Electronic Supplementary Information on Unveiling the electronic origin of anion order in $\text{CrO}_{2-x}\mathbf{F}_x$

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This Electronic Supplementary Information includes information on material synthesis, structural and chemical analysis, magnetic measurements, transmission electron microscopy characterizations, electronic structure calculation methods and related discussion.

SM.1 - High-pressure synthesis of $CrO_{2-x}F_x$ (x = 0.10, 0.12, 0.14)

Polycrystalline $\operatorname{CrO}_{2-x} \operatorname{F}_x$ (x = 0.10, 0.12, 0.14) samples were synthesized on a multi-anvil high-pressure facility. The chemicals are CrO_2 (MagtrieveTM) and CrF_2 power. The starting materials were well-mixed in the ratio as shown in the formula and kept at about 1473 K, 6 GPa for 2 hours [1]. There is a little second-phase (CrOOH) in the as-synthesized samples. The following annealing in O₂ flow at 623 K eliminated it and a pure phase was obtained [2]. The raw material CrO_2 power was also annealed in air at 623 K for investigation on possible oxygen vacancies.

SM.2 - Powder X-ray diffraction and chemical analysis

X-ray diffraction (XRD) experiments were performed using a Rigaku D/Max-RB X-ray diffractometer with Cu K α radiation. The nature of single phase was confirmed by the XRD patterns of $\text{CrO}_{2-x}\text{F}_x$ (x = 0.10, 0.12, 0.14), where only Bragg reflections of rutile-typed structure appeared. The calculated cell dimensions are summarized in Table SM. I. Compared with the starting material CrO_2 (MagtrieveTM) where a = 0.44191(2)nm and c = 0.29153(4)nm, the cells of doped samples obviously expand. However, for doped samples with different F level, the differences of lattice parameters are not significant since the F levels are pretty close. Our results are well consistent with those of Chamberland et al, which suggests that our samples may have similar actual composition with those reported by Chamberland et al.[1]

X-ray photoelectron spectroscopy (XPS) were collected on an ESCALAB250 surface analysis system with carbon peak at 284.6 eV as standard. The XPS profiles of ${\rm CrO}_{2-x}{\rm F}_x$ show a peak at 685.0 eV, which can be assigned as ${\rm F}^-$ 1s [3] and is indicative of the ${\rm F}^-$ doping, as shown in Fig. SM.1. As shown in Fig. SM.1, the intensity of this peak grows with heavier doping. XPS profile from high-resolution scanning around binding energy (B.E.) window of metal cations show two broadened peaks, which are assigned to $2p_{1/2}$ and $2p_{3/2}$, respectively. As displayed in Fig. SM. 3, the data is well fitted as a mixture of ${\rm Cr}^{4+}$ and ${\rm Cr}^{3+}$, where peaks of $2p_{1/2}$ and $2p_{3/2}$ for ${\rm Cr}^{4+}$ appear at around 586.2 eV and 576.4 eV, while those for ${\rm Cr}^{3+}$ at 589.2 eV and 579.2 eV, respectively. In Fig. SM.4, we plot the XPS profiles for ${\rm Cr}^{4+}$ and ${\rm Cr}^{3+}$, after subtracting the background, respectively. The growing peaks of ${\rm Cr}^{3+}$ with increasing doping is consistent with situation of F⁻ 1s peak in Fig. SM. 2, indicative of the systematical change of charge with varying composition. It should be noted that the signals of ${\rm Cr}^{3+}$ for x=0.10, 0.12 come close to the background while x=0.14 clearly displays the contribution from ${\rm Cr}^{3+}$.

SM.3 - Magnetism measurements

Magnetic properties were measured on a SQUID magnetometer (MPMS-XL, Quantum Design). Fig. SM.5 shows the temperature dependencies of magnetization for $\text{CrO}_{2-x}F_x$ (x = 0.10, 0.12, 0.14) at field-cooled (FW) and field-warmed (FW) conditions.

Nominal composition	Actual composition	Lattice a (nm)	Lattice c (nm)
0.10	-	0.44379(4)	0.29221(5)
	0.10	0.44360(8)	0.29210(7)
0.12	-	0.44390(1)	0.29222(1)
	0.122	0.44381(7)	0.29221(6)
0.14	-	0.44504(4)	0.29270(6)
	-	0.44431(8)	0.29237(6)

TABLE SM.1: Comparison of structure and composition of $\text{CrO}_{2-x}F_x$ with published data. First row is for our results while the data in the second row is from Ref [1]. The standard errors are given in the brackets.

SM.4 - Transmission electron microscopy characterizations

Fine powder of annealed samples was well-dispersed in alcohol by ultrasonic vibrator and then was transferred to copper grids coated with holy-carbon support films. The specimens were examined with an FEI Tecnai G^2 F20 transmission electron microscopy (TEM) and a JEOL JEM-2100 TEM equipped with an in-situ heating holder (Gatan 652), operated at 200 kV. In Fig. SM.6(a), we show the high-resolution lattice image of [010] zone-axis, which simultaneously displays (1/3, 0, 1/3) and (-1/3, 0, 1/3) superstructures. Fig. SM.6(b) displays typical morphology of reduced CrO_2 and the related electron-diffraction pattern of [010] zone-axis (inset). The superstructure models are shown in Fig. SM.6, which is obtained by the structural optimization of first-principle calculation. The experimentally observed superlattice diffraction spots can be reproduced on this model, as shown in Fig. SM. 6 (c). Induced by F doping, this superlattice diffraction is attributed to the structural distortion that is clear in Fig. SM. 6 (b).

SM.5 - Electronic structure calculations

We have carried out first-principle electronic structures calculations on $\text{CrO}_{1.90}\text{F}_{0.10}$ ($\text{Cr}_{54}\text{O}_{102}\text{F}_{6}$) within a plane wave pseudo-potential implementation of density functional theory using projected augmented wave potential within VASP [4]. The generalized gradient approximation was used for the exchange, and electrons were considered by including a Hubbard U of 3 eV on Cr, similar with most of studies reported [5, 6]. The calculation was performed on a $3 \times 3 \times 3$ supercell of rutile-typed structure, where F⁻ anions are arranged along <111> direction, as the model shown in Fig. SM.7(a). The difference of charge of two kind of Cr cations is about 0.3, which is much smaller than the ideal integral valence change expected at the purely ionic limit. However, this similar deviation from integral valence changes usually observed in mixed-valence systems including K₂Cr₈O₁₆ [7]. We defined the higher charge state (about 2.75) as Cr³⁺ while the lower charge state (about 2.45) as Cr⁴⁺. A half-metallic behavior is suggested at ferromagnetic (FW) coupling while an insulating behavior with a gap of about 0.2 eV at antiferromagnetic coupling.

SM.6 - Discussion

In $\operatorname{Sr}_2\operatorname{CuO}_2\operatorname{F}_{2+\delta}$, the Madelung energies calculation suggests an apical site-preference of $\operatorname{F}^-[8]$. In the sense of critical effect of charge rather than structure on anion ordering, therefore, $\operatorname{CrO}_{2-x}\operatorname{F}_x$ is similar with cuprates, even if they are very different structural and electronic systems. This might imply a universality that the electrostatic interaction likely underlies anion ordering in mixed-anion systems. Indeed, such argument is strongly supported by the fact that there is same anion ordering in $\operatorname{Sr}_2\operatorname{CuO}_2\operatorname{F}_2$ and $\operatorname{Sr}_2\operatorname{CuO}_2\operatorname{Cl}_2$, also in $\operatorname{Sr}_2\operatorname{CuO}_3\operatorname{X}(\operatorname{X}=\operatorname{F},\operatorname{Cl},\operatorname{Br})$, though halide anions are quite different in radius [9]. Our result might be helpful for understanding the anion ordering in other mixed-anion systems like oxynitrides [10].

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FIG. SM.1: XPS profiles of $CrO_{2-x}F_x$ up to to 1000 eV. The signature of F^- is highlighted at 685 eV by the arrow. The intensity is normalized by C peak.



FIG. SM.2: XPS profiles fitting of $CrO_{2-x}F_x$ for Cr cations.



FIG. SM.3: XPS profiles of Cr cations after subtraction of background in $\text{CrO}_{2-x}F_x$. The intensity is scaled by $I(E)/I_{max}$.



FIG. SM.4: The temperature dependence of FC and FW magnetization for $CrO_{2-x}F_x$ (x = 0.10, 0.12, 0.14)at magnetic field of 0.05 T.



FIG. SM.5: (a) The high-resolution lattice image of [010] zone-axis of $CrO_{1.90}F_{0.10}$ at room temperature, where (1/3, 0, 1/3) and (-1/3, 0, 1/3) superstructures are all shown. (b) Typical morphology of reduced CrO_2 and the related electron-diffraction pattern of [010] zone-axis (inset).



FIG. SM.6: (a) Optimized structure model of $Cr_{54}O_{102}F_6$ by first-principle electronic structure calculations. (b) The apical and equatorial bond length bond length for CrO_6 (left) and CrO_4F_2 (right) octahedra in this optimized structure. (c) Calculated electron diffraction pattern of $[1\overline{3}\overline{1}]$ zone-axis based on the optimized structure.



FIG. SM.7: (a) The model $Cr_{54}O_{102}F_6$ for electronic structure calculation. Blue, red and cyan spheres indicate Cr, O and F, respectively. (b) Electronic density of state (DOS) at FM coupling. (c) (d) and (e) Partial electronic DOS (PDOS) for various ions at FM coupling, respectively. The arrows depict the spin polarization orientation.