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Suppression of magnetism in Ba$_5$AlIr$_2$O$_{11}$: Interplay of Hund's coupling, molecular orbitals, and spin-orbit interaction

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The electronic and magnetic properties of Ba$_5$AlIr$_2$O$_{11}$ containing Ir-Ir dimers are investigated using the generalized gradient approximation (GGA) and GGA + spin-orbit coupling (SOC) calculations. We found that the strong suppression of the magnetic moment in this compound recently found by Terzic *et al.* [Phys. Rev. B **91**, 235147 (2015)]] is not due to charge ordering but is related to the joint effect of the spin-orbit interaction and strong covalency, resulting in the formation of metal-metal bonds. They conspire and act against the intraatomic Hund's rule exchange interaction to reduce total magnetic moment of the dimer. We argue that the same mechanism could be relevant for other 4d and 5d dimerized transition metal compounds.

I. INTRODUCTION

The study of 4d and especially 5d transition-metal compounds, in particular those of Ir, is now at the forefront of research in the physics of correlated electron systems. This is largely connected with effects caused by strong spin-orbit coupling (SOC). In particular, for Ir^{4+} with t_{2g}^5 electronic configuration, with spin $S = 1/2$ and effective orbital moment $L_{\rm eff} = 1$, strong SOC can stabilize for an isolated ion the state with $J = 1/2$, which can explain the Mott insulating character of Sr$_2$IrO$_4$ [1] or for honeycomb systems Li$_2$IrO$_3$ and Na$_2$IrO$_3$ could lead to special states like those described by the Kitaev model [2] (see also Ref. [3]). But no less interesting could be possible nontrivial properties of systems with Ir^{5+} and Ru^{4+}, with ionic configuration t_{2g}^4 ($S = 1$, $L_{\rm eff} = 1$), which in the case of isolated ions are in a nonmagnetic $J = 0$ state [4]. And, indeed, for electron spin resonance (ESR) community Ir^{5+} is a classical nonmagnetic ion, even sometimes used for nonmagnetic dilution. However, in concentrated solids the intersite interaction, if strong enough, can in principle lead to magnetic ordering in such systems, the phenomenon known as singlet magnetism; see, e.g., Ch. 5.5 in Ref. [5] and Ref. [6]. Apparently such magnetic state was discovered in double perovskite Sr$_2$YIrO$_6$ in Ref. [7], although the properties of this and similar systems is still a matter of debate [8].

An interesting system Ba$_5$AlIr$_2$O$_{11}$[9] was recently experimentally studied in detail in Ref. [10]. The main building blocks of it are dimers of face-sharing IrO$_6$ octahedra with, on average, mixed valence Ir$^{4.5+}$, which may be expected to combine both the properties typical for Ir^{4+} and for Ir^{5+}. However, in contrast to the single-site physics (leading to the $J = 1/2$ state for Ir^{4+} and $J = 0$ for Ir^{5+} ions), here we deal with a strongly coupled pair of Ir ions, in which, for example, intersite electron hopping can easily be of order or even larger than the intraatomic parameters such as the Hund's rule coupling J_H and spin-orbit coupling λ, and can

compete with the intraatomic Hubbard repulsion U. Indeed, in going from 3d to 4d and 5d ions, U decreases, from ∼5 eV for 3d to 2–3 eV for 4d and to 1–2 eV for 5d. Similarly, $J_H \sim$ 0.7–0.9 eV for 3d, 0.5–0.6 for 4d, and ∼0.5 eV for 5d systems [11]. At the same time, the size of d orbitals, and with it the pd and dd hoppings, increase in this series, and can easily reach 1–1.5 eV for 4d–5d systems [12–14]. In this situation, there may occur strong modification of the behavior expected for isolated 5d (e.g., Ir) ions. Ba$_5$AlIr$_2$O$_{11}$ may be a good example on which one can investigate relative importance of single-site versus intersite effects.

The crystal structure of Ba$_5$AlIr$_2$O$_{11}$ consists of Ir-Ir dimers, which form chains, as shown in Fig. 1. At $T_S = $ 210 K, there occurs a structural phase transition accompanied by the metal-insulator transition [10]. While even at room temperature there is a certain difference in the average Ir-O distance for two classes of Ir (Ir2 occupies octahedra, which share their corners with AlO$_4$ tetrahedra; Ir1 is in the center of the remaining octahedra), it increases at T_S. Thus, one could speak about certain charge ordering even for $T > T_S$, if this high-temperature phase was insulating. The real charge disproportionation in limiting case 2Ir$^{4.5+} \rightarrow$ Ir^{4+} + Ir^{5+} seems to occur only in the insulating phase below T_S as manifested by a strong dielectric anomaly at T_S and by increasing difference in the average Ir-O bond distance for two classes of Ir [10].

Below $T_M = 4.5$ K there appears a long-range magnetic order in Ba$_5$AlIr$_2$O$_{11}$, apparently an antiferromagnetic one, consistent with negative Curie-Weiss temperature ($\theta = -14$ K). The effective magnetic moment, obtained by the high-temperature fit of susceptibility, is $\mu_{\rm eff} = 1.04\,\mu_B$/dimer, much smaller than one would expect from the values of spin moments corresponding to Ir^{4+} ($\mu_s = 1\,\mu_B$/Ir) or Ir^{5+} ($\mu_s = 2\,\mu_B$/Ir) [10]. The mechanism of such a strong suppression was proposed in Ref. [10]. It was argued that it is related to the joint effect of the strong spin-orbit coupling and formation of singlet molecular orbitals for part of Ir 5d orbitals.

In this paper, we theoretically investigate this problem using *ab initio* band-structure calculations. We demonstrate that indeed in this material, as possibly also in other 5d
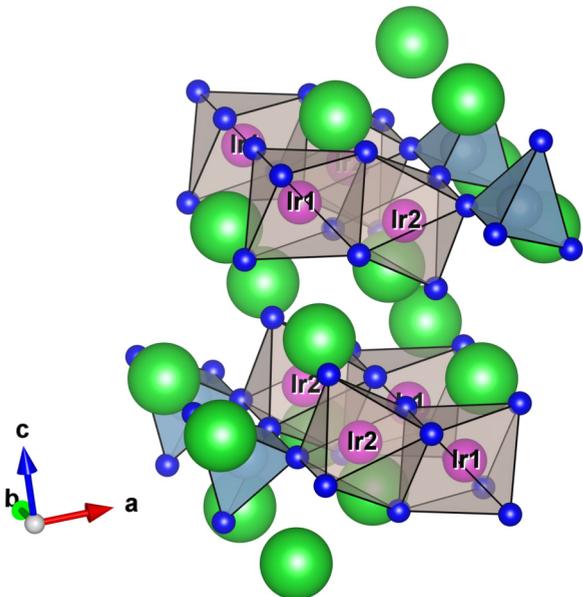
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FIG. 1. Crystal structure of $Ba_5AlIr_2O_{11}$. Ir ions (violet balls) are in the oxygen (small blue balls) octahedra. Two nearest IrO_6 octahedra form dimer, sharing their faces. Al (large blue balls) ions are in the oxygen tetrahedra and Ba (green balls) sits in the voids.

FIG. 2. The sketch, which shows (a) the level splitting in the dimer constructed out of face-sharing octahedra: the largest bonding-antibonding splitting corresponds to a_{1g} orbitals, directed to each other in this geometry. Panels (b) and (c) illustrates two possible states in such a system with different values of total spin.

compounds, there exist strong interplay of covalent bond formation, Hund's rule coupling and spin-orbit interaction, which results in particular in strong suppression of magnetic moment on Ir ions and which strongly modifies intradimer exchange interaction. These results give good explanation of unusual properties of $Ba_5AlIr_2O_{11}$ and show the general trend expected in similar materials with competing intrasite and intersite effects.

II. IONIC TREATMENT

Before presenting the results of the real band-structure calculations, we discuss what one might expect in this system starting from the ionic consideration. Since the $t_{2g} - e_g^\sigma$ crystal-field splitting is huge for $4d$ and especially $5d$ transition-metal oxides, first we have to fill t_{2g} orbitals. Two neighboring IrO_6 octahedra form a dimer, sharing their faces. In such geometry, there will be two sets of orbitals, different by symmetry: a_{1g} orbitals pointing to each other will have stronger hopping, t_a, than e_g^π orbitals, t_e; see Fig. 2(a) [15]. Having nine $5d$ electrons per Ir-Ir dimer one may fill these orbitals in two different ways: to have maximum ($S_{tot} = 3/2$) and minimum ($S_{tot} = 1/2$) total spins, Figs. 2(b) and 2(c), respectively.

The first configuration with $S_{tot} = 3/2$ can be called a double exchange (DE) state, since the electron (hole) on delocalized a_{1g} antibonding orbital with the largest hopping t_a moves from one site to another in the dimer and makes other two electrons (holes) have the same spin projection. In the second state with $S_{tot} = 1/2$, the antibonding a_{1g} orbital stays unoccupied and the total magnetic moment is suppressed. One may call this state an orbital-selective (OS) state [16], since e_g^π and a_{1g} orbitals behave very differently in this state.

One may consider this situation within the two-site–two-orbital (a_{1g} being orbital 1 and e_g^π being orbital 2) model in the simplest ionic approximation, taking into account intra-atomic Hund's rule coupling:

$$H_{Hund} = - \sum_{i,mm'} J_H \left(\frac{1}{2} + 2\vec{S}_{im}\vec{S}_{im'} \right) \quad (1)$$

(here i numerates sites in a dimer, $i = \{a,b\}$, m and m' are orbital indexes $m,m' = \{1,2\}$; the sum runs once over each pair of m and m'), and the kinetic energy is given by hopping parameters between the a_{1g} and e_g^π orbitals, t_a and t_e respectively. With our definition of Hund's exchange, (1), in the mean field, the Hund's energy is equal to $J_H \times$ (number of parallel spins).

For the DE state, with two localized electrons (on orbital 1 and sites a and b, i.e., $|c_{a,1}^\dagger\rangle$ and $|c_{b,1}^\dagger\rangle$), and a "delocalized" electron on a bonding orbital $|(c_{a,2}^\dagger + c_{b,2}^\dagger)/\sqrt{2}\rangle$, all with the same spins and with the total spin of a dimer $S_{tot} = 3/2$, we have the energy of this bonding state with one electron $-t_a$ and the Hund's energy $-J_H/2$ per site. Taking into account the fact that localized e_g^π electrons still can hop with amplitude $-2t_e$ we find that the total energy of this DE state is $E_{DE} = -t_a - 2t_e - J_H$.

On the other hand, the energy of an OS state with two electrons in a singlet state on bonding orbital, $|(c_{a,2\uparrow}^\dagger + c_{b,2\uparrow}^\dagger)(c_{a,2\downarrow}^\dagger + c_{b,2\downarrow}^\dagger)/2\rangle$, and with the remaining localized electron on any of the sites, e.g., at a site a with spin $\uparrow$, we have the bonding energy of "itinerant" electrons $-2t_a$ and the reduced Hunds energy $J_H/2$. Thus, $E_{OS} = -2t_a - t_e - J_H/2$. In effect, the DE will be realized if

$$J_H > 2(t_a - t_e) = 2\Delta_{ae}. \quad (2)$$

The Hund's rule exchange for Ir is ~ 0.5–0.7 eV [17,18], while both hopping parameters can be found from real *ab initio* calculation. If Δ_{ae} would be large enough, one could explain experimentally observed suppression of magnetic moment only by the covalency, i.e., by formation of metal-metal bonds.

III. CALCULATION DETAILS

We used full-potential WIEN2K code [19] and generalized gradient approximation (GGA) [20]. The atomic sphere radii were set as follows: $R_{Ir} = 1.91$ a.u., $R_{Ba} = 2.35$ a.u., $R_{Al} = 1.63$ a.u., and $R_O = 1.63$ a.u. The spin-orbit coupling (SOC)

TABLE I. Magnetic moments obtained in the GGA + SOC calculations.

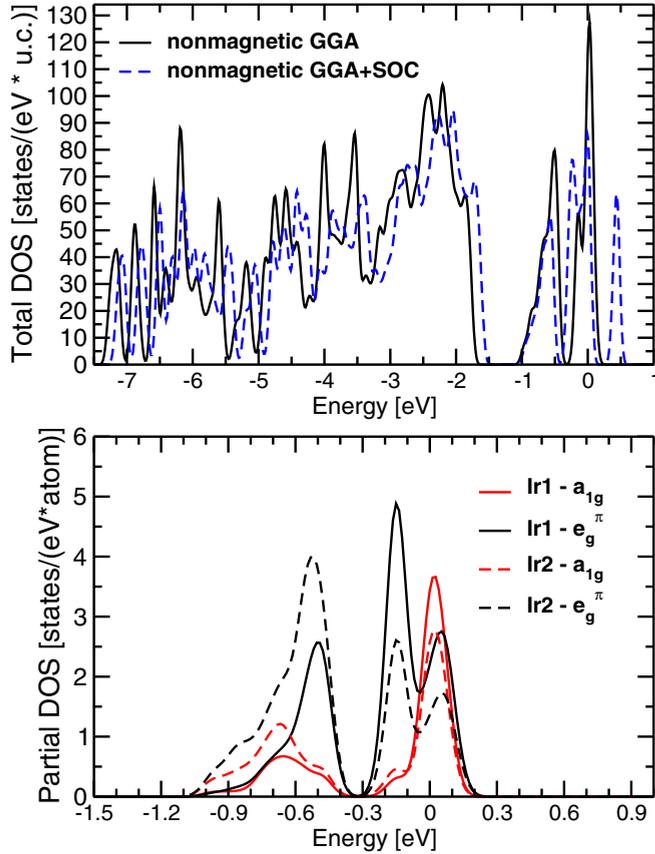| Ion	Spin moment, μ_B	Orbital moment, μ_B	μ_j(Ir), μ_B
Ir1 (Ir^{5+})	(0.02, 0.00, 0.53)	(−0.08, 0.00, −0.09)	0.44
Ir2 (Ir^{4+})	(0.09, 0.00, 0.24)	(−0.01, 0.00, −0.11)	0.15

FIG. 3. Upper panel: total DOS in the nonmagnetic GGA and GGA + SOC calculations. Lower panel: partial DOS in the nonmagnetic GGA in the local coordinate system (LCS), when the z axis looks along the vector connecting two Ir in the dimer. This choice of LCS is not ideal, since the symmetry is very low and octahedra are strongly distorted, but one may see that the rightmost peak mostly corresponds to the antibonding a_{1g} orbital, while the one centered at ≈ -0.16 eV corresponds to the antibonding e_g^π states. Fermi energy is set to zero.

was treated in a second variational way. Then 160 k-points were used for the Brillouin-zone integration. The parameter of the plane-wave expansion was chosen to be $R_{MT}K_{\max} = 7$, where R_{MT} is the smallest atomic sphere radii and $K_{\max}$ is the plane-wave cutoff. The calculations were performed for the crystal structure obtained by x-ray diffraction at $T = 90$ K [10].

IV. CALCULATION RESULTS

Our nonmagnetic GGA calculation for low-temperature phase indeed indicates a sizable bonding-antibonding splitting (see lower panel in Fig. 3), which is natural for IrO$_6$ octahedra forming dimers. As we have seen above, the key parameter which defines the ground-state electronic configuration is the splitting between antibonding a_{1g} and e_g^π orbitals, Δ_{ae}. Using the linearized muffin-tin orbital method [21], the local density approximation, and Wannier projection technique [22], we estimated that $\Delta_{ae} \sim 0.2$ eV. In contrast to our expectations, this value is smaller than $J_H/2$. Therefore, in contrast to experimental finding [10], according to Eq. (2) the DE, not

the OS, state with small magnetic moment should win in this case.

Indeed, in the magnetic GGA calculations the total spin moment is ~ 2.0 μ_B/dimer (smaller than the ionic value due to hybridization effects [23]), while $|\mu_S(\text{Ir1})| = 0.9$ μ_B and $|\mu_S(\text{Ir2})| = 0.6$ μ_B. It is remarkable that the spin moments on the two Ir ions forming dimers are ferromagnetically coupled (antiferromagnetic solution does not converge in the GGA). Therefore, the exchange coupling between these ions without SOC is governed by the DE. Furthermore, there is an unusually large moment ~ 0.5 μ_B/dimer in the interstitial space between the atomic spheres related to the formation of the bonding state, favoring bond-centered spin densities. Thus, we see that the covalency alone (the formation of bonding and antibonding states in Ir dimers) is in this system not sufficient to suppress DE and strongly reduce magnetic moment. As we show below, the situation changes drastically when we take into account spin-orbit interaction.

Before presenting these results, we note that there is significant difference between two inequivalent mean Ir-O distances for the two face-sharing octahedra: $\delta = d[\text{Ir2-O}]-d[\text{Ir1-O}] = 0.016$ Å (recalculated from experimental structure in the low-temperature phase [10]), compared to $\delta \sim 0.055$ Å for a full Ir^{4+}/Ir^{5+} charge order [24]. The Bader analysis [25] shows that corresponding charge disproportionation is $\delta n_{Ir1/Ir2} \sim 0.3$ electrons (Ir1 is closer to Ir^{5+} and Ir2 to Ir^{4+}), indicating the existence of a charge order.

An account of the SOC in the magnetic GGA + SOC calculations strongly changes the situation. It reduces the total moment, $\mu_z^{\text{GGA+SOC}} \sim 0.8$ μ_B/dimer, which is much smaller than in GGA, where $\mu_z^{\text{GGA}} \sim 2$ μ_B/dimer, and which is now consistent with the experimental value. This suggests the importance of the SOC. However, the SOC does not simply reduce the total moment due to direct contribution of orbital moment, which is expected to be antiparallel to spin; see Table I. This effect, commonly used for the description of the spin singlet state of Ir^{5+} ion (which for isolated ion could give a nonmagnetic state [4–6]), leads in Ba$_5$AlIr$_2$O$_{11}$ to a decrease of the total moment only by ~ 0.2 μ_B/dimer. Thus, the observed reduction of the total moment of a dimer is not caused by the formation of $J = 0$ state on Ir^{5+}. This is due to the fact that we are dealing not with the isolated ions but with a dimer with significant hopping between sites and with the average mixed valence of Ir$^{4.5+}$. It is clearly seen from Fig. 4 that the 5d orbitals of Ir1 and Ir2 are strongly hybridized and cannot be considered as ionic. The main reason for the reduction of the total moment is related to strong changes in the electronic structure and to breaking of the delicate balance between DE and OS states by the SOC.

These changes are easier to see in the nonmagnetic GGA + SOC calculations. One may notice in the upper panel of Fig. 3
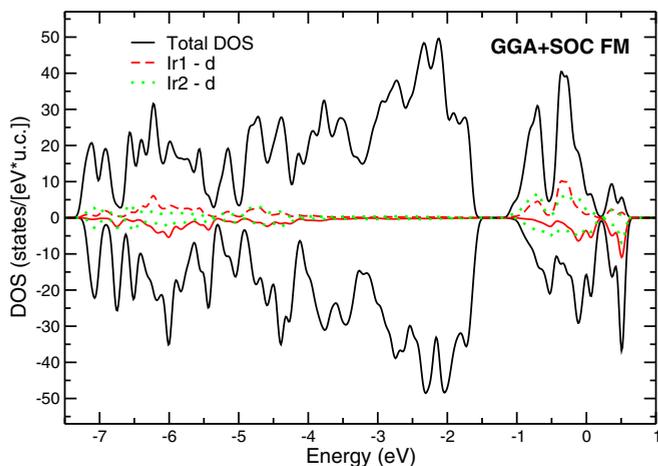
FIG. 4. Results of the ferromagnetic GGA + SOC calculations. Positive (negative) values correspond to spin majority (minority). Fermi energy is set to zero.

that the SOC basically shifts part of the antibonding MO to higher energy, due to formation of $j_{\mathrm{eff}} = 1/2$ and $j_{\mathrm{eff}} = 3/2$ subbands. The DOS center of gravity calculations shows that the splitting due to SOC is $\Delta_{\mathrm{SOC}} \sim 0.6$ eV. This, together with the bonding-antibonding splitting, is already sufficient to overcome the Hund's rule coupling and to suppress DE. Indeed, it is clearly seen in Fig. 4 that the SOC does not spoil main feature of the GGA band structure, the presence of bonding-antibonding splitting, but additionally lifts one of the antibonding orbitals up so that in effect $\Delta_{ae} + \Delta_{\mathrm{SOC}} > J_H/2$; cf. Eq (2). Thus, the SOC plays on the side of covalency against DE. It also decreases the moment in the interstitial region down to 0.27 μ_B and mixes spin-up and spin-down states, reducing spin moments on Ir sites, as shown in Table I. On the other hand, the SOC does not act against charge disproportionation, which is given by the lattice distortions: $\delta n_{Ir1/Ir2}$ stays ~ 0.3 electrons in the GGA + SOC calculations.

These theoretical results are consistent with experimental results. Particularly, considerably weakened μ_{eff} is a result of common action of the SOC and covalency. As mentioned above, Ir ions forming dimers should not be considered as isolated ions, but rather represent a single quantum-mechanical object having, due to the joint effect of the SOC and covalency, strongly reduced magnetic moments. These moments can be coupled between dimers antiferromagnetically as usually occurs in insulating TM oxides [5]. This agrees with the low temperature of the magnetic transition and with negative θ_{CW}. It is important to note that small moment is experimentally seen already at temperatures much higher than the temperature of charge ordering; therefore, it is not related with the formation of Ir^{4+} and Ir^{5+} ions (and correspondingly with $J = 0$ physics) but is rather explained by the competition between (covalency + SOC) and Hund's exchange.

In the end, we would like to comment on the importance of the strong Coulomb correlations in $Ba_5AlIr_2O_{11}$. It is known that the correlation effects have to be take into account for correct description of the electronic and magnetic properties of various transition-metal oxides [5,26]. We used the GGA + U + SOC method to check how strongly the results of the

TABLE II. Magnetic moments obtained in the GGA + U + SOC calculations.

Ion	Spin moment, μ_B	Orbital moment, μ_B	μ_j(Ir), μ_B
		$U = 1$ eV	
Ir1 (Ir^{5+})	(0.02, 0.00, 0.64)	(−0.06, 0.00, −0.07)	0.56
Ir2 (Ir^{4+})	(0.07, 0.00, 0.35)	(−0.02, 0.00, −0.06)	0.29
		$U = 1.5$ eV	
Ir1 (Ir^{5+})	(0.01, 0.00, 0.69)	(−0.05 0.00 −0.03)	0.66
Ir2 (Ir^{4+})	(0.05, 0.00, 0.42)	(−0.03 0.00 −0.01)	0.40

DFT calculations depend on the Hubbard U [27,28]. Typical values of U used in the literature for Ir ions changes from 1 to 1.5 eV, while Hund's intra-atomic exchange J_H is ~ 0.5 eV [8,29–31]. On-site correlation effects usually lead to increase of the electron localization and growth of the spin moment, but the question is whether Hubbard U can overcome joint efforts of the SOC and strong covalency resulting in the formation of the metal-metal bonds and make one Ir^{4+} ($\mu_s = 1\,\mu_B$) and another Ir^{5+} ($\mu_s = 2\,\mu_B$). The results of the GGA + U + SOC calculations for $U = 1$ and 1.5 eV are shown in Table II. One may see, that while Hubbard correlations do lead to increase of the magnetic moments, they are far from been strong enough to overwhelm the SOC and the covalency.

V. CONCLUSIONS

To sum up, with the use of the *ab initio* calculations we show in the present paper that it is the combined action of the spin-orbit coupling and strong covalency which leads to suppression of magnetic moment in $Ba_5AlIr_2O_{11}$. Formation of the metal-metal bonds (covalency) alone is here not strong enough to suppress double exchange, which would favor the state with maximum spin. The spin-orbit coupling alone also would not be able to efficiently suppress magnetic moments on Ir, a result of the incomplete Ir^{4+}/Ir^{5+} charge ordering apparently caused by strong intersite electron hopping. Only the combined action of both these mechanisms leads to the state with properties observed experimentally. We suppose that a similar situation may also be met in other $4d$ and $5d$ transition-metal compounds, e.g., in $Ba_3LnIr_2O_9$ [32], where Ln is lanthanide.

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