Electronic structure and magnetic properties of CaCrO$_3$

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Electronic structure and magnetic properties of CaCrO$_3$ have been calculated by using a variety of functionals within density-functional theory, ranging from hybrid-exchange density functional theory PBE0 to more sophisticated range-separated functional, including HSE06 and HISS. The AFM band gap is as low as 1.44 eV from HSE06 functional. The ferromagnetic, A-type anti-ferromagnetic, C-type anti-ferromagnetic, and G-type anti-ferromagnetic states (defined in the text) have been investigated carefully. The computed magnetic ground state has a G-type anti-ferromagnetic configuration (Néel state). The computed nearest-neighbouring exchange interaction along c-axis is anti-ferromagnetic. The nearest-neighbouring exchange interaction in the ab-plane is ferromagnetic, which is consistent with the in-plane anti-ferro-orbital ordering as shown in the spin density patterns. However, this magnetic state is frustrated by the anti-ferromagnetic next-nearest-neighbouring exchange interaction. More interestingly, a jump of the FM band gap $\sim$0.1 eV between 90 K and 100 K has been found, which shows a strong link to the previous optical conductivity measurements. Thus this work point to the half-metallicity as an alternative explanation for this material showing abnormal electronic properties.

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I. INTRODUCTION

Transition-metal oxides (TMOs) are an important family of strongly-correlated materials in condensed matter physics. For example, yttrium-barium-copper-oxide (YBCO) is the first high-transition-temperature (unconventional) superconductor ever found in nature [1]. This surprising yet challenging discovery [1] has triggered extensive experimental and theoretical efforts on YBCO and other related TMOs. Moreover, chromium dioxide (CrO$_2$), which is a half metal (conducting in one spin channel but insulating in the other), has a great potential for the application in spintronics [2], which can store and transport information encoded in the electron spin. These fascinating physical phenomena, as well as the important applications in the materials technology, are closely linked to the interactions (i) between the localised $d$-electron of transition metals and $p$-electron of oxygen and (ii) between the spin and orbital degrees of freedom. These interactions and underlying physics are manifested in the phenomena of fundamental interest, such as spin ordering and orbital ordering.

Cr$^{4+}$-based perovskites, such as CaCrO$_3$, SrCrO$_3$, and PbCrO$_3$, have attracted considerable attention recently [3][4]. Especially in CaCrO$_3$ (whose crystal structure is shown in Fig.1), the complicated interplay between magnetism, conductivity, and lattice vibration in CaCrO$_3$ has been a major obstacle for the clear observation of its electronic ground state [3][4]. The question, whether CaCrO$_3$ is metallic or insulating, is still under active debate. A comprehensive experimental study has suggested that the anomalous properties of CaCrO$_3$ are related to the Cr-O bond instabilities owing to the spin and orbital orderings, which could result in a crossover from localised to itinerant behaviour [3]. However, a more recent study, combining experiments and first-principles calculations, has shown that CaCrO$_3$ is a rare case of anti-ferromagnetic metal owing to the co-existence of anti-ferromagnetism and metallic Fermi surface [4][5]. The theoretical work therein, in the framework of LSDA+$U$ (local spin density approximation), supported that c-type anti-ferromagnetic (AFM) state, in which the spins are in ferromagnetic (FM) ordering along c-axis but AFM in the ab-plane, is the ground state [5]. The electronic state was predicted to be metallic within LSDA, but insulating once $U$ was included. Another set of first-principles calculations [6] based on GGA + $U$ (generalised gradient approximation) have suggested that under an inter-
mediated $U$, the $c$-type AFM is a metallic state. This is consistent with that calculated by using LSDA + $U$ [6]. To the author's knowledge, most of the previous theoretical work has been done within the framework of either pure density-functional theory (DFT) or DFT + $U$. The electronic correlation can be taken into account by including $U$ parameter in DFT, as performed previously [6, 7]. On the other hand, recently developed functionals, including hybrid-exchange PBE0 [8], range-separated (short-range, medium-range, and long-range-corrected ones), would also be able to include electronic correlation by mixing exact Fock exchange with that from GGA exchange functional.

In this paper, the electronic structure of CrO$_2$ was first benchmarked within the theoretical frame of PBE0 [8] and HSE06 [9], a hybrid-exchange density functional free of any adjusting parameter. Following this, the electronic structure and magnetic properties of CaCrO$_3$ were then calculated systematically. The total energies of ferromagnetic (FM), A-type AFM (AFM-A, AFM along the c-axis but FM in the $ab$ plane), C-type AFM (AFM-C), and G-type AFM (Néel state, AFM-G) states were computed carefully. The nearest-neighbouring (NN) and next-nearest-neighbouring (NNN) exchange interactions were then extracted by comparing the total energies of different magnetic states. We have found that AFM-G spin configuration is the ground state, which is different from that observed and predicted in Ref. [11]. However, the total energy difference is $\sim 30$ meV within the reach of room-temperature. The calculations of exchange interactions suggest that there is a frustration in the $ab$-plane, co-existing with the anti-ferro-orbital ordering. The rest of the discussion is organised as the following: in [III] the computational details are given, in [IV] the calculation results are presented and discussed, and in [V] some more general conclusions are drawn.

II. COMPUTATIONAL DETAILS

Calculations for the electronic structures and magnetic properties of CrO$_2$ and CaCrO$_3$ were carried out by using DFT and a variety of approximate-exchange-correlation functionals, including PBE0 [8], HISS [10], and HSE06 [9] implemented in the CRYSTAL 14 code [11]. The experimentally determined lattice parameters and atomic coordinates are adopted here [12]. The basis sets of Ca [13], Cr [14], and O [15] that are developed for solid-state calculations were used. The Monkhorst-Pack samplings [16] of reciprocal space are carried out choosing a grid of shrinking factor to be $7 \times 7 \times 5$ to be consistent with the ratios among reciprocal lattice parameters. The truncation of the Coulomb and exchange series in direct space is controlled by setting the Gaussian overlap tolerance criteria to $10^{-6}, 10^{-6}, 10^{-6}, 10^{-6}, 10^{-6}$, and $10^{-12}$ [11]. The self-consistent field (SCF) procedure is converged to a tolerance of $10^{-7}$ a.u. per unit cell (p.u.c). To accelerate convergence of the SCF process, all calculations have been performed adopting a linear mixing of Fock matrices by 30%.

Electronic exchange and correlation have been described using the PBE0 hybrid-exchange, short- (HSE06), and middle (HISS)-range-corrected functionals. Apart from a partial elimination of the self-interaction error, PBE0 functional balances 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 [8]. The performance of the hybrid functional, e.g., B3LYP or PBE0 has previously been shown to provide an accurate description of the electronic structure and magnetic properties for both inorganic and organic compounds [18, 19].

The Heisenberg model [17] for the spin-spin interactions in CaCrO$_3$ is defined here as,

$$\hat{H} = J_c \sum_{ij \in c} \hat{S}_i \cdot \hat{S}_j + J_{ab} \sum_{ij \in ab} \hat{S}_i \cdot \hat{S}_j + J'_{ab} \sum_{ij \in ab'} \hat{S}_i \cdot \hat{S}_j,$$

(1)

where $J_c$ is the exchange interaction between NN spins along c-axis, $J_{ab}$ between NN spins in the $ab$ plane, and $J'_{ab}$ between NNN spin in the $ab$ plane, respectively. The i and j label the Cr sites. The exchange interactions are determined by

$$E_{FM} - E_a = 8S^2J_c,$$

(2)

$$E_{FM} - E_c = 16S^2(J_{ab} + J'_{ab}),$$

(3)

$$E_{FM} - E_g = 8S^2J_c + 16S^2J_{ab},$$

(4)

where $E_{FM}$, $E_a$, $E_c$, and $E_g$ are the total energies for a conventional cell in the FM, AFM-A, AFM-C, and AFM-G states, respectively. And $S = 1$ is adopted for a Cr$^{4+}$ ion throughout the remaining discussion.

III. RESULTS AND DISCUSSIONS

A. Benchmark: electronic structure of CrO$_2$

First of all, the electronic structure of CrO$_2$ is benchmarked for the AFM and FM spin configurations. The zero-energy is set to be the Fermi surface. The DFT calculations based on the three functionals, including PBE0, HSE06 and HISS, have predicted that (i) its ground state of CrO$_2$ is FM, and (ii) it is a half metal (Fig. 2). This result is in agreement with the previous experimental and theoretical results [2]. The projected density of states (PDOS) onto the d-orbitals suggests that the conduction band is dominated by d-electrons. It would therefore be worth carrying on to perform calculations for CaCrO$_3$ by using PBE0 functional.

The projected density of states (PDOS) onto the d-orbitals of Cr (the first row), 2p-orbitals of O (the second row), and spin densities (the third row) of AFM-A, AFM-C, and AFM-G states, are shown in Fig. 3. The electronic states of FM, AFM-A, AFM-C, and AFM-G were pre-
AFM-C is as small as 4. Especially the energy difference between AFM-A and energy scale of room temperature. These results are different from the previous theoretical and experimental work. As shown in the spin density of AFM-A (Fig.3g), the spins are anti-aligned along c-axis, but aligned in the ab-plane. In AFM-C (Fig.3h), the spins are aligned along c-axis, but anti-aligned in the ab-plane. And in AFM-G, a neél state is in present, i.e., anti-aligned both in the ab-plane and along c-axis. Although there is a clear difference between these spin states, they share a feature that there exists an anti-ferro-orbital ordering (illustrated by yellow arrows) in the ab-plane, whereas the orbital ordering along c-axis is not obvious.

We have also analysed the spin densities projected to d-orbitals. As shown in Table III the spin densities are dominated by $d_{xz}$, $d_{yz}$, and $d_{xy}$ orbitals ($\sim 1.7\mu_B$ for these three orbitals) from all the functionals used here. The $d_{z^2}$ is occupied mainly because the tetragonal distortion, which will lower $d_{z^2}$ and lift up the $d_{xy}$ orbitals. The PDOS calculated here (Fig.3) is in a good agreement with this physical picture. The $d_{z^2}$ population is strengthened largely in AFM-C state as compared to AFM-G and AFM-A states. The mixture of $d_{xz}$ and $d_{yz}$ is in agreement with the previous theoretical results that claimed an orbital ordering [6]. The calculations presented here also support that these two d-orbitals are responsible for the complex orbital ordering as shown in Fig.3g, h, and i.

Komarek, et. al. [20] have observed the change of the crystal structure of CaCrO$_3$ at different temperatures. According to these crystal structures, the electronic structures have also been computed mainly by using HSE06 hybrid functional. The DFT band gaps of the majority spins in the FM configuration as a function of temperatures have been plotted in Fig.4. Notice that there is a jump $\sim 0.1$ eV between 90 K and 100 K, which coincides with the jump in the measurements of resistivity and optical conductivity [20]. In contrast, the minority band gap in FM configuration maintains as 2.7 eV. Other band gaps have not been affect the temperatures as much as FM ones; AFM-C band gap is $\sim 1.4$ eV.

### B. Exchange interaction

The exchange interactions defined in eq.1 can be extracted by comparing the total energies of the four magnetic states aforementioned according to eq.2. The computed $J_{cc}$, $J_{ab}$, and $J'_{ab}$ using the three functionals have been tabulated in Table III. Although these exchange interactions predicted to be insulating as shown in Fig. The band gap in different AFM spin configurations, computed by using three functionals, are listed in Table I. The lowest band gap is given by HSE06 in AFM-C state, which is $\sim 1.44$ eV. Such narrow band gap could result in high conductivity, thus near the transition point of metal-insulator transition. However, PBE0 and HISS have shown larger band gaps. The AFM-G state is predicted to be the most stable state, but the difference between these three AFM states is up to $\sim 38$ meV, which is close to the energy scale of room temperature. These results are different from the previous theoretical and experimental work [1]. Especially the energy difference between AFM-A and AFM-C is as small as $\sim 4$ meV. The resulting exchange interactions have been tabulated in Table III. Therefore, the stability of these magnetic states is fragile respected to thermal fluctuation and lattice vibration. This will further induce a magnetic disorder, which could prevent a proper observation of the electronic state in CaCrO$_3$.

The d-orbital PDOS near VBM is dominated by that from $d_{x^2-y^2}$, $d_{xz}$, and $d_{yz}$. The 2p-orbital PDOS of O in the AFM spin configurations share the similar feature; one significant peak is near the VBM with the other close to $-3.7$ eV. The comparison between the PDOS of d-orbital and 2p-orbital suggests there could exist a strong hybridisation between them, which is especially strong near the VBM. This might be able to shed some light on the explanation of the electronic state of CaCrO$_3$.

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FIG. 3: (Colour on line.) The PDOS of Cr $d$-orbitals, O $2p$ orbitals, and spin densities on Cr are shown for A-type, C-type, and G-type AFM spin configurations for CaCrO$_3$ in columns. The PDOS for $d_{z^2}$ is depicted in red, $d_{xz}$ in green, $d_{yz}$ in blue, $d_{x^2-y^2}$ in cyan, and $d_{xy}$ in black. The PDOS for $p_x$ is depicted in red, $p_y$ in blue, and $p_z$ in black. Zero-energy is chosen to be at the valence band maximum. In spin densities, spin-up is in red and spin-down in green. Notice that the orbitals are anti-ferro-ordered in the $ab$-plane (the orientation of orbital is illustrated by the yellow arrows).
interactions are computed within different functionals, they have qualitatively the same structure. Notice that the NNN exchange interaction in the ab-plane is even slightly larger than the NN one. The spins are coupled anti-ferromagnetically along the c-axis, but frustrated in the ab-plane as the NN exchange interactions in the ab-plane is FM while the NNN one is AFM. As suggested by the spin densities, there is an anti-ferro-orbital ordering in the ab-plane, which is consistent with the computed exchange interaction. It might be worthwhile performing a comparison between this work and that based on DFT+U in the future, which would inspire more discussions about this fascinating material.

C. Comparison with the previous experiments

The computed PDOS are qualitatively consistent with the X-ray absorption spectroscopy (XAS) as shown in Fig.2a of Ref.5. The measured energy gap between O 2p-orbital and d-orbital peaks is \(~\sim\) 5 eV, which is slightly larger than the predicted \(~\sim\) 3.7 eV. To improve the theoretical description, the more advanced computational methods, such as GW, is needed. However, this is beyond the scope of this paper. The Néel temperature \(T_N\) has been measured from the \(1/\chi\) versus \(T\) curve, which is \(\sim\) 90 K in Ref.3, 4. This is close to the computed exchange interaction \(J_c\). In addition, the experimentally observed magnet moments which were measured to be \(3.7\mu_B\) in Ref.3, which is much larger than the computed \((2.0\mu_B)\). This might be due to the FM ordering in the ab-plane. However, the observed \(1.2\mu_B\) reported in Ref.4 seems an indication of the existence of itinerant magnetism. An alternative explanation for this reduced magnetic moment is the in-plane magnetic anisotropy, induced by the local crystal field. The inconsistency between the measured magnetic moment could be attributed to the spin disorder as mentioned previously in this paper.

IV. CONCLUSION

In summary, the electronic structure and magnetic properties of \(\text{Cr}^{4+}\)-based perovskites, \(\text{CaCrO}_3\) have been calculated within DFT by using hybrid-exchange density functional PBE0. The magnetic ground state is AFM-G configuration. The analysis of the exchange interactions shows that there exists a spin frustration in the ab-plane. The PDOS have suggested a strong hybridization between \(d\) and \(2p\) orbitals. Moreover, the spin densities have shown an anti-ferro-orbital ordering in the ab-plane, which is consistent with the computed exchange interaction. It might be worthwhile performing a comparison between this work and that based on DFT+U in the future, which would inspire more discussions about this fascinating material.
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