Comment on “Sodium Pyroxene NaTiSi$_2$O$_6$: Possible Haldane Spin-1 Chain System”

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A rather rare phenomenon of an opening of the spin gap in transition metal oxides was observed in pyroxene NaTiSi$_2$O$_6$ and was interpreted as a formation of singlet Ti-Ti dimers [1, 2]. However, in the recent Letter [3] the authors challenged this picture. On the basis of spin polarized GGA calculations they argued that with decrease of the temperature this compound evolves into a Haldane phase, characterized by formation of one-dimensional S=1 chains.

This novel interpretation, however, is highly questionable. The authors claim that “direct overlap between 3d orbitals centered on closer Ti ions, ..., indicates that two electrons of the same spin, occupying those states, are shared by two Ti ions” (cursive ours). This picture however contradicts typical situation for short metal-metal bonds in insulating solids, especially those of spin S=1/2 ions.

Most probably the defect lies in the neglect of electronic correlations in the calculation method used in [3]. NaTiSi$_2$O$_6$ is known to be strong Mott insulator with the energy gap close to 2 eV [4], whereas the calculations of Ref. 3 lead to very small energy gaps 0.2-0.3 eV.

In order to take into account strong electronic correlations in Ti-3d shell, we performed for the LT phase (T=100 K) of NaTiSi$_2$O$_6$ the LDA+U calculations [5], which was proven very successful in similar cases [6, 7, 8]. The calculation scheme was realized in the framework of the linear muffin-tin orbitals method [9]. Crystal structure parameters were taken from Ref. 10. The values of on-site Coulomb interaction $U = 3.3$ eV and Hund’s rule exchange $J_H = 0.8$ eV parameters for Ti-3d shell were obtained in constrained supercell calculation [7].

In contrast to Ref. 3, the fully antiferromagnetic state (AFM) was found to have lowest total energy (see Tab.1). The total energy of F+AF state (ferromagnetically coupled antiferromagnetic dimers on short Ti-Ti bonds) is just a little bit larger. This indicates that the coupling between dimers is pretty small, $J_{\text{inter}} = 7$ K. On the contrary, the exchange interaction within Ti dimers is antiferromagnetic and rather strong: from the comparison of total energies of totally AFM and AF+F states we find $J_{\text{intra}} = 626$ K. Direct calculation of exchange integrals using the scheme of Ref. 11 gives very similar values for J’s. Thus, our results confirm the formation of singlet Ti-Ti dimers in the LT phase of NaTiSi$_2$O$_6$ as originally proposed [1, 2]. The spin-gap would be even bigger then the one found in the experiment, $\Delta_{\text{exp}} \sim 500$ K [1]. The obtained value of the band gap $E_g = 1.71$ eV is also of the right order [4]. Thus our calculations give a quite reasonable description of the main physical properties of NaTiSi$_2$O$_6$, very different from that proposed in Ref. 3.

In conclusion, we stress that by neglecting correlation effects [3] one gets incorrect description of magnetic properties of NaTiSi$_2$O$_6$, which definitely Mott insulator. Our calculations demonstrate the formation of singlet Ti-Ti dimers in LT phase of NaTiSi$_2$O$_6$ driven by corresponding orbital ordering [2], which strongly disagrees with the results and interpretations of Ref. 3.

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[1] M. Isobe et al., J. Phys. Soc. Jpn. 71, 1423 (2002)
[2] M.I. Konstantinović et al., Phys. Rev. B 69, 020409(R) (2004); T. Hikihara and Y. Motome, Phys. Rev. B 70, 214404 (2004).
[3] Z.S. Popović, Ž.V. Šljivančanin, and F.R. Vukajlović, Phys. Rev. Lett. 93, 036401 (2004).
[4] The color of NaTiSi$_2$O$_6$ sample is grayish green (M. Isobe, private commun.). It means that the band gap is of order of 2 eV.
[5] V.I. Anisimov et al., Phys. Rev. B 44, 943 (1991).
[6] I. Leonov et al., cond-mat/0508378;
[7] S.V. Streltsov et al., Phys. Rev. B 71, 245114 (2005).
[8] A. Seidel et al., Phys. Rev. B 67, 020405 (2003).
[9] O.K. Andersen and O. Jepsen, Phys. Rev. Lett. 53, 2571 (1984).
[10] G.J. Redhammer et al., Acta Cryst. B59, 730 (2003).
[11] M.I. Katsnelson and A.I. Lichtenstein, Phys. Rev. B 61, 8906 (2000).
TABLE I: Total energies (per dimer), values of magnetic moment and band gap for different magnetic solutions. Ti ions forming dimers with short Ti-Ti distances are connected by “−”.

| Magnetic ordering | Total energy (meV) | Spin moment (μB) | Band gap (eV) |
|------------------|--------------------|-----------------|---------------|
| AFM ↑ − ↓ ↑ − ↓  | 0                  | 0.91            | 1.71          |
| F+AF ↑ − ↓ ↓ − ↑ | 0.6                | 0.91            | 1.66          |
| AF+F ↑ − ↑ ↓ − ↓ | 54                 | 0.92            | 1.5           |
| FM ↑ − ↑ ↑ − ↑   | 53                 | 0.93            | 1.35          |