On the possibility of excitonic magnetism in Ir double perovskites

K. Pajskr,1 P. Novák,2 V. Pokorný,3,4 J. Koloreně,3 R. Arita,5,6 and J. Kunes3,†

1Charles University in Prague, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
2Institute of Physics, Academy of Sciences of the Czech Republic, Cukrowicza 10, 162 53 Praha 6, Czech Republic
3Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 182 21 Praha 8, Czech Republic
4Theoretical Physics III, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, D-86135 Augsburg, Germany
5RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan
6IST ERATO Isobe Degenerate π-Integration Project, Advanced Institute for Materials Research (AIMR), Tohoku University, Sendai, Miyagi 980-8577, Japan

(Dated: December 3, 2015)

We combine several numerical and semi-analytical methods to study the 5d double perovskites Sr2YIrO6 and Ba2YIrO6 which were recently proposed to exhibit excitonic magnetism. Starting from the density functional theory and constrained random phase approximation we construct effective multi-band Hubbard models. These are analyzed by means of static and dynamical mean-field theories and strong coupling expansion. We find both materials to be insulators, but, contrary to the experimental claims, with a large spin gap of several hundreds meV preventing formation of an ordered state at low temperature.

PACS numbers: 71.70.Ej,71.27.+a,75.40.Gb

I. INTRODUCTION

The discovery of new spin-orbit related phenomena and states of matter lead to an immense increase of interest in materials containing 5d elements, Ir and Os in particular. Among the new effects, Khalilullin recently proposed a possibility of excitonic condensation in d materials with cubic local symmetry. The singlet atomic ground state \( |s\rangle \) promises no interesting low-energy physics. However, if the energy of the lowest excitation, a magnetic moment carrying triplet \(*\rangle\), is sufficiently small, the inter-atomic exchange due to electron hopping may lead to formation of an ordered state - excitonic magnet. Thanks to the singlet-triplet exchange processes, the \( t_\alpha \) excitations can be viewed as mobile quasi-particles propagating on the singlet background with a non-trivial dispersion. If the the bottom of this dispersion touches the singlet level a phase transition (Bose-Einstein condensation) takes place. In some systems pairwise creation and annihilation of \( t_\alpha \)'s on the neighboring atoms plays a role similar to the \( t_\alpha \) hopping.

Realization of the Khalilullin’s proposals is an interesting challenge since the spin-orbit coupling must be strong enough to enhance the correlation physics, but not too strong to allow sufficiently small singlet-triplet gap. Recently, a curious magnetic behavior was observed in Sr2YIrO6 (SYIO), which was interpreted as excitonic magnetism. In particular, it was argued that non-cubic crystal field splits the triplet state and thus reduces the first excitation energy of the Ir ion. Subsequent band structure calculations found only moderate non-cubic crystal field on Ir site and found that the physics of SYIO is similar to its cubic analog Ba2YIrO6 (BYIO). The GGA+U calculations to a magnetically ordered ground state, which the authors interpreted as confirmation of the experimental data.

In article we combine several methods to analyse the physics of BYIO and SYIO. Our results contradict the conclusions of Refs. as we find BYIO and SYIO to be insulators with singlet local ground state. We show that using the same GGA+U approach as in Ref. a solution corresponding to the singlet ground state has a lower energy than the solution containing magnetic moments. This result is supported by dynamical mean-field theory (DMFT) calculations performed with full interaction vertex. We conclude with a sufficient margin for uncertainties of various model parameters that the inter-atomic exchange processes in the studied double perovskites are too weak to overcome the singlet-triplet splitting due to the spin-orbit coupling. This result can be put to the perspective of the recent observation of signatures of excitonic magnetism in Ca2RuO4 a 4d perovskite where spin-orbit coupling is weaker and Ru-Ru hopping is stronger than in Ir double perovskites.

The paper is organized as follows. After introducing the computational methods in Sec. II we discuss the bonding in double perovskite structure and construct an effective Hubbard model on the basis of band structure calculations (Sec. III A). To compare with previous studies we have performed Hartree-like GGA+U calculations reported in Sec. III A 3. In the rest of the paper we analyze the multi-band Hubbard model. First, we study the single-site problem with the focus on singlet-triplet splitting and van Vleck susceptibility using exact diagonalization (Sec. III B). Next, we calculate the one-
II. COMPUTATIONAL METHODS

In this work we combine several numerical and semi-analytical approaches. All the below described calculations were performed for cubic BYIO. The key steps were performed also for orthorhombic SYIO.

We start with GGA\(^{10}\) density functional calculations employing the Wien2k\(^{11}\) package. All the results reported here were obtained with the spin-orbit coupling included\(^{5}\). The crystallographic as well as other parameters used in the calculations are summarized in Supplemental Material (SM\(^{9}\)).

To include the correlation effects on the Ir site beyond the effective non-interacting picture of GGA we follow two paths. First, we use the static mean-field approach of GGA+U. Since this approach is known to often lead to multiple solutions we have run series of calculations for various initial conditions. In particular, we used the spin-polarized GGA solution and atomic ground state as starting points. The calculations were performed for interaction parameters \(U\) of 2, 4 and 6 eV and \(J\) from 0.1 to 0.7 eV. The so called ‘fully localized limit’ double counting correction was used\(^{12}\). Although it should be a standard for systems with strong spin-orbit coupling, we note explicitly that spin-off-diagonal terms of the ‘+U’ orbital potential were included in the calculation.

Second, we use the non-spin-polarized GGA band structures to construct effective Hubbard models. Employing wien2wannier\(^{13}\) and wannier90\(^{14}\) codes to construct the Wannier representation of the GGA bands we can extract the crystal-field\(^{12}\) and spin-orbit parameters as well as theinter-atomic hoppings. For the calculation of the partially screened Coulomb interaction, we used the density response code for Eli\(^{15}\). In the calculation of the constrained susceptibility, we excluded the contribution of particle-hole excitations within the target bands (the \(t_{2g}\) bands for the \(d\)-model, and \(t_{2g}\) and \(O\) \(p\) bands for the \(pd\) model) and took 80 unoccupied bands. We used \(4 \times 4 \times 4\) \(k\) and \(q\) meshes for the double Fourier transform with the cutoff \(|G+q|=1, 2, 3.5\) (1/a.u.), where \(G\) is the reciprocal vector, and then extrapolated the result to \(|G+q|=\infty\).

We study two types of model Hamiltonians: (i) \(d\)-model in the space of Ir-like \(t_{2g}\) bands and (ii) \(pd\)-model covering the space of Ir-\(d\) and O-\(p\) bands. The two models were expressed in two bases: (a) real cubic harmonics with sharp spin and (b) the eigenbasis of the local one-particle Hamiltonian with \(j_{1/2}\) doublet and \(j_{3/2}\) quadruplet (\(jj\)-basis). The two bases are equivalent and their use followed numerical convenience. We use both \(d\)- and \(pd\)-model primarily to demonstrate robustness of our results. The questions of \(d\) vs \(pd\) model was discussed by several authors in the context of oxides of 3d elements.

The basic difference between the two models consists in how they describe low-energy one-particle excitations, whose orbital character is a mixture of atomic-like Ir-\(d\) and O-\(p\) orbitals. In \(d\)-model these excitations are molecular orbitals (anti-bonding \(pd\) combinations) whose structure is determined solely by the \(pd\) hybridization and does not depend on the interaction strength. In the \(pd\)-model the orbital structure of the excitations is affected by the interaction and can evolve from the non-interacting molecular orbital limit to the Heitler-London limit where the double occupancy of the atomic orbitals is suppressed. While the \(pd\)-model, which can describe richer physics, appears superior to the \(d\)-model, in practice it is not necessarily so. Larger Hilbert space of the \(pd\)-model involves more uncertainties in its construction, the most prominent of which is the so called double-counting correction which is directly related to the \(pd\) charge transfer energy.

The basic information about the models is obtained by analyzing the local electronic structure. We performed exact diagonalization of the single-site \(d\)-model where the six \(t_{2g}\) Wannier orbitals are treated as the atomic \(d\) orbitals, and iterative Lanczos diagonalization of the \(IrO_6\) cluster where the complete Ir \(d\) shell is hybridized with the O \(p\) states. This step served to determine the singlet-triplet splitting and to assess the differences between the two models, mainly the consequences of the explicit inclusion of the \(pd\) hybridization in the cluster model.

To extend the many-body calculations on the lattice we have run DMFT simulations for both the \(d\) and the \(pd\) model with the interaction parameters obtained in the cRPA calculations. To this end we used our implementation of the self-consistent cyclic\(^{16}\) and the TRIQS hybridization-expansion continuous-time quantum Monte Carlo solver\(^{16}\) (based on the TRIQS library\(^{17}\)). The calculations, with full Coulomb vertex \(U_{ijkl}c_ikc_jlc_k\), were performed in \(j_{1/2-j_{3/2}}\) basis (\(jj\)-basis) in which the on-site one-particle Hamiltonian is diagonal. This choice of basis helps to avoid the Monte Carlo sign problem.\(^{18}\) The reported calculations were performed at the temperature of 290 K. The spectral functions were obtained by analytic continuation of the self-energy using the maximum entropy method\(^{19}\).

While our DMFT calculations were limited to studying one-particle dynamics, we use large-\(U\) expansion of the \(d\)-model to investigate the two-particle excitations. We have eliminated the charge fluctuations by the Schrieffer-Wolf transformation\(^{20}\) to the second order and constructed an effective Hamiltonian on a local Hilbert space spanned by the singlet and lowest triplet states. The dynamics of this effective model was studied in the linear spin wave approximation. To check the consistency of our results we have started from two different one-particle bases: the real cubic harmonics and \(jj\)-basis.
III. RESULTS AND DISCUSSION

A. GGA

First, we report the unpolarized GGA solution for BYIO, which served as a starting point to construct the effective models. The results for lower-symmetry SYIO are similar.

1. Molecular orbitals

Unlike in simple perovskites, where the $O_6$ octahedra around neighboring metal atoms share corners, in double perovskites the Ir$O_6$ octahedra are not touching. This geometry suggests that the double perovskites can be possibly viewed as molecular crystals built out of Ir$O_6$ molecules plus some filler atoms. Irrespective of whether this picture is useful for interpretation of the physics, one can use molecular orbitals (MOs) - linear combinations of atom-centered Wannier functions (WFs) on the $O_6$ octahedron - as an alternative to the atom-centered WF basis.

In Fig. 1 we show the GGA spectral density decomposed into the projections on the MOs classified by their symmetry. First, we note the magnitude of the $pd$ hybridization. Nominally Ir-$d$ orbitals around Fermi level are superpositions of the atomic Ir-$d$ orbital and its MO partner. For $j_{3/2}$ states the mixture is essentially fifty-fifty, while for $j_{1/2}$ and $e_g$ states the Ir-$d$ weight is somewhat larger. We further observe that bands of distinct symmetry exhibit little hybridization. The filled non-bonding MOs therefore do not play an active role in the low-energy physics. In Fig. 2 it is demonstrated that they can be dropped from the model. We compare the GGA band structure with the bands of a truncated $pd$ model where only Ir and $O_6$ $t_{2g}$ orbitals were kept, while the $e_g$ and non-bonding orbitals were simply left out without any adjustment of the $t_{2g}$ subspace. The model dispersion reproduces very well the anti-bonding bands around the Fermi level and does a fairly good job also for the bonding bands which overlap with the $e_g$ and $a_{1g}$ bands. This suggests that the molecular crystal provides a useful picture of the studied double perovskites. The large bonding–anti-bonding splitting allows straightforward construction of the Wannier representation of the bonding bands only - the $d$ model.

2. cRPA

The cRPA calculations were performed for $d$ and $pd$ models. The calculated direct and exchange interaction parameters in the low frequency limit can be found in SM. In our model calculations we make the common assumption of atomic form of the interaction, which is then parametrized by $U$ and $J$ which are chosen to match the cRPA data. For the $d$-model we can fairly accurately fit the cRPA data with the values $U=1.8$ eV and $J=0.4$ eV, while we get $U=4$ eV and $J=1.1$ eV for the $pd$-model. The values of $J$ should be viewed as upper estimates obtained by the extrapolation of the Fourier cut-off to infinity. Our main conclusions in this work hold for smaller $J$, but eventually break for large $J$. Therefore we try to use conservative (upper limit) values in our calculations.
3. Spin-polarised solution and GGA+U

Allowing ferromagnetic spin-polarized solutions we arrive at similar results as reported in Ref. [1] However, these solutions are metallic, contrary to experiment, suggesting that inclusion of electronic correlations beyond GGA is desirable. The GGA+U approach provides a computationally cheap way to include the electronic correlations on a Hartree-Fock level. The GGA+U method is formally analogous to the Weiss mean-field theory and as such it is prone to multiple self-consistent solutions that could be thermodynamically unstable. The authors of Ref. [2] started from their spin polarized solutions for BYIO and SYIO and including the +U orbital potential they found these solutions to be modified, but qualitatively unchanged. While we were able to find similar spin-polarized solutions (SM), we extended the search for possible stable solutions by starting from the occupation matrices corresponding to the atomic ground state reported below. This way we obtained non-magnetic solutions with energies lower than their spin polarized counterparts. The spectral density of the non-magnetic solution for BYIO, shown in Fig. 3 confirms the picture of a local singlet ground state with filled j_{3/2} orbitals and empty j_{1/2} ones.

B. Multi-orbital Hubbard model

In the following, we present the results obtained for the d and pd models of SYIO and BYIO. The parameters of the models obtained using the Wannier projection can be found in SM.

1. Single-site physics

We start by discussing the physics of an isolated lattice site. The key quantity of interest is the singlet-triplet excitation energy $\Delta_s$. In Fig. 4(a) we show the single-ion spectra of BYIO and SYIO of the d-model obtained by diagonalization of the single-site Hamiltonian with 4 electrons. Similar to Ref. [2] we find that the non-cubic crystal-field in SYIO has only minor effect and the spectrum is controlled by the spin-orbit coupling and Hund’s exchange $J$ (Note that the isotropic part $U$ of the on-site interaction does not affect level splitting within a given valence state.) Since the singlet-triplet splitting decreases with $J$, the excitation energy $\Delta_s$ of 270 meV is a conservative lower estimate.

Besides the multiplet structure we have calculated the van Vleck susceptibility of the Ir atom in the d-model of SYIO. The susceptibility increases with $J$ and it exhibits an anisotropy: for $J=0.4$ eV its values along a, b and c axes are 0.0011, 0.0016 and 0.0009 emu/mol (the corresponding values for $J=0.2$ eV are 0.0009, 0.0009 and 0.0008 emu/mole). These numbers correspond rather well to the experimental data of Ref. [3] which exhibit only a weak temperature dependence above 50 K ($\sim 0.0015$ emu/mole@50 K and $\sim 0.0011$ emu/mole@330 K).

Next, we study the local physics of BYIO within the pd-model, i.e. we diagonalize the IrO$_6$ cluster. We treat the O-p states as non-interacting and put the interaction on the central Ir atom only. Unlike for the isolated d-shell above, the isotropic part of the interaction $U$ affects the results strongly. The dependence of the excitation spectrum on $U$ is, however, to a large extent compensated by the double-counting correction $E_{dc}$ which renormalizes the splitting between the d and p orbital energies and
which must be included to take into account the interaction energy present in GGA. Since $E_{d_{c}}$ is not rigorously defined, we treat it as an adjustable parameter. In Fig. 1 we show the singlet-triplet excitation energy $\Delta_{t}$ for the IrO$_{6}$ cluster. Rather than $E_{d_{c}}$, we plot our results as a function of the closely related Ir-$d$ occupancy $n_{d}$ with clear physical meaning. For fixed $n_{d}$ the excitation energy $\Delta_{t}$ is practically independent of $U$. We take the Ir-$d$ occupancies between $6-7$ ($n_{d} = 6.35$ is the GGA value) to be physically reasonable. The corresponding singlet-triplet splitting falls into the interval 190-280 meV and is consistent with 270 meV obtained from the $d$-model.

As a side remark we point out that a popular approximation of the interaction to the density-density terms in the $jj$-basis leads to the substantially smaller values of singlet-triplet splitting of around 100 meV. This can be traced back to the missing pair-hopping terms which contribute to lowering of the singlet energy.

2. DMFT

In the following, we extend our analysis to the lattice problem. We address three questions. Is there a charge gap in the one-particle spectrum and what is its nature? It there a global ground state with broken symmetry predicted by Ref. 2? What is the dynamics of two-particle excitations and can they condense in the sense proposed by Khalilullin?24 The first and, to some extent, the second questions are studied using DMFT. The second and the third questions are addressed using the effective strong coupling Hamiltonian.

The DMFT technique incorporates local quantum and thermal fluctuations and does not typically suffer from the problem of multiple solutions with distinct local states. When several local states are quasi-degenerate the method can naturally describe their statistical mixture (most common example being local moment fluctuations). When several local states are quasi-degenerate the method can naturally describe their statistical mixture (most common example being local moment fluctuations). When several local states are quasi-degenerate the method can naturally describe their statistical mixture (most common example being local moment fluctuations). The classical ground state of singlets. The excitations in the limit of low $^s$-density are described by an effective Hamiltonian describing propagation of a single $t$-excitation, i.e., we neglect for example interactions between $t_s$.

$$H = \varepsilon \sum_{i,s} t_{is} t_{is}^\dagger$$

$$+ \frac{1}{2} \sum_{i,R,s,s',t} (A_{ss'}^{R} | s, s; i, t \rangle \langle t + R | s, s') + \Gamma_{ss'}^{R} | t_{s}' \rangle \langle t_{s}' + R | s, s') + H.c. \quad (1)$$

Here, $\varepsilon$ is the singlet-triplet splitting $\Delta_{t}$ renormalised by hopping processes of the type $| s, s \rangle \rightarrow | s, s \rangle$ and $| s, t_{s} \rangle \rightarrow | s, t_{s} \rangle$, $A_{ss'}^{R}$ is the amplitude of the process $| s, t_{s} \rangle \rightarrow | t_{s}', s \rangle$ and $\Gamma_{ss'}^{R}$ is the amplitude of the process $| s, s \rangle \rightarrow | t_{s}', t_{s} \rangle$. Hopping to the first and second neighbors on the fcc lattice is considered. In Fig. 6 we present the spectrum of $\Gamma$ along the high symmetry directions of the cubic lattice. The main observation is the large excitation gap. In the language of the Khaliullin’s proposal the excitonic condensation takes place when the energy of the lowest triplet excitation touches the singlet (vacuum) level. Our results show that the width of the $t$-dispersion is at least an order of magnitude too small for that to happen. Since the parameters of $\Gamma$ for SYIO are of similar magnitude as for BYIO we conclude that our result holds for SYIO as well.
The double perovskite structure with large Ir-Ir distance and small hopping amplitude $t$ is not very promising for observation of excitonic magnetism. The electronic bandwidth $W \sim Zt$ does not have to be unusually small thanks to the high number of nearest neighbors $Z$. The effect of small $t$ is much more pronounced in the dispersion of two-particle excitations with a bandwidth $W_1 \sim Zt^2$ which scales as $1/Z$ for fixed $W$.

IV. CONCLUSIONS

We have combined several theoretical approaches to study the low-energy properties of Ir double perovskites BYIO and SYIO. The two compounds are quite similar, in particular, the non-cubic crystal field of SYIO is found to be rather weak, a result that agrees with the conclusions of theoretical study of Bhowal et al. Our main conclusion is that excitonic magnetism in BYIO and SYIO is not favored. Small Ir-Ir hopping in double perovskite structure gives rise to valence and conduction bands that are sufficiently narrow to become orbitally polarized and gapped by a moderate on-site Coulomb repulsion. Another consequence of the small electron hopping are small amplitudes for propagation of two-particle excitations. The bandwidth of such excitations is an order of magnitude smaller than the singlet-triplet excitation energy determined by the spin-orbit coupling and Hund's exchange $J$, which prevents the possibility of their exciton condensation.

Our conclusions contradict the conclusions of the experimental study\footnote{See Supplemental Material, URL \url{http://www.fzu.cz/~kunes/papers/BYIO_sm.pdf}}. While our calculated van Vleck susceptibility reproduces quite well the experimental susceptibility of Ref.\cite{3} above 50 K, we do not find any tendency towards a magnetic phase transition at low temperatures. Instead, we predict a large spin gap in the 200 meV range. Our results thus call for reexamination of the experimental data considering the possibility of an extrinsic origin of the observed low temperature behavior.

Acknowledgments

We acknowledge discussions with Z. Jiráš, K. Kužek and J. Hejtmánek. We acknowledge support of the Czech Science Foundation through the project 13-25251S (JKu and PN), German Research Foundation through FOR1346 (VP) and Grants-in-Aids for Scientific Research on Innovative Areas (15H05883) from JSPS (RA). Access to computing and storage facilities owned by parties and projects contributing to the National Grid Infrastructure MetaCentrum, provided under the programme ”Projects of Large Infrastructure for Research, Development, and Innovations” (LM2010005), is greatly appreciated.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Dispersion of a triplet excitation in singlet background obtained from $d$-model with $U = 1.8$ eV and $J = 0.4$ eV.}
\end{figure}
J. Kuneš, V. I. Anisimov, A. V. Lukoyanov, and D. Vollhardt, Phys. Rev. B 75, 165115 (2007).

P. Seth, I. Krivenko, M. Ferrero, and O. Parcollet, arXiv:1507.00175.

O. Parcollet, M. Ferrero, T. Ayral, H. Hafermann, I. Krivenko, L. Messio, and P. Seth, Comput. Phys. Commun. 196, 398 (2015).

T. Sato, T. Shirakawa, and S. Yunoki, Phys. Rev. B 91, 125122 (2015).

M. Jarrell and J. Gubernatis, Physics Reports 269, 133 (1996).

J. R. Schrieffer and P. A. Wolff, Phys. Rev. 149, 491 (1966).

P. Novák, K. Knížek, M. Maryško, Z. Jirák, and J. Kuneš, J. Phys.: Condens. Matter 25, 446001 (2013).

J. Kuneš and P. Augustinský, Phys. Rev. B 90, 235112 (2014).

J. Kuneš, Phys. Rev. B 90, 235140 (2014).

H. Park, K. Haule, and G. Kotliar, Phys. Rev. Lett. 107, 137007 (2011).

L. Boehnke and F. Lechermann, Phys. Rev. B 85, 115128 (2012).