Low-energy electronic interactions in ferrimagnetic Sr₂CrReO₆ thin films

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Sample preparation

90 nm (001) Sr_2CrReO_6 films were grown by off-axis magnetron sputtering on different substrates to achieve different strain states: -1% (compressive) on (LaAlO₃)_{0.3}(Sr_2AlTaO_6)_{0.7} (LSAT), +1% (tensile) on a relaxed $SrCr_{0.5}Nb_{0.5}O_3$ (SCNO) and 0% (unstrained) on $SrTiO_3$ (STO). The absence of additional phases, the quality of the epitaxy and the lattice parameters are checked by x-ray diffraction.



Figure S1: (103) Reciprocal Space Map (RSM) for a) unstrained Sr_2CrReO_6 on STO, b) compressive Sr_2CrReO_6 on LSAT and c) tensile Sr_2CrReO_6 on SCNO/LSAT substrates. The Sr_2CrReO_6 Bragg peaks are aligned in-plane (Qx) with SCNO or LSAT, indicating a coherently strained state for both strained samples.

RIXS experiments

The q-dependent RIXS measurement of compressive Sr_2CrReO_6 is performed at a temperature of 17 K. The temperature-dependent characterization is done at q=(6.4, 0.34, 6.8) for compressive and q=(6, 0.34, 7.2) for tensile Sr_2CrReO_6 films, in the double perovskite system. The in-plane angle between the incident beam and the <100> crystal axis of Sr_2CrReO_6 films α was maintained between 0 and 5 degrees. We used the following method to remove the elastic line from each RIXS spectrum: i) baseline correction of the spectrum with a horizontal line leveled on the gain side, ii) defining the elastic line by mirroring the gain side from 0 to 0.3 eV, iii) fitting the mirrored elastic line with a pseudo-Voigt function, iv) subtraction of the fitting result from the data. The excitation positions are determined with fitting of the RIXS spectra with a linear background, a pseudo-Voigt function for the elastic lines and Gaussian functions for all non-elastic features.

We also characterized with fewer statistics the Sr_2CrReO_6 thin film on STO substrate, leading to 0% strain in the film.



Figure S2: Momentum-dependent RIXS spectra for an unstrained Sr_2CrReO_6 thin film on $SrTiO_3$ substrate. No dispersion is observed. The Gaussian functions are centered at 0.14, 0.56, 0.73 and 1.00 eV.

RIXS calculations

The RIXS calculations were performed using EDRIXS, an open-source toolkit for simulating XAS and RIXS spectra based on exact diagonalization of model Hamiltonians. It is developed as part of the COMSCOPE project in the Center for Computational Material Spectroscopy and Design, Brookhaven National Laboratory [17]. We use single atomic multiplet model, considering single Re⁵⁺ (d^2) ion. We obtain the crystal field splitting parameters from the Wannier function projections on Re d states [29], and use these parameters as an initial guess. Then we explored large phase space of parameters near the set of initial values. We fix the e_g-t_{2g} splitting (10Dq) of 3.23 eV from Wannier projection, since 10Dq is very large and thus only t_{2g} orbitals are important on the RIXS spectra below 1.5 eV.

Sr₂CrReO₆ is ferrimagnetic with a Curie temperature higher than 600K [5], suggesting a strong exchange field that drives the Re ions in a high-spin state S=1. For tensile (compressive) strain, modeled with a negative (positive) value of the crystal field ($-\Delta_{tens}<0$ and $-\Delta_{comp}>0$), the d_{xy} state stands lower (higher) in energy than the degenerate d_{xz} and d_{yz} levels. Thus, the ground states of compressive and tensile Sr₂CrReO₆ have one electron in the spin-down d_{xz} and one electron in the spin-down d_{xz}/d_{yz} bands, and two electrons in the spin down d_{xz}/d_{yz} bands, respectively.

In Figure S3, we compare the calculated RIXS with different crystal field splitting (CF) and experimental data for tensile SCRO. As the magnitude of CF decreases to zero, the energy of the lowest energy peak become smaller, and closer to 0 eV. Note that the elastic peak is removed in the experimental data in Figure S3, and if the energy of the low energy peak become close to 0 eV, the peak will be hidden in the elastic peak. Therefore, at high temperature, CF will be close to zero, and the lowest energy peak will be hidden in the elastic peak.



Figure S3: Calculated RIXS spectra for tensile Sr₂CrReO₆ with different crystal field splitting cf (= Δ_t), compared to the experimental data (a) without elastic peak, and (b) with elastic peak. cf= 0 indicates cubic symmetry while cf \neq 0 refers to tetragonal symmetry. Here we use λ =0.3, J=0.25, U=2, and |M|=0.05 eV. Negative values of cf are chosen to describe the material under tensile strain.

Spin-wave theory

We follow the analogy from Toth et. al [25] and create a linear approximation of the complex spin dynamics by keeping only the lowest order of the boson operator b_{nj}^{\dagger} and b_{nj} :

$$S''_{nj}^{+} = \sqrt{2S_j} b_{nj}$$
$$S''_{nj}^{-} = \sqrt{2S_j} b_{nj}^{+}$$

$$S^{\prime\prime}{}^{z}_{nj} = S_j - b^{\dagger}_{nj}b_{nj}$$

where b_{nj}^{\dagger} and b_{nj}^{\dagger} are creation and annihilation operators of spin quantum number. After Fourier transformation, the Hamiltonian can be written in matrix form:

$$H = \sum_{k \in B.Z.} x^{\dagger}(k)h(k)x(k)$$

where x is the column vector of the bosonic operators:

$$x(k) = \left[b_1(k), \dots, b_N(k), b_1^{\dagger}(k), \dots, b_N^{\dagger}(k)\right]$$

The magnon mode x'_j is given by a linear combination of b'_j and b'_j^{\dagger} normal modes:

$$x_i = \sum_j T_{ij} x_j'$$

i.e.,

$$x' = T^{-1}x$$

In the case of SCRO, we define a_k and b_k as boson operators for Cr and Re, respectively. Then magnon modes $x(k) = \left[\alpha_k, \beta_k, \alpha_{-k}^{\dagger}, \beta_{-k}^{\dagger}\right]$ are given by

$$\begin{bmatrix} a_k \\ b_k \\ a_{-k}^{\dagger} \\ b_{-k}^{\dagger} \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} & T_{13} & T_{14} \\ T_{21} & T_{22} & T_{23} & T_{24} \\ T_{31} & T_{32} & T_{33} & T_{34} \\ T_{41} & T_{42} & T_{43} & T_{44} \end{bmatrix} \begin{bmatrix} \alpha_k \\ \beta_k \\ \alpha_{-k}^{\dagger} \\ \beta_{-k}^{\dagger} \end{bmatrix}$$

Therefore, we obtain

$$\begin{bmatrix} \alpha_k \\ \beta_k \\ \alpha_{-k}^+ \\ \beta_{-k}^+ \end{bmatrix} = \begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} & \tau_{14} \\ \tau_{21} & \tau_{22} & \tau_{23} & \tau_{24} \\ \tau_{31} & \tau_{32} & \tau_{33} & \tau_{34} \\ \tau_{41} & \tau_{42} & \tau_{43} & \tau_{44} \end{bmatrix} \begin{bmatrix} a_k \\ b_k \\ a_{-k}^+ \\ b_{-k}^+ \end{bmatrix}$$

where τ is the matrix element of the inverse matrix T^{-1} .

The weight of the Re spin mode (P_i) presented in Figure 4 in the manuscript is defined by

$$P_i = \frac{\tau_{i2}}{\sqrt{\tau_{i1}^2 + \tau_{i2}^2 + \tau_{i3}^2 + \tau_{i4}^2}}$$

REXS experiments and modeling

The energy-dependent REXS intensity $I(E) = |F(E)|^2$ of the OO-induced reflection is calculated from

$$F = F_{NR} + (f'_{Re1} + if''_{Re1}) \sum_{Re1} e^{i2\pi(r \cdot q)} + (f'_{Re2} + if''_{Re2}) \sum_{Re2} e^{i2\pi(r \cdot q)} + (\Delta f'_{Re2-1} + i\Delta f''_{Re2-1}) \sum_{Re2} e^{i2\pi(r \cdot q)}$$

where F_{NR} is the non-resonant (energy independent) contribution to the reflection intensity, computed with the DFT-derived atomic positions of Sr, Cr and O in a doubled Sr₂CrReO₆ unit cell (under tensile, compressive, or relaxed strain) and the Cromer-Mann coefficients. f''_{Re1} and f''_{Re2} are extracted following an iterative process starting from the XAS spectra of the Re1 and Re2 that result from the RIXS calculations in the presence of orbital-ordering (and for different θ_i , ϕ , and polarization state) and f' is related to f'' by the Kramers-Kronig relationship.

The calculated and measured intensities are corrected for the self-absorption following:

$$I_{cor}(E) = \frac{I(E)}{exp\left(-\frac{2r_e\lambda}{a^3}\left(2\frac{(\sum_{u.c.}f'')h}{\sin\theta_{in}}\right)\right)}$$

where h = 90 nm is the film thickness, a^3 the unit cell (u.c.) volume, r_e the Bohr radius, $\lambda = \lambda(E)$ the wavelength and θ_{in} the incident angle. $\sum_{u.c.} f''$ represents the sum of f'' from all atoms in the unit cell with $f''_{Re} = f''_{Re}(E)$, which is calculated from the experimental fluorescence spectra during the REXS experiment.



Figure S4: REXS calculation (dashed lines) and experimental data (solid lines) at $(0, 0, \frac{1}{2})$ for compressive and tensile Sr₂CrReO₆. No ϕ -dependent signal is found, as expected from orbital-ordering.