

Orbital Driven Spin Ordering in the One Dimensional Chains of Titanium Pyroxene

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Abstract. In this paper we present a model description of the one dimensional titanium chains found in titanium pyroxene. The model we present can be used to understand the available experimental data regarding the magnetic and the lattice properties of the compound, as well as account for the conflicting results found in different calculational approaches. From this work we conclude that a novel type of 'orbital Peierls' transition occurs in the chains of $NaTiSi_2O_6$.

Keywords: Orbital Order, Spin Chains, Titanates

PACS: 75.10.-b; 75.25.+z; 71.27.+a

INTRODUCTION

Transition metal compounds with strongly interacting electrons are interesting systems to study because they display an extremely wide range of different possible orderings and excitations. The occurrence of this large variety of physical phenomena is mainly due to the fact that the electrons in these systems can be regarded as having separate and independent degrees of freedom related to their charges, spins and orbitals and to the lattice. Of these the orbital degree of freedom is of particular interest since it can couple on one hand to the spins via the superexchange interaction, and on the other hand to the lattice via the cooperative Jahn Teller effect [1, 2]. Couplings of this kind are hard to observe in most systems since they can be very easily obscured by more profound magnetic effects. In the pyroxene compound $NaTiSi_2O_6$ however, the coupling of spins and lattice via the orbitals may be visible, and in fact gives rise to a novel kind of phase transition: the orbital Peierls transition.

Titanium Pyroxene

The crystal structure of titanium pyroxene consists of chains of $Ti^{3+}O_6$ octahedra, separated by SiO_4 tetrahedra and Na^+ ions, as pictured in figure 1A [3]. The TiO_6 octahedra are edge-sharing, so that the titanium ions lie on separated zig-zag chains. Since the titanium ions all have one electron in the d-shell, these chains are effectively one dimensional spin 1/2 chains. The d-orbitals of the titanium atoms are split by the surrounding crystal field into low lying t_{2g} orbitals, and energetically less favorable e_g orbitals. For the low energy physics of this system we thus need to consider one

dimensional zig-zag chains with on each site a spin 1/2 occupying one of three possible, degenerate t_{2g} orbitals [3, 4, 5]. The orientation of the orbitals within the crystal structure is such that there are three different uniform orderings, as shown in figure 1B: the orbitals can be oriented completely parallel to both neighbors (d_{zx} orbitals); in this case there is negligible overlap between neighboring orbitals and thus also no exchange coupling between neighboring spins. Another possibility is the d_{xy} orientation. In that case the lobes of the orbitals point directly toward the neighbor on the same xy -plane, but they are exactly parallel to the orbitals on different xy -planes. Consequently there is an exchange coupling present between neighboring spins on the same xy plane, but there is no coupling to the spins on other planes. Finally, in the d_{yz} orientation the situation is just opposite to that of the d_{xy} case; now there is an overlap and an exchange coupling within the yz plane but not within the xy plane. Already at this level of the description it thus becomes clear that the orbital and spin ordering will necessarily be strongly dependent upon each other. We will see that eventually this will give rise to an orbital driven transition in which spin dimers are formed: the orbital Peierls transition.

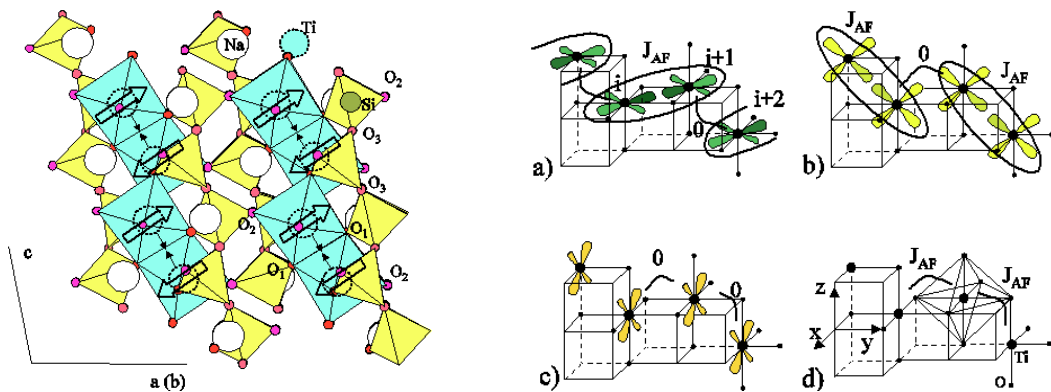


FIGURE 1. (A, left): The crystal structure. An indication of a possible spin ordering and dimerization has been added. (B, right): Possible uniform orbital orderings (a-c) and a schematic indication of the orientation of the TiO_6 octahedra (d).

EXPERIMENTAL DATA

Before we turn to the detailed description of our model of titanium pyroxene, let's first consider what experimental and calculational data that model will have to account for.

Powder samples of $NaTiSi_2O_6$ were first studied by Isobe et al. in 2002 [3]. They found that the temperature dependence of the magnetic susceptibility displays a peak at a temperature of 210 K, corresponding to the opening of a spin gap at that temperature. This behavior is quite different from what has been found in other pyroxene compounds (for example those containing vanadium or chromium instead of titanium): all of these display low temperature antiferromagnetic order [4]. From the fact that titanium pyroxene consists of one dimensional spin 1/2 chains, Isobe et al. concluded that instead of the antiferromagnetic ordering, there should be a kind of spin Peierls transition, possibly aided by the appearance of orbital order. The formation of a dimer phase at low temperatures was further supported by their finding a peak in the x-ray diffraction data which

splits into two exactly at 210 K. This splitting of the x-ray Bragg peak is indicative of the lowering of the crystallographic symmetry; in this case from a high temperature monoclinic phase to a low temperature triclinic phase.

Raman spectra of $\text{NaTiSi}_2\text{O}_6$ taken by Konstantinović et al., show that the phonon modes of the crystal are also affected by the transition at 210 K [4]. A couple of phonon modes shift in energy exactly at this temperature, and almost all modes get broadened above the transition temperature. This broadening of the modes is explained as an indication of having a high temperature dynamical Jahn Teller phase in which orbital fluctuations dominate. The transition at 210K should then correspond to a freezing of the orbitals. Because of the peculiar orientation of the orbitals and their effect on the size of the exchange integral, this in turn will lead to the formation of spin dimers, and thus to the opening of a spin gap. This scenario is further supported by the formulation of a model Hamiltonian for the spin and orbital degrees of freedom in the titanium chains.

Calculational Data

A crystal field analysis of the orbital dimer model however, has lead to a different explanation of the data [6]. In their calculations Bersier et al. find that the t_{2g} orbitals of the titanium ions are split in energy by the surrounding crystal field to such an extent that they can no longer be considered degenerate. Instead Bersier et al. propose that $\text{NaTiSi}_2\text{O}_6$ undergoes a structural transition, in which the crystal field produced by the oxygens rotates at 210 K. At high temperatures then, the ground state for the t_{2g} orbital configuration will be uniform in its overlaps along the chain, whereas at lower temperatures the rotation of the crystal field will induce a rotation of the orbitals, and thus lead to a dimerization of the lattice, and of the spin structure.

Yet another suggestion for explaining the experimental data is made by Popović et al., who used a density functional approach to study the system [7]. After calculating the bandstructure and density of states of the conduction electrons they arrive at the conclusion that the ground state of titanium pyroxene should not be a valence bond state, but rather a Haldane spin one chain: the dimerization of the titanium atoms should then cause the spins to align with their closest neighbor in order to effectively create a spin one, spread out over two neighboring titanium sites. These effective spins in turn tend to align antiferromagnetically, as is depicted in figure 2.

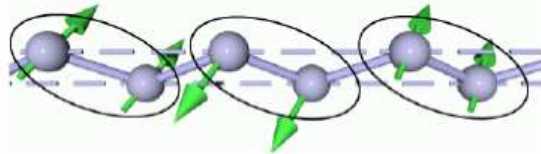


FIGURE 2. The ground state configuration as proposed by Popović et al. Upon inclusion of the quantum fluctuations, the *antiferromagnetic* bonds will turn into spin valence bonds.

In this paper we argue that all of the above observations, including both the experimental data and the results of the calculational studies, can be explained using the spin orbital model, originally proposed in Konstantinović et al. [4, 5]. We will show that the transition indeed should be considered an orbital Peierls transition; i.e. an orbital ordering transition which causes both a lattice dimerization and the formation of a spin

valence bond state. We will also predict an upper bound for the crystal field splitting of the titanium t_{2g} orbitals, and we will show that the Haldane chain can be obtained from the same model if we ignore quantum fluctuations.

THE MODEL

As mentioned before, the $Ti^{3+}O_6$ octahedra in titanium pyroxene form separated, quasi one dimensional zig-zag chains within the crystal structure. The Coulomb interaction between electrons on the same titanium site is so large that all exchange interactions can be determined by second order perturbation theory in the electron hopping parameter. For a single titanium site, the cubic surrounding formed by the oxygen octahedron splits the $3d$ states into three low lying t_{2g} states and two e_g states of higher energy. The Ti^{3+} ($3d^1$) ion then has one electron with spin $1/2$ which can be in any of the three degenerate t_{2g} orbitals. These orbitals have an overlap, and thus an allowed hopping path and magnetic interaction, with at most one neighbor (see figure 1B). Because the d_{zx} can be considered inert, we will neglect them in the following model description, and only focus on the remaining two t_{2g} orbitals. If we label these remaining orbitals as the eigenstates of some Ising like operator (for example the z -projection of some pseudospin: $T_i^z = 1/2$ corresponds to d_{xy} and $T_i^z = -1/2$ to d_{yz} being occupied on site i), then we can write the effective model Hamiltonian as [4, 5]:

$$H_0 = J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j \left[\frac{1}{4} + T_i^z T_j^z + \frac{(-1)^i}{2} (T_i^z + T_j^z) \right], \quad (1)$$

where i and j are on neighboring sites, J is the exchange integral and T^z are the orbital operators. The part between square brackets is such that this Hamiltonian will only give a nonzero result if it acts on a state in which xy (or yz) orbitals are occupied on neighboring sites and these orbitals also are in the same xy (or yz) plane. The ground state of this Hamiltonian will clearly be a state in which the orbitals are all in the same configuration (ferro-orbital order), and in which a spin singlet is formed on all of the bonds on which hopping is allowed by symmetry. The dimerization of the lattice that is seen in x-ray diffraction should then be explained as being due to the Jahn-Teller distortions associated with the orbital ordering. The ordering will in fact tend to lengthen the distance between orbital wavefunctions with lobes pointing towards each other and thus effectively reduce the distance between sites which are not magnetically coupled. At higher temperatures the orbital order will melt, and the spin valence bond pattern will disorder accordingly, thus explaining the disappearance of the spin gap at the transition. The result is a state with large orbital fluctuations which lead to an effective rising of the symmetry of the lattice (since the Jahn Teller distortions are averaged out), and thus a shift in some of the phonon frequencies. The fluctuations at the same time broaden the phonon peaks, and especially those of the modes along the $Ti - O$ bonds.

Crystal Field and Interchain Interactions

For the valence bond scenario to be applicable it is clearly important that the two active t_{2g} orbitals are at least nearly degenerate. To be able to determine the effects of a small crystal field splitting, we will include it in our model Hamiltonian.

On top of this, we will need to raise the dimensionality by introducing some weak interchain coupling parameter in order to be able to describe a true phase transition with our model. This interchain coupling will be done in a mean field fashion in our model.

Finally, we will also add an extra “bare” orbital-orbital interaction to the model which has been shown by Hikiara et al. to come directly from the tight binding perturbation theory, but has been neglected up to this point [8]:

$$H_1 = H_0 + (J_{CF} + J_{IC}) \sum_i T_i^z + \frac{J}{4} \sum_{\langle i,j \rangle} T_i^z T_j^z, \quad (2)$$

where J_{CF} is the size of the crystal field splitting, J_{IC} is the mean orbital field of all neighboring chains, given in terms of the small interchain coupling parameter J' (which in the present approach is approximated to be of the order of $J/10$), the number of neighboring chains z and the mean value for the orderparameter per site:

$$J_{IC} = \frac{zJ'}{N} \left\langle \sum_i T_i^z \right\rangle. \quad (3)$$

THE ANALYSIS

In our analysis of the model Hamiltonian (2), we have used three different calculational techniques. First we have neglected all quantum fluctuations by turning all spin operators into Ising operators, so that the Hamiltonian has an exact solution. We have also used a mean field treatment to solve the model including quantum fluctuations, but in doing so we needed to restrict our focus to XY spins. Finally then we have examined the behavior of the full Hamiltonian by doing a Monte Carlo simulation of the system.

Ignoring Quantum Fluctuations

If we turn off quantum fluctuations by projecting all spin operators onto the z -axis, then Hamiltonian (2) turns into:

$$H_{Ising} = J \sum_{\langle i,j \rangle} \left(\frac{1}{4} T_i^z T_j^z + S_i^z S_j^z \left[\frac{1}{4} + T_i^z T_j^z + \frac{(-1)^i}{2} (T_i^z + T_j^z) \right] \right) + J_{CF} \sum_i T_i^z, \quad (4)$$

neglecting the interchain coupling for the moment. It is trivial to see that the groundstate of this (classical) Hamiltonian is given by the configuration in which the orbitals are all aligned, and each spin is anti-aligned with its neighbor along the bond formed by the orbitals. In principle the relative orientation of the spins along the remaining bonds is

completely free, giving rise to an infinitely degenerate groundstate. This degeneracy will however be lifted by higher order effects that have been neglected in the approximation so far. As was shown in the work of Hikihara et al. the Hund's rule coupling will be the dominant higher order effect along the bonds where (4) gives no magnetic interaction [8]. The resulting groundstate then is no longer infinitely degenerate but consists of a ferro-orbital state with a chain of alternating ferro and antiferromagnetically aligned spins on top of it. This chain is exactly the ground state found by Popović et al. The fact that ignoring quantum fluctuations leads to the same ground state as the one observed through density functional calculations should come as no surprise: in density functional calculations these quantum fluctuations of the electron spin are neglected as well. Notice that the strongest spin-spin interaction in our model is in fact the antiferromagnetic coupling. The formation of a Haldane-chain like structure will therefore probably not be sustainable if we include quantum fluctuations: in that case the antiferromagnetic bonds will turn into spin valence bonds, and the small residual Hund's rule coupling will play no role in the transition (see figure 2).

Including Quantum Fluctuations

Now that we understand the groundstate of the classical model, let's go back to the full Hamiltonian (2), including all of the quantum fluctuations and the interchain coupling. To get some further analytical understanding of this Hamiltonian we will decouple spin-orbit interaction by introducing mean fields for their respective orderparameters:

$$\begin{aligned}
H_{MF}^S &= J \sum_{\langle i,j \rangle} (t + (-)^i \delta t) \vec{S}_i \cdot \vec{S}_j \\
H_{MF}^T &= J \sum_{\langle i,j \rangle} \left(\frac{1}{4} + s + (-)^i \delta s \right) T_i^z T_j^z + \sum_i (\delta s J + J_{CF} + J_{IC}) T_i^z, \quad (5)
\end{aligned}$$

where we have recursively defined the mean fields through the equations:

$$\begin{aligned}
s + (-)^i \delta s &= \langle \vec{S}_i \cdot \vec{S}_j \rangle \\
t + (-)^i \delta t &= \left\langle \frac{1}{4} + T_i^z T_j^z + \frac{(-1)^i}{2} (T_i^z + T_j^z) \right\rangle.
\end{aligned}$$

Even after decoupling the spin and orbital part of the Hamiltonian, the spin part still is a bit too involved to be solved head on. Instead we introduce a further approximation by using XY spins instead of full Heisenberg spins (so we project the spin vectors onto the xy plane). This way we do still include spin quantum fluctuations, so we expect the results to be qualitatively correct. Having done the projection, we are now in a position to solve the two parts of the coupled problem independently in terms of the mean fields.

The XY Spins

Let's first consider the spin part of the problem. Since we only have XY-spins left, we can simplify the problem by turning the spins into fermions, using the Jordan-Wigner transformation $S_i^+ S_{i+1}^- = a_i^\dagger a_{i+1}$. If we then also switch to Fourier space, we find:

$$H_{MF}^S = J \sum_k \left(t \cos(k) a_k^\dagger a_k + i \delta t \sin(k) a_{k+\pi}^\dagger a_k \right). \quad (6)$$

This fermion Hamiltonian can be forced into the diagonal form $H = \sum_q \epsilon_q c_q^\dagger c_q$ by introducing transformed fermions c^\dagger through $a_k^\dagger = \sum_q c_q^\dagger U_{qk}$. The ϵ_q and U_{qk} are then simply given by the eigenvalues and eigenvectors of the matrix

$$h_{qk} = t \cos(q) \delta_{q,k} + i \delta t \sin(q) \delta_{q+\pi,k}.$$

Having found this diagonal form it has then become trivial to check that the expressions for the mean spin field and the corresponding susceptibility are given by:

$$\begin{aligned} s &= \left\langle \frac{1}{N} \sum_i \left(a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i \right) \right\rangle = \frac{2}{N} \sum_{k,q} \left(\frac{1}{1 + e^{\beta \epsilon_k}} \cos(q) U_{kq} U_{qk}^\dagger \right) \\ \delta s &= \left\langle \frac{1}{N} \sum_i (-)^i \left(a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i \right) \right\rangle = i \frac{2}{N} \sum_{k,q} \left(\frac{1}{1 + e^{\beta \epsilon_k}} \sin(q) U_{k,q+\pi} U_{qk}^\dagger \right) \\ \chi_s &= \frac{\beta}{N} (\langle S_{tot}^z S_{tot}^z \rangle - \langle S_{tot}^z \rangle \langle S_{tot}^z \rangle) = \frac{\beta}{N} \sum_q \left(\frac{1}{1 + e^{\beta \epsilon_k}} \left[1 - \frac{1}{1 + e^{\beta \epsilon_k}} \right] \right). \end{aligned} \quad (7)$$

Here we have used the Jordan-Wigner transformation to define $S^z = -\frac{1}{2} + a_i^\dagger a_i$.

The Orbitals

Having diagonalized the spin sector, let's turn to the orbital part of the problem (5). Since the Hamiltonian involves only Ising operators, it is effectively classical. We can therefore solve this sector by adopting a transfer matrix approach. If we write the classical configuration as a state vector $\prod_i |T_i^z\rangle$, with every $T_i^z = \pm 1/2$, then we can write the partition function for the classical Hamiltonian H_{MF}^T in (5) as:

$$Z_{MF}^T = \sum_{T_1^z \dots T_N^z} \prod_{j=1}^{N/2} \left(\left\langle T_{2j}^z \left| \hat{R}^{even} \right| T_{2j+1}^z \right\rangle \left\langle T_{2j+1}^z \left| \hat{R}^{odd} \right| T_{2j+2}^z \right\rangle \right), \quad (8)$$

where the matrices \hat{R} , written out in the one particle basis $(+1/2, -1/2)$, are given by:

$$\hat{R}^{even} = \begin{pmatrix} e^{-\frac{\beta}{4}(J[3\delta s + s + 1/4] + 2J_{CF} + 2J_{IC})} & e^{-\frac{\beta}{4}(J[\delta s - s - 1/4] + 2J_{CF} + 2J_{IC})} \\ e^{\frac{\beta}{4}(J[3\delta s + s + 1/4] + 2J_{CF} + 2J_{IC})} & e^{\frac{\beta}{4}(J[\delta s - s - 1/4] + 2J_{CF} + 2J_{IC})} \end{pmatrix}$$

$$\hat{R}^{odd} = \begin{pmatrix} e^{-\frac{\beta}{4}(J[\delta s+s+1/4]+2J_{CF}+2J_{IC})} & e^{-\frac{\beta}{4}(J[3\delta s-s-1/4]+2J_{CF}+2J_{IC})} \\ e^{\frac{\beta}{4}(J[\delta s+s+1/4]+2J_{CF}+2J_{IC})} & e^{\frac{\beta}{4}(J[3\delta s-s-1/4]+2J_{CF}+2J_{IC})} \end{pmatrix}.$$

In the form (8), we can do the summations over the one particle states, to find that the value for the partition function in terms of the eigenvalues λ_{\pm} of $\hat{R} = \hat{R}^{odd}\hat{R}^{even}$, is simply given by:

$$Z_{MF}^T = \lambda_+^{N/2} + \lambda_-^{N/2}. \quad (9)$$

All that remains then, is to relate the quantities of interest to the partition function. This can easily be done if we use the relation $\langle \partial H / \partial x \rangle = -\beta / Z \partial Z / \partial x$:

$$\begin{aligned} t &= \frac{1}{N} \left\langle \sum_i \left(\frac{1}{4} + T_i^z T_{i+1}^z + \frac{(-)^i}{2} [T_i^z + T_{i+1}^z] \right) \right\rangle = \frac{1}{4} - \frac{1}{\beta N Z} \frac{\partial Z}{\partial s} \\ \delta t &= \frac{1}{N} \left\langle \sum_i \left(\frac{(-)^i}{4} + (-)^i T_i^z T_{i+1}^z + \frac{1}{2} [T_i^z + T_{i+1}^z] \right) \right\rangle = -\frac{1}{\beta N Z} \frac{\partial Z}{\partial \delta s} \\ \chi_T &= \frac{\beta}{N} (\langle T_{tot}^z T_{tot}^z \rangle - \langle T_{tot}^z \rangle \langle T_{tot}^z \rangle) = \frac{1}{\beta N} \left(\frac{1}{Z} \frac{\partial^2 Z}{\partial J_{CF}^2} - \left[\frac{1}{Z} \frac{\partial Z}{\partial J_{CF}} \right]^2 \right). \quad (10) \end{aligned}$$

These expressions, combined with the earlier expressions (7), enable us to solve for the mean fields self consistently, and in the process find the corresponding values for the mean field susceptibilities as well. Since we can do all of this as a function of temperature, we can then identify magnetic and orbital transition temperatures as being the peaks in the corresponding susceptibilities.

Monte Carlo

Apart from the above analytical considerations, we can also examine the full Hamiltonian (2) numerically, without any further approximations. A Monte Carlo treatment of this system turns out to be particularly easy to implement. Because magnetic interactions exist only along the bonds formed by neighboring orbitals, there can be no spin structures that spread beyond two sites: the spatial orientation of the orbitals allow for bonding with one of its neighbors only. This greatly simplifies the problem, since depending on the orbital configuration, a spin is now either isolated or in a two-spin valence bond state (either singlet or triplet). In both cases we can represent the spin variable by a classical variable, just like the orbitals, and thus we can get away with doing classical Monte Carlo instead of quantum Monte Carlo. We have therefor studied the system (2) using a one dimensional, classical Monte Carlo code for a chain of 100 sites, which we then couple to surrounding chains via the mean field. By varying the external fields in our simulation we were able to extract the spin and orbital susceptibilities as a function of temperature. Again we then identified the top in these susceptibility plots as the transition temperature of the material.

THE RESULTS

As we have seen the analysis of the model ignoring quantum fluctuations gave us the same groundstate as Popović et al. found in their calculations. However, our system consists of quasi one dimensional spin 1/2 chains, so quantum fluctuations can be expected to be important. These quantum fluctuations are taken into account in our mean field approach, as well as in the Monte Carlo simulation. The transition temperatures at which the spin and orbital order emerges in these calculations, are plotted as a function of the crystal field splitting in figure 3. In the region below $J_{CF} \simeq J$ both analyses clearly lead to a coincidence of the transition temperatures. This corresponds nicely to the observed opening of a spin gap combined with phonon shifts at 210 K.

A rough estimate for the crystal field splitting can be found by trying to fit our Monte Carlo data to the experimental data taken by Isobe et al. The results of this fitting procedure are shown on in figure 3B. The fit captures all qualitative features of the experimental curve, for a value of the crystal field splitting of $J_{CF} \simeq 0.8J$. Quantitatively it is a little off at the top of the susceptibility curve, but noticing the simplicity of the model, and the fact that we have only one fitting parameter (i.e. J_{CF}), this was to be expected. On the other hand, the crystal field analysis of Bersier et al. lead to a value for the crystal field splitting that was much higher than the exchange coupling. The actual value in titanium pyroxene, is expected to be lower than the value found in their calculations because of the approximations they were forced to make. With our result of figure 3, we can now turn around the reasoning, and make a new prediction: assuming that our model captures the correct physics of the transition in $NaTiSi_2O_6$, we can predict that the crystal field splitting J_{CF} will be no larger than the exchange coupling J .

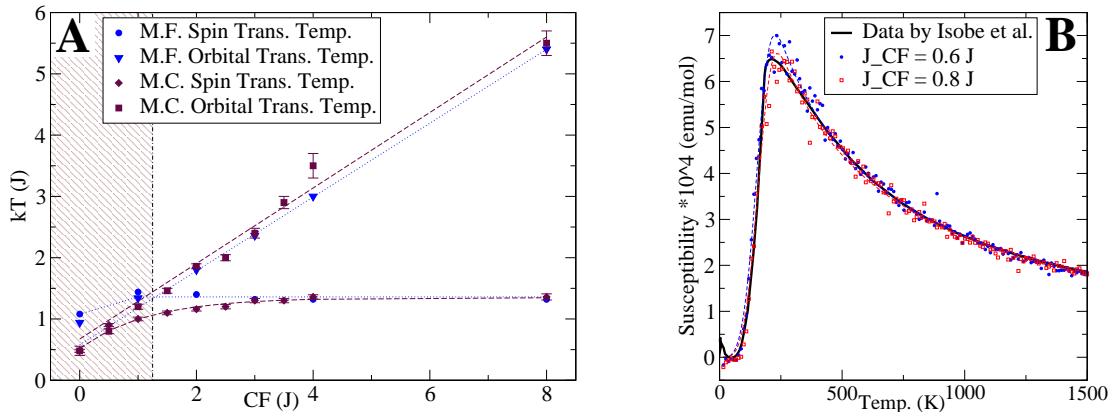


FIGURE 3. (A): The transition temperature as a function of the crystal field splitting, as found in the mean field and Monte Carlo calculations. The mean field data have been adjusted to account for the difference in energy between the excitations for XY spins and full Heisenberg spins. (B): A fit of the experimental data using the Monte Carlo results.

CONCLUSIONS

We have examined the microscopic model Hamiltonian originally proposed by Konstantinović et al. using a Monte Carlo simulation augmented by a mean field treatment and a classical approximation scheme. The model Hamiltonian incorporates both spin and orbital degrees of freedom, and was extended to also include the local crystal field splitting. All treatments of the model have provided strong support for the idea that an orbital Peierls transition occurs in the titanium chains of $NaTiSi_2O_6$. This transition is characterized by the uniform ordering of the orbitals, accompanied by a lattice dimerization and the formation of spin valence bonds.

Using these calculations we were able to understand all previously published data, including the density functional data which seemed to suggest the formation of a spin one Haldane chain. From the results of our calculations we were furthermore able to abstract a firm upper bound on the size of the crystal field splitting in this material: it should not be larger than the strength of the magnetic exchange interaction.

We thus conclude that our microscopic description is consistent with all available data, and that at 210 K, titanium pyroxene undergoes an orbital Peierls transition.

ACKNOWLEDGMENTS

We thank Jan Zaanen and Milan Konstantinović for fruitful discussions. This work was supported by FOM and the Dutch Science Foundation.

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