A hybrid-exchange density-functional theory study of the electronic structure of MnV$_2$O$_4$: exotic orbital ordering in the cubic structure

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The electronic structures of MnV$_2$O$_4$, including the cubic and tetragonal structures, have been studied by using hybrid-exchange density functional theory. The computed electronic structure of the tetragonal MnV$_2$O$_4$ shows an anti-ferro orbital ordering on V sites and a ferrimagnetic ground state (the spins on V and Mn are anti-aligned). These results are in a good agreement with the previous theoretical result obtained from LDA (local-density approximation) + U methods [S. Sarkar, et. al., Phys. Rev. Lett. 102, 216405 (2009)]. Moreover, the electronic structure, especially the density of states of the cubic MnV$_2$O$_4$ has been predicted with a good agreement with the recent soft x-ray spectroscopy experiment. Similar to the tetragonal MnV$_2$O$_4$, the spins on V and Mn in cubic structure favour the ferrimagnetic configuration. Most interesting is that the computed charge densities of the spin-carrying orbitals on V in the cubic MnV$_2$O$_4$ show an exotic orbital ordering, i.e., a ferro-orbital ordering along [110] but an anti-ferro-orbital ordering along [110].

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I. INTRODUCTION

Many fascinating phenomena in condensed-matter physics were discovered in transition-metal oxides (TMOs) and their closely related compounds such as the first high transition temperature superconductor YBaCuO$_{1.85}$, whose superconductivity is closely related to the strong electron correlation. Another interesting phenomenon, orbital ordering (OO) has a long history in condensed matter physics, which occurs when the orbital degeneracy is lifted by typically the interaction with the lattice environment [3,4]. The best-known example of OO is the Jahn-Teller (JT) distortion observed in LaMnO$_3$ [5]. Therein the five $d$-orbitals are first separated into two degenerate manifolds, $e_g$ (comprising $d_{x^2-y^2}$ and $d_z$) and $t_{2g}$ ($d_{xy}$, $d_{xz}$, and $d_{yz}$), in a cubic environment, and then the $e_g$ manifold is further split by the JT distortion owing to the partially filled $e_g$ manifold. The physics here has been well accounted for by the so-called Kugel-Khomskii model [6]. Most experimental and theoretical works so far are focused on the system containing transition-metal ions with partially filled $e_g$ orbitals, i.e., $e_g$ active. This type of orbital occupancy can lead to the strongest JT effect because the related $d$-orbitals directly point to ligands and strongly hybridize with $s$-orbitals of the anion.

Recently, much attention has been paid to vanadium spinels AB$_2$O$_4$ (A=Mg, Zn, and Cd) and MnV$_2$O$_4$ [7], which are, however, $t_{2g}$-active, in contrast to most of known TMOs showing OO. In this type of compound, the V$^{3+}$ ions on the B sites form a pyrochlore lattice. The two $d$-electrons on V, occupying two $t_{2g}$ orbitals, leads to a total spin of $S=1$, resulting in a $t_{2g}$-active OO. The OO in this type of compounds is further complicated by their intrinsic geometrical frustration. In 1939, the ordering of electrical charge on the B-site pyrochlore lattice was proposed to cause a sharp increase of the electrical resistivity when cooling below ~120 K in Fe$_3$O$_4$ (the ‘Verwey’ transition) [8]. Anderson was the first to realise the intimate relationship between the proton ordering in the ice, the Verwey charge ordering, and the ordering of Ising spins [9]. Regardless of the specific material types, geometrical frustration plays a crucial role to determine the spin or charge configurations, in order to minimise exchange or Coulomb energies.

In the cases that A-site ion is nonmagnetic (A=Mg, Zn, and Cd), these vanadium spinels share the common feature that a magnetic ordering follows a structural transition from cubic to tetragonal symmetry when lowering the temperature [10]. In contrast to these vanadium spinels, MnV$_2$O$_4$ (see Fig.1), in which the Mn$^{2+}$ ion is in a $d^8$ half-filled high-spin configuration ($S=\frac{3}{2}$), first experiences a magnetic transition to the collinear ferrimagnetic state at $T=56$ K, and then a structural distortion at a slightly lower temperature, $T=53$ K along with a transition to the non-collinear ferrimagnetic state [12,16]. The observed magnetic ordering below $T=56$ K is ferrimagnetic, i.e., the magnetic moments on Mn$^{2+}$ and V$^{3+}$ are anti-aligned. In the structural transition, the symmetry is lowered from cubic to tetragonal. The orbital ordering of the ground state in the tetragonal MnV$_2$O$_4$ structure has been shown theoretically [11] as an A-type antiferro-orbital ordering with a propagation vector of (002). The orbital and magnetic orderings of the tetragonal MnV$_2$O$_4$ have been extensively studied both theoretically [11] and experimentally [10]. On the other hand, the electronic structure and magnetic properties of the cubic MnV$_2$O$_4$ are yet to be studied in details.

Previously, the electronic structure and magnetic properties of the tetragonal MnV$_2$O$_4$ have been investigated theoretically using LDA (local-density approximation) +...
II. COMPUTATIONAL DETAILS

The calculations of the electronic structures of tetragonal and cubic MnV$_2$O$_4$ were carried out by using DFT and hybrid-exchange functional PBE0 as implemented in the CRYS TAL 09 code [24]. The crystal structures of the cubic (symmetry group $Fd\overline{3}m$) and tetragonal (symmetry group $I4_1/amd$) MnV$_2$O$_4$ experimentally determined in Ref. [11] have been adopted here to perform all the calculations. The basis sets for the atomic orbitals centered on the Mn [25], V [20], and O [27] atoms, which are designed for solid-state compounds, were used throughout all the calculations. The Monkhorst-Pack samplings of reciprocal space are carried out choosing a grid of shrinking factor to be $6 \times 6 \times 6$ ($6 \times 6 \times 5$) in order for a consistency with the ratios among reciprocal lattice parameters for the cubic (tetragonal) MnV$_2$O$_4$. The truncation of the Coulomb and exchange series in direct space is controlled by setting the Gaussian overlap tolerance criteria to $10^{-6}, 10^{-6}, 10^{-6}, 10^{-6}$, and $10^{-12}$ [24]. The self-consistent field (SCF) procedure is converged to a tolerance of $10^{-6}$ a.u. per unit cell (p.u.c). To accelerate convergence of the SCF process, all the calculations have been converged by using a linear mixing of Fock matrices by 30%.

Electronic exchange and correlation are described using the PBE0 hybrid functional [20], free of any empirical or adjustable parameter. The advantages of PBE0 include a partial elimination of the self-interaction error and balancing the tendencies to delocalize and localize wave-functions by mixing a quarter of Fock exchange with that from a generalized gradient approximation (GGA) exchange functional [20]. The broken-symmetry method [28] is used to localize collinear opposite electron spins on atoms in order to describe the anti-ferromagnetic state. The performance of the hybrid functionals including B3LYP [30] and PBE0 have previously been shown to provide a good description of the electronic structure and magnetic properties for both inorganic and organic compounds [18, 19].

III. RESULTS AND DISCUSSIONS

A. Electronic structure

The projected densities of states (PDOS) of the cubic and tetragonal MnV$_2$O$_4$ structures for the AFM configuration (the spins on Mn and V are anti-ligned) have been shown in Fig. 2. The magnetic structure could be much more complicated owing to the exchange interaction between the nearest-neighbouring Mn (V) atoms [12] and the spin-orbit coupling (SOC), which will cause the non-collinear magnetic ordering. However, this topic is beyond the scope of this paper that is focused on the electronic structure and the magnetic ground state within collinear magnetism. The zero energy is align with the valence band maximum (VBM). In the cubic and tetragonal structures, Mn 3d PDOS (Fig. 2a and b) shows that five d-orbitals including $d_{xz}$, $d_{yz}$, $d_{x^2-z^2}$, and $d_{xy}$ are singly occupied, thus giving a spin $\frac{5}{2}$. In the Mn $d$-orbital PDOS, the lower and upper $d$-bands of Mn can be seen clearly and gapped by a large energy $\sim 10$ eV. From the analysis of Mulliken spin densities and V 3d PDOS (Fig. 2c and d), the two electrons occupying $t_{2g}$ state, including $d_{xz}$, $d_{yz}$, and $d_{xy}$, would incur a Jahn-Teller distortion; this can be identified as the origin of the orbital ordering in MnV$_2$O$_4$. Similar to Mn $d$-bands, the upper and lower Hubbard $d$-bands of V are shown in the PDOS, which are gapped by the on-site Coulomb interaction $\sim 7$ eV. The O 2p PDOS (Fig. 3).
FIG. 2: (Color online.) The PDOS of the $d$-orbitals on Mn, the $d$-orbitals on V, and the $p$-orbitals on O of the cubic (left) and tetragonal (right) MnV$_2$O$_4$ are shown. The PDOS onto $d_{x^2-y^2}$ is in green, $d_{z^2}$ in red, $d_{xz}$ in blue, $d_{yz}$ in purple, and $d_{xy}$ in black, respectively. For $p$-orbitals, the PDOS onto $p_x$ is in green, $p_y$ in red, and onto $p_z$ in black, respectively. In (g) and (h), the total PDOS onto Mn $d$-orbitals is in red, V $d$-orbitals in green, and O $p$-orbitals in black, respectively.
and f) for the cubic MnV_2O_4 is much more delocalized than those for the tetragonal. This might be due to the elongation of the lattice vector a and b in the tetragonal structure. The O 2p PDOS are particularly dominant at approximately 5 eV below the VBM for both the cubic and tetragonal structures, which overlap with the rather weak Mn 3d and V 3d PDOS. The O 2p orbitals involved here will give rise to the so-called oxygen bonding states that represent the hybridisation between the d-orbitals on transition metals and p-orbitals on O atoms. In addition, it can be observed by comparing the spin-up and spin-down PDOS, that the O 2p states have been strongly spin-polarized by the magnetic moments on Mn and V.

The PDOS onto the V sites have also been compared with the previous results obtained by the LDA+U [11], which suggests that there is a qualitative agreement between them except that the DFT band-gap computed here (∼ 3 eV) is larger than the previously computed one (∼ 1 eV) in Ref. [11]. The computed PDOS is in good agreement with recent soft x-ray microscopy; the combination of the theoretical work and experiments will be published in a forthcoming paper [31].

The computed crystal-field splitting between t_{2g} and e_g states of Mn^{2+} and V^{2+} ions in cubic MnV_2O_4 can be read from Fig.2a, which is ∼ 1 eV. On the other hand, in tetragonal MnV_2O_4, for both Mn^{2+} and V^{2+}, d_{3z^2} and d_{xy} are closely aligned while the other three 3d-orbitals overlap well, as shown in Fig.2. This picture is consistent with the previous calculations reported in Ref. [11]. The crystal-field splitting between these two groups is ∼ 1 eV. The on-site Coulomb interaction U can be approximated by observing the gap between occupied d-orbitals and unoccupied ones (approximately 5 eV for Mn site, and 7 eV for V), which is much larger than the crystal-field splitting that can be approximated by the splitting in the peaks of Mn and V PDOS. This would result in a high-spin state for Mn^{2+} and V^{2+} ions as well as is consistent with the experiments [10].

The Mulliken spin densities on Mn and V sites for the cubic (tetragonal) MnV_2O_4 are 4.8 (4.7)μ_B and −2.0 (−1.9)μ_B, respectively. They are close to the expected values, i.e. 5μ_B for Mn and −2μ_B for V (anti-aligned). For tetragonal (cubic) structure, the computed total energies for a conventional cell with the spins on Mn and V aligned (ferromagnetic) is higher than the tetragonal. Similarly we can estimate the exchange interaction for the cubic structure, which is ∼ 23 meV. On the other hand, the exchange interaction between the spins on Mn and V can also be estimated by using the super-exchange formalism, where t can be quantified in the PDOS, which is ∼ 0.5 eV for Mn and ∼ 1 eV for V. Therefore, the exchange interaction between Mn and V, which can be estimated by using $U_{MnV}^{\text{exchange}}$ ($U = U_{Mn} + U_{V}$), which is ∼ 59 meV. This is in the same order as that calculated from the total energy differences aforementioned (here an average value is taken for on-site Coulomb interaction). A detailed discussion about the exchange interaction, taking into account all the d-orbitals on both Mn and V would be great, but beyond the scope of this paper.

B. Orbital ordering

The OO in cubic and tetragonal MnV_2O_4 can be illustrated by the spin densities on V (see Fig.3) – the difference between the charge densities of spin-up and spin-down orbitals (essentially the charge densities of the spin-carry orbitals). In the tetragonal structure, the relative orientation rotation of neighbouring orbitals is illustrated by the red arrows in Fig.3b; this is consistent with the previous calculations presented in Ref. [11] in which an anti-ferro-orbital ordering (AFOO) has been predicted. The orbital orientations for the nearest-neighbouring (NN) orbitals are perpendicular to each other, which was defined as AFOO. In sharp contrast, for the cubic structure the NN orbitals (labeled by X and Y in Fig.3a) are organized in an exotic way, in which the orbitals on one of the four symmetry-inequivalent V atoms in the unit cell has a different orbital orientation (labeled by Y), perpendicular to the others (labeled by X). The orbital orientations corresponding to Fig.3a are further illustrated in Fig.3(d), (e), and (f), which are the views of the spin densities from the lattice direction [100] (⃗a), [010] (⃗b), and [001] (⃗c), respectively. This leads to an exotic orbital ordering, i.e., along the lattice direction [110] (blue arrow in Fig.3), a ferro-orbital ordering (FOO) is predicted, whereas along [110] (red arrow in Fig.3) exists an AFOO. This OO can probably be attributed to (i) the crystal field environment formed by neighbouring oxygen atoms and (ii) the Coulomb interaction between d-orbitals, leading to this exotic OO. This interesting OO has been further confirmed by the calculations with the exchange-correlation functional, B3LYP [30], which relies on the empirical parameters for mixing exact exchange and GGA exchange functional. The spin densities on V predicted by using B3LYP functional are shown in Fig.3, in which FOO is along [110] and AFOO [110] (all the atoms are made partially transparent).

In order to see the orbitals involved more clearly, the atomic orbital composition of the bands at the Γ point that contribute most to the two peaks at −0.26 eV and −0.64 eV in the V PDOS has been investigated. The bands VB−13 and VB−14 contribute the most to the peak at −0.26 eV, whereas VB−26 and VB−27 to the one at −0.64 eV. Although the atomic coefficients for d-orbitals are slightly different among V atoms, approximately the most dominant linear combinations of d-orbitals for each V atoms contained in these bands read,
FIG. 3: (Colour on line.) The spin densities on V of the AFM state in the conventional unit cell of the cubic (a) and tetragonal (b) structures of MnV$_2$O$_4$ are shown. In the tetragonal an anti-ferro-orbital order is found. In contrast, in the cubic structure, the rotation of the orbital orientation illustrates an exotic OO, in which an ferro-orbital ordering is along [110], while anti-ferro-orbital ordering along [100]. This exotic OO is further confirmed by the calculation from B3LYP functional; the resulting spin densities are shown in (c). The B3LYP spin-density calculation is performed in a unit cell, but shown in a conventional cell. The views from $[100]$ (a), $[010]$ (b), $[001]$ (c) lattice directions are shown in (d), (e), and (f), respectively. The isovalue is chosen as 0.04 e/Å$^3$.

\[ \phi_{VB-13} = 0.2|d_{xz}\rangle + 0.2|d_{yz}\rangle, \]  
\[ \phi_{VB-14} = 0.2|d_{xz}\rangle + 0.2|d_{xy}\rangle, \]  
\[ \phi_{VB-26} = 0.2|d_{xz}\rangle + 0.2|d_{xy}\rangle, \]  
\[ \phi_{VB-27} = 0.2|d_{xz}\rangle - 0.1|d_{yz}\rangle - 0.2|xy\rangle. \]  

The corresponding spherical harmonic functions have been plotted in Fig.4 to see the contributions of d-orbitals. From the perspectives of linear combination of atomic orbitals (LCAO), the strong variations of the orbital orientation illustrated in Fig.3 and Fig.4 result from the minimisation of total energy respective to the atomic coefficients. On the other hand, this can be seen as the orbital re-orientation driven by Coulomb and crystal-field interactions.

There are two concepts that are closely related to this exotic orbital ordering, including orbital glass state and orbital ice configuration. The orbital glass state is formed by the randomly orientated orbitals, which result from Jahn-Teller distortion and orbital frustrations in a similar manner to spin frustrations. In light that orbital glass states have been observed in the spinel compounds FeCr$_2$S$_4$ and LuFe$_2$O$_4$ (which has similar chemical formula to a spinel, but a different structure), this is not unexpected in cubic MnV$_2$O$_4$. Therefore, these calculations could suggest that at $T = 53$ K, there is not only a structural transition, but also an orbital-ordering transition from the exotic OO illustrated in Fig.3 to antiferro orbital ordering, when lowering temperature. In addition, previously an ice model consisting of triplet orbital variables (such as $p$-orbital) has been presented, which is however closely related to orbital-driven many-body phenomena in optical lattice. The analogue of spin-interacting Hamiltonian, an orbital-exchange model describing Coloumb interactions has been used therein. The exotic ordering presented here is closely related to the newly proposed concept of the orbital ice, similar
FIG. 4: (Colour online.) The linear combination of harmonic spherical functions are shown. $Y_{xz} + Y_{yz}$ (corresponding to eq. (1)) are shown in (a), $Y_{xz} + Y_{xy}$ (corresponding to eq. (2)) in (b), and $2Y_{xz} - Y_{yz} - 2Y_{xy}$ (corresponding to eq. (4)) in (c). Notice that the linear combination illustrated in (c) changes the orientation of orbitals significantly away from their original ones, which is closely related to the exotic OO shown in Fig. 3a.

to the spin ice.

IV. CONCLUSION

The electronic structures of the cubic and tetragonal MnV$_2$O$_4$ structures have been computed by using hybrid-exchange density functional theory PBE0 and B3LYP. The calculated PDOS of the tetragonal structure has been in a good agreement with previous theoretical results. The most important finding here is that the charge densities of spin-carrying orbitals suggest a possible existence of an exotic orbital ordering mixing different types of OO, i.e., FOO along [110] and AFOO [T10], which could be related to orbital glass state and orbital ice state in the cubic MnV$_2$O$_4$. The theoretical prediction presented here could be validated in the future experiment. For example, different OO along those two directions aforementioned could lead to different electron transport properties. More advanced theoretical methods such as dynamical mean-field theory [35] is also needed to further understand the electronic structure of MnV$_2$O$_4$. The ground state the spins on Mn and V are predicted to be anti-aligned, suggesting a ferrimagnetic state for both structures, which is good agreement with previous theoretical and experimental results. The lower and upper Hubbard bands of Mn and V d-electrons have been shown clearly below and above the band gap. The on-site Coulomb interaction can be estimated by using the gap between the lower and upper Hubbard bands, which is $\sim$ 7 eV for V and $\sim$ 10 eV for Mn. The transfer integral responsible for the delocalization is in the order of 1 eV, which should be attributed to a combination of the first-order direct hopping between Mn and V and the second-order effect via O atoms. The d-orbital PDOS overlapping with O PDOS in energy originates from the correlation between Mn/V and O. The comparison between DFT energy difference between AFM and FM states and the super-exchange formalism suggests that the super-exchange could be dominant in the magnetic properties in both structures.

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