Sodium Pyroxene $NaTiSi_2O_6$: Possible Haldane Spin-1 Chain System

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Using a density functional approach, we study the structural and magnetic properties of the pyroxene compound $NaTiSi_2O_6$. While all previous workers are taking that $NaTiSi_2O_6$ is a quasi-one-dimensional $S = 1/2$ system, our theoretical results indicate that this is a Haldane $S = 1$ chain compound below the phase transition at 210 K. A good agreement is obtained between the calculated and the measured Ti-Ti distances in the dimerized low temperature phase. We present a simple explanation of the flow of the unusual phase transition which is taking place in this compound.

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Quantum fluctuations in chain and ladder magnetic systems produce such exotic phenomena as the Haldane gap in integer spin chains and the spin-Peierls (SP) transition in one-dimensional (1D) half-integer spin systems. The alkali metal pyroxene compounds $AM^{3+}B_2O_6$ ($A =$ alkali metal; $B =$ Si, Ge; $M =$ cations with valence state of 3^+) with transition metal M^{3+} have drawn considerable attention as low-dimensional magnets recently [1–5]. Several dilemmas already appeared in the attempts to describe the behavior of measured magnetic susceptibility, lattice parameters, and specific heat as functions of temperature. In $LiVGe_2O_6$ Millet *et al.* [1] proposed the presence of biquadratic exchange interaction and SP transition in the spin $S = 1$ chain, while in Ref. [2], the antiferromagnetic (AF) state driven by ferromagnetic (F) interchain couplings was suggested as the low-temperature state. In $NaTiSi_2O_6$, Isobe *et al.* [3] reported a typical behavior of magnetic susceptibility in a $S = 1/2$ $1D$ magnet, followed by a SP-like transition at 210 K, while Konstantinović *et al.* [5] indicated that the high temperature dynamical Jahn-Teller (JT) phase exibits a spontaneous breaking of translational symmetry into a dimerized, JT distorted, orbital ordered state under the formation of spin valence bonds.

The sodium-silicon system with titanium $NaTiSi_2O_6$ crystallizes in the space group $C2/c$ with monoclinic symmetry at room temperature [6,7]. The structure includes well-isolated zigzag chains of TiO_6 octahedra. Since titanium is in the Ti^{3+} valence state with all Ti ions in equivalent crystallographic positions, the chains are usually regarded as uniform linear chains with $S = 1/2$ being a candidate to show SP phase transition. Recently a transition at $T_c \sim 210$ K was observed in this compound [3,4]. The low temperature phase was identified to be of triclinic $P\bar{1}$ symmetry with the spin-gapped ground state [4]. The authors of Ref. [4] reported x-ray and neutron diffraction results with clear crystallographic evidence for the alternation of the Ti-Ti distance within the chain of edge shared TiO_6 octahedra in the low temperature phase. The transition is similar to SP transition in some respects but, strangely enough, transition occurs at a temperature significantly higher ($\sim$30 K) than that at the maximum point of the Boner-Fisher curve. The authors of Refs. [3,4] properly noted that the lack of well-developed short-range magnetic correlations within their $S = 1/2$ chain excludes magnetoelastic instability as a driving force for the transition at 210 K.

Phase transition in this compound is not well understood and it is not a standard one. Further theoretical and experimental investigations are obviously needed in order to answer the questions that had been raised by previous workers [3–5]. We saw here fertile ground for the first principles density functional theory (DFT) band structure calculations. A complex and striking crystal deformation seen and precisely measured by x-ray and neutron diffraction [3,4], together with the results of high quality magnetic susceptibility [3] and Raman scattering technique [5] measurements, inspired us to search for a more peculiar cause in order to explain the phase transition in $NaTiSi_2O_6$.

The purpose of the present Letter is to clarify the electronic structure of $NaTiSi_2O_6$ and to investigate the crystal structure stability by first principles calculations within the framework of a spin-dependent generalized gradient approximation (GGA) [8]. Only valence wave functions were treated explicitly and valence-core interactions were described by ultrasoft pseudopotentials [9,10] and nonlinear core corrections [11]. All atoms were allowed to relax until the 2-norm of the total force on them was less than 0.05 eV/Å. The basis set for the electron wave function is restricted to plane waves with a maximum kinetic energy of 35 Ry. An energy cutoff of 240 Ry was used for augmented electron density. Brillouin-zone integrations were done using a $(2 \times 2 \times 1)$ $\mathbf{k}$-point grid. To increase the stability of our iterative convergence procedure, the occupation numbers were taken according to a Fermi distribution function defined by a temperature of $k_bT_c = 0.03$ eV. The experimental lattice parameters used in the present calculations are [4] $a =$ 9.6955 Å, $b =$ 8.8851 Å, $c =$ 5.2968 Å, $\beta = 106.702°$

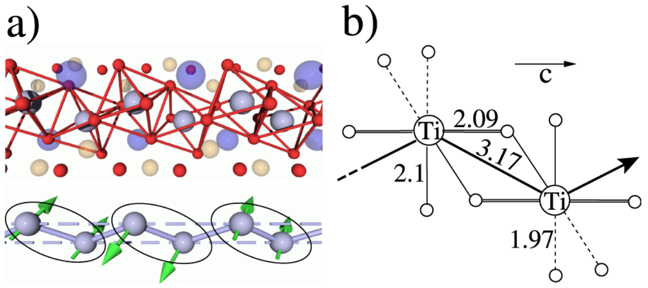

FIG. 1 (color online). (a) Schematic representation of the structure with mixed AF + F order for $C2/c$ symmetry of NaTiSi$_2$O$_6$. Large spheres represent Na atoms, middle-size bright spheres Si atoms, while small spheres represent O atoms. The Ti atoms are drawn in the cages of O atoms (upper part) and with spins on them (lower part). (b) Schematic representation of two-neighboring Ti^{3+} ions with their surrounding oxygen octahedra.

($C2/c$ at 300 K) and $a = 6.627$ Å, $b = 8.845$ Å, $c = 5.2895$ Å, $\alpha = 90.180°$, $\beta = 102.230°$, $\gamma = 47.031°$ ($P\bar{1}$ at 100 K). Figure 1(a) shows the experimental crystal structure of NaTiSi$_2$O$_6$ for $C2/c$ crystal symmetry with emphasized well isolated zigzag chain of titanium atoms. In this compound titanium atoms are located in the distorted oxygen octahedra with two opposite shorter and two longer bonds. Two bonds are of the same length, which we take to point into the c direction [$c/\bar{a} = 1.027$; cf. Fig. 1(b) and Ref. [4]].

We performed both nonmagnetic (P) and spin-polarized GGA calculations. Spin-polarized calculations were done for F, AF, and one calculation with *mixed magnetic order* (AF + F) [cf. Fig. 1(a)]. Starting from the experimental crystal structures with $C2/c$ and $P\bar{1}$ symmetries for the initial atomic configurations, we have calculated the electronic structure and carry out the optimization of the atomic positions. Our results are concisely presented in Table I and in Figs. 2 and 3. We have found that the optimized atomic positions with $P\bar{1}$ symmetry of NaTiSi$_2$O$_6$ were slightly more stable in all performed GGA calculations. The most stable solution has been obtained for ferromagnetically ordered spins along the titanium zigzag chains for both $P\bar{1}$ and $C2/c$ crystal symmetry. An insulating state is obtained in all cases, with modest d-d-type band gaps, whose magnitude is well known to be underestimated in the DFT calculations [12].

TABLE I. The total energies per formula unit calculated for the optimized atomic positions. The lowest energy for the two observed crystal structures is obtained for F order and this is taken as zero energy in both cases. We also present calculated magnetic moments at Ti sites (the sphere radii are equal to 1.2 Å), and the energy gap values.

Mag.	$C2/c$			$P\bar{1}$		
orders	E (meV)	$\mu_{\mathrm{Ti}}(\mu_B)$	E_g (eV)	E (meV)	$\mu_{\mathrm{Ti}}(\mu_B)$	E_g (eV)
F	0	0.83	0.28	0	0.83	0.2
AF + F	90	0.79	0.33	45	0.79	0.32
AF	370	0.54	0.38	260	0.25	0.49
P	595	0	0.08	425	0	0.09

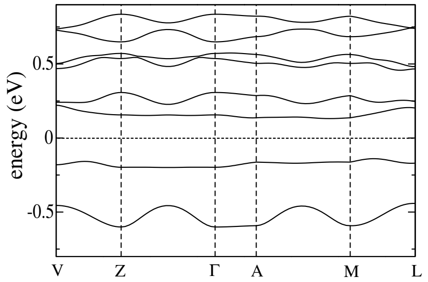

FIG. 2. Band structure of monoclinic structure with $C2/c$ symmetry calculated by the GGA for the AF + F state.

Figure 2 shows a spin-polarized AF + F band structure between -0.8 and 0.8 eV, which has predominantly Ti $3d$ character, along the high symmetry points of the monoclinic BZ. The oxygen O-$2p$-type bands are between -10.0 and -5.0 eV, approximately (for clarity, these bands are not shown). We additionally present in Fig. 3 the DOS close to the gap region for AF + F magnetic ordering for the $C2/c$ phase. The electronic structure of the AF + F magnetic ordering for the $C2/c$ phase is further analyzed by plotting the highest occupied and lowest unoccupied KS orbitals at Γ point. The KS wave functions (i) in Fig. 3 show a clear bonding between Ti $3d$ orbitals localized on closer Ti ions. The orbitals with different spin projections are positioned on neighboring titanium pairs. Direct overlap between $3d$ orbitals centered on closer Ti atoms, observed in the KS wave function (i), and a similar overlap of the $3d$ orbitals in a KS wave function at -0.53 eV below Fermi level (not plotted here), indicate that two electrons of the same spin, occupying those states, are shared by two Ti ions. Hence, two

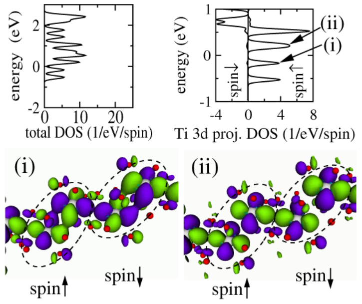

FIG. 3 (color online). Density of states (DOS) obtained by use of optimized atomic positions with $C2/c$ symmetry and AF + F magnetic order. Contour plots of the Kohn-Sham (KS) wave functions at (i) -0.18 eV (highest occupied states) and (ii) 0.18 eV (lowest unoccupied states) at the Γ point in the Brillouin zone (BZ). The KS wave functions for both spin projections are plotted. The change in color from bright gray to dark gray corresponds to the phase difference of π radians. Only Ti (large gray balls) and O (small dark grey balls) atoms are shown.

closer Ti ions can be considered as an effective site carrying magnetic moment of $2\mu_B$. The magnetic ordering between the effective sites is antiferromagnetic. At variance to the KS wave function (i), the KS wave function (ii) in Fig. 3 does not show bonding between respective Ti $3d$ orbitals. The lack of the bonding character gives rise to an energy increase of 0.36 eV with respect to the KS wave functions (i). The results of a similar analysis in the case of the F magnetic ordering show the strong bonding and nonbonding character of highest occupied and lowest unoccupied Kohn-Sham orbitals, respectively. Now that the band structure and DOS are plotted in this way, it seems evident that this compound is quasi-one-dimensional with the topmost valence bands of Ti $3d$ character.

The intention of present work is not to discuss all the details which follow from our quite complete band structure calculations [13]. In what follows we concentrate on the results of calculated stability of the supposed magnetic orderings in $NaTiSi_2O_6$ with $C2/c$ symmetry in order to comprehend the transition to the spin-gapped state observed in this compound at ~210 K. The question of significant interest is the nature of two topmost titanium $3d$ valence bands. With the appropriately chosen local coordinate system, we have obtained that these bands for AF + F ordering are of $3d_{xy}$ and $3d_{yz}$ character [14]. It should be probably explained here why we put our trust on the mixed magnetic ordering, which is denoted by AF + F, and schematically depicted in Fig. 1(a). At the beginning, we started with ordinary AF and F order in titanium chains of $NaTiSi_2O_6$. After we found a significant difference in the stability of these two phases, lack of dimerization in Ti chains for more stable F phase, noticeable reduction in the value of magnetic moments at Ti sites for the AF solution (cf. Table I), not even to mention technical difficulties to stabilize true AF solution, we became aware that we should check if some more specific magnetic ordering is possible in this compound. Subsequently, we realized that titanium zigzag chains in $NaTiSi_2O_6$ with the mentioned mixed AF + F magnetic order could be that specific ordering. It is easy to figure out that definite deformation of a standard two-leg ladder with usual AF interaction along the legs and spin singlets (or even spin triplets) on the rungs could bring us to the supposed mixed AF + F ordering [cf. Fig. 1(a)]. This magnetic ordering has stability comparable with the ferromagnetic one and produces a dimerized solution in both $C2/c$ and $P\bar{1}$ crystalline phases of the investigated compound. The shorter distance between the titanium atoms for $C2/c$ ($P\bar{1}$) symmetry is 2.95 (2.94) Å, while the longer distance is 3.18 (3.19) Å. Respective experimental results are [4] 3.05 and 3.22 Å.

In this compound the Ti atoms are positioned in a distorted oxygen octahedra [Fig. 1(b)] with two shorter, two longer, and two equal opposite Ti-O bonds. Because of the experimental fact that these octahedra are elongated, $c/\bar{a} = 1.027$ [4], we should take that three t_{2g} orbitals split into a low lying doublet (d_{xy}, d_{yz}) and a single orbital d_{xz} above this doublet [15]. Our band structure results about the character of the two topmost valence Ti $3d$ bands are in accordance with this well-known fact.

Although the ferromagnetic state is the most stable one for the $C2/c$ symmetry of the $NaTiSi_2O_6$ compound, we believe that the electronic structure for the mixed AF + F state is more appropriate than the one for the F state. Experimentally observed magnetic susceptibility [3] is not in accordance with the ferromagnetism. By optimizing the atomic positions in $C2/c$ symmetry we were unable to get dimerization for the supposed F ordering.

We can also put some qualitative reasons to support our decision to use the AF + F state in order to comprehend physical properties of this compound. For ions with t_{2g} states, orbital degrees of freedom can order in the same way as spin moments do, and the magnetic structure can be strongly dependent on orbital ordering. Besides that, local spin density approximation–based calculations for semiconductors and insulators underestimate the tendency for the localization and the values for local magnetic moments.

All previous workers treated pyroxene $NaTiSi_2O_6$ as a quasi-one-dimensional spin 1/2 magnetic system [3–5]. The system evidently got into the spin-gapped dimerized state with alternate internuclear distances of 3.05 and 3.22 Å in the linear chain and quite unordinary temperature dependence of magnetic susceptibility [3,4].

The new natural picture is emerging from our band structure and crystal stability calculations.

First, AF order in a titanium quasi-one-dimensional chain is energetically less stable than mixed AF + F order. In the chain with a degenerate t_{2g} orbital at titanium sites, which are magnetically coupled by the close to 90° superexchange through neighboring oxygen atoms, pure AF order is not probable.

Second, materials with electrons on degenerate d orbitals display features typical for the JT effect; however, there is an important difference between the t_{2g} ions compared to the e_g ions. For the latter the orbital moment is quenched, and the spin orbit (SO) interaction is ineffective in such systems. For t_{2g} ions there exists a nonzero orbital moment $l_{\mathrm{eff}} = 1$ and correspondingly there is a SO interaction $\lambda \mathbf{l} \cdot \mathbf{s}$. In the seminal paper of Kugel and Khomskii [15] it is precisely explained how the SO interaction can, by itself, lift the orbital degeneracy. In typical situations it leads to a distortion (usually called magnetostrictive distortion) opposite in sign to the one caused by the JT effect. In the compounds which contain electrons on t_{2g} orbital levels, octahedra around $3d$ ions may distort along different "channels." In some of them the ground state is determined by JT distortion and then the octahedra are compressed ($c/a < 1$), while in the others, which distort "along the spin-orbit channel," a magnetostricive deformation of opposite sign is in action (elongation $c/a > 1$, exactly what we have for the $C2/c$

symmetry in our system [4]). A lifting of the degeneracy, which occurs simultaneously with the magnetic ordering, is the characteristic feature of the compounds in which $\mathbf{l} \cdot \mathbf{s}$ coupling determines the ground state. In typical systems where the JT effect dominates this happens independently and usually at higher temperatures than any magnetic ordering. Let us note that, although the Ti-O bonding asymmetry looks large enough that one might easily expect significant crystal field splittings and effective SO interaction quenching, this does not happen. Both our band structure results, which have given the character of Ti 3*d* bands in the gap region, and the recent experimental results, which have shown that the $NaTiSi_2O_6$ crystal is effectively more symmetric (on larger time scales the TiO_6 octahedra appear to be less distorted at high temperatures [5]), support the point of view about unquenched SO interaction and its importance for lifting of the quasidegeneracy.

Third, when directions of the spins are random, degenerate orbital states are equally occupied. Below the spin ordering temperature, however, the direction of the spins which are subject to a strong exchange field is fixed and consequently the orbital states, which are coupled with the spin, are no longer equally occupied and the shape of the electronic cloud changes its symmetry. The crystal distortion, which produces the maximum energy lowering of an orbital state, will be favored [16].

This is exactly what is going on at the transition temperature in the system we are investigating. Because of the elongated octahedra around titanium atoms we have obtained double quasidegeneracy of respective 3*d* valence states, e.g., the two topmost valence bands are of d_{xy} and d_{yz} character for $C2/c$ symmetry. Lifting of double quasidegeneracy goes along the spin-orbit channel.

When the system passes over into the mixed AF + F ordered state, we get effectively AF chains of spin $S_{\mathrm{eff}} = 1$, SO interaction becomes effective, dimerization with transition to $P\bar{1}$ symmetry starts, and the Haldane spin gap opens. This can be seen from the much faster lowering of the magnetic susceptibility below 210 K than in the case of spin 1/2 antiferromagnetic chains with SP transition [3].

In the present Letter we show that the experimentally observed deformations of octahedra around Ti atoms could explain the simultaneous appearance of magnetic and structural transition in the $C2/c$ structural phase. More precisely, magnetic ordering which is most probable in our *ab initio* calculations confirm and supplement the picture which follow from careful observation and investigation of experimentally observed crystallographic data.

In conclusion, we suggest a new theoretical explanation of the very peculiar magnetostructural phase transition with dimerization in one-dimensional titanium zigzag well-isolated chains, spin gap formation in the spectrum of magnetic excitations, and spin triplet states formation which transforms a $NaTiSi_2O_6$ system from spin $S = 1/2$ to a Haldane spin $S = 1$ one-dimensional system. By analyzing the energy dispersion and the position of Ti 3*d* states, rendered by first principle calculations, we conclude that the picture of the transition emerging from our calculations is in accordance with the experimentally observed crystallographic details.

We thank Z.V. Popović for stimulating our interest in this compound and E. Ninomiya for sending us the structural data for $P\bar{1}$ symmetry. Support is acknowledged from the Serbian MNTR under Grant No. 2013. The calculations were performed at the central computational facilities of the Ecole Polytechnique Fédérale de Lausanne and of the Swiss Center for Scientific Computing.

[1] P. Millet *et al.*, Phys. Rev. Lett. **83**, 4176 (1999).

[2] M. D. Lumsden *et al.*, Phys. Rev. B **62**, R9244 (2000).

[3] M. Isobe *et al.*, J. Phys. Soc. Jpn. **71**, 1423 (2002).

[4] E. Ninomiya *et al.*, Physica (Amsterdam) **329B**, 884 (2003).

[5] M. J. Konstantinović *et al.*, Phys. Rev. B **69**, 020409 (2004).

[6] H. Ohashi *et al.*, J. Jpn. Assoc. Mineral., Petrol. Econ. Geol. **77**, 305 (1982).

[7] After submission of this Letter, we learned that very extensive experimental investigation of the title compound was carried out by G. J. Redhammer *et al.*, Acta Crystallogr. Sect. B **59**, 730 (2003).

[8] J. P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).

[9] A. Pasquarello *et al.*, Phys. Rev. Lett. **69**, 1982 (1992); K. Laasonen *et al.*, Phys. Rev. B **47**, 10 142 (1993).

[10] We used computer code DACAPO developed by B. Hammer *et al.*, http://www.fysik.dtu.dk

[11] S. G. Louie *et al.*, Phys. Rev. B **26**, 1738 (1982).

[12] Very small band gaps were obtained on the basis of *P* GGA calculations. We expect this small gap to disappear for a denser **k**-point grid. Present *P* results were obtained by using a (4 × 4 × 2) **k**-point grid (calculations are very time-consuming). Besides that, our linear-muffin-tin-orbital (LMTO) calculations gave metallic solutions for both $C2/c$ and $P\bar{1}$ symmetry.

[13] We did complete GGA pseudopotential and LMTO calculations and a more detailed paper is in preparation [Z. S. Popović *et al.* (to be published)].

[14] The local *z* axes are going from Ti(1)/Ti(2) to the oxygen atoms in the *c* direction [cf. Fig. 1(b)].

[15] K. I. Kugel and D. I. Khomskii, Sov. Phys. Usp. **25**, 232 (1982).

[16] This exposition of lifting the near twofold degeneracy in the spin chain system $NaTiSi_2O_6$ is practically the same as the explanation of the similar splitting in several systems with a long-range AF order: J. Kanamori, J. Appl. Phys. **31**, 14S (1960).