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Can the highly symmetric $SU(4)$ spin-orbital model be realized in α-$ZrCl_3$?

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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 α-$ZrCl_3$ with one electron residing in the relativistic $j_{\rm eff} = 3/2$ 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 α-$ZrCl_3$. 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 α-$RuCl_3$ [6] for the structural optimization of α-$ZrCl_3$ as a starting point and relaxed all possible parameters in magnetic GGA. As a result α-$ZrCl_3$ 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 α-$RuCl_3$ 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 armchair geometry is rather close in energy and one might expect that dimers might start to flow over the lattice in α-$ZrCl_3$ at temperatures ~ 500 K in the same way they do in Li_2RuO_3 [18].

We found that α-$ZrCl_3$ appears to be an insulator even at the GGA level in contrast to metallic α-$RuCl_3$. 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 in the non-magnetic ground state, while α-$RuCl_3$ is magnetic.

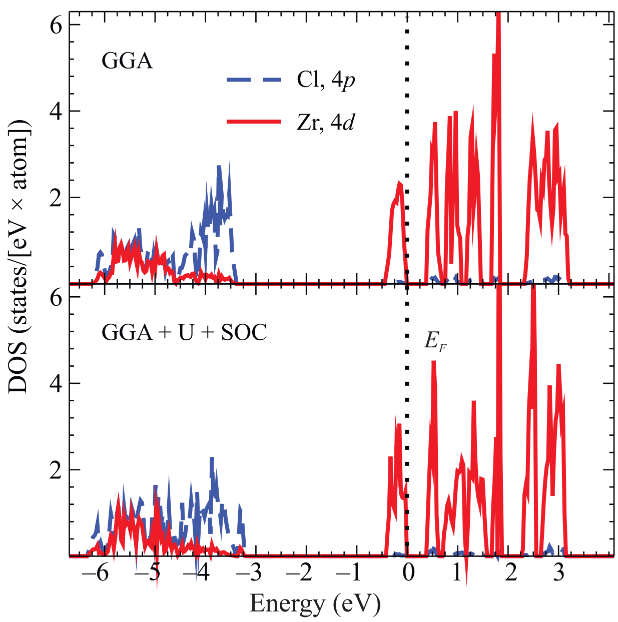

Fig. 1. (Color online) The partial densities of states of α-$ZrCl_3$ calculated in the GGA and GGA + U + SOC approximations for the dimerized structure with parallel dimers

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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 $j_{\rm eff} = 3/2$ 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 $t^{oo}_{ij} = -1.262$ eV and $t^{ou}_{ij} = 0.136$ eV in α-$ZrCl_3$. 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 α-$ZrCl_3$.

One may notice, that formation of molecular orbitals helps to quench orbital moment, which is tiny ($\sim 10^{-3}\mu_B$) for α-$ZrCl_3$. However, in some dimerized or trimerized structures the spin-orbit coupling may play some role [20–22].

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