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RIXS Evidence for the Order–Disorder Antiferroelectric Transition in $CuCrP_2S_6$

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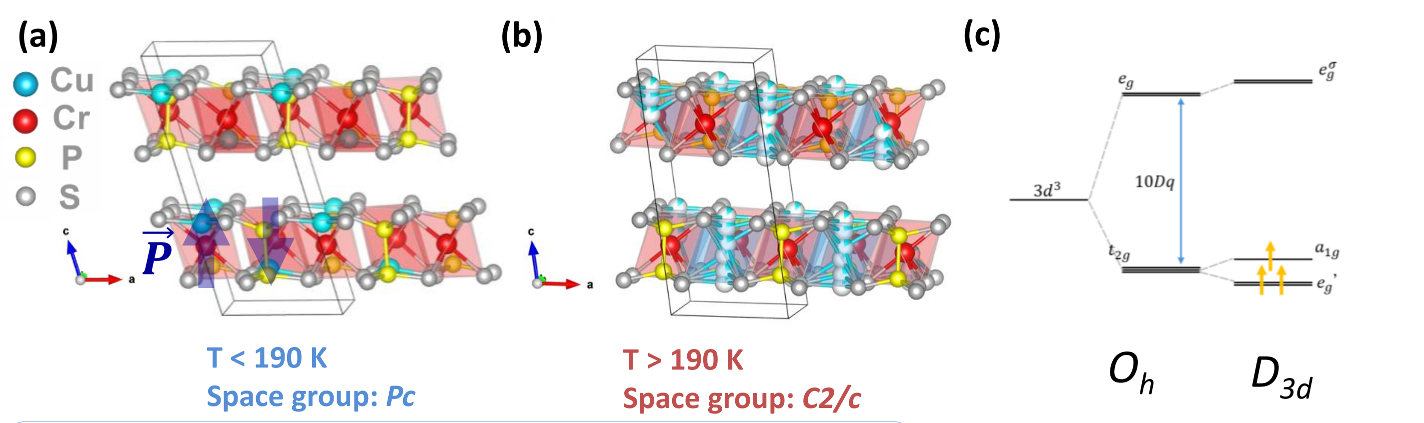
ABSTRACT

We report polarization-dependent resonant inelastic X-ray scattering (RIXS) measurements that reveal the order–disorder nature of the antiferroelectric (AFE)–paraelectric (PE) transition in the van der Waals multiferroic $CuCrP_2S_6$. The RIXS transition from the high-spin ground state to a state with $^4T_{1g}$ symmetry splits into two *dd* excitations at 2.0 and 2.15 eV, arising from the splitting of $^4T_{1g}$ into ^4E and $^4A_2$ due to trigonal distortion. The excitation energies remain nearly unchanged across the AFE–PE transition, indicating that the average Cr-centered trigonal crystal-field strength is insensitive to the Cu positions within RIXS resolution. However, in the AFE phase, these two peaks exhibit a distinct polarization contrast between RIXS excitations with π and σ polarizations, which evolves strongly with temperature. This polarization contrast vanishes in the PE phase, indicating that while the local trigonal splitting persists, Cu^+ ions become dynamically disordered, thereby washing out the polarization anisotropy. These observations support a Cu-driven order–disorder mechanism for the AFE–PE transition, rather than a displacive transition.

Introduction

Van der Waals multiferroic $CuCrP_2S_6$



T < 190 K
Space group: *Pc*

T > 190 K
Space group: *C2/c*

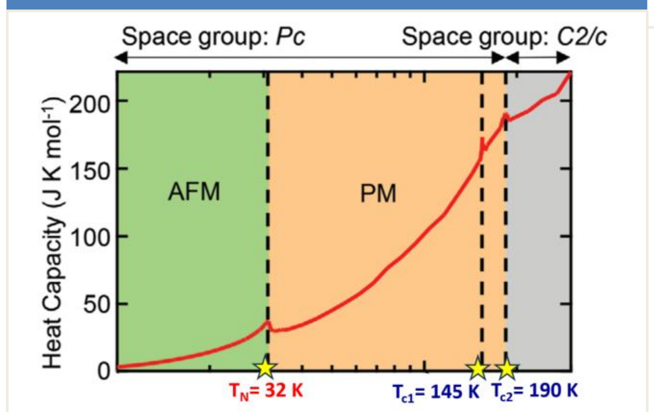
Cu^+: d^{10} Ferroelectricity
Cr^{3+}: d^3 Ferromagnetism

a= 5.9098 , b= 10.2447, c=13.3644 (Å)
α=γ=90°, β= 106.974°,
Space group: monoclinic

Above 190 K, the system crystallizes in a centrosymmetric *C2/c* structure, whereas below 190 K it adopts a noncentrosymmetric *Pc* space group. In the intermediate temperature range between 145 and 190 K, a quasi-antipolar phase emerges, followed by a fully developed antiferroelectric (AFE) phase below 145 K, characterized by long-range antipolar ordering of strongly off-centered Cu cations.

Under an elongated trigonal distortion, the t_{2g} manifold splits into a doublet e_g' and a singlet a_{1g}, with the e_g' doublet stabilized as the ground state. The a_{1g} orbital has lobes oriented along the trigonal axis and is most sensitive to distortions along this direction, whereas the e_g' doublet lies predominantly in the plane perpendicular to the trigonal axis.

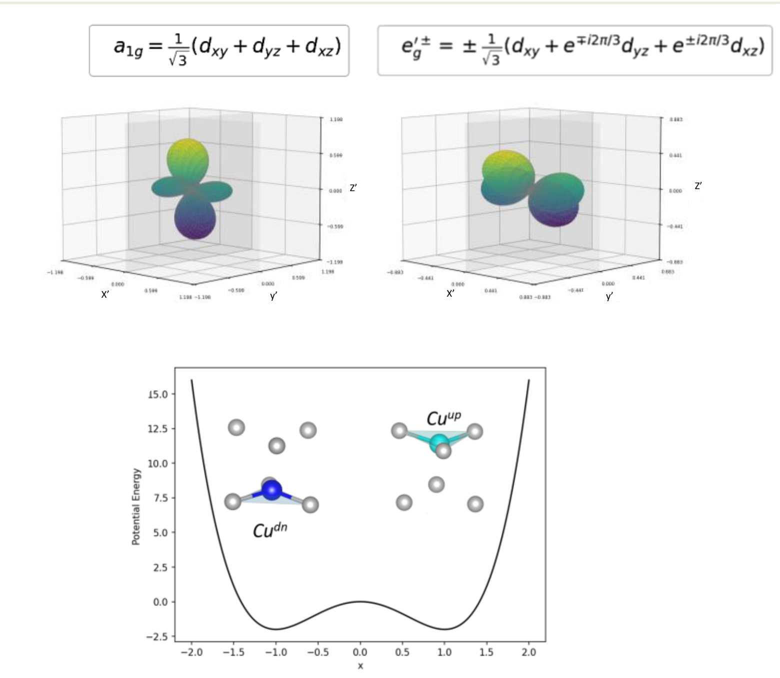
Phase diagram



Aoki S et al., Adv Mater. **36**, 2312781 (2024)

Heat-capacity measurements reveal anomalies at 32, 145, and 190 K, indicating three phase transitions. Below 32 K, $CuCrP_2S_6$ develops an A-type antiferromagnetic order, in which Cr spins are ferromagnetically aligned within each layer and antiferromagnetically coupled between neighboring layers along the *c*-axis. The two higher-temperature anomalies correspond to structural transitions.

$a_{1g} = \frac{1}{\sqrt{3}}(d_{xy} + d_{yz} + d_{xz})$ $\quad$ $e_g'^{\pm} = \pm\frac{1}{\sqrt{3}}(d_{xy} + e^{\pm i2\pi/3}d_{yz} + e^{\pm i2\pi/3}d_{xz})$



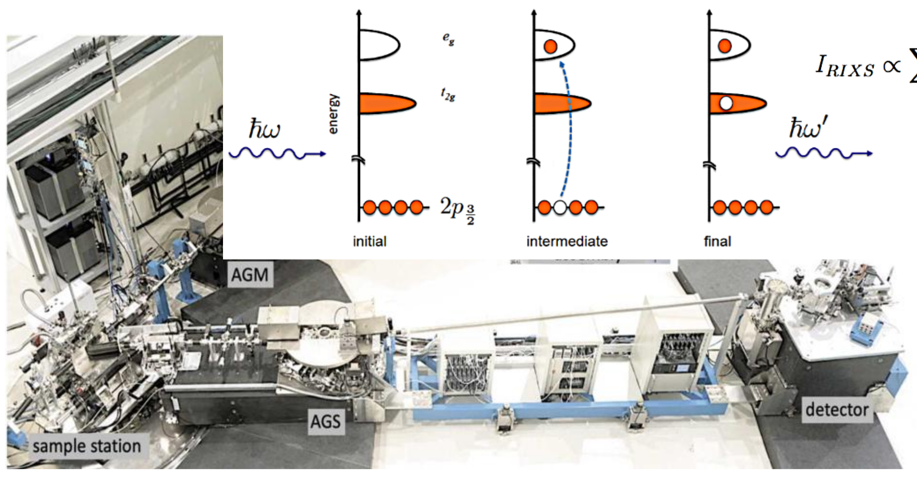
The AFE transition in $CuCrP_2S_6$ is driven by Cu^+ off-centering, which can be described by a local **double-well potential** with two symmetry-related polar minima.

- **T < 145 K:** Antiferroelectric, 100:0 %
- **145 < T < 190 K:** Quasi-antipolar, 30:70 %
- **T > 190 K:** Paraelectric, 50:50 %

We combine temperature- and polarization-dependent resonant inelastic X-ray scattering (RIXS) to elucidate the underlying mechanisms of the AFE transition in $CuCrP_2S_6$. RIXS measurements probe the local electronic structure of Cr *3d* and its evolution throughout the transition.

Resonant inelastic X-ray scattering (RIXS)

TPS 41A RIXS end station



Kramers-Heisenberg Formula

$$I_{RIXS} \propto \sum_f \left| \sum_n \frac{\langle f|\mathcal{D}^\dagger_{\vec{k}',\vec{\epsilon}'}|n\rangle\langle n|\mathcal{D}_{\vec{k},\vec{\epsilon}}|i\rangle}{E_n - E_i - \hbar\omega_k + i\Gamma_n/2} \right|^2 \delta(E_f - E_i - \hbar\omega)$$

$\mathcal{D}_{\vec{k},\vec{\epsilon}} = \sum_{i=1}^{N} \vec{\epsilon}\cdot\vec{r}_i$ Dipole operator

- Two-photon process: dipole-forbidden *dd* excitations

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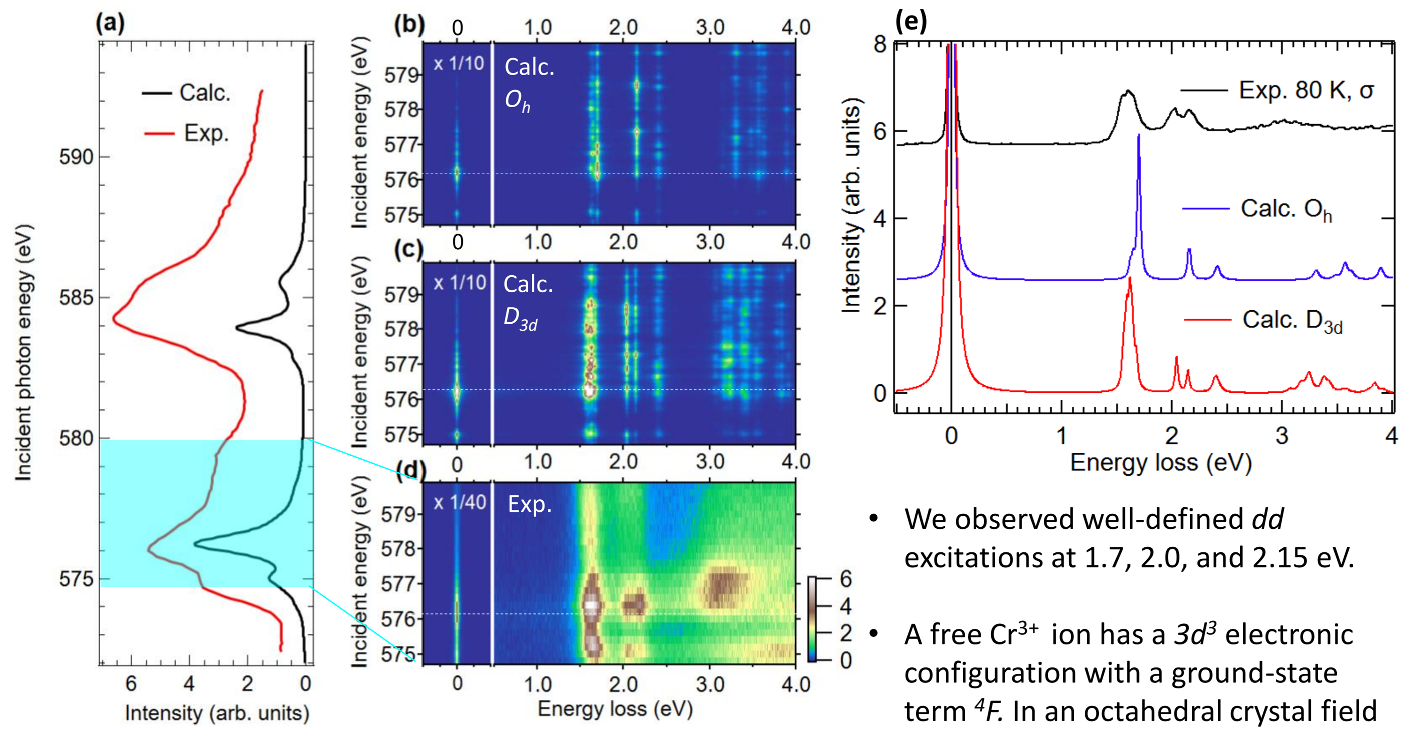
Results & Crystal-field multiplet calculations

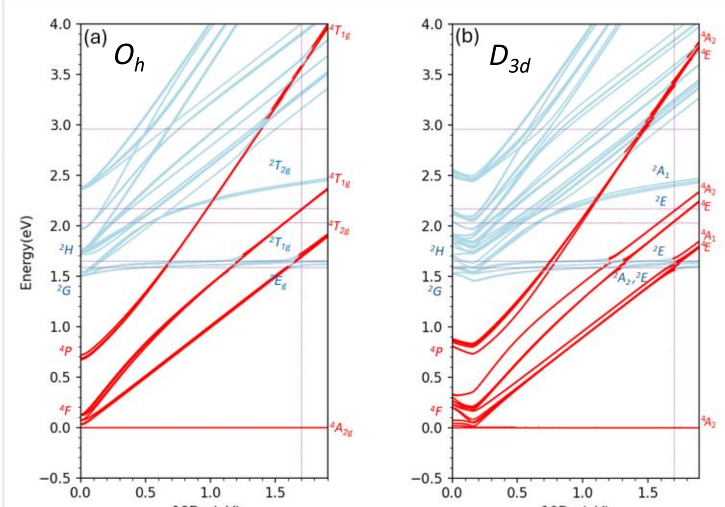
Cr $L_{2,3}$-edge RIXS intensity maps



Comparisons between experimental and crystal–field multiplet calculations of **(a)** XAS and **(b)-(d)** RIXS intensity maps show the crystal-field symmetry of the Cr site can be approximated by D_{3d} symmetry. The white dotted lines are the slice cuts for Cr *L*-edge , as shown in Fig. **(e)**.

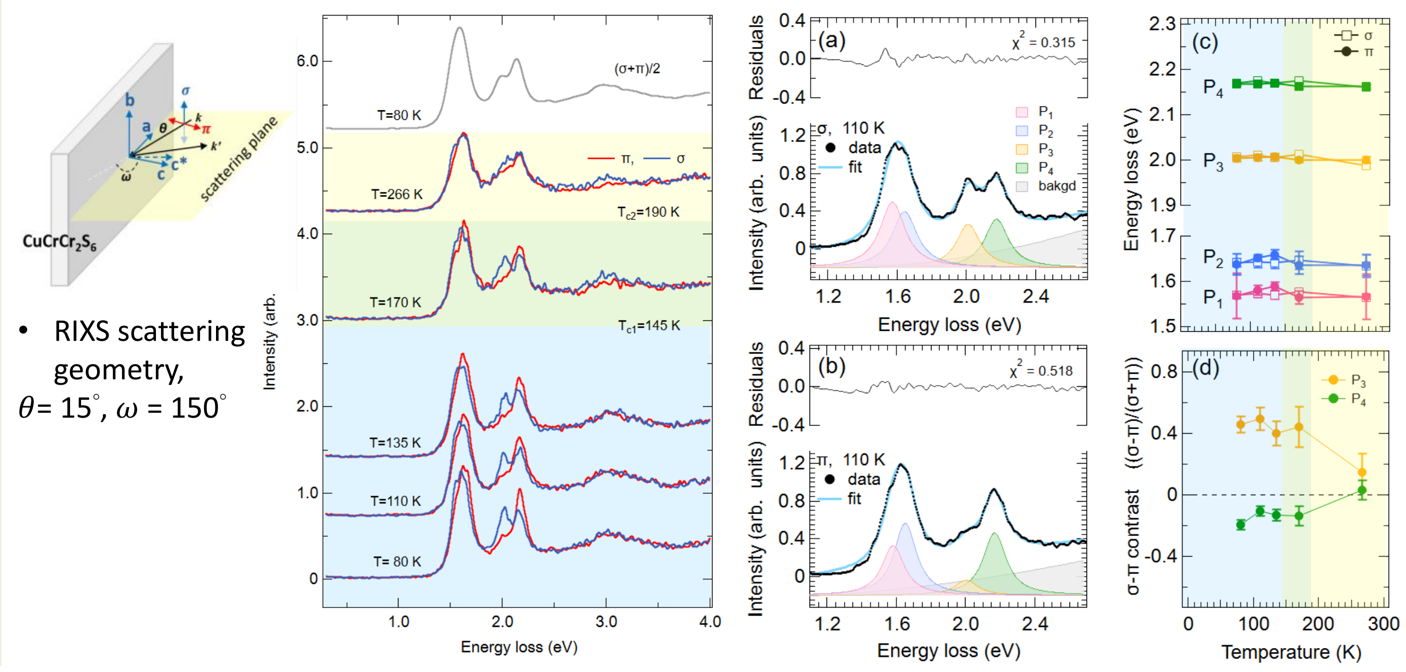
- We observed well-defined *dd* excitations at 1.7, 2.0, and 2.15 eV.
- A free Cr^{3+} ion has a *3d³* electronic configuration with a ground-state term ^4F. In an octahedral crystal field (symmetry O_h), this term is split as: $^4F \rightarrow {}^4A_{2g} + {}^4T_{2g} + {}^4T_{1g}$, and the ground state is $^4A_{2g}$.
- For a trigonal distortion corresponding to an elongation along the threefold axis, the orbitally triply degenerate $^4T_{1g}$ state further splits according to $^4T_{1g} \rightarrow {}^4A_2 + {}^4E$, and the energy of the $^4A_2$ state is higher than that of the ^4E state.

d^3 Tanabe-Sugano diagram



- The branching of O_h to D_{3d} can be visualized by d^3 Tanabe-Sugano diagram with **(a)** O_h and **(b)** D_{3d} symmetry as a function of *10Dq* . The purple dashed lines in the horizontal direction are the indications of multiplets observed in the RIXS spectra. The spin quartets and doublets are colored by red and blue color, respectively.

Temperature- & Polarization-dependent RIXS



- RIXS scattering geometry, θ= 15°, ω = 150°

- From the polarization-dependent RIXS results, we assign the higher-energy 2.15 eV peak to the $^4A_2$ singlet and the lower-energy 2.0 eV peak to the ^4E doublet.
- These excitation energies remain unchanged across the antiferroelectric (AFE)–paraelectric (PE) transition, indicating that the average Cr-centered trigonal crystal field is insensitive to Cu^+-driven structural changes.
- Polarization contrast between π and σ channels evolves strongly with temperature. Upon heating into the PE phase, **the local symmetry axis will fluctuate away from the c^*-axis** to gain entropy. The unwell-defined local symmetry makes the polarization contrast largely collapses, even though the local and instantaneous trigonal splitting remains finite.
- These findings support a Cu-driven order–disorder mechanism for the AFE–PE transition, rather than a displacive one. In the low-T AFE phase, static Cu^+ ordering produces strong polarization-dependent RIXS contrast; in the PE phase, dynamic Cu^+ disorder erases this anisotropy while preserving Cr-centered trigonal splitting.