

Can the highly symmetric $SU(4)$ spin-orbital model be realized in $\alpha\text{-ZrCl}_3$?

A. V. Ushakov⁺, I. V. Solovyev^{+*×}, S. V. Streltsov^{+*1)}

⁺*Institute of Metal Physics, Russian Academy of Sciences, 620041 Ekaterinburg, Russia*

^{*}*Ural Federal University, 620002 Ekaterinburg, Russia*

[×]*International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

Submitted 1 October 2020

Resubmitted 12 October 2020

Accepted 18 October 2020

DOI: 10.31857/S1234567820220097

Highly symmetric models play a special role not only in the condensed matter physics, but in a whole physics. A special efforts were put into studying of highly symmetric spin and spin-orbital models, since they are important for description of magnetic materials. In particular it was shown that in case of the common-face geometry the Kugel-Khomskii spin-orbital Hamiltonian has unexpectedly high symmetry [1, 2]. Another example is the Kitaev model, which naturally appears in layered materials with the honeycomb lattice and heavy transition metal ions, such as Ir^{4+} or Ru^{3+} [3–7] with a possibility of spin-liquid ground state realization. Recently Yamada and co-authors [8] noticed that $\alpha\text{-ZrCl}_3$ with one electron residing in the relativistic $j_{\text{eff}} = 3/2$ manifold can be a physical realization of $SU(4)$ symmetric spin-orbital model.

In the present paper we performed *ab initio* study to check the hypothesis about realization of this model in $\alpha\text{-ZrCl}_3$. We used the generalized gradient approximation (GGA) [9] and projector augmented-wave (PAW) method as realized in the VASP code [10] for the calculations.

We used data of $\alpha\text{-RuCl}_3$ [6] for the structural optimization of $\alpha\text{-ZrCl}_3$ as a starting point and relaxed all possible parameters in magnetic GGA. As a result $\alpha\text{-ZrCl}_3$ dimerizes (Zr-Zr distance turns out to be smaller than in Zr metal [11]). The dimers are parallel to each other. Similar dimerization has been observed in $\alpha\text{-RuCl}_3$ under pressure [12], TiCl_3 [13] and many other titanites [14–17]. While the lowest in energy configuration corresponds to parallel dimers, the other one with arm-chair geometry is rather close in energy and one might expect that dimers might start to flow over the lattice in

$\alpha\text{-ZrCl}_3$ at temperatures ~ 500 K in the same way they do in Li_2RuO_3 [18].

We found that $\alpha\text{-ZrCl}_3$ appears to be an insulator even at the GGA level in contrast to metallic $\alpha\text{-RuCl}_3$. The lowest in energy t_{2g} orbitals looking towards each other in edge-sharing geometry form molecular orbitals and this results in strong bonding-antibonding splitting seen in the density of states plot (Fig. 1). Two electrons of the dimer occupy the bonding state leading to the non-magnetic ground state, while $\alpha\text{-RuCl}_3$ is magnetic.

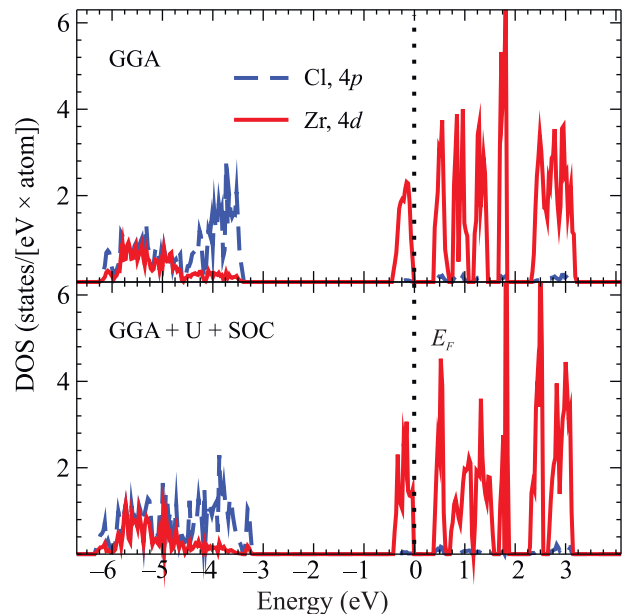


Fig. 1. (Color online) The partial densities of states of $\alpha\text{-ZrCl}_3$ calculated in the GGA and GGA + U + SOC approximations for the dimerized structure with parallel dimers

¹⁾e-mail: streltsov.s@gmail.com

Further we construct an effective five-orbital Hubbard-type model for Zr 4d bands using the Wannier functions technique and dimerized crystal structure, obtained from the optimization in the frameworks of GGA [19]. Without spin-orbit coupling, the t_{2g} levels are split by 8 and 186 meV, separating the lowest-middle and middle-highest levels, respectively. The spin-orbit coupling constant has been estimated to be about 70 meV. It additionally splits the lowest t_{2g} levels. Thus, the crystal field, though not particularly strong, lifts the orbital degeneracy, substantially modifies the $j_{\text{eff}} = 3/2$ character of the lowest energy states and kills $SU(4)$ invariance of the spin-orbital model.

The hopping integrals connecting occupied (o) states and unoccupied (u) states of the nearest sites i and j have been calculated to be $t_{ij}^{oo} = -1.262$ eV and $t_{ij}^{ou} = 0.136$ eV in $\alpha\text{-ZrCl}_3$. A very large hopping between occupied orbitals results in bonding-antibonding splitting ~ 2.5 eV. Using superexchange theory and estimates for U and J_H we found exchange coupling of the Heisenberg model as rather weak $J \sim 0.26$ meV. The constrained random phase approximation (cRPA) [19] yields $U = 1.53$ and $J_H = 0.58$ eV. These values were used in the subsequent GGA + U + SOC calculations. Basically U renormalizes GGA energy differences between different solutions discussed above, but it does not change the ground state of $\alpha\text{-ZrCl}_3$.

One may notice, that formation of molecular orbitals helps to quench orbital moment, which is tiny ($\sim 10^{-3}\mu_B$) for $\alpha\text{-ZrCl}_3$. However, in some dimerized or trimerized structures the spin-orbit coupling may play some role [20–22].

S. Streltsov is grateful to A. Gubkin for help with analysis of structural data in [23], to H. Jeschke for consultations on the crystal optimization of $\alpha\text{-RuCl}_3$ and especially to G. Jackeli and D. I. Khomskii for various stimulating discussions on spin-orbital physics.

This work was supported by the Russian Science Foundation through RSF 20-62-46047 research grant.

Full text of the paper is published in JETP Letters journal. DOI: 10.1134/S002136402022004X

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