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Crystal growth engineering and origin of the weak ferromagnetism in antiferromagnetic matrix of orthochromates from $t$-$e$ orbital hybridization

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Highlights
The lack of large and good-quality single crystals of orthochromates has been solved
Nature of the weak ferromagnetism in a main antiferromagnetic matrix has been revealed
$t$-$e$ orbital hybridization is the microscopic origin
Relationship between microscopic and macroscopic properties has been correlated

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Crystal growth engineering and origin of the weak ferromagnetism in antiferromagnetic matrix of orthochromates from t-e orbital hybridization

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SUMMARY
We report a combined experimental and theoretical study on intriguing magnetic properties of quasiferroelectric orthochromates. Large single crystals of the family of RECrO3 (RE = Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) compounds were successfully grown. Neutron Laue study indicates a good quality of the obtained single crystals. Applied magnetic field and temperature dependent magnetization measurements reveal their intrinsic magnetic properties, especially the antiferromagnetic (AFM) transition temperatures. Density functional theory studies of the electronic structures were carried out using the Perdew-Burke-Ernzerhof functional plus Hubbard U method. Crystallographic information and magnetism were theoretically optimized systematically. When RE3+ cations vary from Y3+ and Eu3+ to Lu3+ ions, the calculated t-e orbital hybridization degree and Neél temperature behave similarly to the experimentally determined AFM transition temperature with variation in cationic radius. We found that the t-e hybridization is anisotropic, causing a magnetic anisotropy of Cr3+ sublattices. This was evaluated with the nearest-neighbor J1-J2 model. Our research provides a picture of the electronic structures during the t-e hybridization process while changing RE ions and sheds light on the nature of the weak ferromagnetism coexisting with predominated antiferromagnetism. The available large RECrO3 single crystals build a platform for further studies of orthochromates.

INTRODUCTION
Multiferroic materials have received considerable attention because of their potential application in electric and magnetic devices (Fiebig et al., 2016; Huang et al., 2021; Hur et al., 2004; Jones et al., 2014; Spaldin and Ramesh, 2019). Within the materials, long-range orders such as ferroelectric and magnetic coexist and may interact strongly on each other, providing multi-tunable parameters for tailoring the macroscopic functionalities. There are significant challenges for a complete understanding of the microscopic mechanisms underlying their intriguing macroscopic properties.

Chromium-based perovskites have attracted considerable interest because of their intriguing magnetic and ferroelectric properties as well as potential technique applications. The set of chromium-based RECrO3 (RE = rare earths) compounds was suggested to be another family of multiferroic materials, usually displaying ferroelectricity, weak ferromagnetism, and a wide application in fields of catalyst, thermistor, solid-oxide fuel cell, and nonvolatile memory devices (Figure 1) (Oliveira, 2017). The formation of Cr3+ magnetic orders has a strong effect on the ferroelectric property, i.e., there may be a magnetoelectric coupling (Oliveira et al., 2020; Rajeswaran et al., 2012). Chromium ions in RECrO3 compounds hold a single-valence state, i.e., Cr3+(2t2g3e2g), naturally discarding the eg orbital ordering as well as its perturbation on the t2g electrons. This results in a tightly localized electric environment, an ideal platform for the potential coexistence of ferroelectricity and magnetism. The ferroelectric transition temperature, \( T_C \approx 473 \text{ K} \), of YCrO3 compound is much higher than that of the antiferromagnetic (AFM) phase transition of Cr3+ ions \( T_N \approx 141.5 \text{ K} \) (Serra et al., 2005; Zhu et al., 2020a). An isosymmetric structural phase transition was observed at \( T_C \approx 900 \text{ K} \) in a neutron powder diffraction study on the pulverized YCrO3 single crystal, where...
the incompressibility of lattice constants $a$, $b$, and $c$ is anisotropic, and there exist obvious atomic displacement and charge subduction on the Y and O$_2$ sites (Zhu et al., 2020b). Net electric polarization was observed for polycrystalline LuCrO$_3$ and ErCrO$_3$ samples below $T_{Cr N}$, indicating the presence of a possible ferroelectric state, whereas this is clearly absent above $T_{Cr N}$. Most importantly, the study demonstrates that the paramagnetic (PM) nature of RE sites is not necessary to accommodate the ferroelectricity in orthochromates (Preethi Meher et al., 2014). In addition, the polarizations attain maximum values of $\sim 90 \mu C/m^2$ (at $E = 165$ kV/cm for LuCrO$_3$ compound) and $\sim 70 \mu C/m^2$ (at $E = 174$ kV/cm for ErCrO$_3$ compound). Both polarizations are reversal and can be explained by either the Cr$^{3+}$ off-centering or the ferroelasticity or their couplings and even by Cr$^{3+}$ vacancies (Preethi Meher et al., 2014). The SmCrO$_3$ compound demonstrates an electric polarization with the maximum value of $\sim 8 \mu C/m^2$ at $E = 1.43$ kV/cm and $\sim 15$ K (El Amrani et al., 2014), which was ascribed to a breaking of the local symmetry via Cr$^{3+}$ off-centering (El Amrani et al., 2014). It was observed that electric dipoles exist in the DyCrO$_3$ compound, which was attributed to the displacement of Cr$^{3+}$ cations (Yin et al., 2018). Electric polarizations were observed in TbCrO$_3$ and TmCrO$_3$ compounds at $E = 1.43$ kV/cm below $T_{Cr N}$ (Rajeswaran et al., 2012), whereas the existence of electric dipoles in the TmCrO$_3$ compound remains a debate (Yoshii and Ikeda, 2019).

Most previous studies focused on polycrystals, nanocrystals, and thin films. Single crystal growths of rare-earth orthochromates utilize mainly two methods: (i) one is the flux method (Yin et al., 2015). Unfortunately, impurities from the flux exist in the grown single crystals and have strong effects on macroscopic properties of the host (Cooke et al., 1974; Li et al., 2021; Looby and Katz, 1954; Zhu et al., 2020c). In addition, single crystals grown by the flux method are small, normally millimeter in size, and not suitable for some studies that make excessive demands in sample’s quality and mass. (ii) The other is the floating-zone (FZ) method with a mirror furnace. Unfortunately, the intense volatility of Cr element because of its high vapor pressure at melting points of orthochromates (Philipp et al., 2003) can practically reduce the heating power of the mirror furnace (Li, 2008). This makes it not so easy to stably grow the single crystals of orthochromates. As a consequence, the lack of large single crystals has been a long-standing obstacle for studying their intrinsic properties and realizing some potential applications of orthochromates.

One of the long-standing unsolved issues existing in the family of RECrO$_3$ orthochromates is the microscopic origin of the weak ferromagnetism. This is introduced by the canted AFM structure. The Cr$^{3+}$ state ($t_{2g}^3e_{g}^0$) in orthochromates enables a virtual charge transfer (VCT) of Cr$^{3+}$ ($t_{2g}^3$) $\rightarrow$ Cr$^{3+}$ ($e_{g}^0$) and a possible ferromagnetic (FM) competition with superexchange interactions $J \sim b^2/U$ (Landron and Lepetit, 2008), where $b$ is the overlapping integral, and $U$ denotes the on-site Coulomb interactions (Slater and Koster, 1954; Zhu et al., 2010). The overall Cr-O-Cr superexchange comprises two major contributions: One is from the $t_{2g}$ $\rightarrow$ $t_{2g}$ hopping, producing an AFM component; the other is from the $t_{2g}$ $\rightarrow$ $e_{g}$ orbital hybridization, generating FM couplings. The hybridization strength depends on the lattice distortion (Siddique et al., 2021), on-site Coulomb interaction (Besbes et al., 2019; Yekta et al., 2021), and $t_{2g}$ $\rightarrow$ $e_{g}$ crystal field.
splitting (Ko et al., 2007). The spin-orbit coupling induced Dzyaloshinskii-Moriya (DM) exchange would favor a magnetic structure with spins perpendicular to each other to minimize the total energy of the system (Coffey et al., 1991; Dmitrienko et al., 2014). To describe the effect of RE sites on the Cr$^{3+}$-$\text{O}^{2-}$-Cr$^{3+}$ super-exchange interactions, one can utilize density functional theory (DFT) based first-principles calculations to optimize the atomic information and correlate it with the superexchange interactions in RECrO$_3$ compounds. This provides a quantitative description of the t-e hybridization process. In addition, the AFM transition temperatures can be further calculated for a qualitative comparison to those measured from the grown single crystals.

In this paper, we report on a successful single crystal growth of the family of RECrO$_3$ compounds by a laser-diode FZ technique. Large single crystals measuring centimeters in size were obtained with the largest mass >10 g. The results from in-house characterizations on grown single crystals are in agreement with those from our first-principles calculations. Our research reveals that the t-e hybridization process can be tuned by RE-ions and induce FM interactions in the main AFM matrix and sheds light on the coexistence of weak ferromagnetism with antiferromagnetism and ferroelectricity in orthochromates.

**RESULTS**

**Grown single crystals**

Single-crystal materials hold translational symmetry of long-range building blocks; therefore, they provide reliable information of structures and properties of matters (Cheng, 2017; Li et al., 2018; Sun et al., 2019; Xiong et al., 2021; Zhang, 2020). Exploring and optimizing the single crystal growth parameters are time-consuming and labor-intensive processes (Li, 2008). For the first time, we have grown large single crystals of the family of RECrO$_3$ (RE = Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) compounds. Photos of some representative single crystals as-grown are exhibited in Figures 2A and 2B, where the YbCrO$_3$ (Figure 2A, ~7 cm in length) and LuCrO$_3$ (Figure 2B, ~10 cm) crystals have a diameter of 4–6 mm and very shining surfaces. So far, the largest single crystal of orthochromates we have grown is >10 g for the EuCrO$_3$ compound. Our crystal growth engineering of RECrO$_3$ compounds produced a China invention patent (Li et al., 2021).

**Neutron Laue diffraction patterns**

We investigated the grown single crystals with a neutron Laue diffraction study. The top panels of Figures 2C–2E show the monitored neutron Laue patterns of a YCrO$_3$ single crystal with the three axes perpendicular to the paper: a axis (Figure 2C), b axis (Figure 2D), and c axis (Figure 2E). All patterns display symmetric and very strong diffraction spots, indicating a good quality of the grown single crystal. As shown in the bottom panels of Figures 2C–2E, we theoretically simulated the three patterns by using the OrientExpress software (Ouladdiaf et al., 2006), which further confirmed the good quality of our single crystals.

**Magnetic properties**

To clearly show features of dc magnetization in the vicinity of magnetic phase transitions, we present temperature-dependent data in the temperature range of 1.8–200 K. For the whole-temperature data (1.8–400 K), please refer to Figure S1. We measured the zero-field cooling (ZFC) magnetization at zero applied magnetic field, trying to explore the negative magnetization behavior and address whether the observed weak ferromagnetism is spontaneous.

We measured the ZFC magnetization data at 1000 Oe in the temperature range of 250–350 K and calculated the inverse magnetic susceptibility $\chi^{-1} = B/M$, which can well fit with the Curie-Weiss (CW) law for a pure paramagnetic (PM) state (Li et al., 2006, 2007, 2009; Zhu et al., 2020b),

$$\chi^{-1}(T) = \frac{3k_BT}{N_A\mu_{eff}^2},$$

(Equation 1)

where $k_B = 1.38062 \times 10^{-23}$ J/K is the Boltzmann constant, $\Theta_{CW}$ is the PM CW temperature, $N_A = 6.022 \times 10^{23}$ mol$^{-1}$ is Avogadro’s constant, and $\mu_{eff}$ is the effective PM moment. We fit the data to Equation (1), extracting experimental values of the AFM transition temperature $T_{N_\perp}$, $\Theta_{CW}$, and $\mu_{eff\_meas}$ of RECrO$_3$ single crystals. These measured values were listed in Table 1. For the RECrO$_3$ compounds, it is pointed out that both RE$^{3+}$ and Cr$^{3+}$ ions contribute to the effective PM moment; therefore, the theoretical total
effective PM moment 

\[
\mu_{\text{eff-theo}}^{\text{total}} = \sqrt{\left(\mu_{\text{eff-theo}}^{\text{RE}}\right)^2 + \left(\mu_{\text{eff-theo}}^{\text{Cr}}\right)^2},
\]

where 

\[
\mu_{\text{eff-theo}}^{\text{RE}} = g_m B \sqrt{J(J+1)},
\]

and 

\[
\mu_{\text{eff-theo}}^{\text{Cr}} = g_m B \sqrt{S(S+1)} = 3.873 \mu_B \quad (\text{where } S = 3/2).
\]

The quantum numbers of RE\(^{3+}\) and Cr\(^{3+}\) ions and the calculated values of \(\mu_{\text{eff-theo}}^{\text{RE}}\) and \(\mu_{\text{eff-theo}}^{\text{CR}}\) were listed in Table 1 for a comparison to the corresponding experimental values. Within 250–350 K, the fits coincide well with the measured magnetization of RECrO\(_3\) (RE = Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu) single crystals. As temperature decreases from 250 to 220 K, the measured data did not show obvious deviation from the Curie-Weiss law fitting (short-dashed line), which confirms the validity of our theoretical fits and that the RECrO\(_3\) (RE = Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu) single crystals remain a pure PM state in the temperature range of 220–350 K.

Magnetic hysteresis loops at the low-field regimes were measured. The isothermal field dependence of magnetization with applied magnetic field from −14 to 14 T was supplemented in Figure S2.

In the following, we present analyses of the magnetic properties of RECrO\(_3\) (RE = Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu) single crystals one by one.

**EuCrO\(_3\)**

EuCrO\(_3\) demonstrates negative magnetization behavior at zero magnetic field below \(T_N^{\text{EuCrO}_3}\) (Figure 3A), whereas the ZFC magnetization at \(B = 50\) Oe increases sharply below \(T_N^{\text{EuCrO}_3}\) within a thermal regime of ~ 1.2 K and then flattens to 1.8 K upon cooling. The field-cooling (FC) magnetization at 100 Oe increases by ~ 18% at 1.8 K. The magnetization measured at 50 and 100 Oe resembles the features of a weak FM state. We determined that \(T_N^{\text{EuCrO}_3} = 181.6(1)\) K for an EuCrO\(_3\) single crystal. Below \(T_N^{\text{EuCrO}_3}\) EuCrO\(_3\) enters a canted AFM state, probably because of the Dzyaloshinskii-Moriya interactions of Cr\(^{3+}\) ions.

To avoid the effect of non-intrinsic magnetic contributions at low applied magnetic fields, we used the ZFC magnetization measured from 250 to 350 K at 1000 Oe for CW fitting (Figure 3B). This produces an effective
hysteresis loops are observed at 1.8 and 20 K, and there is nearly no difference between them. Remanent field dependence of magnetization measured at 1.8 K is displayed in Figure 3C, where clear magnetic loop closes at 0.322 (1) emu g⁻¹ T⁻¹ (Figure S2A). Given that the theoretical saturation moment (\(M_{\text{sat-theo}}\)) for RE³⁺ ions in RECrO₃ single crystals based on the Hund’s rule (Table 1) is considerably larger than the theoretical value \(\mu_{\text{eff-theo}} \approx 3.873 \mu_B\) for 4f (4d for \(Y^{3+}\) ion) electrons, spin \(S\), orbital \(L\), total angular momentum \(J\), Landé factors \(g_J\), and the ground-state term \(2S+1_L_J\). The values of \(\theta_{\text{CW}}\) were extracted from the M-T measurements by the CW-law fitting. The values of \(M_{\text{sat-theo}}\) were extracted from the M-B data. The numbers in parenthesis are the estimated standard deviations of the (next) last significant digit. Some parameters of YCrO₃ (Zhu et al., 2020a) and GdCrO₃ (Zhu et al., 2020c) were referred to in our previous studies.

### Table 1. Calculated theoretical quantum numbers of RE³⁺ ions in RECrO₃ single crystals based on the Hund’s rule: number of 4f (4d for \(Y^{3+}\) ion) electrons, spin \(S\), orbital \(L\), total angular momentum \(J\), Landé factors \(g_J\), and the ground-state term \(2S+1_L_J\)

<table>
<thead>
<tr>
<th>RE³⁺ =</th>
<th>Y³⁺</th>
<th>Eu³⁺</th>
<th>Gd³⁺</th>
<th>Tb³⁺</th>
<th>Dy³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>4d⁺ ion</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4f⁺ ions</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0</td>
<td>3</td>
<td>7/2</td>
<td>3</td>
<td>5/2</td>
</tr>
<tr>
<td>L</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>J</td>
<td>0</td>
<td>0</td>
<td>7/2</td>
<td>6</td>
<td>15/2</td>
</tr>
<tr>
<td>(g_J)</td>
<td>–</td>
<td>–</td>
<td>2</td>
<td>1.5</td>
<td>1.33</td>
</tr>
<tr>
<td>(2S+1_L_J)</td>
<td>(\frac{1}{2}S_0)</td>
<td>(\frac{3}{2}F_0)</td>
<td>(\frac{3}{2}S_{7/2})</td>
<td>(\frac{7}{2}F_2)</td>
<td>(\frac{6}{2}H_{15/2})</td>
</tr>
<tr>
<td>(\mu_{\text{eff-theo}})</td>
<td>3.95</td>
<td>6.44</td>
<td>8.40</td>
<td>10.51</td>
<td>11.35</td>
</tr>
<tr>
<td>(\mu_{\text{sat-theo}})</td>
<td>3.873</td>
<td>3.873</td>
<td>8.832</td>
<td>10.464</td>
<td>11.328</td>
</tr>
<tr>
<td>(M_{\text{sat-theo}})</td>
<td>(-0.147)</td>
<td>0.245 (1)</td>
<td>6.43</td>
<td>6.248 (1)</td>
<td>4.834 (1)</td>
</tr>
<tr>
<td>(\theta_{\text{CW}})</td>
<td>141.5 (1)</td>
<td>181.6 (1)</td>
<td>169.3 (1)</td>
<td>157.9 (1)</td>
<td>148.5 (1)</td>
</tr>
</tbody>
</table>

PM moment \(\mu_{\text{eff-theo}} = 6.44 \mu_B\), which is considerably larger than the theoretical value \(\mu_{\text{theo}} = 3.873 \mu_B\) (Table 1) and a CW temperature \(\theta_{\text{CW}} = -450.4(15)\) K.

The field dependence of magnetization measured at 1.8 K is displayed in Figure 3C, where clear magnetic hysteresis loops are observed at 1.8 and 20 K, and there is nearly no difference between them. Remanent magnetization \(M_r \approx 0.91\) emu g⁻¹ and coercive field \(B_c \approx 95\) Oe were determined. The magnetic hysteresis loop closes at \(B_c \approx 867\) Oe, after which the ZFC magnetization increases linearly as a function of the magnetic field, with a slope of d\(M\)/d\(B\) = 0.322 (1) emu g⁻¹ T⁻¹ (Figure S2A). Given that the theoretical saturation...
magnetic moment of Cr\(^{3+}\) ions is 
\[ M_{\text{Cr}}^{\text{sat}} = g_J m_B S = 3 m_B, \]
where \( g_J = 2 \) and \( S = \frac{3}{2} \) for pure ionic Cr\(^{3+}\) ions (Table 1), it is inferred that attaining a full magnetic saturation state requires \( B > 203 \, T \). At 1.8 K and 14 T, a magnetization of \( M_{\text{meas}} = 0.245 \) (1) \( \mu_B/\text{Cr} \) was reached (Figure S2A), which is equal to \( \approx 8.2\% \) of the theoretical value \( M_{\text{total}}^{\text{sat}}/C_0^{\text{theo}} = 3 \mu_B/\text{Cr} \).

Our study indicates a possible existence of competition between FM and AFM exchange interactions. We did not observe the magnetic ordering of Eu\(^{3+}\) ions, which is consistent with a previous study on polycrystalline EuCrO\(_3\) samples (Taheri et al., 2016).

\( \text{TbCrO}_3 \)

We determined that \( T_{\text{Cr}}^N = 157.9(1) \, K \) for a TbCrO\(_3\) single crystal (Figure 4A). Below \( T_{\text{Cr}}^N \), the ZFC magnetization at 0 Oe was negative, whereas the magnetization curves at 50 and 100 Oe increased gradually after a sharp enhancement around \( T_{\text{Cr}}^N \) within \( \approx 0.56 \, K \). Below \( \approx 70 \, K \), the ZFC magnetization at 100 Oe evidently exceeded that measured at 50 Oe. At \( \approx 7.7 \, K \), a kink appeared in the magnetization at 50 and 100 Oe (ZFC at 50 and 100 Oe: downturn; FC at 100 Oe: upturn), indicating the formation of Tb\(^{3+}\) spin ordering. Below \( \approx 4.5 \, K \), a sharp decrease in the magnetization at 50 and 100 Oe and a sharp increase in that at 0 Oe were observed. Below \( \approx 3 \, K \), the ZFC magnetization at 0, 50, and 100 Oe approached zero. Therefore, we observe elaborate magnetic phase transitions with temperature in the TbCrO\(_3\) single crystal.

The CW fitting result of \( \mu_{\text{eff-meas}} = 10.51 \) \( \mu_B \) (Figure 4B) is nearly equal to the theoretical value \( \mu_{\text{total}}^{\text{eff-theo}} = 10.464 \) \( \mu_B \). The CW temperature \( \Theta_{\text{CW}} = 53.3(1) \, K \) indicates a weak competition between the FM and AFM interactions in our TbCrO\(_3\) single crystal.

A clear magnetic hysteresis loop was observed with \( M_r \approx 2.75 \) emu g\(^{-1}\) and \( B_c \approx 48 \) Oe at 15 K (Figure 4C), indicating a weak FM state of the Cr\(^{3+}\) ions. When \( T = 1.8 \) K, both Tb\(^{3+}\) and Cr\(^{3+}\) spins order, and the observed magnetization loop was stretched along the \( B \) axis and squeezed along the magnetization axis, leading to a parallelogram-shaped hysteresis loop with \( M_r \approx 1.82 \) emu g\(^{-1}\) and \( B_c \approx 2500 \) Oe (Figure 4C). Such a twisted loop has not been previously observed in either polycrystalline or single-crystalline (grown by the flux method) samples (Vagadia et al., 2018; Yin et al., 2016). This indicates a stronger coupling between the Cr\(^{3+}\) and Tb\(^{3+}\) spins in our TbCrO\(_3\) single crystal. As \( B \) increased, the loop at 1.8 K gets a quick saturation at \( B_s \approx 1.67 \, T \), whereas that at 15 K increased.
smoothly and attained a plateau at ~6.8 T. At 1.8 K and 14 T, the magnetization reached $M_{\text{meas}} = 6.248(1)\, \mu_B$, which is ~34% smaller than the theoretical value $M_{\text{total\,sat\,theo}} = 9.487\, \mu_B$ (Table 1).

TbCrO$_3$ entered a long-range canted AFM state of Cr$^{3+}$ ions below $T_{\text{N\,Cr}} = 157.9(1)$ K. The possible long-range AFM order of Tb$^{3+}$ ions was formed below $T_{\text{N\,Tb}} = 7.7$ K. Strong coupling was observed between the spin orders of the Cr$^{3+}$ and Tb$^{3+}$ ions. In addition, a weak competition between the FM and AFM interactions of the Cr$^{3+}$ ions was observed.

DyCrO$_3$

The DyCrO$_3$ single crystal underwent a magnetic phase transition from the PM state to a canted AFM phase at $T_{\text{N\,Cr}} = 148.5(1)$ K (Figure 5A), corresponding to the formation of Cr$^{3+}$ spin ordering. A kink appeared at $T_{\text{Cr}} = 38$ K in the magnetization at 0, 50, and 100 Oe (Figure 5B), which is attributed to the spin reorientation of the Cr ions. A similar observation was previously reported for DyCrO$_3$ single crystals grown by the flux method, where the appearance of the kink was believed to be caused by the spin reorientation of Dy$^{3+}$ ions (Yin et al., 2016). Below $T_{\text{Cr}}$, the magnetization increased smoothly until the onset of a sharp enhancement at ~17 K, reaching a maximum at ~2.54 K and then followed by a quick reduction. Therefore, we observed an AFM phase transition of the Dy$^{3+}$ ions at $T_{\text{Dy}} = 2.8$ K.

The CW fitting produces $\mu_{\text{eff\,meas}} = 11.35\, \mu_B$ (Figure 5C), which is nearly equal to the theoretical value $\mu_{\text{total\,meas\,theo}} = 11.328\, \mu_B$. CW temperature, $\Theta_{\text{CW}} = -56.5(1)$ K (Table 1).

Isothermal magnetic hysteresis loops were observed at 1.8 (M$_r \sim 4.7$ emu g$^{-1}$; $B_c \sim 639$ Oe) and 10 K (M$_r \sim 1.1$ emu g$^{-1}$; $B_c \sim 41$ Oe) (Figure 5D), confirming that Cr$^{3+}$ spins hold a canted AFM state. For the Dy$^{3+}$ sublattices, we could only conclude that the spins form an AFM state. At both 1.8 and 10 K, the magnetization curves finally flattened with $M_{\text{meas}} = 4.834(1)\, \mu_B$ at 14 T (Figure 5C). This value was ~53.7% less than the theoretical value of $M_{\text{total\,sat\,theo}} = 10.440\, \mu_B$ (Table 1).

HoCrO$_3$

We determined that $T_{\text{N\,Cr}} = 143.2(1)$ K for a HoCrO$_3$ single crystal (Figure 6A). Below $T_{\text{N\,Cr}}$, the ZFC magnetization at 0 Oe was negative, whereas those at 50 and 100 Oe were positive and increased smoothly in the
temperature regimes of \( \sim 19 \) K (at 50 Oe) and \( \sim 47 \) K (at 100 Oe) and then flatten until \( T_H = 7 \) K, at which \( Ho^3+ \) ions order antiferromagnetically. Below \( \sim 2.4 \) K, all curves were flattened. When \( 2.4<K<T_H \), the magnetization curves at ZFC (down turn) and FC (up turn) 100 Oe demonstrated an inverse trend; above \( T_H \), they coincided. The degree of canting of the \( Cr^3+ \) AFM structure determines the strength of the resulting ferromagnetism along the \( c \) axis. This prevents the formation of an AFM structure of the \( Ho^3+ \) ions. The difference between the ZFC and FC magnetization at 100 Oe is controlled by the competition between the Zeeman energy generated by the applied magnetic field, crystal field, AFM interaction strength of \( Ho^3+ \) ions, and magnetic anisotropy (Li, 2016).

We obtained \( \mu_{\text{eff-meas}} = 11.03 \mu_B \), which is comparable to \( \mu_{\text{eff-theo}} = 11.292 \mu_B \), and \( \Theta_{\text{CW}} = 19.6(1) \) K (Figure 6B and Table 1). The previous study on polycrystalline \( HoCrO_3 \) sample shows \( \mu_{\text{eff-meas}} = 11.55 \mu_B \) and \( \Theta_{\text{CW}} = -24.0 \) K (Su et al., 2011). Obtaining evidence of short-range exchange interactions and magnetic fluctuations of \( Ho^{3+} \) spins reported previously by quasielastic and inelastic neutron scattering studies on \( HoCrO_3 \) powder samples (Chatterji et al., 2017; Kumar et al., 2016) necessitates more in-house characterizations with the \( HoCrO_3 \) single crystal.

At 1.8 and 15 K, we observed magnetic hysteresis loops in step-increasing mode (Figure 6C). We extracted \( M_s \sim 3.5(1.8 \) K) and 1.9 (15 K) emu g\(^{-1}\) and the corresponding \( B_{\text{K}} \sim 140 \) and 72 Oe, respectively. At 15 K, the magnetization increased linearly at \( B \leq 618 \) Oe and then proceeded smoothly into a plateau at \( \sim 3.2 \) T; in contrast, at 1.8 K and \( B \leq 1092 \) Oe, the magnetization almost increased linearly with increasing magnetic field and then attained \( M_{\text{meas}} = 3.999(1) \mu_B \) at 14 T (Figure S2D). This value was only \( \sim 38.3\% \) of the theoretical value \( M_{\text{sat-theo}} = 10.440 \mu_B \) (Table 1).

**ErCrO\(_3\)**

Below \( T_{C} = 135.4(1) \) K (Eibschütz et al., 1970), there was a small sharp enhancement in the magnetization within \( \sim 0.72 \) K, which then increased smoothly until an onset of a sudden decrease at \( T_{SR} = 9.7 \) K (Figure 7A). The decrease in magnetization is attributed to the spin reorientation of \( Cr^{3+} \) ions from \( I_4(G_x, A_y, F_z; F_y) \) to \( I_1(A_x, G_y, C_z; C_y^2) \) or the \( I_1(0) \) spin configuration (Su et al., 2010b, 2012). Below
Er/CrO$_3$, the magnetization at 0, 50, and 100 Oe decreased linearly. No difference was found in the ZFC and FC magnetization at 100 Oe.

The CW fitting resulted in an effective PM magnetic moment of $10.20 \, \mu_B$, in agreement with the theoretical value of $10.334 \, \mu_B$, and a CW temperature of $30.0(1) \, K$ (Figure 7B and Table 1).

No magnetic hysteresis loop appeared in the $M$-$B$ measurements (Figure 7C). In contrast, clear hysteresis loops were observed previously for polycrystalline ErCrO$_3$ samples (Shi et al., 2018). For the magnetization curve at 1.8 K, a gate magnetic field of $650 \, Oe$ existed. When $0 \leq B \leq B_{gate} = 650 \, Oe$, the magnetization increased linearly from 0 to $0.45 \, emu \, g^{-1}$. Then, it quickly flattened when $B/0.617 \, T$ and attained $M_{meas} = 6.385(1) \, \mu_B$ at 14 T (Figure S2E).

TmCrO$_3$

We determined that $T^\chi_{Cr} = 125.9(1) \, K$ for the TmCrO$_3$ single crystal (Figure 8A), which is consistent with a previous study of polycrystalline TmCrO$_3$ (Wang et al., 2016a; Yoshii, 2012). Below $T^\chi_{Cr}$, the ZFC magnetization at 0 Oe was negative. The magnetization at 50 and 100 Oe was positive and increased sharply within $\sim 1 \, K$. This is because Cr$^{3+}$ spins order into a canted AFM state of the $I_2$ configuration ($F,C,G$) (Tamaki et al., 1977; Yoshii, 2012). Upon further cooling, the magnetization increased smoothly until it reached a maximum at $T^\chi_{Cr,max} \sim 74 \, K$. After that, the magnetization reduced smoothly and attained negative values suddenly at $T_{SR} \sim 37.2 \, K$ (for ZFC at 50 and 100 Oe) and $\sim 40.1 \, K$ (for FC at 100 Oe), followed by a sharp increase with positive values appearing again at a compensation temperature $T_{comp} \sim 28.72 \, K$. The sharp drop observed at $\sim 40.1 \, K$ could be ascribed to the spin reorientation of Cr$^{3+}$ ions accompanied by a 90$^\circ$ rotation of the spins, that is, from one crystallographic axis to another, probably because of the competition between anisotropic exchanges and single-ion anisotropy (Li, 2016). This feature became smooth in the polycrystalline samples (Wang et al., 2016a; Yoshii, 2012). Our study revealed a reversal of the magnetization behavior. The ZFC and FC magnetization at 100 Oe nearly coincided with each other. This is different from the observations with polycrystalline TmCrO$_3$ (Yoshii, 2012). We observed a magnetic phase transition at $T^\chi_{Cr} = 19.6 \, K$, which probably correlates with the AFM order of Tm$^{3+}$ ions. This was not observed in polycrystalline TmCrO$_3$ samples (Wang et al., 2016a; Yoshii, 2012).
We obtained $m_{\text{eff-meas}} = 8.35 \, \mu_B$, which is almost identical to the theoretical value $m_{\text{total eff}}/C_0 = 8.495 \, \mu_B$, and $Q_{\text{CW}} = 17.4(4) \, \text{K}$ (Figure 8B and Table 1).

We observed different magnetic hysteresis loops (Figure 8C): (i) at 20 K, a parallelogram-shaped loop with $M_r \sim 1.4 \, \text{emu g}^{-1}$ and $B_c \sim 111 \, \text{Oe}$. (ii) At 1.8 K, a twisted loop with $M_r \sim 0.75 \, \text{emu g}^{-1}$ and $B_c \sim 38.2 \, \text{Oe}$. The magnetization reached $M_{\text{meas}} = 2.868(1) \, \mu_B$ at 14 T (Figure S2F and Table 1).

**YbCrO$_3$**

We determined that $T_{\text{Cr}} = 117.9(1) \, \text{K}$ for the YbCrO$_3$ single crystal (Figure 9A), which is the lowest magnetic phase transition temperature of Cr$^{3+}$ sublattices among all rare-earth orthochromates. Below $T_{\text{Cr}}$, the ZFC magnetization at 0 Oe reduced sharply to negative values, whereas the magnetization at 50 and 100 Oe increased sharply and attained the maximum values at $T_{\text{Cr}} \approx 99.3 \, \text{K}$ (for ZFC at 50 Oe), 86.3 K (for ZFC at 100 Oe), and 69.6 K (for FC at 100 Oe), followed by smooth decreases to negative values at compensation temperatures $T_{\text{comp1}} \approx 63.7 \, \text{K}$ (for ZFC at 50 Oe), 47.5 K (for ZFC at 100 Oe), and 15.5 K (for FC at 100 Oe). The positive values of magnetization at 0, 50, and 100 (ZFC) Oe reappeared at $T_{\text{comp2}} \approx 5.5 \, \text{K}$ (for ZFC at 50 Oe), 17.6 K (for ZFC at 100 Oe), and 19.5 K (for ZFC at 100 Oe), whereas the magnetization at FC 100 Oe still remained negative. Below $T_{\text{Yb}} \approx 7 \, \text{K}$, all the ZFC magnetization curves flattened (Su et al., 2010a). Notably, a large difference exists between the curves of the ZFC and FC magnetizations at 100 Oe. The FC magnetization at 100 Oe resembles that observed in the polycrystalline samples (Wang et al., 2016b).

The CW fitting resulted in $m_{\text{eff-meas}} = 5.63 \, \mu_B$, which was slightly lower than the theoretical value $m_{\text{total eff}}/C_0 = 5.964 \, \mu_B$, and $\Theta_{\text{CW}} = -17.4(4) \, \text{K}$ (Figure 8B and Table 1).

No magnetic hysteresis loop appeared in the ZFC $M$-$B$ curves at 15 and 300 K, whereas we observed magnetic hysteresis loops with a similar shape at 1.8 K ($M_r \sim 0.24 \, \text{emu g}^{-1}$; $B_c \sim 1200 \, \text{Oe}$), 25 K ($M_r \sim 0.14 \, \text{emu g}^{-1}$; $B_c \sim 1200 \, \text{Oe}$), and 40 K ($M_r \sim 0.25 \, \text{emu g}^{-1}$; $B_c \sim 1780 \, \text{Oe}$) (Figure 9C). The measured magnetization $M_{\text{meas}} = 0.883(1) \, \mu_B$ at 1.8 K and 14 T, which is merely $17.7\%$ of $M_{\text{total eff}}/C_0 = 5 \mu_B$ (Figure S2G and Table 1).
The LuCrO$_3$ single crystal exhibited magnetic behaviors similar to those observed in single-crystal TmCrO$_3$ (Figures 8A and 10A). We determined $T_{C_{\text{max}}}$ = 122.3(1) K, $T_{SR}$ = 33 K (for ZFC at 50 Oe) and 31 K (for ZFC and FC at 100 Oe), $T_{\text{comp2}}$ = 28 K (for all data), and $T_{N}$ = 2.3 K for the LuCrO$_3$.

**Figure 8.** Magnetic property of TmCrO$_3$

(A) Magnetization as a function of temperature from 1.8–200 K measured at 0, 50, and 100 Oe. We performed both zero-field and field-cooling measurements at 100 Oe.

(B) Zero-field cooling inverse magnetic susceptibility $\chi^{-1}$ (solid circles) at an applied magnetic field of 1000 Oe as a function of temperature in the range of 220–350 K. The solid lines represent the fits with a Curie-Weiss law from 250–350 K. The Curie-Weiss law fits were extrapolated to low temperatures shown as short-dashed lines.

(C) Magnetic hysteresis loops measured at low applied magnetic fields with selected temperatures.

**Figure 9.** Magnetic property of YbCrO$_3$

(A) Magnetization as a function of temperature from 1.8–200 K measured at 0, 50, and 100 Oe. We performed both zero-field and field-coolings measurements at 100 Oe.

(B) Zero-field cooling inverse magnetic susceptibility $\chi^{-1}$ (solid circles) at an applied magnetic field of 1000 Oe as a function of temperature in the range of 220–350 K. The solid lines represent the fits with a Curie-Weiss law from 250–350 K. The Curie-Weiss law fits were extrapolated to low temperatures shown as short-dashed lines.

(C) Magnetic hysteresis loops measured at low applied magnetic fields with selected temperatures.
LuCrO$_3$ single crystal. No clear difference was observed in the ZFC and FC magnetization at 100 Oe. Our LuCrO$_3$ single crystal demonstrated magnetic behaviors different from those of previous polycrystalline samples (Durán et al., 2014).

The CW fitting results in $\mu_{\text{eff-meas}} = 4.98 \mu_B$, which is ~ 28.1% higher than the theoretical value $\mu_{\text{total-theo}} = 3.873 \mu_B$, and $\theta_{\text{CW}} = -110.4(2)K$ (Figure 10B and Table 1).

We observed magnetic hysteresis loops at: 1.8 K ($M_r \sim 0.13 \text{ emu g}^{-1}$; $B_c \sim 25 \text{ Oe}$), 15 K ($M_r \sim 0.14 \text{ emu g}^{-1}$; $B_c \sim 32 \text{ Oe}$), 25 K ($M_r \sim 0.054 \text{ emu g}^{-1}$; $B_c \sim 125 \text{ Oe}$), and 40 K ($M_r \sim 0.12 \text{ emu g}^{-1}$; $B_c \sim 28 \text{ Oe}$) (Figure 10C). The measured magnetization, $M_{\text{meas}} = 1.197(1) \mu_B$, at 1.8 K and 14 T is merely ~ 39.9% of $M_{\text{total-sat-theo}} = 3\mu_B$ (Figure S2H and Table 1).

We summarize the magnetic behaviors of single-crystal RECrO$_3$ compounds as follows: (i) TbCrO$_3$, DyCrO$_3$, and ErCrO$_3$ displayed similar temperature dependencies as did TmCrO$_3$ and LuCrO$_3$ single crystals. (ii) DyCrO$_3$ and ErCrO$_3$ did not exhibit negative magnetization, whereas the others did. (iii) Reversal magnetic behaviors (positive $\rightarrow$ negative $\rightarrow$ positive) occurred for TmCrO$_3$, YbCrO$_3$, and LuCrO$_3$ single crystals. (iv) We did not observe any indication of Eu$^{3+}$ magnetic ordering, which may require lower temperatures. (v) Obvious magnetic hysteresis loops were observed for RECrO$_3$, except for ErCrO$_3$. (vi) The measured magnetization at 1.8 K and high magnetic fields plateaued for RECrO$_3$ (RE = Tb, Dy, Ho, Er, and Lu) single crystals. (vii) The measured effective PM moments of EuCrO$_3$ and LuCrO$_3$ were not consistent with the theoretical values. (viii) The applied magnetic field of 14 T was far less to saturate RECrO$_3$ at 1.8 K. (ix) Only HoCrO$_3$ demonstrated a positive CW temperature. Finally, we observed the complex and coupled magnetic phase transitions of RE$^{3+}$ (except for Eu$^{3+}$) and Cr$^{3+}$ ions.

We also summarize the magnetic structures of RE$^{3+}$ and Cr$^{3+}$ ions in RECrO$_3$ (RE = Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) compounds in the literature (Table 2). The magnetic SR transition of Cr$^{3+}$ ions has been reported for GdCrO$_3$ (Cooke et al., 1974) and ErCrO$_3$ (Hornreich, 1978; Shamir et al., 1981) compounds. The detailed magnetic structures of Tm$^{3+}$ and Yb$^{3+}$ ions in TmCrO$_3$ (Shamir et al., 1981) and YbCrO$_3$ (Shamir et al., 1981) compounds remain controversial. A $F_\alpha$ magnetic component of Yb$^{3+}$ ions had to be included for a satisfactory fit of the neutron powder diffraction data of YbCrO$_3$ in the temperature range.
of 1.5–120 K (Deepak et al., 2021). Unraveling the nature of the magnetic phase transitions necessitates neutron scattering studies on single-crystal samples with modern techniques (Li, 2008).

**DISCUSSION**

Superexchange interactions between the neighboring spins of transition metals can be realized through VCT via intermediate O\(^{2−}\) ions. During this process, the tilting of the oxygen octahedron corresponds to the change in the metal-oxygen-metal bond angles and may lead to \(t_{2g}\) and \(e_g\) orbital overlapping. This facilitates the hopping of \(t_{2g}\) electrons via the bridge of O\(^{2−}\) ions to occupy the empty \(e_g\) band and the interaction with filled \(t_{2g}\) electrons at the same site, that is, the intersite t–e orbital hybridization (Zhou et al., 2010; Zhou and Goodenough, 2008). In the framework of t–e hybridization, the superexchange parameter \(J\) consists of the following two parts (Zhou et al., 2010):

\[
J = J^t - J^\text{hb},
\]

(Equation 2)

where \(J^t\) denotes AFM coupling via the VCT of \(t_{2g}\) O\(^{2−}\)–O–\(t_{2g}\) and \(J^\text{hb}\) represents FM coupling via the VCT of \(t_{2g}\) O\(^{2−}\)–\(e_g\). Both processes are schematically depicted in Figure 11A for Cr\(^{3+}\) ions. For example, for a half-filled 3d metal like Fe\(^{3+}\) (\(t_{2g}\) e\(_g^0\)), the effect of t–e hybridization on superexchange interactions may not be evident because the electron hoppings of Fe\(^{3+}\) (\(t_{2g}\) e\(_g^0\)) – O\(^{2−}\) – Fe\(^{3+}\) (\(t_{2g}\)) and Fe\(^{3+}\) (\(t_{2g}\)) – O\(^{2−}\) – Fe\(^{3+}\) (\(e_g^0\)) themselves are AFM couplings already (Zhou et al., 2010; Zhou and Goodenough, 2008). In contrast, for less than half-filled 3d electrons like Cr\(^{3+}\) ions (\(t_{2g}\) e\(_g^0\)) in RECrO\(_3\) compounds, the t–e orbital hybridization favors the VCT of Cr\(^{3+}\) (\(t_{2g}\)) – O\(^{2−}\) – Cr\(^{3+}\) (\(e_g^0\)) (Qian et al., 2014; Siddique et al., 2021; Zhou et al., 2010). Electron hopping of \(t_{2g}\) O\(^{2−}\)–\(e_g^0\) can increase the FM coupling component \(J^\text{hb}\).

To quantitatively describe the Cr\(^{3+}\)-O\(^{2−}\)-Cr\(^{3+}\) superexchange interactions as well as the \(t_{2g} - e_g\) (t–e) orbital overlapping degree as a function of the ionic radii of the RE\(^{3+}\) ions, we calculated the exchange parameters and electronic structures of RECrO\(_3\) (RE = Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) compounds. We mainly considered the NN exchange parameters of the Cr\(^{3+}\) sublattices within the crystallographic ab plane \((J_{ab})\) and along the c axis \((J_c)\) (Figure 11B). We extracted the values of \(J_1\) and \(J_2\) using the so-called energy mapping method with four types of magnetic structures (A–AFM, C–AFM, G–AFM, and FM) (Figure S3). We obtained the total energy of each magnetic structure using DFT calculations, projecting each collinear spin state onto the following spin Hamiltonian of a Heisenberg model

**Table 2. Summary of the previously reported magnetic structures of RE\(^{3+}\) and Cr\(^{3+}\) ions in RECrO\(_3\) (RE = Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) compounds.**

<table>
<thead>
<tr>
<th>RECrO(_3)</th>
<th>RE(^{3+})</th>
<th>Cr(^{3+})</th>
<th>SR</th>
<th>Cr(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((T &lt; T_{N}^{RE}))</td>
<td>((T &lt; T_{N}^{CR}))</td>
<td>((T &lt; T_{SR}^{CR}))</td>
<td>((T &gt; T_{SR}^{CR}))</td>
</tr>
<tr>
<td>GdCrO(_3)</td>
<td>(F_yC_y)</td>
<td>(F_yG_y)</td>
<td>(1)</td>
<td>(G_yF_y)</td>
</tr>
<tr>
<td>TbCrO(_3)</td>
<td>(F_yC_y)</td>
<td>(1)</td>
<td>(F_yG_y)</td>
<td></td>
</tr>
<tr>
<td>DyCrO(_3)</td>
<td>(G_yA_y)</td>
<td>(1)</td>
<td>(G_y)</td>
<td></td>
</tr>
<tr>
<td>HoCrO(_3)</td>
<td>(-F_x-C_y)</td>
<td>(-)</td>
<td>(-)</td>
<td>(G_y)</td>
</tr>
<tr>
<td>ErCrO(_3)</td>
<td>(-C_y)</td>
<td>(G_y)</td>
<td>(1)</td>
<td>(G_yF_y)</td>
</tr>
<tr>
<td>TmCrO(_3)</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
<td>(F_yG_y)</td>
</tr>
<tr>
<td>YbCrO(_3)</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
<td>(F_yG_y)</td>
</tr>
<tr>
<td>LuCrO(_3)</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
<td>(F_yG_y)</td>
</tr>
</tbody>
</table>

The crystal structure is orthorhombic with the \(Pbnm\) space group (No. 62). Here \(T_{N}^{RE}\) = AFM transition temperature of RE\(^{3+}\) ions; SR = spin reorientation; \(T_{SR}^{CR}\) = SR temperature of Cr\(^{3+}\) ions; \(T_{N}^{CR}\) = AFM transitions temperature of Cr\(^{3+}\) ions. The check mark (\(\checkmark\)) represents that there exists a magnetic SR phase transition. These were summarized from the following references: GdCrO\(_3\) (Cook et al., 1974), TbCrO\(_3\) (Gordon et al., 1976), DyCrO\(_3\) (Berlaut, 1963; Krynetskii and Matveev, 1997; Tamaki et al., 1973), HoCrO\(_3\) (Shamir et al., 1981; Su et al., 2011), ErCrO\(_3\) (Hornreich, 1978; Shamir et al., 1981), TmCrO\(_3\) (Shamir et al., 1981), YbCrO\(_3\) (Shamir et al., 1981), and LuCrO\(_3\) (Shamir et al., 1981).
where $J > 0$ represents FM interactions, and $J < 0$ denotes AFM couplings. Using Equation (3), we can solve for $J_1$ and $J_2$ as (Bernal et al., 2021; Fujioka et al., 2008)

$$J_1 = \frac{(E_G + E_C - E_A - E_f)}{8S^2},$$

and

$$J_2 = \frac{(E_G - E_C + E_A - E_f)}{4S^2}.$$  \hspace{1cm} (Equation 4)  

Thus, we can calculate the Néel temperatures of the RECrO$_3$ compounds using the mean-field approximation (MFA) (Fujioka et al., 2008), that is,

$$T_N = \frac{2S(S+1)}{3k_B} (4J_1 - 2J_2).$$  \hspace{1cm} (Equation 5)

To depict the hybridization degree, we calculated the overlap of $t_{2g}$ and $e_{g}$ (Table 3) using their DOS (Figure S4) product over the corresponding energy region.

$$I_{t_{2g}-e_{g}} = \int_{E_F}^{E_C} D_{t_{2g}}(E)D_{e_{g}}(E)dE,$$

where $D_{t_{2g}}(E)$ and $D_{e_{g}}(E)$ are the DOSs for the $t_{2g}$ and unoccupied $e_{g}$ states of Cr$^{3+}$ ions, respectively. $E_F$ and $E_C$ represent the Fermi level and cutoff energy of the $t_{2g}$ and $e_{g}$ hybridization, respectively. With Equation (7), we could quantitatively describe the t-e hybridization in RECrO$_3$ orthochromates (Table 3).

To illustrate the effect of on-site Coulomb interactions of Cr$^{3+}$ ions on the superexchanges in rare-earth orthochromates, we chose YbCrO$_3$ as an example and carried out a calculation of $U_{\text{eff}}$ scan from 0 to 5 eV as shown in Figure 12A, where we can see the $U_{\text{eff}}$-dependent evolution of t-e orbital hybridizations from the DOSs. Based on these calculations, the $U_{\text{eff}}$-dependent exchange parameters of $J_1$ and $J_2$ were extracted and shown in Figure 12B. The increase in on-site Coulomb interactions enhances both the crystalline-field splitting and the exchange splitting (with a relatively larger enhancement). The overall superexchange interactions could be expressed as (Zhou et al., 2010)

$$J = J_0 \left[ (b^*)^2 - \eta (b^b)^2 \right],$$

and

$$\eta = \frac{U + \Delta_{\text{ex}}}{U + \Delta_{\text{c}}},$$

where $b^*$, $b$, $\Delta_{\text{ex}}$, and $\Delta_{\text{c}}$ are electronic parameters, $U$ is the on-site Coulomb interaction, and $\Delta_{\text{ex}}$ and $\Delta_{\text{c}}$ are the exchange and crystal-field splitting parameters, respectively.

### Figure 11. Process of virtual charge transfer and crystal structure

(A) Crystal field splitting of the 5-fold degenerate $d$ orbitals of Cr$^{3+}$ ions ($3d^6$) in a cubic environment that splits the $d$-level into 2-fold degenerate $e_g$ and 3-fold degenerate $t_{2g}$ levels. The arrows represent the spins of chromium. We schematically show the virtual charge transfers, leading to FM and AFM states, respectively.

(B) Refined crystal structure of RECrO$_3$ in one unit cell (solid lines) with $Pbnm$ space group (No. 62). The RE, Cr, O1, and O2 ions are labeled. $J_1$ and $J_2$ represent the NN spin-exchange parameters within the ab plane and along the c axis, respectively.
where $U$ denotes the on-site Coulomb interactions, $\Delta_{\text{ex}}$ and $\Delta_c$ are the exchange splitting and the crystalline-field splitting, respectively (Zhou et al., 2010). In the RECrO$_3$ system, different RE$^{3+}$ ions lead to different crystallographic structures of RECrO$_3$. The increase of $U_{\text{eff}}$ favors the ferromagnetic component in the entire superexchange interactions, leading to a strong competition between ferromagnetic and antiferromagnetic components, and finally may result in $J_2 > 0$, that is, ferromagnetism would be generated along the crystallographic $c$ axis.

Different $U_{\text{eff}}$-value settings have a relatively minor effect on the $t$-$e$ hybridization; therefore, our calculations are based on the on-site Coulomb interactions between Cr$^{3+}$ ions using Hubbard $U_{\text{eff}} = 3.3$ eV derived under the framework of a linear-response ansatz, which is in good agreement with the measured band gaps (Singh et al., 2018). Meanwhile, the electron dispersions are not largely influenced by fixing $U_{\text{eff}}$, which assures the calculation of reliable $t$-$e$ orbital hybridizations of RECrO$_3$ orthochromates by considering only the influence of RE$^{3+}$ ions.

Based on the foregoing discussion, we first optimized the structural parameters of RECrO$_3$ orthochromates (Tables S1 and S2) (Kumar et al., 2008). Our calculations also indicate that the G-type AFM is the most stable magnetic structure for all the RECrO$_3$ orthochromates (Figure S3 and Table S3). Subsequently, we extracted the optimized values of $J_1$, $J_2$, Neél temperature ($T_{\text{N,MFA}}$), and the $t_{2g} - e_g$ orbital overlapping degree ($l_{t_{2g} - e_g}$) (Table 3).

When RE$^{3+}$ ions vary from Eu to Lu, the changes of the calculated $l_{t_{2g} - e_g}$ (Figure 13A), $T_{\text{N,MFA}}$ (Figure 13B), and $\angle$ Cr-O1-Cr and $\angle$ Cr-O2-Cr (Figure 13C) demonstrated a similar trend, indicating a strong correlation between them and a clear effect of the RE$^{3+}$ radii (Winter, 2021) on the superexchange interactions. The calculated $T_{\text{N,MFA}}$ coincided with the experimental $T_{\text{N,exp}}$ values (Table 1, Figure 13B). The average value ($\langle \angle$ Cr-O1-Cr $\rangle$) of the $\angle$ Cr-O1(2)-Cr bond angles changed from 148.34° (EuCrO$_3$) to 142.81° (YbCrO$_3$) (Tables S1 and S2), leading to the $t$-$e$ hybridization ($l_{t_{2g} - e_g}$) changing from −2.2104 (EuCrO$_3$) to −2.5394 (YbCrO$_3$) and the corresponding $T_{\text{N,MFA}}$ deceased from 245.7 (EuCrO$_3$) to 80.5 K (YbCrO$_3$) (Table 3). Therefore, the decrease in bond angles of $\angle$ Cr-O1(2)-Cr facilitated $t$-$e$ hybridization by enhancing the FM component ($J_{\text{eff,FM}}$) within the entire superexchange interaction. Both our experimental and theoretical studies produced the minimum AFM transition temperature for YbCrO$_3$ in the system (Figure 13B), which is inconsistent with a previous study on polycrystal RECrO$_3$ samples, where the minimum $T_{\text{N}}$ and $\langle \angle$ Cr − O − Cr $\rangle$ occurred to LuCrO$_3$ (Zhou and Goodenough, 2008).

Our DFT calculations demonstrate that the magnetic anisotropy of Cr$^{3+}$ sublattices can be tuned by RE$^{3+}$ ions. The ratio of $J_2/J_1$ is a good parameter that inversely expresses anisotropy. It indeed reduces from $J_2/J_1 \approx 0.98$ (EuCrO$_3$) to $\sim 0.01$ (YbCrO$_3$) (Table 3) and strongly correlates with the values of the $\angle$ Cr-O1(2)-Cr bond angles. The $\angle$ Cr-O1-Cr angle was outside the $ab$ plane, and its value was smaller than that of $\angle$ Cr-O2-Cr within the $ab$ plane (Inset, Figure 13C). Therefore, we infer that the VCT of $t_{2g}^3 - O^{2-} - t_{3g}^1$ produces
the major AFM spin interactions within the ab plane, whereas the VCT of t$_{2g}$/t$_{2g}$ can generate strong FM couplings along the c axis. This is in good agreement with the previously proposed magnetic model (Van der Ziel and Van Uitert, 1969). The difference between the Cr-O1(2)-Cr values increases when RE$^{3+}$ varies from Eu to Lu, indicating that the competition between in-plane AFM interactions and out-of-plane FM couplings becomes increasingly strong with an enhancement of FM interactions. The largest difference between Cr-O1-Cr and Cr-O2-Cr occurred for YbCrO$_3$, leading to the smallest $J_2/J_1$ ratio (~0.01), and thus the largest magnetic anisotropy.

The FM coupling $J_{ab}$ directly acts on the overall Cr-O-Cr superexchange. This is induced by the t$_{2g}$-$t_{2g}$ orbital hybridization and could compete with AFM coupling, leading to an overall exchange $J = J_t - J_{ab}$ (Zhou et al., 2010). The state of Cr$^{3+}$, that is, the 3d$^3$ configuration with half-filled t$_{2g}$ orbital and empty e$_g$ orbital, makes it a special ion compared with other elements such as V, Fe, and Mn (Streltsov and Khomskii, 2008). By chemical engineering (Yaresko, 2008) or applying high pressure (Fita et al., 2021), one may strengthen t$_{2g}$ - t$_{2g}$ hopping but simultaneously weaken t$_{2g}$ - t$_{2g}$ hopping. Eventually, this could result in an overall FM component superexchange between neighboring Cr$^{3+}$ cations. The weak ferromagnetism results from competition between the Heisenberg exchange and DM interactions in orthochromates. This is one case of an AFM structure with a small canting, leading to a noncollinear spin configuration and thus a net FM component. Unraveling the competing degree of different spin interactions necessitates inelastic neutron scattering studies on single-crystal orthochromates.

The grown crystals are centimeter (gram)-scale with a good quality. We performed magnetization measurements as functions of temperature and applied magnetic field, providing more reliable and intrinsic magnetic properties. We theoretically investigated the t-e hybridization by quantitatively calculating the t$_{2g}$ and e$_g$ orbital overlapping degree (t$_{2g}$ – e$_g$) based on DOS calculations. As RE$^{3+}$ ions change from Eu to Lu, the calculated AFM transition temperatures demonstrate a similar trend with those determined experimentally. The changes in the Cr-O1(2)-Cr bond angles strongly influence the weight factor of FM couplings.
within the entire superexchanges interactions by (dis)favoring the VCT of $t$-$e_g$/CoCo. This may be the origin of the weak ferromagnetism appearing within the main AFM matrix of RECrO$_3$. The difference between the $t$-$e$ orbital overlapping degree ($f_{t-e}$) and the $t_{2g}$ overlapping degree $f_{t_{2g}}$ (right) and calculated ($T_{N}^{MFA}$) (left) AFM transition temperatures. The change of $t$-$e$ hybridization coincides well with that of $\angle$Cr-O1(2)-Cr and that of $T_{N}^{MFA}$. Our research sheds light on the origin of the intriguing magnetism in the RECrO$_3$ system.

**Limitations of the study**

The single crystal growth of orthochromates is extremely difficult. First, traditional FZ furnaces equipped with four IR-heating halogen lamps and four ellipsoidal mirrors (such as Model FZ-T-10000-H-VI-VPO-PC from Crystal Systems Inc.) cannot even access the melting temperature of orthochromates so that the seed and feed rods could not be melted, thus the crystal growth could not be performed. Second, the evaporation of Cr-based oxides is very heavy like a thick haze. Third, the process of crystal growth is time-consuming and labor-intensive, and one needs to optimize various growth parameters. Presently, we are unable to measure magnetic properties as a function of the crystallographic orientation because of technique difficulties, which is left for future work.

**STAR Methods**

Detailed methods are provided in the online version of this paper and include the following:

- **Key Resources Table**
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  - Materials availability
  - Data and code availability
- **Method Details**
SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.104111.

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AUTHOR CONTRIBUTIONS


DECLARATION OF INTERESTS

The authors declare the following competing financial interest(s): Y. H. Zhu, S. Wu, and H.-F. Li have a 2021 China Invention Patent (CN110904497B) through University of Macau based on this work: A method of centimeter-sized single crystal growth of chromate compounds and related storage device.

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REFERENCES


Dmitrienko, V.E., Ovchinnikova, E.N., Collins, S.P., Nisbet, G., Beutier, G., Kvashnin, Y.O.,


RCrO₃ (R = La, Nd, Eu, Dy, and Y). Solid State Sci. 85, 70–75.


STAR★METHODS

KEY RESOURCES TABLE

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<th>REAGENT or RESOURCE</th>
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RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Prof. Dr. Hai-Feng Li (haifengli@um.edu.mo).

Materials availability
This long-term project produced a series of RECrO₃ (RE = Y, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu) single crystals utilizing the innovative method described in the China Invention Patent (CN110904497B). We welcome potential collaborations.

Data and code availability
- All data reported in this article will be shared by the lead contact upon request.
- Code with instructions reported in this article will be shared by the lead contact upon request.
- Any additional information required to reanalyse the data reported in this study is available from the lead contact upon request.

METHOD DETAILS

Single crystal growth procedure and parameters
Using raw materials of Y₂O₃ (Alfa Aesar, 99.9%), Gd₂O₃ (Alfa Aesar, 99.9%), Tb₂O₃ (Alfa Aesar, 99.9%), Dy₂O₃ (Alfa Aesar, 99.9%), Ho₂O₃ (Alfa Aesar, 99.9%), Er₂O₃ (Alfa Aesar, 99.9%), Tm₂O₃ (Alfa Aesar, 99.9%), Yb₂O₃ (Alfa Aesar, 99.9%), Lu₂O₃ (Alfa Aesar, 99.9%), and Cr₂O₃ (Alfa Aesar, 99.6%), polycrystalline RECrO₃ samples were synthesized with solid-state reactions. We first obtained homogeneous polycrystalline powder with a single phase. After that, cylindrical feed rods with additional treatments (Li et al., 2021) were shaped by a hydrostatic pressure of ~70 MPa (Wu et al., 2020; Zhu et al., 2020b). Then RECrO₃ single crystals were grown by a laser-diode floating-zone furnace (Model: LD-FZ-5-200W-VPO-PCUM). The floating-zone method assures no introduction of impurities (Li, 2008). The growth speed was fixed at 5–15 mm/h to attain a stable growth state. Due to the intense volatility of chromium oxides, we added extra...
5–15% mole raw chromium oxide for the synthesis of polycrystalline samples and for the growth of single crystals.

**Neutron Laue diffraction**

To determine the quality of the grown single crystals, we performed a neutron Laue diffraction study on the diffractometer, OrientExpress, located at ILL, Grenoble, France. Simultaneously, we simulated the recorded neutron Laue patterns along the three crystallographic axes with the software of OrientExpress (Ouladdiaf et al., 2006) to confirm the quality of the grown crystals.

**Magnetization measurements**

Magnetization was measured using the option of a vibrating sample magnetometer of Quantum Design physical property measurement system. Small RECrO₃ single crystals (5–15 mg) were glued on a quartz sample holder with GE Varnish. The dc magnetization was measured at applied magnetic fields of 0, 50, and 100 Oe with zero-field cooling and field cooling modes in the temperature range of 1.8–400 K. The magnetic field dependent hysteresis loops were measured from −14 to 14 T at different temperatures within 1.8–300 K.

**First-principles calculations**

The first-principles calculations of RECrO₃ compounds were carried out within density functional theory. The exchange and correlation term in Kohn-Sham equation was treated with the Perdew-Burke-Ernzerhof (PBE) and (PBE + U) functionals (Perdew et al., 1996; Franchini et al., 2007a, 2007b; Shick et al., 1999) using the Vienna Ab-initio Simulation Package (Kresse and Furthmüller, 1996a, 1996b). The core electrons were frozen, and the projected-augmented-wave method was used (Kresse and Joubert, 1999). The Cr 3d₄s, RE (RE = Eu–Lu) elements 5p5d6s, Y (4s4p5s4d), and O 2s2p electrons were treated as valence electrons. It is well known that the 4f orbitals are tightly localized in comparison to the d orbitals. In the present study, we aim mainly to unravel the effect of lattice variation on Cr³⁺-O²⁻-Cr³⁺ superexchange interactions, and the energy scale of RE³⁺-RE³⁺ exchange interactions is about two magnitudes smaller than that of Cr³⁺-Cr³⁺, hence the 4f electrons of lanthanide ions could be frozen reasonably. A Gaussian broadening of 0.05 eV was chosen. The set of plane-wave basis with an energy cutoff of 500 eV was used. Brillouin-zone integrations were performed with a Gamma-point-centered 7 x 7 x 5 Monkhorst-Pack k-point mesh (Monkhorst and Pack, 1976). The ionic relaxation was performed with a convergency criterion of 10⁻⁶ eV/primitive cell for each relaxation step and stopped moving when residual force <0.01 eV/Å. A convergency accuracy of 10⁻⁶ eV per conventional cell was chosen for subsequent static self-consistent calculations.

We first optimized the structures with collinear magnetic configurations of FM and A-type, C-type, and G-type AFM, to determine the magnetic ground state of each compound. Furthermore, to avoid an underestimation of the band gap, the Hubbard U value (U_{eff} = U – J) of each compound was calculated using the linear response ansatz (Dudarev et al., 1998; Cococcioni and de Gironcoli, 2005). With appropriate Hubbard U value, static electronic self-consistent calculations were performed using the (PBE + U) method to obtain the exact total energy of the four magnetic states. The exchange parameters, J, under classical Heisenberg model could be deduced with the energy mapping method, as does T_{C}^{C} based on the mean-field approximation (MFA). Finally, the electronic structures of the RECrO₃ compounds were calculated with reading the charge density of ground state of the magnetic configuration.

**QUANTIFICATION AND STATISTICAL ANALYSIS**

Sensitivity analysis (one-at-a-time) was carried out to see the effects of parameters in the numerical model.