Electronic and magnetic properties of the Jahn-Teller active fluoride NaCrF$_3$ from first-principles calculations

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In perovskite-type compounds, the interplay of cooperative Jahn-Teller effect, electronic correlations and orbital degree of freedom leads to intriguing properties. NaCrF$_3$ is a newly synthesized Jahn-Teller active fluoroperovskite where the CrF$_{6}^{2-}$ octahedrons are considerably distorted. Based on the first-principles calculation, we analyze its electronic structure and magnetic properties. Our numerical results show that the Cr$^{2+}$ ions adopt the high-spin $t_{2g}^{3}e_{g}^{1}$ configuration with $G$-type orbital ordering. We also estimate the magnetic exchange couplings and find that the in-plane and interplanar nearest-neighbor interactions are ferromagnetic and antiferromagnetic, respectively. The ground state of this material is $A$-type antiferromagnetic, in agreement with the experiments. Reasonable Curie-Weiss and Néel temperatures compared to the experiments are given by mean-field approximation theory. Our results give a complete explanation of its electronic structure, magnetic and orbital order, and help to further comprehend the behaviors of Jahn-Teller active perovskite-type fluoride.

I. INTRODUCTION

In strongly correlated electron systems, the interplay between charge, spin, orbital and lattice degrees of freedom gives rise to profuse and exotic physics properties [1]. Especially, the orbital physics is usually significant and inevitable for understanding this complexity [2, 3]. A fascinating example is the cooperative Jahn-Teller (JT) effect, which refers to a symmetry-lowering structural deformation driven by the coupling between the degenerate orbital states and the collective lattice vibrations [4–8]. Accompanied with strong electronic correlations and orbital degree of freedom, the cooperative JT effect gives rise to intriguing behaviors in perovskite-type compounds [6, 9]. The best known example is the parent material of colossal magnetoresistance (CMR) manganites, LaMnO$_3$ [10, 11], where the cooperative JT effect plays a fundamental role in stabilizing the $A$-type antiferromagnetic (AFM) spin and $C$-type orbital ordering (OO) [12–15]. Moreover, it arouses the formation of polaron which is regarded as a key mechanism in CMR effect [16–18].

Besides in the perovskite oxides, the cooperative JT effect also causes various remarkable magnetic and structural effects in fluoroperovskites [19–35]. In the paradigmatic example, tetragonal KCuF$_3$, two distinct types of collective JT distortions lead to two isoenergetic structural polytypes [19–22]. The cooperative JT effect is not only essential for stabilizing the antiferro-orbital order in KCuF$_3$ at high temperature [23], but also makes this compound one of the most ideal one-dimensional antiferromagnets with $S = \frac{1}{2}$ [9, 19]. Similar uniform AFM chains induced by cooperative JT effect are also found in triclinic AgCuF$_3$ and NaCuF$_3$ [26, 27]. Additionally, chromium fluoroperovskites are also able to activate cooperative JT effect, such as KCrF$_3$ [28–30]. This material has rich structural phase-transitions ($Pm3m \rightarrow I4/mcm$ at 973K and $I4/mcm \rightarrow I112/m$ at 250K) [28–30] and exhibits an ordering of staggered $3d_{xy}$, $d_{yz}$ and $3d_{x^2−y^2}$ orbitals in $ab$-plane which is rotated by $90^\circ$ in consecutive layers along the $c$-direction at room temperature [28, 29]. The ample structural and magnetic behaviors of KCrF$_3$ have attracted much interest in theoretical study in recent years [31–35].

Recently, another chromium fluoroperovskite NaCrF$_3$ was successfully synthesized with a novel wet chemistry method [36]. Incorporating the JT active Cr ions, this material exhibits obvious cooperative structural distortions. Neutron powder diffraction experiments revealed that NaCrF$_3$ adopts a canted $A$-type AFM ground state at low temperature [36]. The Curie-Weiss temperature and Néel temperature were given by -4K and 21.3K, respectively [36]. Its Néel temperature is much lower than KCrF$_3$ (79.5 K) [30], indicating its weak antiferromagnet nature. Isostructural with triclinic NaCuF$_3$ [26, 36], NaCrF$_3$ has considerably lower crystal symmetry than KCrF$_3$. Meanwhile, the Cr ions of NaCrF$_3$ have $3d^4$ electronic configuration, which are different from the $3d^9$ Cu ions in KCuF$_3$. Thus, it will be worthwhile to investigate the electronic structure and magnetic properties of this distinct compound.

In this paper we systematically analyze the electronic and magnetic properties of NaCrF$_3$ by using the first-principles calculation. Band structure and partial density of states (PDOS) show clearly the splitting of $e_g$ orbitals of Cr$^{2+}$ ions caused by the axial elongation of CrF$_6^{3-}$ octahedrons. Our numerical results show that this material exhibits $G$-type antiferro-orbital ordering while the Cr$^{2+}$ ions adopt the high-spin $t_{2g}^{3}e_{g}^{1}$ configu-
A-type AFM spin state is found to own the lowest total energy in accordance with the experiments. Based on energy-mapping procedure, a ferromagnetic (FM) in-plane nearest-neighbor (NN) coupling, an AFM interplanar NN interaction and a non-negligible interplanar next-nearest-neighbor (NNN) exchange parameter are estimated. Through mean-field approximation theory, we calculate the Curie-Weiss and Néel temperatures, which are in reasonable agreement with the results of experiments. The ground magnetic state of A-type magnetic order can be understood based on the electronic configuration of Cr$^{2+}$ ions and the Cr-F-Cr superexchange pathways.

II. METHOD AND CRYSTAL STRUCTURE

The density functional calculations have been performed by utilizing the full potential linearized augmented plane wave (LAPW) method as implemented in Wien2k code [37]. Local spin density approximation (LSDA) is adopted as the exchange-correlation potential [38]. To take into account the Coulomb repulsion of the Cr-3d electrons, LSDA + $U$ scheme is also performed [39]. The value of $U_{eff}$ ($U_{eff} = U - J$, the Hund exchange parameter $J$ is set to be 0), which varies from 4 eV to 8 eV, has been widely used in previous first-principle calculation [20, 31]. We found that our numerical essential properties do not depend on the value of $U_{eff}$ in this range and the results of $U_{eff} = 6$ eV are mainly presented here. The muffin-tin sphere radii are chosen to be 2.06, 1.81 and 1.90 Bohr for Na, F and Cr atoms, respectively. The plane wave cut-off $K_{max}$ is determined by $R_{min}K_{max} = 7$, where the $R_{min}$ is the smallest of all atomic sphere radii. The convergence criterion of the crystal total energy is set to be 0.01 mRy per conventional unit cell, and a sufficient large k mesh is used for the integration over the Brouillon zone. In addition to the FM configuration, five possible AFM configurations (shown in Fig. 4) have also been taken into consideration to explore the magnetic properties of NaCrF$_3$.

The experimental crystal structure (Fig. 1(a)) obtained by high-resolution synchrotron X-ray and neutron powder diffraction is used in the calculation [36]. NaCrF$_3$ belongs to the triclinic crystal system (space group $P1$), with lattice constants $a=5.48428(11)$ Å, $b=5.67072(11)$ Å and $c=8.13620(15)$ Å. The angles between the lattice vectors are $\alpha=90.3860(10)^{\circ}$, $\beta=90.2816(8)^{\circ}$ and $\gamma=86.3255(8)^{\circ}$ [36]. Four inequivalent crystallographic sites are occupied by the Cr cations (Fig. 1(a)), which form distorted corner-sharing CrF$_6$ octahedrons enclosed in Na cage with the surrounding F anions. Each axially elongated CrF$_6$ octahedra has 2 long and 4 short Cr-F bonds. It should also be noted that, the CrF$_6$ octahedrons connect with each other through alternating long-short Cr-F bonds within the (110) plane, while all the interplanar connection consists of short bonds (Fig. 3(a)).

III. RESULTS AND DISCUSSION

LDA calculation is carried out firstly to clarify the basic electronic features. The band structures and the density of states (DOS) are given in Fig. 2(a) and 3. The z-direction of local coordinate system is defined along the longest Cr-F bond of each CrF$_6$ octahedron in the analysis of PDOS. There are 12 F ions in the unit cell. As shown in Fig. 2(a) & 3, 36 F-2$p$ bands mainly locate in the energy range from -9 eV to -6 eV, indicating that the F-2$p$ orbitals are nearly full occupied. In comparison, the F-2$p$ bands of KCuF$_3$, which locates between -7 eV and -3 eV, are closer to the Fermi level due to the stronger electronegativity of Cu than Cr. As shown in Fig. 3, the main contribution of Na bands is above the Fermi level, while there is also small distribution of Na states between -9 and -6 eV, indicating the non-negligible hybridization between Na and F states. Thus the nominal chemical valence of F and Na can be regarded as -1 and +1, respectively. As a consequence, the nominal valence of Cr is +2 and the outer shell electronic configuration of Cr ion is 3d$^4$. Our results also show that the bands around the Fermi level consists mostly of the Cr-3d electrons (Fig. 3). In each axially elongated CrF$_6$ octahedron, two long Cr-F bonds are collinear, while the angles between the long bonds and the short bonds deviate slightly from the right angle (ranging from 84.50$^{\circ}$ to 96.17$^{\circ}$) [36]. Though the CrF$_6$ octahedrons deform from the ideal ones, the Cr-3d orbitals are still roughly divided into 12 $t_{2g}$ bands (from -0.46 eV to 0.25 eV) and 8 $e_g$ bands (from 0.46 eV to 2.53 eV), as shown in Fig. 2(a) & 3. Furthermore,
influenced by the axial elongation of the CrF₆ octahedrons, the $e_g$ states split into 4 $d_{3z^2-r^2}$ bands from 0.46 eV to 0.91 eV and 4 $d_{x^2-y^2}$ bands from 1.08 eV to 2.53 eV, as shown in Fig. 2(a) and 3. The energy splitting between the band centers of $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ states is estimated to be about 1.05 eV.

As shown in Fig. 3, the DOS at Fermi level is quite large, which indicates the electronic instability. To explore its magnetic properties, the LSDA + $U$ calculation of FM configuration is performed. The band structures are shown in Fig. 2(b) & 2(c). The spin exchange splitting is relatively large and the down-spin bands lie far away from the Fermi level. As shown in the band structure and DOS (Fig. 2(b) & 2(c) & 3), the $t_{2g}$ and $d_{3z^2-r^2}$ orbitals in spin-up channel are fully occupied, while the $d_{x^2-y^2}$ orbitals are entirely empty in the FM structure. Thus, the Cr 3d⁴ configuration can be regarded as holding a $t_{2g}^1e_g^1$ high-spin state. Enhanced by the combination of JT effect and electronic correlation, the energy splitting between the weight-centers of $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states in spin-up channel is estimated to be 4.5 eV. Note that the occupied $d_{3z^2-r^2}$ orbitals form a G-type orbital ordering pattern, as shown in Fig. 3(a). The high-spin state Cr²⁺ ions and G-type orbital order show remarkable similarity with those of KCrF₃ [31–33, 35].

In order to study the magnetic ground state of NaCrF₃, five AFM configurations have been taken into consideration in addition to the FM state (See Fig. 4 for the schematic descriptions of the different AFM configurations). AFM-1 and AFM-2 are two different A-type AFM structures where the AFM couplings are in [1 ¯10]- and [001]-direction, respectively. The Cr²⁺ ions of AFM-3 configuration couple anti-ferromagnetically in the (1 ¯10)-plane, but ferromagnetically in [1 ¯10]-direction. And in AFM-4, the magnetic moments are anti-parallel in (001)-plane, but parallel in [001]-direction. In the spin configuration AFM-5, each spin is set to be anti-parallel to all its
nearest neighbors. Our numerical results reveal that different magnetic configurations have minor influence on the electronic configuration and the orbital ordering of this material, and all magnetic configurations have the same high-spin $t_{2g}^3e_{g}^1$ state and the $G$-type orbital order. The differences between total energies and magnetic moments of Cr$^{2+}$ of various magnetically ordered structures for LSDA $+ U$ calculations are summarized in Table I. The results show that the AFM-1 configuration has the lowest total energies under different $U$ values, which is in agreement with the experimental results [36]. The calculated magnetic moments of different spin configurations are similar, which indicates that the magnetism of NaCrF$_3$ is quite localized and the total energy differences mainly originate from the inter-atomic exchange interactions. Thus, it allows us to perform the energy-mapping procedure to estimate the exchange couplings.

The exchange couplings are analyzed by using the Heisenberg Hamiltonian:

$$H = \sum_{i<j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$  \hspace{1cm} (1)$$

where $J_{ij}$ stands for the spin exchange parameter between two spins at sites $i$ and $j$. We have calculated the exchange parameters $J_{ij}$ by using the relative total energies of different magnetic ordering systems. The exchange interactions that we consider are shown in Fig. 4(a), where $J_1$ and $J_3$ denote the NN and NNN interactions between the $(1\bar{1}0)$-planes, while $J_2$ and $J_4$ represent the NN and NNN couplings within the $(1\bar{1}0)$-planes.

|        | FM | AFM-1 | AFM-2 | AFM-3 | AFM-4 | AFM-5 |
|--------|----|-------|-------|-------|-------|-------|
| $U=4$ eV | 5.15 | 0     | 8.53  | 9.29  | 7.35  | 10.34 |
| $E_{tot}$ | 4.85 | 0     | 6.65  | 5.84  | 5.21  | 7.38  |
| $U=8$ eV | 4.52 | 0     | 5.69  | 4.00  | 4.34  | 5.67  |
| $U=4$ eV | 3.366 | 3.361 | 3.361 | 3.356 | 3.356 | 3.356 |
| $M_{Cr}$ | 3.397 | 3.394 | 3.394 | 3.390 | 3.388 | 3.387 |
| $U=8$ eV | 3.345 | 3.423 | 3.423 | 3.420 | 3.419 | 3.415 |

Table I. Relative total energies ($E_{tot}$ in meV/f.u.) of different magnetic ordering states and corresponding magnetic moment ($M_{Cr}$ in $\mu_B$) of Cr$^{2+}$, total energy of AFM-1 structure is set to be 0.

By applying the spin Hamiltonian model (Eq.1) on the 6 different magnetic configurations, the total energy per conventional unit cell are expressed as:

$$E_{FM} = E_0 + 4(J_1 + 2J_2 + 4J_3 + 2J_4)S^2$$
$$E_{AFM1} = E_0 + 4(-J_1 + 2J_2 - 4J_3 + 2J_4)S^2$$
$$E_{AFM2} = E_0 + 4(J_1 - 2J_2)S^2$$
$$E_{AFM3} = E_0 + 4(J_1 - 2J_2 - 4J_3 + 2J_4)S^2$$
$$E_{AFM4} = E_0 + 4(-J_1 - 2J_2)S^2$$
$$E_{AFM5} = E_0 + 4(-J_1 - 2J_2 + 4J_3 + 2J_4)S^2$$

Here $E_0$ denotes the paramagnetic part of the total energy, which is considered as irrelevant of the change of spin configuration. The values of the exchange parameters $J$ can be evaluated by mapping these energies obtained with LSDA $+ U$ calculations. Since the number of magnetic configurations is larger than the number of exchange parameters, a least squares method is applied.

The calculated exchange couplings from energy-mapping analysis are given in Table II. Generally speaking, the magnetic exchanges are considerably weaker in NaCrF$_3$ than in other materials with similar Jahn-Teller active ions [26, 31, 32, 35]. With the value of $U$ increasing, the values of most magnetic couplings decrease as expected. The dominant terms are $J_1$ and $J_2$, where the positive $J_1$ indicates an interplanar AFM interaction, while the negative $J_2$ reveals a FM coupling within the $(1\bar{1}0)$-plane. The results correspond well with experiments, since the combination of these NN interactions leads to the A-type magnetic ground state. As shown in Table II, $J_1$ and $J_2$ have same order of magnitude, indicating that NaCrF$_3$ exhibits three-dimensional magnetic nature. Moreover, we also get a non-negligible positive interplanar NNN exchange constant $J_3$, which strengthens the AFM interactions between the $(1\bar{1}0)$-planes.

Based on the spin exchange parameters, we calculate the Curie-Weiss and Néel temperature by the mean-field

Fig. 4. Five AFM configurations considered in our DFT calculations. (a), (b), (c), (d) and (e) represent AFM-1, AFM-2, AFM-3, AFM-4 and AFM-5 spin structures respectively. Blue spheres stand for the Cr atoms within the $(1\bar{1}0)$-plane which is represented by the dashed lines. Red arrows denotes the spins in up-direction and yellow arrows denotes the spins in down-direction. The 4 exchange parameters that we take into consideration are shown in (a).
Table II. Calculated exchange constants (meV) for different computational settings.

|         | $J_1$  | $J_2$  | $J_3$  | $J_4$  |
|---------|--------|--------|--------|--------|
| $U=4$ eV   | 0.211  | -0.445 | 0.101  | -0.035 |
| $U=6$ eV   | 0.250  | -0.269 | 0.096  | -0.031 |
| $U=8$ eV   | 0.183  | -0.158 | 0.092  | -0.004 |

theory approximation [40]:

$$\theta = \frac{S(S+1)}{3k_B} \left( \sum_i z_i J_i + \sum_j z'_j J'_j \right)$$  \hspace{1cm} (2)

$$T_N = \frac{S(S+1)}{3k_B} \left( \sum_i z_i J_i - \sum_j z'_j J'_j \right)$$  \hspace{1cm} (3)

where $J_i$ and $z_i$ are the neighbor exchange parameters between the sites with same spin orientation and the corresponding number of adjacent neighbors, whereas $J'_i$ and $z'_j$ represent the magnetic coupling and the coefficients between the sites with opposite spin orientation.

According to the experiments [36], Curie-Weiss temperature $\theta$ is -4 K while Néel temperature $T_N$ is 21.3 K, smaller than that of KCrF$_3$ ($T_N = 79.5$ K) [30]. Since the Curie-Weiss temperature represents sum of all magnetic couplings in the mean-field theory (Eq. 2 & 3), the relative low value of the frustration index $\theta/T_N$ (smaller than 1) reveals the interplay of the FM and AFM interactions [41], in agreement with our results shown in Table II. When $U$ equals 6 eV (reasonable value compared with similar material [20, 31]), Curie-Weiss temperature is estimated to -1.67 K while the Néel temperature is about 57.31 K. The results can be regarded as qualitatively consistent with the experimental ones.

![Diagram of crystal levels of high-spin Cr$^{2+}$ of different Cr$^{2+}$ sites. The notations of the orbitals are given based on the local coordinate system of each Cr$^{2+}$. (a) and (b) stand for two NN Cr$^{2+}$ within the (110)-plane, while (c) represents the NN Cr$^{2+}$ of (b) in another plane. The in-plane $e_g$ electron hopping leads to FM interaction while the interplanar coupling between $t_{2g}$ orbitals results in AFM interaction.](image)

In conclusion, we have presented comprehensive investigation of a newly synthesized JT active ternary fluoroperovskite NaCrF$_3$ through the DFT calculation. The high-spin configuration of Cr$^{2+}$ and the G-type orbital ordering are proposed by our numerical results. We also confirmed the A-type AFM magnetic ground state obtained by the experiments. With the energy-mapping procedure, we estimate the exchange parameters. The interplanar NN interaction $J_1$ is AFM while in-plane NN coupling $J_2$ is FM. Reasonable Curie-Weiss and Néel temperatures are also estimated by using mean-field approximation theory. Based on the GKA rule, the magnetic ground state of A-type AFM order is understood. We hope our calculation of this compound may help to further understand of the behaviors in JT active perovskite fluoride.

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