Can the Highly Symmetric $SU(4)$ Spin–Orbital Model Be Realized in $\alpha$-ZrCl$_3$?

A. V. Ushakov$^a$, I. V. Solovyev$^{a, b, c}$, and S. V. Streltsov$^{a, b, *}$

$^a$ Institute of Metal Physics, Russian Academy of Sciences, Yekaterinburg, 620041 Russia
$^b$ Ural Federal University, Yekaterinburg, 620002 Russia
$^c$ International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044 Ibaraki, Japan

*e-mail: streltsov.s@gmail.com

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We study physical properties of layered $\alpha$-ZrCl$_3$ as a potential candidate for the physical realization of the $SU(4)$ spin–orbital model. Both DFT and DFT $+$ U $+$ SOC calculations show that this material most probably dimerizes at normal conditions. Therefore, it is unlikely that the symmetric $SU(4)$ model can be used for description of magnetic properties of $\alpha$-ZrCl$_3$ at low temperatures. In the dimerized structure electrons occupy molecular orbitals formed by the $\chi_y$ orbitals. One might expect a nonmagnetic ground state in this case. Interestingly the energy difference between various dimer packings is rather small and thus dimers may start to flow over the lattice as they do in Li$_2$RuO$_3$.

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INTRODUCTION

Highly symmetric models play a special role not only in the condensed matter physics, but also in a whole physics. The symmetry of such models of course manifests itself in their solutions, properties of the ground and excited states and finally in various observables. Therefore, a lot of efforts were made in attempts to solve these models and in search for their physical realizations. Special efforts were put into studying of highly symmetric spin and spin–orbital models, since they are especially important for description of magnetic materials. In particular, it was shown that the Kugel–Khomskii spin–orbital Hamiltonian in the case of the common-face geometry 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$^{3+}$. Strong spin–orbit coupling results in formation of effective angular momenta, which in a specific common-edge geometry turns out to be coupled in a very anisotropic way [3]. One of the important results was a possibility of spin–liquid ground state realization in Kitaev materials. The quest of such a state in canonical materials Na$_2$IrO$_3$, Li$_3$IrO$_3$, and $\alpha$-RuCl$_3$ unfortunately failed at normal conditions, see, e.g., reviews [4, 5], but further studies demonstrated that it can be indeed realized in external magnetic field [6, 7].

Meantime, Yamada et al. [8] noticed that other layered materials with the same structural motif, honeycomb lattices, but with one electron instead of one hole ($\chi\eta^4$ instead of $\chi\eta^5$) can be potentially described by a very symmetric spin–orbital Hamiltonian. They proposed that $\alpha$-ZrCl$_3$ with one electron residing in the relativistic $\chi\eta^3 = 3/2$ manifold can be a physical realization of this model. In this work, we performed ab initio study to check the hypothesis about realization of the $SU(4)$ symmetric spin–orbital model in this material.

While the crystal structure of $\alpha$-ZrCl$_3$ has been previously experimentally refined, both small and main unit cell settings presented in [9] do not provide appropriate crystal structures of edge-sharing ZrCl$_6$ octahedra forming honeycomb layers (presented in the left panel of Fig. 1). Therefore, the first important issue is establishing a probable candidate for the crystal structure of $\alpha$-ZrCl$_3$. This can be done by DFT.

In order to test available computational tools we started with a sister material, $\alpha$-RuCl$_3$, which was thoroughly studied in the past decade. Initial structural model for $\alpha$-RuCl$_3$ was based on the space group $P3_12$ [10]. However, more recent combined X-ray diffraction and DFT studies found the space group $C2/m$ is more appropriate [6].

CALCULATION DETAILS

We used the generalized gradient approximation (GGA) [11] and projector augmented-wave (PAW)
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method as realized in the VASP code [12] for the calculations. We utilized hard Cl pseudopotential and considered $s$ states as valent ones for Zr and Ru. For GGA + U calculations, we used its version as presented in [13]. The cutoff energy was chosen to be 600 eV and the mesh of $6 \times 4 \times 4$ points was used for integration over the Brillouin zone. We optimized cell volume, its shape and atomic positions in the structural relaxation, which was performed until the total energy change from one ionic iteration to another was larger than 0.1 meV.

RESULTS

Structural Optimization

It is interesting that without Coulomb correlations (treated on the level of GGA + U method) and the spin–orbit coupling the lowest total energy for $\alpha$-RuCl$_3$ corresponds to the ferromagnetic order with nearly isotropic lattice, the distance between nearest in the honeycomb plane Ru ions is 3.48 Å. For other magnetic structures in GGA, we obtained two slightly different Ru–Ru bonds with bond-length difference of $\delta_{\text{Ru}} \sim 0.06–0.16$ Å (depending on the configuration). This is close to results of [6], where $\delta_{\text{Ru}} \sim 0.04$ Å.

Then, after testing the computational scheme on $\alpha$-RuCl$_3$, one may perform the crystal structure optimization of $\alpha$-ZrCl$_3$. We used data of $\alpha$-RuCl$_3$ as a starting point and relaxed all possible parameters in magnetic GGA (cell volume, cell shape, atomic positions). The results are presented in Table 1.

Surprisingly, the lowest in energy turned out to be not a uniform structure (all Zr–Zr bonds are the same), but the dimerized one with dimers being parallel to each other. It is important that Zr–Zr distance in this state is smaller than in Zr metal [14]. The details of the electronic and magnetic structure as well as exchange interaction will be discussed further on, but already at this point one would expect that the dimerization is a result of formation strong molecular bonding (or orbital order) between two $t_{2g}$ orbitals looking towards each other. Stabilization of a single (per site) electron at the particular orbital will kill $SU(4)$ invariance of the spin–orbital model.

It is worth noting that while $\alpha$-RuCl$_3$ has a structure with nearly regular hexagons (and this is exactly what was obtained for this compound in our calculations), it is known to dimerize under tiny pressure of 0.2 GPa [15]. Furthermore, it dimerizes exactly in the same structure, featured by parallel orientation of the Ru–Ru dimers, as $\alpha$-ZrCl$_3$ in our calculations at the ambient pressure. In yet another material TiCl$_3$ with the same structural motif and the same (as in $\alpha$-ZrCl$_3$) $d^1$ configuration, a drop of magnetic susceptibility was observed experimentally at $\approx 217$ K [16], which is likely associated with the formation of the spin gap due to dimerization. A similar behavior was observed in many other titanates [17–20].

Table 1. Total energies (per formula unit), Zr–Zr bond lengths for various magnetic and structural configurations. Results of magnetic GGA calculations. Note, that Neel AFM structure converges to the nonmagnetic (NM), while stripe AFM to the parallel dimers solution

| Configuration        | Energy, meV | $d$(Zr–Zr), Å   |
|----------------------|-------------|-----------------|
| NM uniform           | 220         | 3.581 × 3       |
| FM uniform           | 176         | 3.607, 3.616 × 2|
| AFM zigzag           | 107         | 3.952, 3.435 × 2|
| Armchair dimers      | 50          | 3.068, 3.972 × 2|
| Parallel dimers      | 0           | 3.089, 3.928, 3.937|

Fig. 1. (Color online) Crystal structure of $\alpha$-ZrCl$_3$ obtained by the optimization of the $\alpha$-RuCl$_3$ structure. Zr–Zr dimers in the honeycomb lattice are marked by the red line.
It is rather interesting that 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 $\alpha$-ZrCl$_3$ at temperatures $\sim 500$ K in the same way they do in Li$_2$RuO$_3$ [21]. This theoretical prediction would be very interesting to check experimentally.

Contrary to $\alpha$-RuCl$_3$, the lowest energy state of $\alpha$-ZrCl$_3$ is no longer ferromagnetic. This is interesting, because for metallic systems at the beginning of the band filling ($t_{2g}$ configuration) one could generally expect the ferromagnetic ground state [28]. However, $\alpha$-ZrCl$_3$ appears to be an insulator even at the GGA level (the band gap is about 0.3 eV). This will certainly break the phenomenological rule [28], resulting in an AFM ground state.

**Electronic Structure**

The electronic structure of $\alpha$-ZrCl$_3$ in the dimerized phase is presented in Fig. 2. It is rather similar to another dimerized transition metal compound with the same structural motif Li$_2$RuO$_3$ [21–23]. These are Zr 4$d$ states, which are in vicinity of the Fermi level. We chose the local coordinate system for any pair of ZrCl$_6$ octahedra in such a way that the axes are directed to Cl ions and the common edge is in the $xy$ plane. Then the $xy$ orbitals looking towards each other in this edge-sharing geometry form molecular orbitals and this leads to strong bonding—antibonding splitting seen in the density of states plot. Two electrons of the dimer occupy the bonding state, resulting in the nonmagnetic ground state. Other $t_{2g}$ states are in between of these bonding and antibonding orbitals. The states at $\sim$3 eV are $e_g$ orbitals of Zr.

In order to gain further insight, 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 framework of GGA [24]. We start with the local, on-site effects: the crystal field splitting. Without spin–orbit coupling, the $t_{2g}$ levels are split by 8 and 186 meV, separating the lowest-middle and middle–highest levels, respectively (Fig. 3). The spin–orbit coupling constant is about 70 meV. Quiet expectedly, it additionally splits the lowest $t_{2g}$ levels, but has little effect on the position of other atomic states. Thus, the crystal field, though not particularly strong, lifts the orbital degeneracy and substantially modifies the $J_{\text{eff}} = 3/2$ character of the lowest energy states.

Other very important parameters are the hopping integrals. One may compute averaged transfer integrals connecting occupied ($o$) states and occupied and unoccupied ($u$) states of the nearest sites $i$ and $j$: $t_{ij}^{oo}$ and $t_{ij}^{ou} = \left( \sum_{b=ao} t_{ij}^{ob} t_{ij}^{bo} \right)^{1/2}$, respectively, where $b$ is the orbital index. Then, for the dimerized structure $t_{ij}^{oo} = -1.262$ eV and $t_{ij}^{ou} = 0.136$ eV. A very large hopping
between occupied orbitals results in bonding–antibonding splitting ∼2.5 eV.

For the uniform structure we have \( t_{ij}^{\text{oo}} = 0.067 \) eV and \( t_{ij}^{\text{ou}} = 0.100 \) eV. Then one can calculate exchange parameters of the Heisenberg model using superexchange theory for this structure. In the simplest approximation, neglecting asphericity of on-site Coulomb (\( U \)) and exchange (\( J_H \)) interactions in the five-orbital model, \( t_{ij}^{\text{oo}} \) contributes to the AFM coupling as \( \frac{(t_{ij}^{\text{oo}})^2}{U} \), while \( t_{ij}^{\text{ou}} \) contributes to both FM and AFM coupling as \( \frac{-(t_{ij}^{\text{ou}})^2}{U} \) and \( \frac{(t_{ij}^{\text{ou}})^2}{U - J_H} \), respectively. Using realistic estimates for \( U \) and \( J_H \) (see below), this yields weak total exchange coupling \( J ∼ 0.26 \) meV.

**Correlation Effects**

It has to be stressed that while all results presented above were obtained without account of on-site Coulomb correlations and the spin–orbit coupling, their inclusion to the calculation scheme does not change the main conclusion that α-ZrCl₃ tends to dimerize.

In order to have realistic estimation of Hubbard \( U \) and Hund’s \( J_H \) parameters, we used the constrained random phase approximation (cRPA) [24], which yields \( U = 1.53 \) eV and \( J_H = 0.58 \) eV. Particularly, the Coulomb interaction \( U \) is strongly screened, as expected at the beginning of the band filling [24]. 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 structure. The energy of the armchair configuration is 68 meV and of the AFM zigzag is 28 meV. Zr–Zr bond lengths in parallel dimers configuration are 3.094 Å.

One also needs to comment on the importance of the spin–orbit coupling. The orbital angular momentum in the lowest in energy structure is tiny (∼0.003 \( \mu_B \)) and therefore one may neglect this interaction in dimerized structure. This is rather natural since dimerization results in a strong deformation of the octahedra, the \( t_{ij}^{\text{oo}} \) manifold is split and the orbital angular momentum is quenched. Formation of molecular orbitals only helps this quenching. We note, however, that in some dimerized or trimerized structures the spin–orbit may play some role [25–27].

**CONCLUSIONS**

Using results of first principles electronic structure calculations, we have argued that the ideal honeycomb structure of α-ZrCl₃ has a strong tendency towards symmetry lowering via the formation of the Zr–Zr dimers, similar to other transition-metal compounds having formal electronic configuration \( d^1 \). Although the dimerization scenario has many interesting aspects, it seems to be at odds with the realization in this material high \( SU(4) \) symmetry required for the formation of the spin–orbital liquid state [8].

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