Charge density functional plus U calculation of lacunar spinel GaM$_4$Se$_8$ (M = Nb, Mo, Ta, and W)

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Abstract – Charge density functional plus $U$ calculations are carried out to examine the validity of molecular $J_{\text{eff}} = 1/2$ and $3/2$ states in lacunar spinel GaM$_4$Se$_8$ (M = Nb, Mo, Ta, and W). With LDA (spin-unpolarized local density approximation)+$U$, which has recently been suggested as a more desirable choice than LSDA (local spin density approximation)+$U$, we examine the band structure in comparison with the previous prediction based on the spin-polarized version of functional and with the prototypical $J_{\text{eff}} = 1/2$ material Sr$_2$IrO$_4$. It is found that the previously suggested $J_{\text{eff}} = 1/2$ and $3/2$ band characters remain valid still in LDA+$U$ calculations while the use of charge-only density causes some minor differences. Our result provides further support for the novel molecular $J_{\text{eff}}$ state in this series of materials, which can hopefully motivate the future exploration toward its verification and the further search for new functionalities.

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**Introduction.** - A series of “lacunar spinel” compounds, GaM$_4$X$_8$ (M = V, Nb, Mo, and Ta; X = S, Se, and Te), has attracted great attention due to their interesting physical properties and promising material characteristics. For example, multiferroicity has been observed in GaV$_4$S$_8$ and GaV$_4$Se$_8$ carrying a great potential for memory device applications [1–4]. In GaTa$_4$Se$_8$, resistive switching phenomena which can be used for resistive random access memory (RRAM) have been reported [5]. In the case of M = Nb and Ta, the insulator-to-metal transition followed by a superconducting transition is known to occur by applying pressure [6,7]. Their intriguing low-temperature behaviors in susceptibility and specific-heat measurement [7–9] can possibly be related to the unconventional superconductivity. Further, novel “molecular $J_{\text{eff}}$” ground states have been suggested recently. According to the first-principles band calculations, the molecular $J_{\text{eff}} = 1/2$ and $3/2$ states are realized in the case of M = Mo, W, and Nb, Ta, respectively, due to the crucial role of spin-orbit interaction while this effect has been ignored in earlier studies [10]. For GaTa$_4$Se$_8$, the novel $J_{\text{eff}} = 3/2$ ground state has been verified by the resonant inelastic x-ray scattering (RIXS) experiment combined with theoretical calculations [11].

One further important step is therefore to study the other materials (i.e., GaNb$_4$Se$_8$, GaMo$_4$Se$_8$, and GaW$_4$Se$_8$) and to confirm their characteristic molecular $J_{\text{eff}}$ states, which can provide a new exciting playground in the search for the novel quantum phenomena [12–21]. While a similar type of experiments such as RIXS and RXMS (resonant x-ray magnetic scattering) can be utilized [11,22], only available at this moment is the band structure prediction [10]. On the one hand, the successful verification of $J_{\text{eff}} = 3/2$ for the case of M = Ta [11] supports the reliability of the previous theoretical prediction [10]. On the other hand, a series of recent DFT (density functional theory)+$U$ studies requires the further investigation. According to recent careful studies, the use of the charge-only density functional (such as LDA and GGA) is more desirable for the DFT+$U$ type of calculation rather than the use of the spin density functional (such as LSDA and SGGA) is more desirable for the DFT+$U$ type of calculation.

1We hereafter clearly distinguish LDA and GGA from LSDA and SGGA.
way [26,27]. Since the previous band-structure prediction of molecular \(J_{\text{eff}}\) states has been based on SGGA+U calculation with the functional form suggested by Dudarev et al. [10,28,29], it is necessary to confirm its validity.

In this paper, we performed LDA+U calculations and confirmed the robustness of the \(J_{\text{eff}}\) band-structure for the 4d and 5d lacunar spinels. It is found that \(J_{\text{eff}} = 1/2\) and 3/2 Mott ground states are well maintained in the reasonably large range of Hubbard \(U\) and Hund \(J\) parameters. By introducing a new quantity \(b_{\text{avg}}\), which is designed to measure the \(J_{\text{eff}} = 1/2\) and 3/2 band separation, we present the quantitative argument in comparison to the previous SGGA+U results and the prototype \(J_{\text{eff}} = 1/2\) material, Sr\(_2\)IrO\(_4\). By confirming the previous theoretical prediction, our result hopefully motivates the further research toward the verification of these exotic quantum states and the search for the new functionality.

**Computation details.** Band structure calculations were carried out using the “OpenMX” software package which is based on the linear combination of pseudo-atomic orbital (LCPAO) formalism [30]. The spin-orbit coupling (SOC) was treated within the fully relativistic \(j\)-dependent pseudo-potential [31–33]. We adopted the energy cutoff of 400 rydberg for a real space grid and \(12 \times 12\) \(k\)-points for the primitive unit cell. The crystal structures were optimized, and for the band structure, we present the 2-formula-unit cell results with the antiferromagnetic inter-cluster order.

LDA+\(U\) calculations were performed with the (so-called) fully localized limit (FLL) functional form [34–37]. Note that in (spin-unpolarized) LDA/GGA plus \(U\) scheme, the spin polarization and the magnetization can for orbitals \(\{\}\).

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\[\text{J}_{\text{[10,28,29]}}\), it is necessary to confirm its validity.\]

\[\text{Considering that our lacunar spinels are all insulating, \text{we used the 25\% larger values of } U \text{ than the cRPA results for elements since the Mott gap is opened at around}}\]

\[\text{these values: } U = 3.4, 4.5, 3.0, \text{ and 4.4 eV for GaNb}_2\text{Se}_8, \text{ GaMo}_4\text{Se}_8, \text{ GaTa}_4\text{Se}_8, \text{ and GaW}_4\text{Se}_8, \text{ respectively.}\]

In order to discuss the robustness of the \(J_{\text{eff}}\) nature in a quantitative way, we introduce a new parameter:

\[b_{n,k} = \frac{|P_{n,k}^{1/2} - P_{n,k}^{3/2}|}{2P_{n,k}^{1/2} + P_{n,k}^{3/2}}.\]

Here

\[P_{n,k}^{1/2} = \left\{ \left| \frac{1}{2} + \frac{1}{2} \langle \psi_{n,k} \rangle \right| \right\}^2\]

\[P_{n,k}^{3/2} = \left\{ \left| \frac{3}{2} + \frac{1}{2} \langle \psi_{n,k} \rangle \right| \right\}^2\]

and

\[P_{n,k}^{1/2} = \left\{ \left| \frac{1}{2} - \frac{1}{2} \langle \psi_{n,k} \rangle \right| \right\}^2\]

\[P_{n,k}^{3/2} = \left\{ \left| \frac{3}{2} - \frac{1}{2} \langle \psi_{n,k} \rangle \right| \right\}^2,\]

where \(n\) and \(k\) represent the band index and the momentum, respectively. Also, the atomic \(J_{\text{eff}}\) states are written as \(\{J_{\text{eff}} m_{J_{\text{eff}}}\}\). The \(b_{n,k}\) quantifies the ratio between \(J_{\text{eff}} = 1/2\) and \(J_{\text{eff}} = 3/2\) with a factor 2 which represents the statistical ratio, 2:1, for the ideal \(t_2g\) or molecular \(t_2\) states. Thus, ideally, \(b_{n,k}\) becomes 0 if the given state is a purely atomic \(t_2g\) or molecular \(t_2\) state (i.e., well identified just by \(xy \pm \sigma\), \(xz \pm \sigma\), and \(yz \pm \sigma\)) while it becomes 1.0 when the eigenstate is identical to the pure \(J_{\text{eff}}\) states. Now the separation of \(J_{\text{eff}} = 1/2\) and \(J_{\text{eff}} = 3/2\) bands of a given material can be represented by taking the average for the entire space:

\[b_{\text{avg}} = \frac{\sum_k \sum_n \left( P_{n,k}^{1/2} + P_{n,k}^{3/2} \right) b_{n,k}}{\sum_k \sum_n \left( P_{n,k}^{1/2} + P_{n,k}^{3/2} \right)}\]

This value therefore provides a single number with which the \(J_{\text{eff}}\) nature of band structure can be expressed. As an example, let us consider the prototypical \(J_{\text{eff}} = 1/2\) material \(\text{Sr}_2\text{IrO}_4\). The calculated \(b_{\text{avg}}\) based on the “(so-called)” Dudarev functional” [28] with \(U = 2.0\) yields \(b_{\text{avg}} = 0.486\). This is the case for the original calculation result by Kim et al. [39]. If we performed the calculation with the SOC turned off, \(b_{\text{avg}}\) would become zero. Here we also performed LDA+U calculation for \(\text{Sr}_2\text{IrO}_4\) with the 25\% larger value of \(U\) than the cRPA value for elemental Ir.

The result remains the same; \(b_{\text{avg}} = 0.487\). Here it should be noted that \(b_{\text{avg}}\) depends on the degree of \(d\)-orbitals hybridization with other orbitals (e.g., oxygen or chalcogen \(p\)), the local structure, and crystal field splitting, etc. Therefore, the interpretation and the comparison of the absolute values of \(b_{\text{avg}}\) need to be careful.

**Results and discussion.** The crystal structure of the lacunar spinel \(\text{GaM}_4\text{Se}_8\) (space group \(F\bar{4}3m\)) can be understood as deduced from the spinel, \(\text{GaM}_2\text{Se}_4\), with half-deficient Ga atoms [7,40]. A characteristic feature is that the well-defined molecular units of \(\text{M}_4\text{Se}_4\) and \(\text{GaSe}_4\) are arranged to be the NaCl structure as shown in fig. 1(a). The 12-fold \(M\)-\(M\) bonding complex is split into 6-fold \(t_2\), 4-fold \(e\) and 2-fold degenerate \(a_1\) states due
Fig. 1: (a) Crystal structure of GaM₄Se₈ (cubic Fd3m). The yellow, red, and grey spheres represent Ga, M (=Nb, Mo, Ta, and W) and Se atoms, respectively. GaM₄Se₈ is composed of M₄Se₄ (red) and GaSe₄ (grey) clusters. (b) Schematic energy level diagrams for the M₄ cluster with and without SOC. Without SOC, t₂ molecular orbital states are 6-fold degenerate. SOC splits them into 2-fold \( J_{\text{eff}} = 1/2 \) and 4-fold degenerate \( J_{\text{eff}} = 3/2 \) states.

The electronic structure near the Fermi level is governed by molecular t₂ states which are derived from the atomic t₂g orbitals of transition metals [7,10,41,45,46]. It is noted that the molecular t₂ orbitals have the same symmetry as atomic t₂g, and the SOC leads them to split into the “effective” angular momentum \( J_{\text{eff}} = 1/2 \) doublet and \( J_{\text{eff}} = 3/2 \) quartet [10]. Depending on the number of valence electrons, GaMo₂Se₈ and GaW₂Se₈ have \( J_{\text{eff}} = 1/2 \) while GaNb₄Se₈ and GaTa₄Se₄ carry \( J_{\text{eff}} = 3/2 \) moment; see fig. 1(b). These “molecular” \( J_{\text{eff}} \) ground states were first predicted by band structure calculation [10], and the case for \( J_{\text{eff}} = 3/2 \) has recently been confirmed for \( M = Ta \) [11].

Figure 2 presents the projected density of states (PDOS; left panels) and the fat-band dispersion (right panels) obtained by LDA+U calculations; (a) GaNb₄Se₈, (b) GaMo₄Se₈, (c) GaTa₄Se₄, and (d) GaW₄Se₈. First of all, we note that the characteristic molecular \( J_{\text{eff}} \) states are well maintained as in the previous calculation of SSGA+U functional [10]. The upper/lower Hubbard bands are predominantly of \( J_{\text{eff}} = 1/2 \) and \( J_{\text{eff}} = 3/2 \) character for GaW₂Se₈ and GaTa₄Se₄, respectively; see fig. 2(c) and (d). For 4d materials, the mixture between the two \( J_{\text{eff}} \) states is noticed in the upper and lower Hubbard parts for GaNb₄Se₈ and GaMo₄Se₈, respectively (see fig. 2(a) and (b)), which is a comparable feature with the case of Sr₂IrO₄ [47].

In particular, for GaTa₄Se₈, the higher-lying \( J_{\text{eff}} = 1/2 \) peak is located at around +0.8 eV and well identified (i.e., having a negligible mixture with other states). This feature together with the lower-lying “p” bands at \(< -0.3 \) eV (see the green-colored PDOS in fig. 2(e)) is mainly responsible for the novel quantum interference observed in a recent RIXS experiment which is the first direct experimental evidence for \( J_{\text{eff}} = 3/2 \) moment in a real material [11]. Thus, our current result provides the further confirmation of the characteristic electronic structure of GaTa₄Se₈ and other lacunar spinels by using the charge-only LDA+U calculations which have recently been suggested as a more desirable functional choice than SSGA+U [25,26].

The differences in the two calculated band structures, namely by LDA+U and LSDA+U, are relatively minor. For all four compounds, the calculated band gaps are smaller in LDA+U than LSDA+U by about 0.1–0.2 eV at the same interaction parameters \( U \) and \( J \). It implies that a larger \( U \) is required to open the Mott gap in LDA+U. The band separation between \( J_{\text{eff}} = 1/2 \) and \( J_{\text{eff}} = 3/2 \) is slightly more pronounced in LDA+U results. This feature can also be seen by comparing the calculated \( b_{\text{avg}} \) which will be discussed below.

One obvious limitation of the Dudarev formalism is its inability to calculate the Hund-\( J \)-dependent electronic structure [10,28]. In order to check the robustness of the \( J_{\text{eff}} \) band character in lacunar spinels, we performed the calculations as a function of Hund \( J \); see fig. 3. The results show that the degree of separation of \( J_{\text{eff}} = 1/2 \) and \( J_{\text{eff}} = 3/2 \) bands as represented by \( b_{\text{avg}} \) is well maintained in the wide range of \( J \), especially for 5d compounds. The calculated \( b_{\text{avg}} \) for GaTa₄Se₈ and GaW₄Se₈ is quite large (\( b_{\text{avg}} > 0.68 \)) in the entire range of Hund \( J \) considered in this study (see the violet and green lines). Due to the smaller SOC, on the other hand, the calculated \( b_{\text{avg}} \) for 4d compounds depends more severely on Hund \( J \). In the large-\( J \) limit, the calculated \( b_{\text{avg}} \) becomes as small as \( \sim 0.49 \) and \( \sim 0.25 \) for GaMo₄Se₈ and GaNb₄Se₈, respectively (see the blue and red lines). In the reasonable range of Hund \( J \approx 0.5 \) eV, \( b_{\text{avg}} \) is about 0.5 for both Nb and Mo cases, which is comparable with the value of Sr₂IrO₄. While \( b_{\text{avg}} \) is just a simple measure of the degree of separation of \( J_{\text{eff}} = 1/2 \) and \( J_{\text{eff}} = 3/2 \) bands based on the calculated electronic structure, our calculation clearly supports the robustness of the molecular \( J_{\text{eff}} \) character of lacunar spinels.

In order to further check if the \( J_{\text{eff}} \) band character remains valid, we calculated \( b_{\text{avg}} \) as a function of \( U \) with the fixed \( J \) to the cRPA values: \( J = 0.45, 0.50, 0.40, 0.45 \) eV for GaNb₄Se₈, GaMo₄Se₈, GaTa₄Se₄, and GaW₄Se₈. In a wide range of the \( U \) value from 2.0 to 4.5 eV, we found that \( b_{\text{avg}} \) does not change much. For 5d compounds of \( M = Ta \) and \( W \), the calculated \( b_{\text{avg}} \) remains well above \( b_{\text{avg}} = 0.6 \) and mainly close to 0.7 for
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Fig. 2: The calculated $J_{\text{eff}}$-projected DOS and the band dispersions for (a) GaNb$_4$Se$_8$ ($U = 3.4 \text{ eV}, J = 0.45 \text{ eV}$), (b) GaMo$_4$Se$_8$ ($U = 4.5 \text{ eV}, J = 0.5 \text{ eV}$), (c) GaTa$_4$Se$_8$ ($U = 3.0 \text{ eV}, J = 0.4 \text{ eV}$) and (d) GaW$_4$Se$_8$ ($U = 4.4 \text{ eV}, J = 0.45 \text{ eV}$). The red, blue, green and violet colors in DOS represent the $J_{\text{eff}} = 1/2$, $J_{\text{eff}} = 3/2$, $e$ and $a_1$ characters, respectively. In the band dispersion, the $J_{\text{eff}} = 1/2$ (red) and $3/2$ (blue) characters are represented by the line thickness.

Fig. 3: The calculated $b_{\text{avg}}$ of four lacunar spinel compounds as a function of Hund $J$. The violet, green, blue, and red colors represent the results of GaW$_4$Se$_8$, GaTa$_4$Se$_8$, GaMo$_4$Se$_8$, and GaNb$_4$Se$_8$, respectively.

$U \leq 4.0 \text{ eV}$. In the case of GaMo$_4$Se$_8$, the calculated $b_{\text{avg}}$ remains not smaller than 0.5. For $M = \text{Nb}$, the calculated $b_{\text{avg}}$ is gradually reduced from 0.43 at $U = 3.0 \text{ eV}$ to 0.33 at $U = 4.5 \text{ eV}$, which is noticeably smaller than the other three compounds. While the quantified $b_{\text{avg}}$ is certainly smaller in 4$d$ materials, we think that GaNb$_4$Se$_8$ can also be well identified as a molecular $J_{\text{eff}} = 3/2$ material especially considering that its material properties are quite similar to those of GaTa$_4$Se$_8$ including the insulator-to-metal transition and superconductivity under pressure [6]. It would be an interesting experimental challenge to confirm this exotic ground state for $M = \text{Nb}$ just as in the recent report on GaTa$_4$Se$_8$ [11].

**Conclusion.** – With LDA+$U$ calculations, we confirm the previous theoretical prediction based on SGGA+$U$ for the molecular $J_{\text{eff}}$ band structures in 4$d$/5$d$ lacunar spinels. By introducing a new parameter, $b_{\text{avg}}$, we performed the quantitative examination of $J_{\text{eff}}$ band separation as a function of $J$ which was not feasible in the previous studies. It is found that 5$d$ compounds have quite robust $J_{\text{eff}}$ band character while both 4$d$ and 5$d$ materials have a well-identified $J_{\text{eff}}$ feature at around the realistic $J$ values. This $J_{\text{eff}}$ nature is also quite well maintained in the reasonable range of $U$. Our results provide the solid guidance for future study of these materials by strengthening the theoretical prediction of the novel material characteristic. In particular, the detailed magnetic property at low temperature and under pressure needs to be further identified and understood, which can also elucidate the nature of superconductivity found in $J_{\text{eff}} = 3/2$ materials.

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