Two Regimes of the Kitaev Materials: Li_2RhO_3 and $Ag_3LiRh_2O_6$

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In this note, with the help of density-functional calculation and Hatree-Fock mean-field data, we build the low-energy effective Hamiltonians for two generation of Kitaev materials Li_2RhO_3 (LRO) and $Ag_3LiRh_2O_6$ (ALRO). Particularly, we show that ALRO is controlled by the Kramers doublet, and the Ising-anisotropy exchange is the only possible one can write down. Furthermore, except for the common effects comming from spin-orbital coupling (SOC) and trigonal distortion, we notice that there is another geometric distortion that breaks the RhO_4 coplane condition. Such distortion is neglegible for ALRO but commensurable in LRO.

尽挹西江，细斟北斗，万象为宾客。扣舷独啸，不知今夕何夕。

—— 张孝祥「水调歌头」

Contents

I. LOW-ENERGY EFFECTIVE HAMILTONIAN

A general strongly-interacting Hubbard-like Hamiltonian with rotational-invariant spin-spin interaction and arbitrary orbital degrees of freedom can be written as

$$H = J_1 \sum_{\langle ij \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \sum_{\langle ij \rangle} J^{\alpha\beta}_{2,ij} \tau^\alpha_i \tau^\beta_j + \sum_{\langle ij \rangle} J^{\alpha\beta}_{3,ij} (\boldsymbol{S}_j \cdot \boldsymbol{S}_j)(\tau^\alpha_i \tau^\beta_j) + \cdots . \tag{1}$$

Since there may be anisotropic terms for the orbital part of exchange like $\tau^z_i \tau^z_j, \tau^x_i \tau^x_j, \tau^x_i \tau^y_i$, etc., the general Hamiltonian (1) is really intractable for theoretical analysis. However, with the help of crystalline symmetry, in real materials many terms turn out to be vanishing. Particularly, we will show at the end of this section that, for ALRO, the allowed low-energy Hamiltonian can only be composed of Ising-like exchanges.

A. Octehedral Crystal Field

It is well-known in crystal field theory [1] that the spherical symemtric $3d$-orbitals will split into two-fold e_g orbitals (omitting the irrelevant radial part)

$$|d_{x^2-y^2}\rangle = \frac{1}{\sqrt{2}}(Y_2^{-2} + Y_2^2), \quad |d_{3z^2-r^2}\rangle = Y_2^0,$$

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and three-fold t_{2g} orbitals

$$|d_{zx}\rangle = \frac{1}{\sqrt{2}}(Y_2^{-1} - Y_2^1), \quad |d_{yz}\rangle = \frac{i}{\sqrt{2}}(Y_2^{-1} + Y_2^1), \quad |d_{xy}\rangle = \frac{i}{\sqrt{2}}(Y_2^{-2} - Y_2^2),$$

in the octahedral oxygen environment, with $Y_\ell^m(\theta, \phi)$ the familiar spherical harmonics, as is shown in FIG. 1.

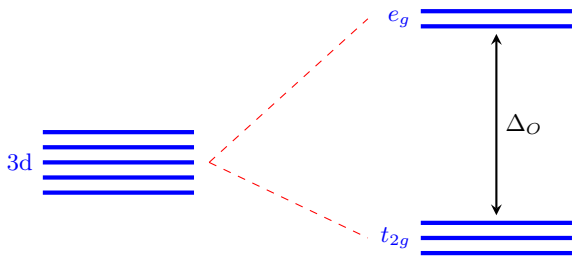

FIG. 1: **Octahedral Crystal Field Splitting.**

Depending on the energy scale between such e_g-t_{2g} splitting Δ_O and spin-orbital coupling (SOC) Δ_{SOC}, we will fall into high-spin and low-spin states with the electrons of $3d^5$ configuration on Rh^{3+}. If $\Delta_{\text{SOC}} > \Delta_O$, by Hunds rule each orbital of e_g and t_{2g} will be half-filled to maximize the total spins, and we are in the high-spin state. In contrast, if the energy scale of e_g-t_{2g} splitting is prominent (or at least comparable) $\Delta_O \geq \Delta_{\text{SOC}}$, then we are able to say that the five electrons occupy six degenerate (including spin degeneracy) t_{2g} orbitals first, leaving only one empty hole so we are in the low-spin state.

To determine which is the case, we can simply take a look at the numerical energy spectrum of relevant ten orbitals. The trick is to first turn off the SOC in the DFT calculation (It can be added back by hand in the analysis of our wannierized tight-binding model). The results are listed in TABLE. I.

	LRO without SOC	LRO with SOC
t_{2g}	8.72285690310658	8.67598932812092
	8.72285690310658	8.675989328120933
	8.752896854397369	8.730099641245802
	8.752896854397376	8.730099641245813
	8.819499295755385	8.884903534921547
	8.819499295755387	8.88490353492155
e_g	11.635763926129755	11.642613587390171
	11.635763926129762	11.642613587390173
	11.789525861249246	11.79621047265392
	11.789525861249246	11.796210472653923

	ALRO without SOC	ALRO with SOC
t_{2g}	9.166541771379567	9.142025045656869
	9.166541771379569	9.142025045656881
	9.42234146297424	9.371810987827514
	9.422341462974245	9.371810987827523
	9.436907961253517	9.50713680312438
	9.436907961253526	9.507136803124386
e_g	12.329049772638278	12.336116219990881
	12.329049772638282	12.336116219990888
	12.406462151678134	12.413564910334824
	12.406462151678145	12.41356491033483

TABLE I: Energy Spectrum of $3d$ Orbitals for both LRO and ALRO with/without SOC.

Although the existence of SOC slightly shift both ten energy levels, the e_g-t_{2g} splitting gap $\Delta_O^{\text{LRO}} \simeq 2.94756\text{eV}$ and $\Delta_O^{\text{ALRO}} \simeq 3.0345\text{eV}$ are large enough so that we can safely conclude that the discussion of low-energy physics can be confined in the subspace of t_{2g} orbitals only. The name of orbitals can also be checked by their eigenstates and ???

There is a well-known phenomena called t_{2g}-p *equivalence* [2] stating that the *effective* angular momentum within t_{2g} subspace quench to have a similar form of that on p-orbitals

$$\mathbf{L}|_{t_{2g}} = -\mathbf{L}|_p. \tag{2}$$

This can be seen more clearly by rotating the aforementioned basis of t_{2g}-subspace to

$$|+1\rangle \equiv \frac{1}{\sqrt{2}}(|d_{zx}\rangle - i|d_{yz}\rangle) = Y_2^{-1}, \quad |0\rangle \equiv i|d_{xy}\rangle = \frac{1}{\sqrt{2}}(Y_2^2 - Y_2^{-2}), \quad |-1\rangle \equiv \frac{1}{\sqrt{2}}(|d_{zx}\rangle - i|d_{yz}\rangle) = -Y_2^1.$$

and express the 5×5 matrix of angular-momentum operator in the basis of $\{|+1\rangle, |0\rangle, |-1\rangle, |d_{3z^2-y^2}\rangle, |d_{x^2-y^2}\rangle\}$

$$L_x = -\frac{1}{\sqrt{2}} \left(\begin{array}{ccc|cc} 0 & 1 & 0 & -\sqrt{3} & -1 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & \sqrt{3} & 1 \\ \hline -\sqrt{3} & 0 & \sqrt{3} & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 \end{array}\right),$$

$$L_y = -\frac{i}{\sqrt{2}}\left(\begin{array}{ccc|cc} 0 & 1 & 0 & \sqrt{3} & 1 \\ -1 & 0 & 1 & 0 & 0 \\ 0 & -1 & 0 & \sqrt{3} & -1 \\ \hline -\sqrt{3} & 0 & -\sqrt{3} & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 \end{array}\right),$$

$$L_z = -\left(\begin{array}{ccc|cc} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2 \\ 0 & 0 & -1 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 \\ 0 & -2 & 0 & 0 & 0 \end{array}\right).$$

Clearly within the subspace of t_{2g} (3×3 block), the angular mometum operator takes exactly the form of that on the $\ell = 1$ p-orbitals (off-diagonal compoents can be igonored due to the large gap Δ_O). While within the subspace of e_g (2×2 block), $\mathbf{L}|_{e_g} \equiv 0$ and the further SOC are *quenched*.

But this is not the end of the story. Due to the competition between SOC and geometric distortion (here is trigonal distortion), we will end up with more fine structure of energy splitting on the t_{2g} orbitals, as may be already noticed in TABLE I.

B. Spin-Orbital Coupling

When spin-orbital coupling (we denote $\boldsymbol{L}|_{t_{2g}} \equiv \boldsymbol{l}_{\text{eff}}$)

$$H_{\text{SOC}} = \lambda \boldsymbol{l}_{\text{eff}} \cdot \boldsymbol{S} \tag{3}$$

is dominant, which is the case for LRO, clearly the t_{2g} triplet $l_{\text{eff}} = 1$ and $S = 1/2$ gives the $j = 1/2$ doublet as the ground state, as is shown in FIG. 2. The small splitting energy $\Delta_{\text{SOC}} \simeq 0.0816$eV can be read from TABLE I.

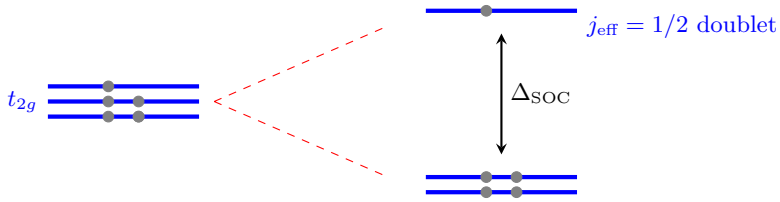

FIG. 2: **Splitting from SOC.**

The superexchange can then be projected to such subspace through a $\tau = 1/2$ pseoduspin operator. The effective Hamiltonian for strongly localized electrons ($U > J_H \gg t$) has already been well-studied for perovskites with 180° exchange, e.g., Sr_2IrO_4, and 90° exchange, i.e., Na_2IrO_3, in [3]. Since in LRO the RhO_6 octahedra is edge-sharing, Jackeli and Khaliullin's result shows that the effective Hamiltonian is Kitaev-like [4]

$$H = -J\sum_{\langle ij\rangle} \mathcal{H}_{ij}^{(\gamma)} = -J\sum_{\langle ij\rangle} S_i^\gamma S_j^\gamma, \tag{4}$$

where $\gamma = \{x, y, z\}$ labeling the types of ij-bonds.

C. Trigonal Distortion with SOC

In reality, chances are the RhO_6 octahedra to be compressed or streched along $\hat{z}$ axis. Such trigonal crystal field breaks the t_{2g} triplet into an a_{1g} singlet [5]

$$|a_{1g}\rangle \equiv |d_{3z^2-r^2}\rangle,$$

and e_g' doublet

$$|e_{g1}'\rangle \equiv \frac{2}{\sqrt{6}}|d_{xy}\rangle - \frac{1}{\sqrt{3}}|d_{zx}\rangle, \quad |e_{g2}'\rangle \equiv \frac{2}{\sqrt{6}}|d_{x^2-y^2}\rangle - \frac{1}{\sqrt{3}}|d_{yz}\rangle,$$

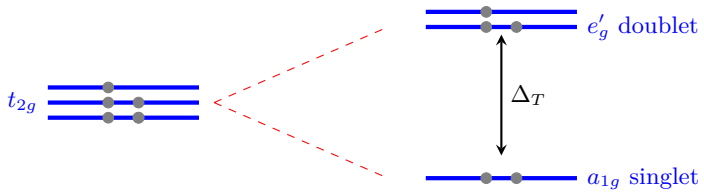

FIG. 3: **Splitting from Trigonal Distortion.**

which is the case for our ALRO, as is show in FIG. 3. This time the energy splitting is a little bit larger $\Delta_T = 0.2630$eV.

Although a first glance of the four-fold degenerate e'_g orbitals in FIG. 3 may pop up the idea that the effective orbital momentum to be $l_{\text{eff}}|_{e'_g} = 3/2$, a careful representation of $\boldsymbol{l}_{\text{eff}}$ in the new basis of $\{|a_{1g}\rangle, |e'_{g1}\rangle, |e'_{g2}\rangle\}$ tells you NOT. In fact, the t_{2g} effective orbital momentum operator now takes a strange form of

$$l_{\text{eff},x} = \left(\begin{array}{c|cc} 0 & \cdots & \\ \hline \vdots & 0 & 0 \\ & 0 & 0 \end{array}\right), \quad l_{\text{eff},y} = \left(\begin{array}{c|cc} 0 & \cdots & \\ \hline \vdots & 0 & 0 \\ & 0 & 0 \end{array}\right), \quad l_{\text{eff},z} = \frac{1}{3}\left(\begin{array}{c|cc} 0 & \cdots & \\ \hline \vdots & 0 & -i \\ & i & 0 \end{array}\right). \tag{5}$$

Again due to the comparable large gap Δ_T, we can safely narrow our discussion in the subspace of e'_g orbitals, giving the only non-vanishing component of angular momentum matrix

$$l_{\text{eff},z}|_{e'_g} \propto \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \equiv \tau^y. \tag{6}$$

Therefore, the effective Hamiltonian (1) drastically simplify to

$$H_{\text{eff}} = J_1 \sum_{\langle ij \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j + \sum_{\langle ij \rangle} J_{2,ij} \tau_i^y \tau_i^y + \sum_{\langle ij \rangle} J_{3,ij} (\boldsymbol{S}_i \cdot \boldsymbol{S}_j)(\tau_i^y \tau_j^y) \tag{7}$$

with Ising-anisotropy.

The above discussion only consider the effect from trigonal distortion. Now if we take the SOC as a perturbation, by adding (7) with (all other components are suppressed in projection into the e'_g subspace)

$$H_{\text{SOC}} = \lambda \tau_y S_y, \tag{8}$$

then clearly the low-energy state is of *two-fold* degenerate

$$|\mu_z = 1\rangle \equiv |\tau_y = 1, S_z = 1/2\rangle, \quad |\mu_z = -1\rangle \equiv |\tau_y = -1, S_z = 1/2\rangle, \tag{9}$$

forming a Kramers doublet.

Within the final low-energy subspace of $\{|\mu_z = \pm 1\rangle\}$, the only possible exchange we can write down is of Ising-like

$$H_{\text{eff}} = \sum_{\langle ij \rangle} \mu_i^z \mu_j^z + \cdots. \tag{10}$$

That is why we expect the ground state of ALRO to be in Ising-like phase (at least along one direction), and the g-factor will be anisotrpic.

D. Extra Distortion

As is shown in the numerical TABLE I, except for the above discussions of SOC and trigonal distortions, the fully-filled $j = 3/2$ quadruplet of t_{2g} orbitals are actually not perfectly degenerate. There exists an extra mecahnism splitting them, with a tiny gap about $\Delta_E^{\text{LRO}} \simeq 0.03$eV, which is quite comparable with Δ_{SOC} (about 36.7%). A similar splitting occurs in ALRO, but the energy scale $\Delta_E^{\text{ALRO}} \simeq 0.0146$eV is much smaller in comparison with Δ_T (about merely 5.56%).

This can be ascribed to the extra distortion we find on the wannier centers of RhO_6 octehedron: For the octahedron with merely trigonal distortion, the RhO_4 plane should keep coplane. But a visualization of wannier centers evidently exihibit a violation of such coplane condition, as shown in FIG. 4.

In light of this extra distortion, the Khaliullin's requirement of a *strong* SOC may not be satisfied in LRO, and their effective Kitaev Hamiltonian may also not be accurate. While for ALRO we belive that the above low-energy analysis won't be altered.

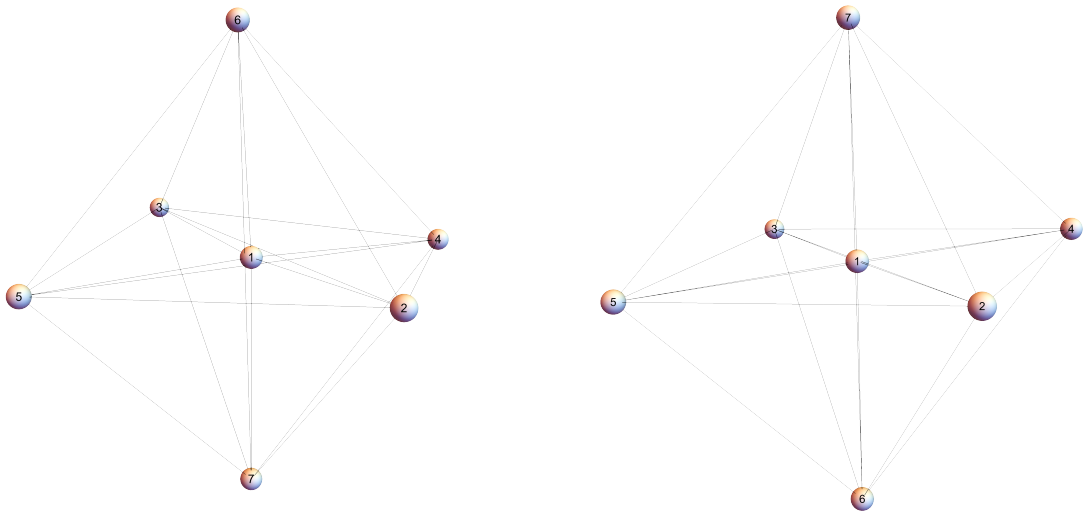

FIG. 4: **Wannier Centers of LRO and ALRO**: The left graphics is for LRO, while the right one is for ALRO. We draw the diagonal line to compare with the O-Rh-O plane. The discrepancy is in accordance with the strength of extra energy splitting we found in numerical results. Thus the extra distortion is much stronger in LRO than that for ALRO.

II. LONG-RANGE ORDER

A. LRO

B. ALRO

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[4] A. Kitaev, Annals of Physics **321**, 2 (2006).
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