  $\text{NaTiSi}_2\text{O}_6$  is the presence of quasi-one-dimensional arrays of edge sharing  $\text{TiO}_6$  octahedra. Besides its spin ( $s = \frac{1}{2}$ ), each  $\text{Ti}^{3+}$  ion has an additional orbital degree of freedom. We determine the properties of the microscopic spin–orbital Hamiltonian for this compound by finite temperature Monte Carlo simulations. We show that for the spin and orbital ordering to occur at the same temperature, the orbital crystal field splitting should be smaller than or comparable to the inter-site superexchange integral. The simulations strongly indicate that in  $\text{NaTiSi}_2\text{O}_6$  there is an orbital–Peierls transition, which is an orbital ordering transition that is accompanied by a lattice dimerization. Magnetically, in this case, the system goes from a high temperature quasi-one-dimensional antiferromagnet to a low-temperature valence bond solid. The experimentally observed spin gap and lattice anomalies are strong evidence for the presence of an orbital–Peierls transition in  $\text{NaTiSi}_2\text{O}_6$ .

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## 1. Introduction

Electrons in strongly correlated transition-metal compounds can be regarded as having separate spin, charge and orbital degrees of freedom. It is the interplay between these, combined with their coupling to the lattice, that gives rise to a wealth of possible spin, charge and orbital orderings. Also, the low-energy elementary excitations—responsible for the rich variety of physical phenomena that are encountered in these materials—are characterized by the complex interplay of these different degrees of freedom [1]. Systems with orbital degeneracy are particularly interesting because orbitals couple to the lattice via the cooperative Jahn–Teller (JT) effect on one hand, and via superexchange interactions to the electronic spin on the other hand. Therefore at an orbital

ordering-phase transition the magnetic susceptibility and phonon properties will be affected at the same time. Experimentally, however, such an interrelation is seldom found: often the dominant orbital–lattice coupling obscures the more subtle magnetic effects due to the superexchange.

In the pyroxene compound  $\text{NaTiSi}_2\text{O}_6$ , however, there is experimental evidence for a canonical orbital ordering transition, coupling both to spin and lattice degrees of freedom. There is a dramatic drop of the magnetic susceptibility below  $T_{\text{OO}} = 210$  K, that is accompanied with a structural change [2,3]. In Ref. [3], a microscopic orbital–spin model is derived for this compound. On the basis of this model it was suggested that orbital ordering is the basis for the magnetic and lattice anomalies. The idea is that the high-temperature quasi-one-dimensional dynamical JT phase of  $\text{NaTiSi}_2\text{O}_6$  exhibits a spontaneous breaking of the translational symmetry into a *dimerized orbital ordered*

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state at low temperature, see Fig. 1. This dimerized orbital state has a spin gap due to the formation of spin valence bonds. Because of the formation of orbital dimers this state is called an orbital–Peierls state.

In order for any orbital ordering transition to occur, it is important that the system is close to a point of orbital degeneracy. In the scenario outlined above for NaTiSi<sub>2</sub>O<sub>6</sub> the t<sub>2g</sub> orbitals of the Ti<sup>3+</sup> ions in the system are supposed to be (quasi-)degenerate. However, recent ionic crystal field calculations indicate that the t<sub>2g</sub> orbital splitting can be substantial, which implies that the assumption of t<sub>2g</sub> orbitals being (quasi-)degenerate is actually not valid [4]. Thus the foundation that underlies the orbital–Peierls scenario seems to break down. On the other hand, it should be noted that ionic calculations that neglect covalency effects, generally overestimate crystal field splittings. An independent measure of the orbital splitting is therefore called for.

We determine the crystal field splitting by comparing model calculations with experimental observations. In this way, we find a robust upper limit for the value for the orbital splitting. Monte Carlo simulations are performed on the spin–orbital model Hamiltonian of Ref. [3], with in addition a crystal field splitting term. We obtain spin and orbital susceptibilities and estimate the corresponding transition temperatures. From the experimental fact that the lattice and spin anomalies occur at about the same temperature, we conclude that in NaTiSi<sub>2</sub>O<sub>6</sub> the crystal field splitting can be of the order of the inter-site exchange coupling, but not much larger. Thus, our calculations strongly support the scenario that in NaTiSi<sub>2</sub>O<sub>6</sub> an orbital–Peierls transition takes place.

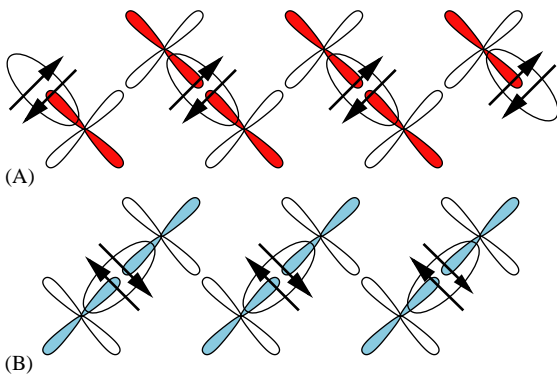


Fig. 1. Schematic representation of the overlap between the  $|xy\rangle$  and  $|yz\rangle$  orbitals of neighboring Ti<sup>3+</sup> ions. Part A is a projection along the  $z$ -axis, part B along the  $x$ -axis. Adjacent uncolored lobes lie on different levels, and do not overlap. Hopping is dominantly between orbitals of the same kind that are pointing toward each other. On these orbital dimers spin singlets will form in the groundstate. In the case of a vanishing crystal field splitting ( $D/J = 0$ ) states A and B are degenerate.

## 2. Model

For a single TiO<sub>6</sub> octahedron the cubic crystal field splits the Ti-states into low lying t<sub>2g</sub> states, occupied by a single electron and empty states of e<sub>g</sub> symmetry at higher energy. The low-energy electronic properties are governed by the three-fold degenerate t<sub>2g</sub> states (the relevant states are  $|xy\rangle$ ,  $|yz\rangle$  and  $|zx\rangle$ ). The Coulomb interaction  $U$  between electrons on the same transition metal atoms is large, so the exchange interactions can be determined by a second-order perturbation expansion in the electron hopping parameters, as is schematically indicated in Fig. 1. For the spin  $S = \frac{1}{2}$  titanium system with chains of edge sharing octahedra one then obtains the Hamiltonian [3]

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

where we use the spin operators  $S$ , orbital operators  $T$  ( $T^z = \frac{1}{2}$  corresponds to an occupied  $|xy\rangle$  orbital and  $T^z = -\frac{1}{2}$  to an occupied  $|yz\rangle$  orbital), and  $i, j$  are neighboring sites and  $D$  is the crystal field splitting between these two orbitals. The  $|zx\rangle$  orbitals turn out to be inert.

## 3. Results

We performed a classical Monte Carlo simulation on the Hamiltonian above for a system of 100 sites for different temperatures and determined the magnetic (spin) and orbital susceptibility,  $\chi^s$  and  $\chi^o$  respectively, from the simulations. The use of classical Monte Carlo instead of quantum Monte Carlo is justified here, since the staircase structure of the  $Ti$  chains and the orientation of the t<sub>2g</sub> orbitals only allow the spin states to be either single spins or dimers. The magnetic susceptibility is shown in Fig. 2 for different values of the crystal field splitting ratio  $D/J$ . For all values of this ratio we observe a vanishing of the susceptibility at low temperatures, characteristic for the spin gap that is present in the ground state. The susceptibility changes continuously with the applied crystal field when the field is not very large ( $D/J < 4$ ). For larger values of the orbital splitting  $\chi^s$  becomes almost independent of the crystal field. This reflects the fact that for such large values of  $D/J$  the orbital degrees of freedom become static and the system is uniformly orbital ordered in the temperature range that we consider. In this limit  $\chi^s$  is due to local singlet–triplet excitations on orbital dimers, see Fig. 1. The magnetic susceptibility from our simulations is very similar to what is observed in experiment [2], with a peak in  $\chi^s$  at around  $T/J \approx 1-2$ , depending on the ratio  $D/J$ . This peak signals the onset

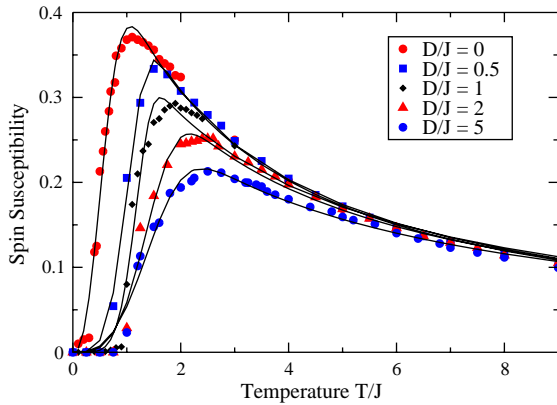


Fig. 2. Spin susceptibility as a function of reduced temperature  $T/J$  for different values of the crystal field splitting ratio  $D/J$ . The solid lines are a fit of the data.

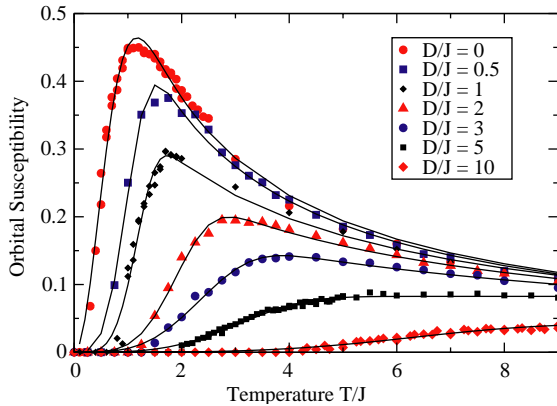


Fig. 3. Staggered orbital susceptibility as a function of reduced temperature  $T/J$  for different values of the crystal field splitting ratio  $D/J$ .

of the magnetic ordering transition and the dependence of the peak position on  $D/J$  is shown in Fig. 4. Note that the simulated system is one dimensional, which a priori excludes the possibility of having a finite-temperature phase transition. However, in the presence of a small inter-chain coupling that makes the model effectively three dimensional, one expects that a finite temperature cross-over in the one-dimensional chain develops into full blown phase transitions of the three-dimensional system. Such is indeed observed when the Monte Carlo simulation in a mean field inter-chain orbital-orbital coupling is included [5].

The orbital susceptibility  $\chi^o$  is shown in Fig. 3. For small values of the crystal field the orbital susceptibility shows a behavior that is very similar to the magnetic

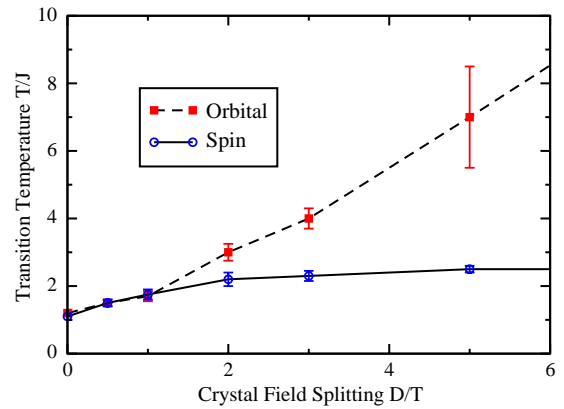


Fig. 4. Spin and orbital susceptibility peak positions as determined from a fit to the magnetic and orbital susceptibilities. The solid line is an extrapolation of the data.

susceptibility  $\chi^s$ . The peak in  $\chi^o$ , indicative of the orbital ordering instability, is at the same position as the peak in  $\chi^s$ , see Fig. 4. For values of  $D/J > 1$ , however, the peak in  $\chi^o$  continues to increase with increasing orbital splitting. This indicates that for larger orbital splittings the orbital ordering phase transition occurs at higher temperature than the magnetic transition. Such is contrary to the experimental observations: the drop in magnetic susceptibility and the turning up of the lattice distortion that is related to the presence of orbital ordering occur both at the same temperature [2,3].

#### 4. Conclusion

Simulations on the microscopic Hamiltonian that incorporates both the orbital and spin degrees of freedom of the titanium ions in the pyroxene compound  $\text{NaTiSi}_2\text{O}_6$  show that in order for the spin and orbital ordering to occur at the same temperature, the orbital crystal field splitting  $D$  cannot be much larger than the inter-site superexchange  $J$ . We thus conclude that at  $T_{\text{OO}} = 210$  K in  $\text{NaTiSi}_2\text{O}_6$  an orbital-Peierls transition occurs, which is an orbital ordering transition that is accompanied by a lattice dimerization and the formation of spin singlet valence bonds.

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