1. Introduction

Transition metal oxides have attracted enormous attention for their vast members, divergent properties, novel physics, and great impact on potential applications based on correlated electrons. In past decades, the overwhelming balance of interest was devoted to those compounds with 3d elements, which showed high-$T_C$ superconductivity, colossal magnetoresistivity, multiferroicity, and so on [1, 2]. However, the 4d and 5d counterparts were of less concern and only in very recent years have a few of them, e.g. Sr$_2$IrO$_4$, been extensively studied [3–5]. In principle, for 4d/5d electrons, the electron–electron repulsion, e.g. Hubbard $U$, is much weaker due to more extended wave functions, while the spin–orbit coupling (SOC) is much stronger due to the large atom number, compared with the 3d electrons [6]. These characteristics may lead to non-conventional physics in 4d/5d metal oxides, e.g. $p$-wave superconductors, spin–orbit Mott insulators, Kitaev magnets, topological materials, and possible high-$T_C$ superconductors [5, 7–11].

Till now, the most studied 4d/5d transition metal oxides possess quasi-two-dimensional layer structures (e.g. Sr$_2$IrO$_4$ and Na$_2$IrO$_3$) or three-dimensional structures (e.g. SrIrO$_3$ and SrRuO$_3$). Recently, those 4d/5d metal oxides with quasi-one-dimensional chains have also been synthesized, which may lead to unique low-dimensional physics, e.g. charge density waves, spin-Peierls transitions, and novel magnetic excitations [12–14]. For example, recent experiments reported the basic physical properties of $R_3MO_7$, which adopts the weberite structure, as shown in figure 1(a) [15]. Since here the 4d/5d electrons are mostly confined in one-dimensional chains instead of two-dimensional plane or three-dimensional
framework, their electronic and magnetic structures, may be markedly different from the higher-dimensional structural 4\textit{d}/5\textit{d} counterparts. Given the decreased electron correlations and increased SOC of the 4\textit{d}/5\textit{d} electrons, the physical behavior of these compounds may also show differences compared with quasi-one-dimensional 3\textit{d} metal oxides [16]. In fact, there is rare 3\textit{d} metal oxide forming the weberite \(R_3\text{MO}_7\) structure. It is therefore physically interesting to study these new systems.

Taking \(La_3\text{OsO}_7\) for example, recent experimental studies reported its structural, transport, and magnetic properties, characterized by magnetic susceptibility, x-ray diffraction, as well as neutron diffraction [17]. The corner-shared OsO\(_6\) octahedra form chains along the [001] direction of the orthorhombic framework. The nearest-neighbor distance of Os–Os is \(3.81\)\,Å within a chain, but \(6.75\)\,Å between chains. The Os-O-Os bond angle within a chain is about \(153^\circ\), implying strong octahedra tilting, which is also widely observed in other oxides. Its ground state is an antiferromagnetic (AFM) insulator. Ca-doped \(La_3\text{OsO}_7\) was also studied. Despite the change of nominal carrier density, surprisingly, this hole-doped system remains an insulator (or a semiconductor), violating the rigid band scenario [17]. Similar robust insulating behavior was also found in some doped iridates [18, 19], which were expected to show superconductivity after doping [10, 20]. In contrast, in many perovskites with 3\textit{d} electrons, the carrier doping can lead to much drastic effects, e.g. insulator-metal (or even insulator-superconductor) transition [1, 21]. Therefore, the experience from 3\textit{d} electronic materials can not be simply applied to the 5\textit{d} systems, while the independent studies are necessary.

In this work, we have performed systematic first-principles calculations to understand the electronic and magnetic properties of \(La_3\text{OsO}_7\) as well as isostructural \(La_3\text{RuO}_7\). The doping effect has also been studied, which may provide a reasonable explanation to the insulating behavior, based on the polaron forming. To our best knowledge, there have been very few theoretical studies on these two materials before. Only Khalifah \textit{et al} calculated several magnetic states of \(La_3\text{RuO}_7\) [22]. Even though, their predicted ground state (see figure 1(b)) seems to be inaccurate, according to our results.

2. Model & methods

All following calculations were performed using the Vienna ab initio Simulation Package (VASP) based on the generalized gradient approximation (GGA) [23, 24]. The newly-developed PBEsol function is adopted [25], which can improve the accurate description of crystal structure compared with the old-fashioned PBE one. The plane-wave cutoff is 550\,eV and Monkhorst-Pack \(k\)-points mesh is centered at \(\Gamma\) points.

Starting from the low-temperature experimental orthorhombic (No. 63 \textit{Cmcm}) structures [17, 26], the lattice constants and inner atomic positions are fully optimized till the Hellman–Feynman forces are all less than 0.01\,eV \(\text{Å}^{-1}\). The Hubbard repulsion \(U_{\text{eff}} (=U – J)\) is imposed on Ru’s 4\textit{d} orbitals and Os’s 5\textit{d} orbitals [27]. Various values of \(U_{\text{eff}}\) have been tested from 0\,eV to 4\,eV. It is found that \(U_{\text{eff}}\) is the best choice to reproduce the experimental structure of \(La_3\text{RuO}_7\), while for \(La_3\text{OsO}_7\) the bare GGA without \(U_{\text{eff}}\) is the best choice. Comparing with experimental values [17, 22], the deviation of calculated lattice constants are only <0.8\% for \(La_3\text{OsO}_7\), and 0.5\% for \(La_3\text{RuO}_7\), providing a good start point to study other physical properties. These choices of \(U_{\text{eff}}\) are quite reasonable considering the gradually deceasing Hubbard repulsion from 3\textit{d} to 5\textit{d}.

Considering the fact of heavy atoms, the relativistic SOC is also taken into consideration, comparing with those calculations without SOC.
3. Results and discussion

3.1. Undoped La$_3$MO$_7$: magnetic orders and reduced moments

First, the magnetic ground state is checked by comparing several possible magnetic orders, including ferromagnetic (FM) state, and various AFM ones (AFM I–IV as shown in figures 1(b)–(e)). For AFM I, III, and IV states, the -up–down-up–down- ordering is adopted within each chain, but with different coupling between chains. Taking the FM state as the energy reference, the energies of all candidates are summarized in table 1, which suggest the AFM IV to be the possible ground state for both $M$ = Os and Ru.

By mapping the system to a classical spin model, the exchange coefficients between neighboring (within each chain and between chains, as indicated in figure 1(a)) spins (normalized to $|| = S_1$) can be extracted as:

$J_1 = 72.00$ meV, $J_2 = 8.34$ meV, $J_3 = 2.96$ meV for $M$ = Os,

$J_1 = 3.45$ meV, $J_2 = 0.66$ meV, $J_3 = 0.37$ meV for $M$ = Ru.

Obviously, the exchanges between Os chains are quite prominent even for the nearest neighbor chains (distance up to 6.75 Å), implying strongly coupled AFM chains, different from the one-dimensional intuition. And these exchanges are much stronger in La$_3$OsO$_7$ than those corresponding in La$_3$RuO$_7$. These characters of La$_3$OsO$_7$ benefit from the more extended distribution of 5d orbitals.

Experimentally, the AFM transition temperatures of La$_3$OsO$_7$ are much higher than the corresponding ones of La$_3$RuO$_7$. For La$_3$OsO$_7$, the intrachain magnetic correlation emerges near $\sim$100 K (mainly due to $J_1$) and the fully three-dimensional AFM ordering occurs at 45 K (also determined by $J_2$ and $J_3$ [22]. In contrast, the signal for magnetic ordering in La$_3$RuO$_7$ appears at $\sim$17 K with short-range characters [22]. Note [22] previously predicted the ground state of La$_3$RuO$_7$ to be AFM I, which is ruled out according to our calculation. More neutron experiments are needed to refine the subtle magnetic order of La$_3$RuO$_7$.

Table 1. The energy difference (in unite of meV) for a minimal unit cell (four f.u.’s), local magnetic moment per $M$ within the default Wigner–Seitz sphere (in unit of $\mu_B$), and band gap (in unit of eV) of La$_3$MO$_7$.

| $M$   | Magnetism | Energy | Moment       | Gap  |
|-------|-----------|--------|--------------|------|
| Os    | FM        | 0      | 0.851, 0.846 | 0.19 |
|       | AFM I     | −689   | 1.670, −1.670| 0.42 |
|       | AFM II    | −228   | 1.435, −1.435| 0    |
|       | AFM III   | −709   | 1.652, −1.652| 0.54 |
|       | AFM IV    | −714   | 1.651, −1.651| 0.53 |
| Ru    | FM        | 0      | 1.958, 1.959 | 0.53 |
|       | AFM I     | −23    | 1.902, −1.902| 0.60 |
|       | AFM II    | −22    | 1.948, −1.948| 0.78 |
|       | AFM III   | −38    | 1.902, −1.902| 0.73 |
|       | AFM IV    | −42    | 1.900, −1.899 | 0.70 |

Figure 2. Density of state (DOS) and projected density of state (PDOS) of La$_3$MO$_7$ ($M$ = Os or Ru). (a)–(b) La$_3$OsO$_7$; (c)–(d) La$_3$RuO$_7$. (a) and (c) SOC-disabled; (b) and (d) SOC-enabled. Right panels: the corresponding near-Fermi-level PDOS of an individual $M$ ion.
$5d$ orbitals have a large SOC coefficient, we also calculate the DOS and PDOS with SOC enabled, which are presented in figure 2(b) for comparison [11]. However, there is no qualitative difference between the SOC-enabled and SOC-disabled calculations. The quantitative differences include: (1) a shrunk band gap $\sim 0.37\,\text{eV}$ (SOC-enabled); (2) a slightly reduced local magnetic moment from 1.661 $\mu_B$/Os (SOC-disabled) to 1.578 $\mu_B$/Os (SOC-enabled). In particular, the magnitude of orbital moment is only $\sim 0.087\,\mu_B$. Note, this local moment is obtained by integrating the wave function within the Wigner–Seitz radius of Os (0.58 $\text{Å}$) and is thus not absolutely precise, even though, the theoretical values are still quite close to the experimental one $\sim 1.71\,\mu_B$/Os [17]. Such a local moment is significantly reduced from the high-spin expectation (3 $\mu_B$/Os) of three $t_{2g}$ electrons as in Os$^{5+}$ here, but agrees with recent neutron diffraction results of Os$^{5+}$ in several double perovskites [28–30].

According to the PDOS (insert of figures 2(a) and (b)), every Os seems to be in the high-spin state, i.e. only spin-up electrons within the Wigner–Seitz radius. So how does one understand the reduced local moment? The above SOC-enabled calculation has ruled out SOC as the main contribution, which can only slightly affect the value of moment. Instead, the real mechanism is the covalency between Os and O. As revealed in PDOS, there exists strong hybridization between Os’s $5d$ and O’s $2p$ orbitals around the Fermi energy level, due to the spatial extended $5d$ orbitals. In fact, the previous neutron study also attributed the reduced moment to the hybridization between Os and O [17].

Furthermore, the same calculations have been done for La$_3$RuO$_7$ and the DOS/PDOS are shown in figures 2(c) and (d), which are qualitatively similar to La$_3$OsO$_7$. The local magnetic moment of Ru$^{5+}$ is 1.892 $\mu_B$ (SOC-enabled) or 1.900 $\mu_B$ (SOC-disabled), and such a negligible difference implies a weaker SOC effect compared with La$_3$OsO$_7$. In particular, the magnitude of orbital moment is only $\sim 0.018\,\mu_B$ per Ru, even lower than that of Os. The total moment is also lower than the ideal 3 $\mu_B$ but higher than the moment of Os, which is also reasonable considering the more localized distribution of $4d$ orbitals than $5d$. The reduced moment of Ru$^{5+}$ is also due to the covalency between Ru and O, as indicated in figure 2(c).

The calculated band gap of La$_3$RuO$_7$ is 0.70 eV, which is higher than the experimental value ($\sim 0.28\,\text{eV}$) extracted from transport [22]. This inconsistency is probably due to the polycrystalline nature of samples and the presence of small amounts of the highly insulating La$_2$Os$_2$O$_7$, as admitted in [22]. More measurements, especially the optical absorption spectrum, are needed to clarify the intrinsic band gap of La$_3$RuO$_7$.

The aforementioned weak SOC effects to magnetism and band structures in La$_3$RuO$_7$ and La$_3$OsO$_7$ seem to contradict the intuitive expectation of strong SOC coefficients for $4d/5d$ electrons. This paradox can be understood as follows. Since in La$_3$MO$_7$ the low-lying $t_{2g}$ orbitals are half-filled ($t_{2g}^3$), the Hund coupling between $t_{2g}$ electrons will prefer the high-spin state, in which the orbit moment is mostly quenched. Then the net effect of SOC is weak even if the SOC efficiency is large.

### Table 2. The energy difference (in unit of meV for 4 f.u.’s) and local magnetic moments of $M$ in unit of $\mu_B$ of doped La$_{12.4}$Ca$_{0.6}$MO$_7$. The SOC is disabled in calculations except for those items with ‘+ SOC’.

| System | Magnetism   | Energy | Moment |
|--------|-------------|--------|--------|
| $M = \text{Os}$ | FM | 0 | 1.690, 1.694, 1.707, 1.709 |
| | AFM I | 79 | 1.559, 1.622, 1.565, 1.219 |
| | AFM II | −63 | 1.647, 1.645, 1.647, 1.699 |
| | AFM III | −315 | 1.393, 1.393, 1.528, 1.511 |
| | (+SOC) | AFM III | 1.298, −1.298, −1.442, 1.449 |
| | AFM IV | −285 | 1.257, 1.617, −1.620, −1.289 |
| $M = \text{Ru}$ | FM | 0 | 1.753, 1.765, 1.797, 1.803 |
| | FM | | 1.749, 1.753, 1.791, 1.792 |
| | (+SOC) | AFM I | 363 | 1.896, 1.912, −1.887, 1.265 |
| | AFM II | 9 | 1.726, 1.735, −1.789, −1.794 |
| | AFM III | 40 | −1.697, 1.706, 1.787, −1.749 |
| | AFM IV | 42 | 1.568, 1.891, −1.892, −1.531 |

Other $5d$ electronic systems with more or less electrons than $t_{2g}$, e.g. Sr$_2$IrO$_4$, can activate the SOC effects.

#### 3.2. Chemical doping and polaron forming

Doping is a frequently used method to tune physical properties of materials. For Mott insulators, proper doping may result in superconductivity (e.g. for cuprates) or colossal magnetoresistivity (e.g. for manganites). One of the most anticipant doping effects on $5d$ metal oxides is the possible superconductivity, as predicted in Sr$_2$IrO$_4$ [10, 20]. However, till now, not only has the superconductivity not been found, but also there is an unsolved debate regarding the metallicity of doped Sr$_2$IrO$_4$. Some experiments reported the metallic transport behavior upon tiny doping and observed Fermi arcs using angle-resolved photoelectron spectroscopy (ARPES) [31–34], while some others reported robust insulating (or semiconducting) behavior even upon heavy doping by element substitution and field-effect gating [19, 35].

Similarly, for La$_3$OsO$_7$, the experiment found that the Ca-doping up to 6.67% could reduce the resistivity but the system remained insulating [17]. Then it is interesting to investigate the doping effect. In our calculation, by using one Ca to replace one La in a unit cell, i.e. 8.33% doping, the crystal structure is re-relaxed with varying magnetism. Then the ground state turns out to be AFM III, a little different from the above Os-based counterpart. As summarized in table 2, whatever the lowest energy FM state or the second lowest energy AFM II state, the in-chain FM order remains robust.

In contrast, when the 8.33% Ca-doping is applied to La$_3$RuO$_7$, our calculations predict that the ground state magnetism would probably be transformed from AFM IV to FM, different from the above Os-based counterpart. As summarized in table 2, whatever the lowest energy FM state or the second lowest energy AFM II state, the in-chain FM order remains unambiguous. This result is also reasonable considering the much weaker in-chain antiferromagnetism (i.e. $J_1$) of...
La$_3$RuO$_7$. Thus the antiferromagnetism of La$_3$RuO$_7$ should be more fragile against chemical doping. Further experiments are needed to verify our prediction.

As shown in figure 3, the DOS’s of doped La$_3$OsO$_7$ and La$_3$RuO$_7$ show finite values at Fermi levels, implying metallic behavior, which seems to be opposite to experimental observation of doped La$_3$OsO$_7$. However, a careful analysis finds that this finite DOS at Fermi level should be due to a technical issue of calculation. The substitution of one La by one Ca will bring one hole into the system. However, the AFM state implies at least doubly degenerate bands (spin-up and spin-down). Then the one hole doping to the system means half hole doping to the spin-up and spin-down bands, respectively. Technically, the minimal unit cell calculation does not allow the forming of sub-bands for the half-filling spin-up (and spin-down) band. Then this half hole doping in the minimal unit cell leads to the

Figure 3. DOS/PDOS and corresponding band structures around the Fermi level of La$_{11/4}$Ca$_{1/4}$MO$_7$ ($M =$ Os or Ru). ((a)–(c)) La$_{11/4}$Ca$_{1/4}$OsO$_7$; ((d)–(f)) La$_{11/4}$Ca$_{1/4}$RuO$_7$. In (e), spin up/down bands are distinguished by blue/red colors. ((g)–(h)) The SOC-enabled DOS/PDOS which are only slightly changed compared with the non-SOC ones.
finite DOS at the Fermi level. In the real system beyond the minimal unit cell, the bands may be split to sub-bands to overcome this issue. Thus, the finite DOS at Fermi level does not guarantee metallicity of Ca-doped La$_3$OsO$_7$, while the metallicity of Ca-doped La$_3$RuO$_7$ needs experimental verification.

The SOC-enabled calculations have also been performed for the doped La$_3$MO$_7$. However, due to the partial hole concentration (~1/4 per M), the SOC effect is not prominent. For example, the near-Fermi-level DOS (figures 3g)-(hi)) are similar to the corresponding non-SOC ones. The local moments for the ground states are also listed in table 2, and are only slightly lower than the original one without SOC, especially for the Ru case.

The PDOS’s of Ca-doped La$_3$OsO$_7$ show that the Os ions can be classified into two types: (a) two near-Ca Os’s (one spin up and one spin down); (b) the other two Os’s. Their PDOS’s are slightly different, and the type-b Os’s are less affected by the Ca-doping, namely the doping effect has a tendency to be localized. In contrast, the PDOS’s of Ca-doped La$_3$RuO$_7$ show that almost all four Ru ions are equally affected by the Ca-doping.

To clarify the effect of doping, the charge density distribution of hole in Ca-doped La$_3$OsO$_7$ is visualized in figure 4(a). Here we only extract the wave function of the above-Fermi-level partial bands, which can represent the hole (half spin-up plus half spin-down hole). Clearly, the orbitals of hole are the $d_{xy}$ type on Os site and the $p_z$ type on O site (the chain direction is chosen as the $z$ axis), implying a spatially extended wave function. According to the Slater–Koster equation [36], the lying-down $d_{xy}$ orbital has a very weak hopping amplitude along the $z$-axis, if not ideally zero. Thus, the hole will be restricted near the Ca dopant by the Coulombic interaction, leading to the semiconducting behavior of Ca-doped La$_3$OsO$_7$.

According to the abundant experience of 3d electron systems, the lattice distortions, e.g. Jahn–Teller modes, will be always activated by partially occupied $t_{2g}$ orbitals (or $e_g$ orbitals) to split the energy degeneration between/among orbitals. By carefully analyzing the bond lengths of oxygen octahedra, it is easy to verify the effect of hole modulated lattice distortions. First, the breathing mode $Q_1$ can be defined as $(l_x + l_y + l_z)/\sqrt{3}$ to characterize the size of oxygen octahedral cage, where $l$ denotes the O-M-O bond length along a particular axis [37, 38]. After the doping, the changes of $Q_1$ are $-5.307$ pm for the near-Ca Os’s and $-3.636$ pm for the other two Os’s. These shrunken octahedral cages are due to the Coulombic attraction between positive-charged hole on Os and negative charged oxygen ions. Second, the Jahn–Teller modes $Q_2$ and $Q_3$ can be defined as $(l_x - l_y)/\sqrt{2}$ and $-(l_y - l_z + 2l_x)/\sqrt{6}$ respectively, which can split the degeneration among triplet $t_{2g}$ orbitals or between doublet $e_g$ orbitals. For La$_3$OsO$_7$, the original Jahn–Teller modes are $Q_2 = 0.100$ pm and $Q_3 = 3.938$ pm. This prominent $Q_3$ mode prefers the $d_{xy}$ orbital for electrons. Therefore, the $d_{xy}$ hole after doping is not driven by this presented lattice distortion, but can only be due to the Coulombic interaction from Ca$^{2+}$ since the spatial distribution of $d_{xy}$ hole is closer to dopant (see figure 4). Then this Coulombic-driven $d_{xy}$ hole will suppress the $Q_3$ mode: $Q_3 = -2.414$ pm for near-Ca Os’s and $-1.007$ pm for the other two Os’s. Meanwhile, the $Q_2$ mode is enhanced: $Q_2 = 0.942$ pm for near-Ca Os’s and 1.152 pm for the other two Os’s.

For doped La$_3$RuO$_7$, the changes of $Q_1$ are $-4.074$ pm for the near-Ca Ru’s and $-3.470$ pm for the other two, similar to the case of doped La$_3$OsO$_7$. For original La$_3$RuO$_7$, the Jahn–Teller modes are: $Q_2 = 0.110$ pm, $Q_3 = 5.351$ pm. In contrast with La$_3$OsO$_7$, this lattice distortion does not favor the $d_{xy}$ orbital (for electron) in energy. Then the Coulombic-driven $d_{xy}$ hole will further enhance this positive $Q_3$ mode: $Q_3 = 7.574$ pm for the near-Ca Ru’s and 7.913 pm for the other two Ru’s. Meanwhile, the $Q_2$ mode is enhanced as in La$_3$OsO$_7$: $Q_2 = 1.227$ pm for the near-Ca Ru’s and 1.129 pm for the other two.
The localization of hole can be further confirmed by calculations of supercells. As shown in figures 4(c), the hole occupancies on four near-Ca Os ions are more prominent than other Os ions which stay only one u.c. space from the dopant. Similar results exist for doped La$_3$RuO$_7$. This localized hole with distorted lattices forms the polaron.

According to previous studies, there are magnetic polarons in manganites, which are ferromagnetic clusters of several Mn sites embedded in AFM background [39]. This scenario is quite possible for La$_3$RuO$_7$ considering the ferromagnetically-aligned Ru ions as revealed in table 2. However, for La$_3$OsO$_7$, both the results of the minimal cell (shown in table 2) and the calculation of doubled-supercell (along the c-axis) do not favor magnetic polaron, at least the small (up to three-site) magnetic polaron. It is also reasonable considering the differences among 3$d^4$4$d^5$/5$d^1$-Mott-insulators. Of course, the difference among 3$d^5$/5$d^1$-Mott-insulators and further tunes the lattice distortions. The experimental observed semiconducting behavior after doping is explained as the forming of polarons.

In short, considering the above results of hole restricted by Coulombic interaction and the lattice distortions following the particular $d_{xy}$-orbital hole, it is reasonable to argue that the carriers generated by Ca doping would be mostly localized near dopant to form polaron and contribute to the semiconducting behavior. This scenario may explain the puzzle why the expected metallicity is absent in some doped 5$d$-Mott-insulators.

4. Conclusion

In summary, two 4$d$/5$d$ metal oxides La$_3$MO$_7$ ($M$ = Os and Ru) with unique quasi-one-dimensional $M$ chains have been studied systematically using the density function theory calculation. Their magnetic ground states are revealed to be identical, in agreement with the recent neutron study of La$_3$OsO$_7$ but different from early calculations on La$_3$RuO$_7$. Due to the half-filled $t_{2g}$ configuration, the spin–orbit coupling is not crucial in these two systems. Moreover, the doping of Ca has been predicted to affect the magnetism somewhat, leading to different effects for $M$ = Os and Ru. In particular, the $d_{xy}$-orbital-sharp hole is formed after Ca dopant. This orbital is driven by the Coulombic interaction, and further tunes the lattice distortions. The experimental observed semiconducting behavior after doping is explained as the forming of polarons.

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References

[1] Dagotto E 2005 Science 309 257–62
[2] Dong S, Liu J M, Cheong S W and Ren Z 2015 Adv. Phys. 64 519–626
[3] Kim B J, Ohsumi H, Komese T, Sakai S, Morita T, Takagi H and Arima T 2009 Science 323 1329–32
[4] Meng Z Y, Kim Y B and Kee H Y 2014 Phys. Rev. Lett. 113 177003
[5] Kim B J et al 2008 Phys. Rev. Lett. 101 076402
[6] Cao G and De-Long L (ed) 2013 Frontiers of 4d And 5d Transition Metal Oxides (Singapore: World Scientific)
[7] Nelson K D, Mao Z Q, Maeno Y and Liu Y 2004 Science 306 1151–4
[8] Kitaev A 2006 Ann. Phys. 321 2–111
[9] Witzcak-Krempa W, Chen G, Kim Y B and Balents L 2013 Annu. Rev. Condens. Matter Phys. 5 57–82
[10] Wang F and Senshti T 2011 Phys. Rev. Lett. 106 136402
[11] Xiang H J and Whangbo M H 2007 Phys. Rev. B 75 052407
[12] Hase M, Terasaki I and Uchinochurako K 1993 Phys. Rev. Lett. 70 3651
[13] Monceaux P, Ong N P, Portis A M, Meerschaut A M and Rouxel J 1976 Phys. Rev. Lett. 37 602
[14] Tennant D A, Cowley R A, Nagler S E and Tsvelik A M 1995 Phys. Rev. B 52 13368
[15] Allpress J G and Rossell H J 1979 J. Solid State Chem. 27 105–14
[16] Comini E, Baratto C, Faglia G, Ferroni M, Vomiero A and Sherveglieri G 2009 Prog. Mater. Sci. 54 1–67
[17] Morrow R, Susner M A, Sumption M D and Woodward P M 2015 Phys. Rev. B 92 134402
[18] Wang J C et al 2015 Phys. Rev. B 92 214411
[19] Lu C, Dong S, Quindeau A, Preziosi D, Hu N and Alexe M 2015 Phys. Rev. B 91 104401
[20] Watanabe H, Shirakawa T and Yunoki S 2013 Phys. Rev. Lett. 110 027002
[21] Imada M, Fujimori A and Tokura Y 1998 Rev. Mod. Phys. 70 1039–256
[22] Khalifah P, Erwin R W, Lynn J W, Huang Q, Batlogg B and Cava R J 1999 Phys. Rev. B 60 9573
[23] Kresse G and Hafner J 1993 Phys. Rev. B 47 558–61
[24] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169–86
[25] Perdew J P, Ruzsinszky A, Csonka G I, Vydrov O A, Scuseria G E, Constantin L A, Zhou X and Burke K 2008 Phys. Rev. Lett. 100 136406
[26] Lam R, Wux F and Greedan J E 2002 J. Solid State Chem. 167 182–7
[27] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Phys. Rev. B 57 1505–9
[28] Kermarrec E et al 2015 Phys. Rev. B 91 075133
[29] Taylor A E, Morrow R, Singh D J, Calder S, Lumsden M D, Woodward P M and Christianson A D 2015 Phys. Rev. B 91 100406
[30] Kanungo S, Yan B, Felser C and Jansen M 2016 Phys. Rev. B 93 161116
[31] Kim Y K, Sung N H, Denlinger J D and Kim B J 2016 Nat. Phys. 12 37–41
[32] Kim Y K et al 2014 Science 345 187–90
[33] de la Torre A et al 2015 Phys. Rev. Lett. 115 176402
[34] Korneta O B, Qi T, Chikara S, Parkin S, DeLong L E, Schlottmann P and Cao G 2010 Phys. Rev. B 82 115117
[35] Calder S, Cao G X, Lumsden M D, Kim J W, Gai Z, Sales B C, Mandrus D and Christianson A D 2012 Phys. Rev. B 86 220403
[36] Slater J C and Koster G F 1954 Phys. Rev. 94 1498–524
[37] Dagotto E, Hotta T and Moreo A 2001 Phys. Rep. 344 1–135
[38] Dong S, Zhang X T, Yu R, Liu J M and Dagotto E 2011 Phys. Rev. B 84 155117
[39] Meskine H, Saha-Dasgupta T and Satpathy S 2004 Phys. Rev. Lett. 92 056401