RIXS study on van der Waals multiferroic $CuCrP_2S_6$

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ABSTRACT

Characterized by the layered structures and weak interlayer interactions, van-der-Waals quasi-2D materials mark a significant milestone in the field of spintronics due to their unique electronic and magnetic properties. Incorporating multiferroicity, these materials exhibit highly-manipulative properties, allowing the exploration of new quantum phenomena and the potential for revolutionary advances in low-power, non-volatile devices. $CuCrP_2S_6$, one of the van-der-Waals multiferroic materials, has ignited our curiosity. Here, we use high-resolution resonant inelastic X-ray scattering (RIXS) to probe its electronic excitations across the transition temperature 32K, 145K and 190 K. Photon energy- and polarization-dependent RIXS results of $CuCrP_2S_6$ will be presented and discussed.

Introduction

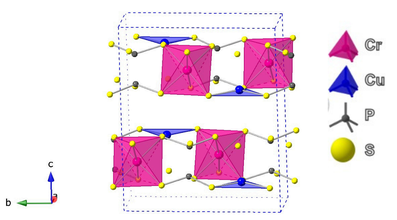
Van-der-Waals Quasi-2D layered structures, together with multiferroicity, have emerged as promising characteristics for advancing the field of spintronics.

vdW material:
- anisotropy
- high tunability

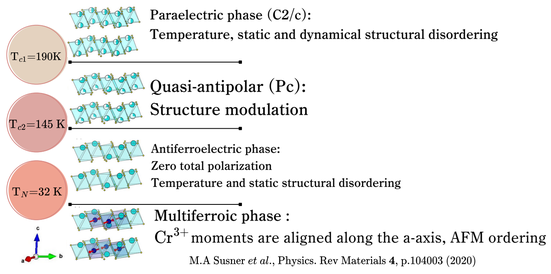
Multiferroics:
- magnetoelectric coupling
- manipulation of electric dipole & spin order with external field

Material $CuCrP_2S_6$

- Coexistence of ferromagnetism and ferroelectricity gives rise to its multiferroic properties. While the staggered displacement of the Cu^+ cations contributes to the ferroelectricity, the dominant intralayer ferromagnetism, coupled with the weak interlayer antiferromagnetism caused by the Cr^{3+} cations, leads to its unique ferromagnetism.
- Two transitions associated with Cu^+ structural disorder happen at 145K and 190 K, and one magnetic transition due to the magnetic moment of Cr^{3+} happens at 32 K.
- The calculated crystal structure suggests that $CuCrP_2S_6$ possesses the crystal field symmetry lower than D_{3d}.



▲ Calculated crystal structure of $CuCrP_2S_6$

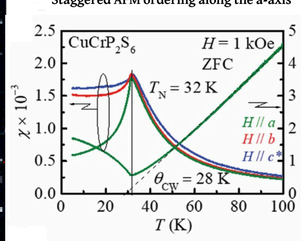


M.A Susner *et al.*, Physics. Rev Materials **4**, p.104003 (2020)

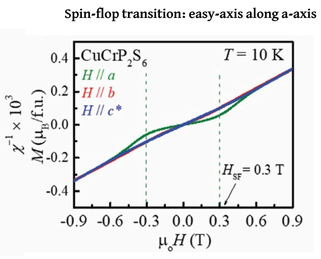
Macroscopic measurement

A. Magnetic susceptibility

Staggered AFM ordering along the a-axis

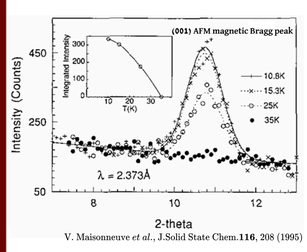


Spin-flop transition: easy-axis along a-axis



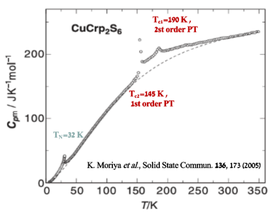
V. Maisonneuve *et al.*, J.Solid State Chem.**116**, 208 (1995)

B. Neutron Powder Diffraction



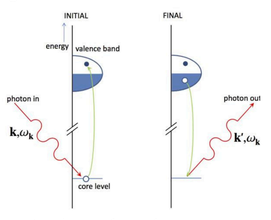
V. Maisonneuve *et al.*, J.Solid State Chem.**116**, 208 (1995)

C. Heat capacity



RIXS

Energy loss and momentum transfer of the photons in RIXS process facilitates the investigation of electronic dynamics in materials. A high flux of incident photons and a large scattering cross section enable one to measure magnetic excitations and fluctuations.

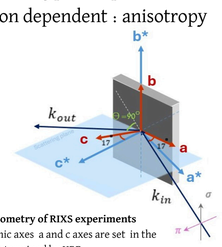


▲ Schematic figure of RIXS process

Ament et al.,Phys. Review of Modern Physics.September 2010

Crucial Characteristics of RIXS

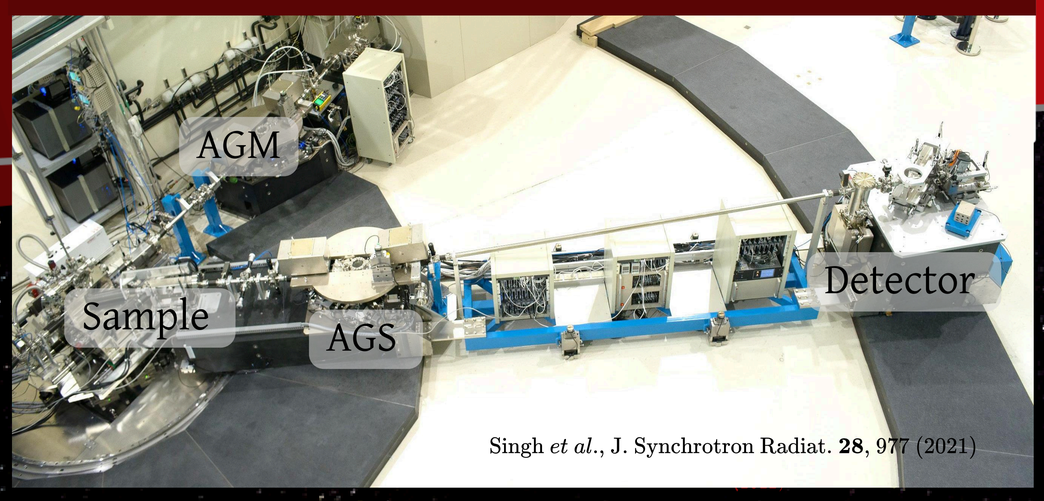
- Chemical, site and orbital specificity
- Small sample volume
- Bulk sensitive
- Large scattering phase space
- Polarization dependent : anisotropy



- **Scattering geometry of RIXS experiments**

The crystallographic axes a and c axes are set in the scattering plane determined by XRD.

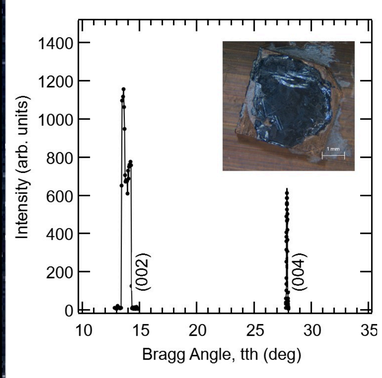
TPS41A beamline



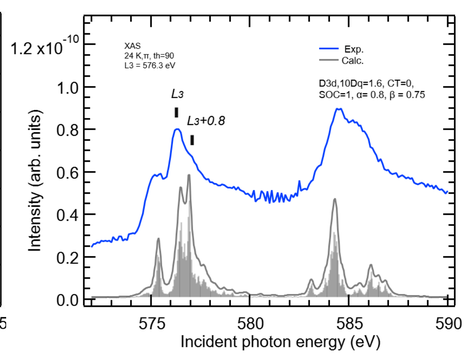
Singh *et al.*, J. Synchrotron Radiat. **28**, 977 (2021)

Experimental results

X-ray Diffraction



Cr $L_{2,3}$-edge XAS



Atomic Multiplet Calculation

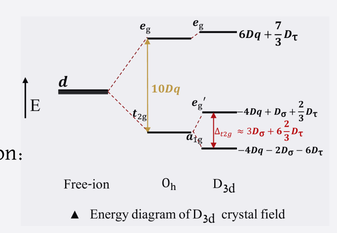
$$F_{\mathrm{RIXS}}(\omega_{\mathrm{in}},\omega_{\mathrm{out}}) = r_e^2 \frac{\omega_{out}}{\omega_{in}} \sum_f \left| \sum_m \frac{\langle f|V_E|m\rangle\langle m|V_I|g\rangle}{\omega_{\mathrm{in}}+E_g-E_m+i\Gamma} \right|^2 \delta(\omega_{\mathrm{in}}+E_g-\omega_{\mathrm{out}}-E_f)$$

Cr^{3+}, D_{3d}, 10Dq=1.6 eV

$D_\sigma = 0.05$ eV, $D_\tau = 0$ eV

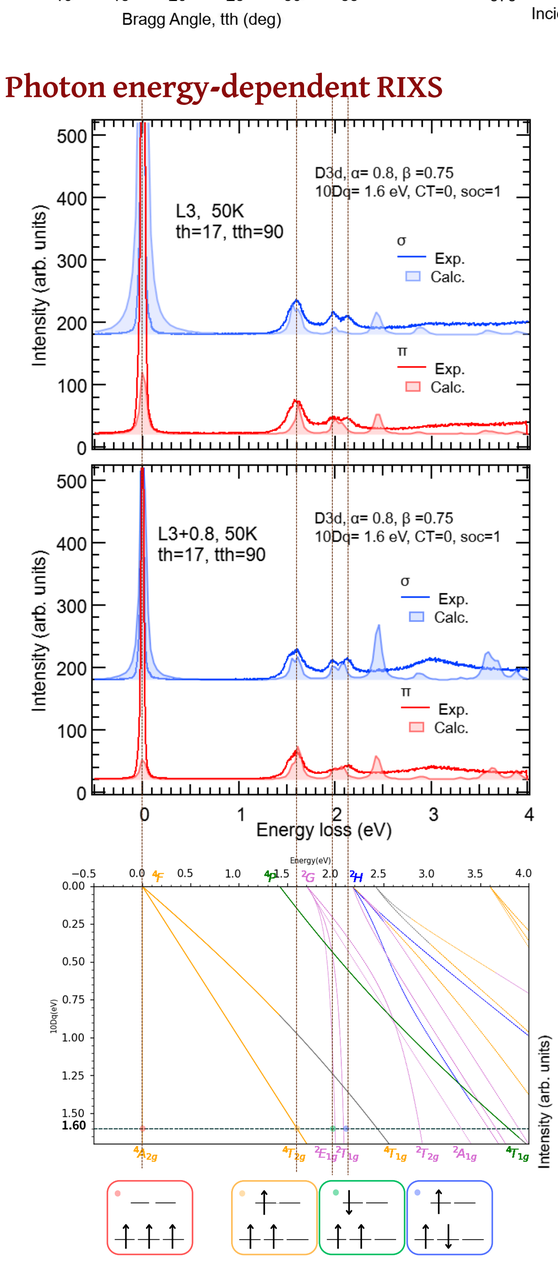
Slater integral reduction:

$\alpha = 0.8, \beta = 0.75$



▲ Energy diagram of D_{3d} crystal field

Photon energy-dependent RIXS



- dd excitations are dipole-allowed in a RIXS process because RIXS involves two dipole transition : XAS and XES. The $t_{2g} - e_g$ excitation energy indicates the value of 10Dq.
- Due to the large spin-orbit coupling for the core hole created in the intermediate state of the RIXS process, a 3d electron in the final state can undergo a spin-flip with respect to that of the initial state.

Cr L_3-edge RIXS intensity maps

- Excitation selectivity : The satellite feature in XAS at L3 +0.8 eV is associated with the antibonding orbitals due to hybridization effects. Tuning to this energy, the charge transfer excitation is selectively excited in RIXS.

Polarization-dependent RIXS

For transitions across 145 K and 190 K, clear evolution of dd excitation at 2 eV is observed, which is sensitive to the electronic structure. In constrast, there are no clear changes in the spectral line shape across 32 K. Probably, one assumption is that the low-energy magnons are beyond the energy resolution of ~ 30 meV at Cr L_3-edge RIXS.

Discussions

- We observed multiplet excitations through polarization-dependent RIXS, and found the the crystal field of Cr^{3+} in $CuCrP_2S_6$ is 1.6 eV with a small trigonal distortion.
- Multiplet calculations using the D_{3d} crystal field symmetry explain the major dd excitations of Cr^{3+}. The comparisons between calculations and RIXS data show that reductions in the Slater integrals are required to explain the data. However, the calculated 2.5-eV dd feature is inconsistent with the data.
- By comparing with d^3 Tanabe-Sugano diagram, the RIXS excitations can be assigned to the states $^4A_{2g}, ^4T_{2g}, ^2E_{1g}$ and $^2T_{1g}$.
- The relative intensity of the double-peak dd excitation may arise from structural disordering dominated by D_σ. At L_3, the double-peak feature is better captured by D_σ ~ -0.03 eV at higher temperature, and captured by D_σ ~ 0.05 eV at lower temperature.