Comment on "Spin-Lattice Coupling and the Emergence of the Trimerized Phase in the $S=1$ Kagome Antiferromagnet $Na_2Ti_3Cl_8$"

Recently it was concluded based on the DFT + U results that one has to invoke complex factors such as biquadratic and ring exachanges to explain the structural transition in $Na_2Ti_3Cl_8$ at 200 K [1]. In this Comment we point out that this conclusion is not justified and that the suggested explanation is not necessary.

The simple picture, which is actually seen from calculations performed in [1], is that of the Peiers distortion. Ti^{2+} ions have an electronic configuration d^2. In the kagome structure of $Na_2Ti_3Cl_8$ the direct $d-d$ hopping between t_{2g}-orbitals would lead to the formation of three one-dimensional ($1D$) bands in three directions, formed by xy, xz, and yz orbitals, Fig. 1. Each Ti atom lies on the intersection of two such chains and would participate in two bands. With two electrons per Ti, each $1D$ band is half filled similar to VO_2, which would immediately lead to Peierls dimerization. And the breathing kagome structure of $Na_2Ti_3Cl_8$ corresponds exactly to such dimerization in all three directions (Fig. 1).

Exactly the same mechanism can explain the formation of trimers in other family of materials—$(Zn, Fe, Ni)_2Mo_2O_8$, which contain a kagome layer of Mo ions with the same electronic configuration [2–4]. This "orbital-driven" Peierls effect also explains the formation of clusters in many other materials, such as spinels [5–7], in another trimerized d^2 $LiVO_2$ and $LiVS_2$ systems [8–10].

Interestingly Peierls-like instability in $Na_2Ti_3Cl_8$ clearly manifests itself in [1]. The authors of [1] focus on the DFT + U results, which do not give lattice instability for the undistorted phase. However, one should stress that phonon frequencies get imaginary, i.e., the lattice becomes unstable, in simple nonmagnetic DFT calculations, see Table I in the Supplemental Material of [1]. Thus, already on the band level the systems tends to distort. This is nothing else but a manifestation of the Peierls instability.

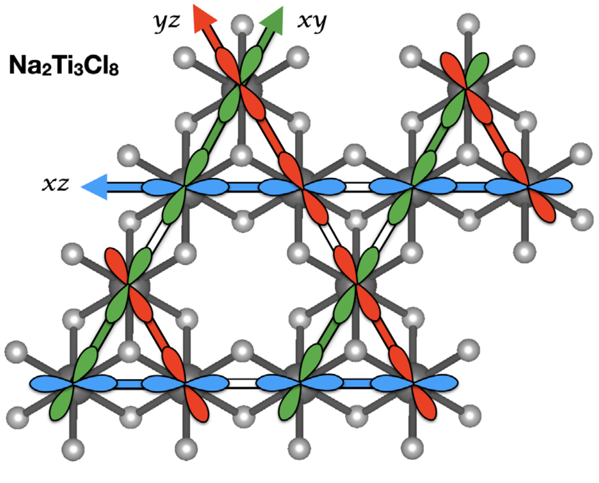

FIG. 1. Formation of Ti_3 trimers in kagome lattice of $Na_2Ti_3Cl_8$ due to dimerization of chains. Colored Ti-Ti bonds are short, white ones are long.

This is a typical situation that including correlations in a simplified way via the DFT + U approach [11] we often worsen the description of a system tending to form clusters. The famous example is VO_2, for which DFT reproduces a dimerized phase observed experimentally [12], while DFT + U stabilizes equally spaced V ions [13]. The tendency to form molecular orbitals, which is well described by a kinetic energy in DFT and which is of order of hopping parameter t, is substituted in DFT + U by a strong exchange coupling, which is typically much weaker $\sim t^2/U$. DFT + U (in contrast to cluster DMFT [14]) was constructed in a way to localize electrons not on molecular bonds, but on atomic orbitals and therefore it is not surprising that for $Na_2Ti_3Cl_8$ this method suppressed tendency to trimer formation.

While DFT band structure is considered in [1] "unphysical," it is actually not clear how one should deal with such situations as in $Na_2Ti_3Cl_8$—starting from the localized limit or, vice versa, first taking into account all band effects and coupling to the lattice, and only then including correlations. In this Comment we want to point out that the relevance of the second approach was overlooked in Ref. [1] and that it can explain the structural transition not only in this, but also in many other similar materials in a conceptually simple and straightforward way.

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