Near Room-Temperature Ferromagnetism and Insulator-Metal Transition in van der Waals Material $CrGeTe_3$

Prof. Dr. Daniel Guterding

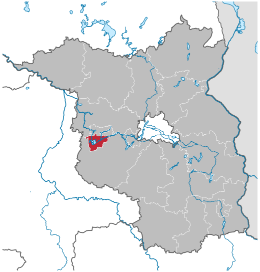
daniel.guterding@th-brandenburg.de

20th February 2025

Technische Hochschule Brandenburg
University of Applied Sciences

Where is TH Brandenburg?

- Located in the city of Brandenburg an der Havel
- Used to be capital city until move to Berlin in 1432
- Third-largest city in state of Brandenburg, 70 km west of Berlin
- Surrounded by nature reserves, lakes, river Havel (mosquitoes!)
- TH Brandenburg founded in 1992
- Public institution with $\sim$ 2000 students in STEM subjects

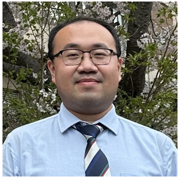


Figures: `https://w.wiki/CYGQ`; `CYGT`; `CYGu`; `CYJ8`

Collaborators on $CrGeTe_3$ projects

Jihaan Ebad-Allah
U Augsburg

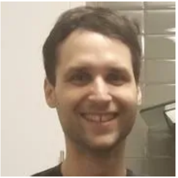
Gili Scharf
Tel Aviv U



Han-Xiang Xu
CAS, Beijing

Makoto Shimizu
Kyoto U

Christine Kuntscher
U Augsburg



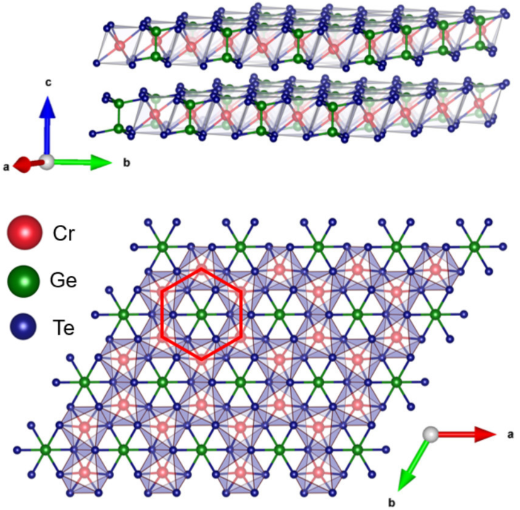
Alon Ron
Tel Aviv U

Junya Otsuki
Okayama U

Harald O. Jeschke
Okayama U

Crystal structure and basic properties of $CrGeTe_3$

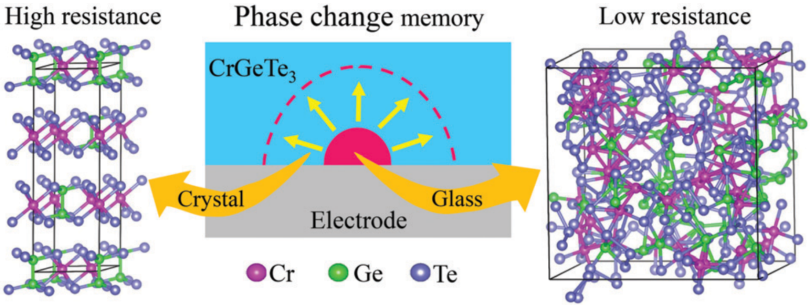
- Layered ferromagnetic semiconductor discovered in 1995 (J. Phys. Condens. Matter **7**, 69 (1995))
- Band gap of about 0.2 eV
- Ferromagnetic with Curie temperature $T_C = 61$ K
- Rhombohedral crystal structure
- Layers bound only by van der Waals forces
- Two-dimensional honeycomb network of Cr^{3+}
- Recently studied as ferromagnetic component in heterostructures, e.g. as substrate for topological insulators



Figures: PRR **4**, L022040 (2022) Supplement

A first story of $CrGeTe_3$: Amorphization and Phase-Change Memory

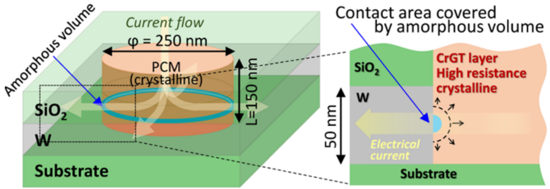
- Phase-change memory for non-volatile random-access memory
- Switch material between crystalline and amorphous state via controlled heating
- In $CrGeTe_3$ the amorphous state has lower resistance than crystal ("inverse resistance")
- Use resistance to encode two states (0 and 1), no continuous current required

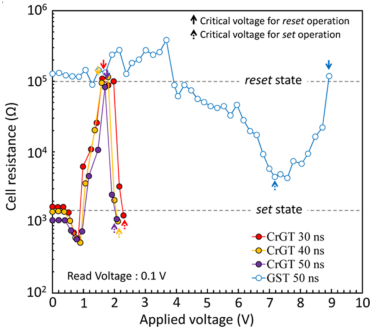


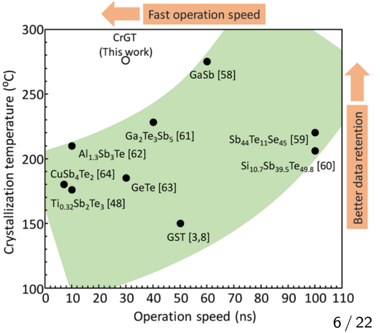
Figures: J. Mater. Chem. C **7**, 9025 (2019)

Phase change memory based on $CrGeTe_3$

- Cycling of devices based on $CrGeTe_3$
- Very sharp transition in resistance
- Low required operating energy for set and reset operations
- Unusually favorable combination of fast operation speed and high crystallization temperature
- Drastic decrease in charge carrier density upon crystallization



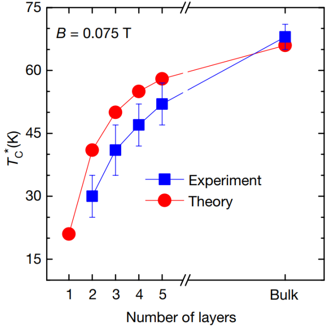


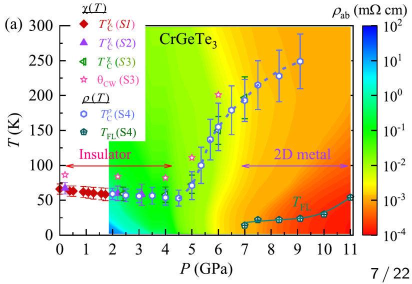


Figures: ACS Appl. Mater. Interfaces **10**, 2725 (2018)

A second story of $CrGeTe_3$: Ferromagnetism and Insulator-metal transition

- Exfoliation of layers from crystal possible
- Ferromagnetism persists down to at least bilayer
- Reduced Curie temperature compared to bulk crystal
- Perfect for magnetic nanoscale devices
- Subsequent experiments with such devices
- Insulator-metal transition under pressure with onset around 5 GPa
- Slow decrease of T_C in insulating regime
- Sharp enhancement of ferromagnetism to near room-temperature at IMT
- Relation to inverse resistance under amorphization? (see also Adv. Electron. Mater. **10**, 2300609 (2024))

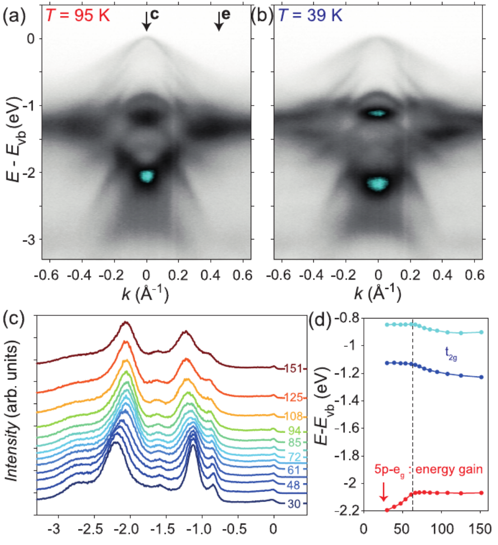


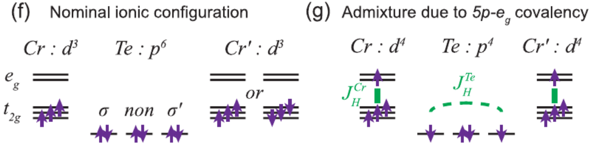


Figures: Nature **546**, 265 (2017); PRL **127**, 217203 (2021)

Ferromagnetism from superexchange in bulk $CrGeTe_3$

- ARPES paper assumes perfect octahedral geometry, but actually trigonal
- In octahedral geometry Cr t_{2g} to Te 5p states hopping would be forbidden
- Superexchange interaction between Cr 3d and Te 5p states (see PRL **123**, 047203 (2019))
- Observe energy gain of Te 5p states upon FM ordering when cooling below T_C
- Evidence for mixed state of Cr $3d^{3.5}$ from XMCD

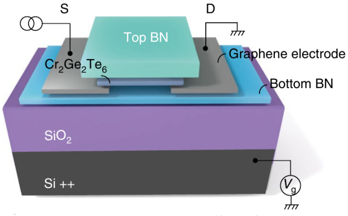


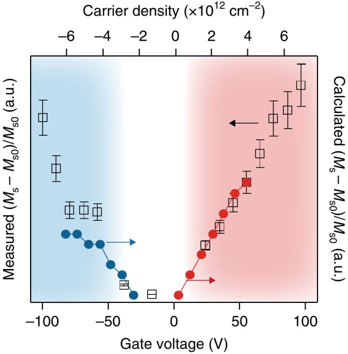


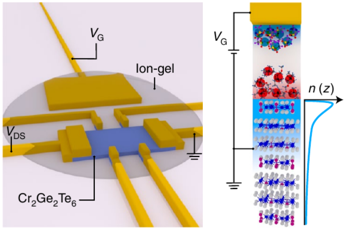
Figures: PRB **101**, 205125 (2020)

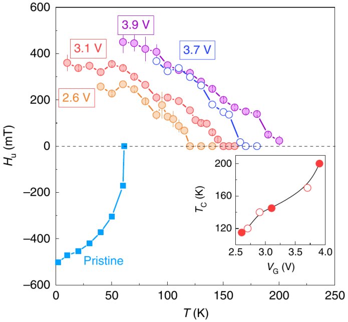
Nanoscale device experiments for $CrGeTe_3$

- First device builds bipolar FET from $CrGeTe_3$
- Allows for gate doping of both conduction and valence bands
- Both directions enhance magnetization, faster increase from electron doping (red)
- Second device uses gating with ionic liquid
- Electron doping leads to enhanced T_C and change of easy axis from out-of-plane to in-plane (magnetic anisotropy energy H_u)





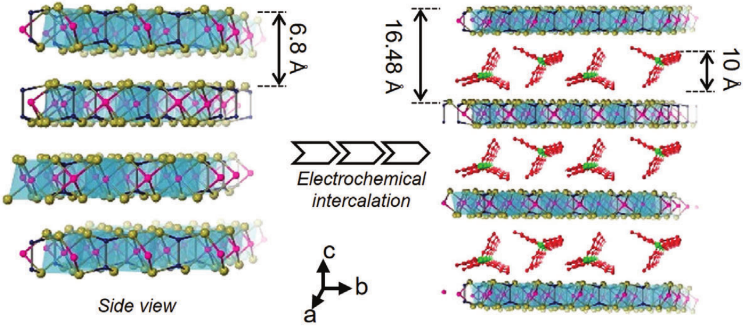


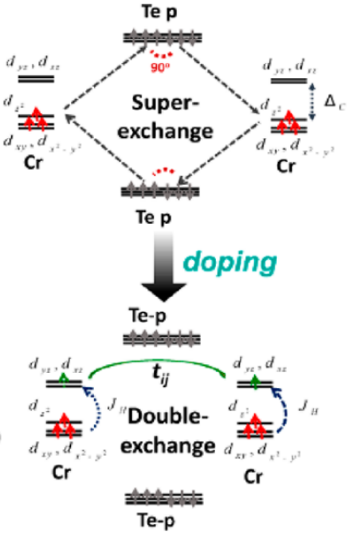


Figures: Nature Nanotech. **13**, 554 (2018); Nat. Electron. **3**, 460 (2020)

Electron doping of bulk $CrGeTe_3$ via intercalation of organic donors

- Intercalation with organic molecules increases layer distance
- Tributylammonium (TBA) acts as electron donor
- Pristine crystal with $T_C = 67$ K
- Enhanced FM with $T_C = 208$ K in $(TBA)CrGeTe_3$
- Change of mechanism behind FM to double-exchange?

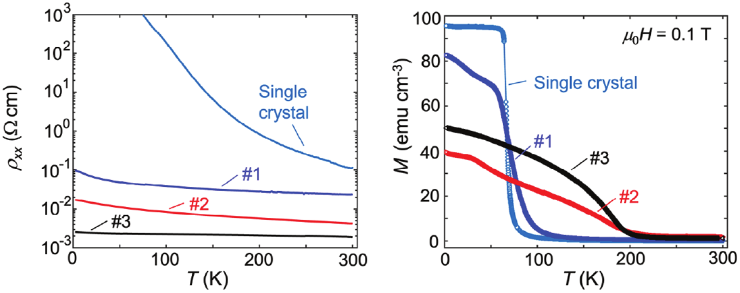


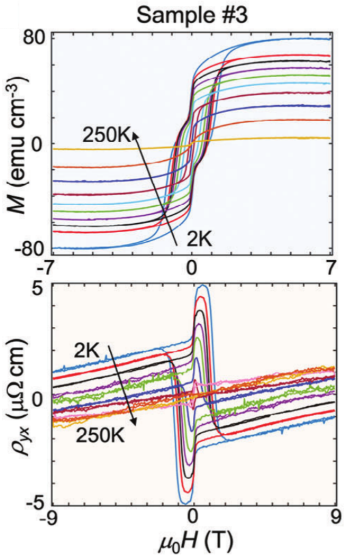


Figures: JACS **141**, 17166 (2019)

Amorphous ferromagnetic metal in irradiated $CrGeTe_3$

- Irradiation of bulk sample with high-energy Xe^{+14} ions
- Becomes amorphous and metallic with lower magnetization
- Small increase in resistance upon cooling due to disorder-induced scattering
- Ferromagnetic T_C increased to $\approx$ 200 K
- AHE with multiple contributions, skew-scattering dominates

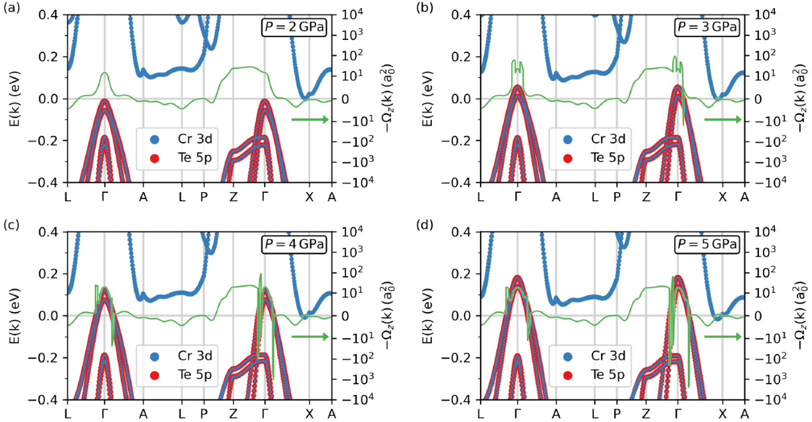




Figures: Adv. Electron. Mater. **10**, 2300609 (2024)

Berry curvature in $CrGeTe_3$ under pressure: electronic band structure

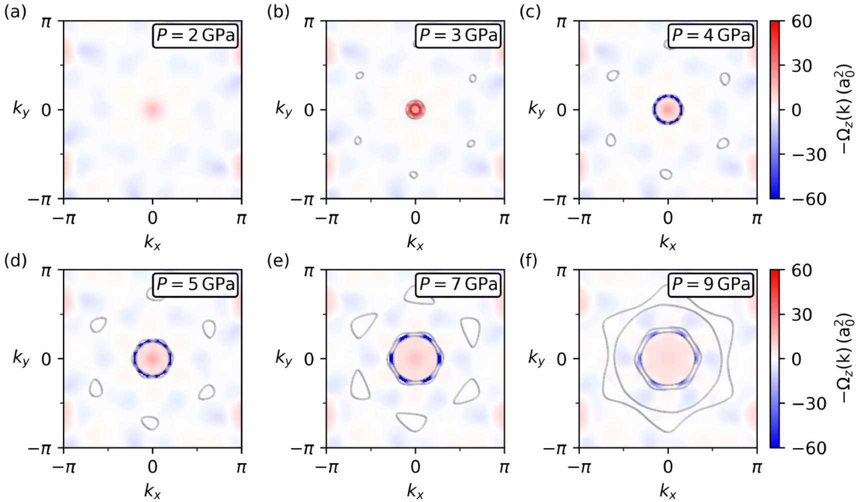
- Full-relativistic DFT calculations with FPLO for $CrGeTe_3$ as a function of pressure in FM state
- Insulator-metal transition clearly visible for $P = 3$ GPa
- Berry curvature strongly modified by shift of hole bands
- Extreme peaks in Berry curvature close to Fermi surface



Figures: PRR **7**, 013127 (2025)

Berry curvature in $CrGeTe_3$ under pressure: Fermi surface

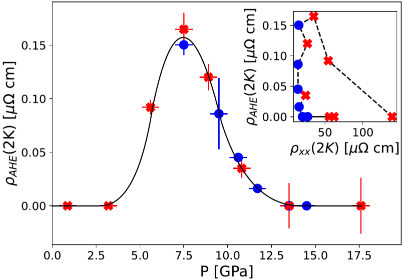
- No Fermi surface in insulating state
- Semi-metallic character with hole and electron pockets visible in cuts at $k_z = 0$ for $P \geqslant 3$ GPa
- Strong modification of Fermi surfaces
- Pressure modulates dominant sign of Berry curvature

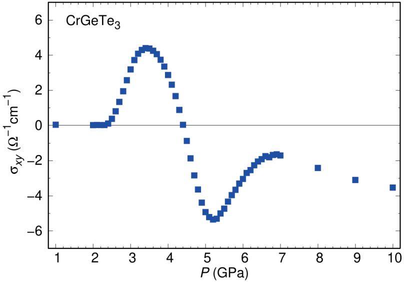


Figures: PRR **7**, 013127 (2025)

Anomalous Hall effect in $CrGeTe_3$ under pressure

- Experiment shows large positive Anomalous Hall resistivity with peak around 8 GPa
- Theoretical calculation for conductivity shows transition from positive to negative AHC under pressure
- Integration of total Berry curvature over Brillouin zone, adaptive Monte Carlo algorithm
- Negative conductivity corresponds to positive resistivity
- Absolute scales of experiment and theory inconsistent
- Extrinsic effects seems to dominate AHC, most likely side-jumps and/or skew scattering
- Similar conclusion as for irradiated $CrGeTe_3$

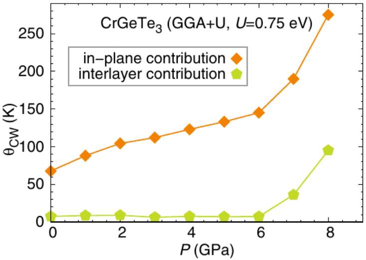


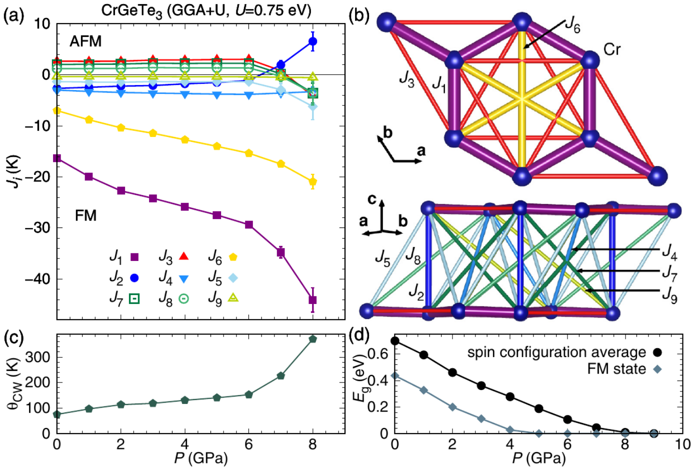


Figures: PRR **7**, 013127 (2025)

Heisenberg Hamiltonian for $CrGeTe_3$ under pressure

- DFT+U calculations with FPLO for magnetic configurations
- Mapping of energies to Heisenberg Hamiltonian
- J_1 and J_6 dominant
- Strong enhancement of FM in metallic phase

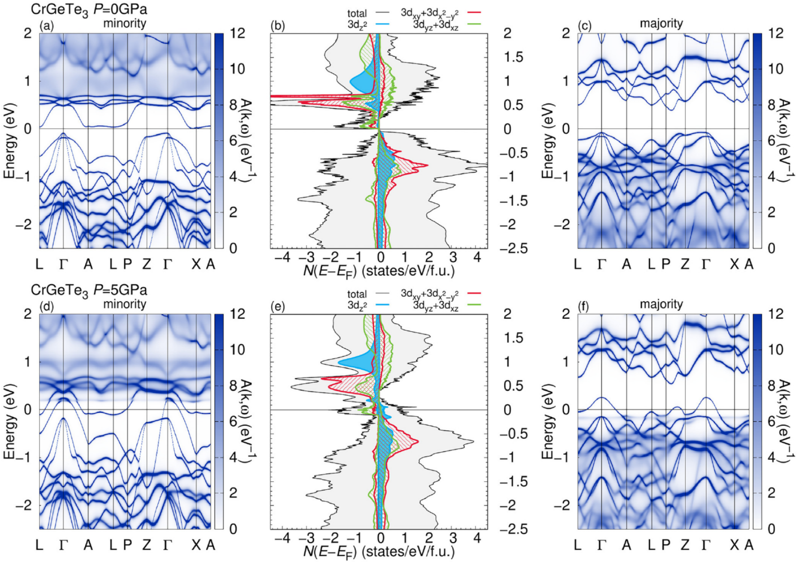




Figures: PRB **108**, 125142 (2023)

Correlated electronic structure of $CrGeTe_3$ under pressure: band structure

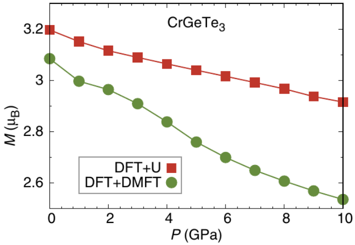
- DFT+DMFT based on FPLO projective Wannier functions and CT-HYB impurity solver
- Insulator to semi-metal transition under pressure reproduced
- Mostly coherent bands around Fermi level
- Almost momentum independent feature slightly above/below Fermi level for minority/majority spins

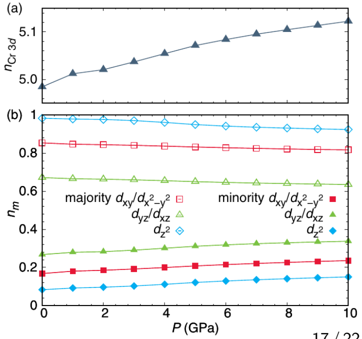


Figures: PRB **108**, 125142 (2023)

Correlated electronic structure of $CrGeTe_3$ under pressure: moments

- Decrease of magnetic moments under pressure
- Moments slightly above 3 μ_B at ambient pressure, consistent with XMCD experiment
- Decrease to around 2.5 μ_B at $P = 10$ GPa
- Filling of Cr states increases slightly under pressure
- Decreasing filling of majority spin states
- Increasing filling of minority spin states
- More pronounced in DFT+DMFT than in DFT+U
- Redistribution likely driven by correlations
- Coulomb repulsion and Hund's rule coupling in presence of minority electrons versus energy gain by delocalization

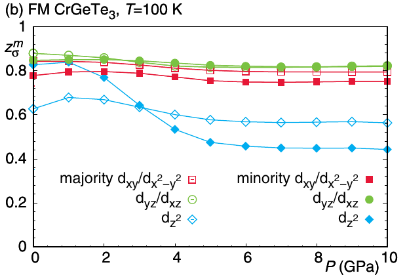


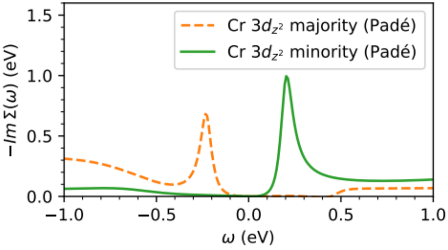


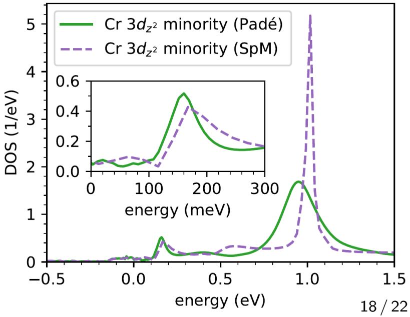
Figures: PRB **108**, 125142 (2023)

Correlated electronic structure of $CrGeTe_3$: quasiparticle weights

- Quasiparticle weight in DFT+DMFT measures correlation strength
- Weight of 1 means no additional correlations over DFT
- Weight of 0 means Mott-Hubbard insulator
- Cr $3d_{z^2}$ orbital most correlated, slightly above half filling
- Self-energy features in metallic phase around ±200 meV
- Corresponding feature in the DOS around 150 meV



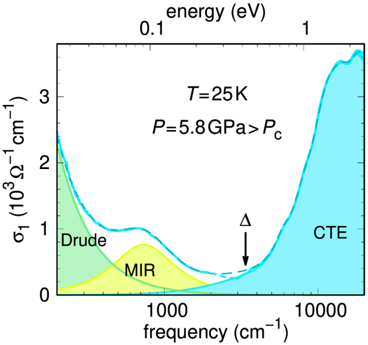


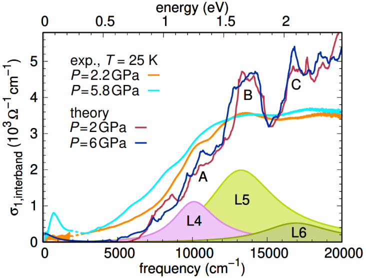


Figures: PRB **108**, 125142 (2023); arXiv:2410.02522

Optical conductivity of $CrGeTe_3$

- Optical conductivity exp. confirms earlier phase diagram
- Additionally provides information about correlations
- Decomposition of experimental conductivity spectrum
- Drude term expected in metallic phase
- Interband transitions above roughly 0.5 eV present in both insulating and metallic phase
- Mid-infrared peak appears in metallic phase
- Almost exactly where we see minority Cr $3d_{z^2}$ feature above the Fermi level
- Interband transitions well explained by DFT in magnetic state
- Detailed assignment of experimental peaks in the paper

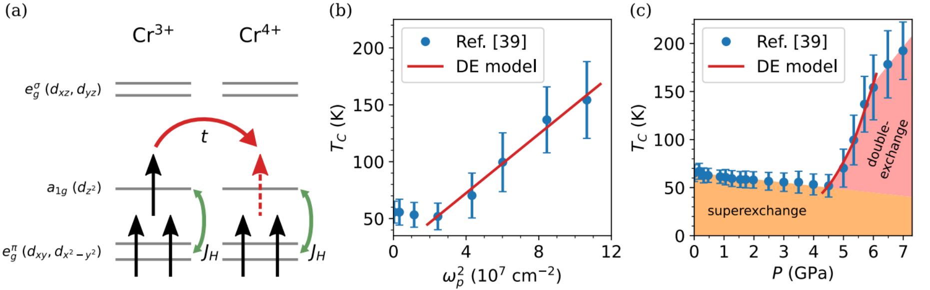




Figures: arXiv:2410.02522

Double exchange model for $CrGeTe_3$

- Mean-field analysis of double exchange model shows $T_C \propto \omega_p^2 \propto \frac{n_e e^2}{\epsilon_0 m_e}$ (PRL **93**, 147202 (2004)), get ω_p^2 from optical conductivity experiment
- Our T_C as function of ω_p^2 looks linear, also fits T_C as function of pressure really well
- Double-exchange may be enabled by holes in majority Cr $3d_{z^2}$ orbital in metallic phase
- Experimental evidence for double-exchange extremely rare
- Superexchange in both phases vs. double-exchange only in metallic phase



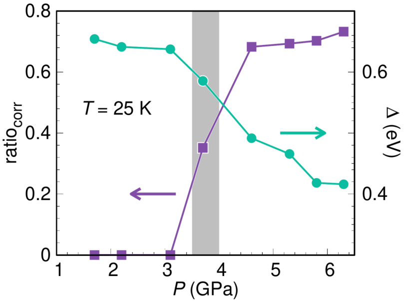
Figures: arXiv:2410.02522

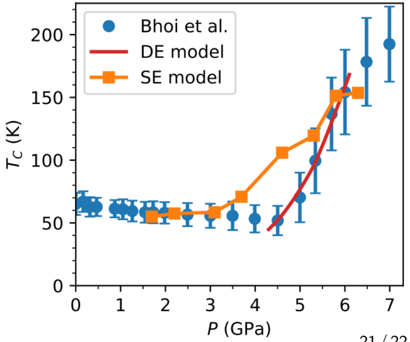
Optical gap and superexchange model

- Collapse of optical gap under pressure was conjectured
- Enhancement of superexchange due to reduced Δ ?

$J_{SE} \propto \frac{t_{pd}^2 t_{p'd'}^2 J_H^{Te}}{\Delta^2(2\Delta+U_p)^2}$ (PRL **127**, 217203 (2021))

- Only moderate decrease from about 0.6 eV to 0.4 eV
- Enough to generate enhanced T_C of observed magnitude
- Continously decreasing gap cannot explain sharp rise of T_C at metal-insulator transition
- Questionable validity of SE formula for metal
- Unclear how superexchange picture could explain nanoscale device, doping and amorphization experiments
- Double-exchange picture can explain those and their similar T_C

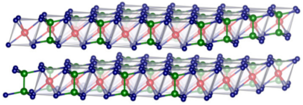


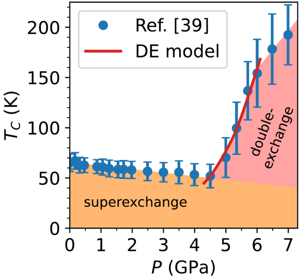


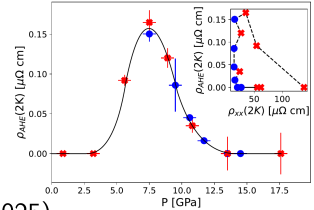
Figures: arXiv:2410.02522

Summary of our findings for $CrGeTe_3$

- Semi-metallic character under pressure, near room-temperature ferromagnet
- Double-exchange picture for high-temperature FM seems likely, strong evidence from optical conductivity
- Consistent with other available experiments on $CrGeTe_3$
- Superexchange mechanism provides low T_C background
- Hole and electron doping possible, but barely explored
- Dynamics of holes and minority spin electrons?
- Experimental evidence for correlations, Hund's physics?
- Puzzling Anomalous Hall effect, role of extrinsic contributions?
- How to use enhanced T_C upon doping or amorphization in devices?







Publications: PRB **108**, 125142 (2023); arXiv:2410.02522; PRR **7**, 013127 (2025)

Appendix: Berry curvature and Anomalous Hall conductivity

- Intrinsic AHE from Berry curvature $\Omega_n(\underline{k}) = \underline{\nabla} \times \underline{A}_n(\underline{k})$ with $\underline{A}_n(\underline{k}) = i \langle u_{n\underline{k}} | \underline{\nabla}_{\underline{k}} | u_{n\underline{k}} \rangle$
- z-Component of Berry curvature tensor:

$$\Omega_{n,z}(\underline{k}) = -2\,\mathrm{Im} \left\langle \frac{\partial u_{n\underline{k}}}{\partial k_z} \middle| \frac{\partial u_{n\underline{k}}}{\partial k_z} \right\rangle$$

- Total Berry curvature $\Omega_z(\underline{k})$ is defined as the sum over all bands n of the band-resolved Berry curvature $\Omega_{n,z}(\underline{k})$ weighted by the respective occupation number $f_n(\underline{k})$:

$$\Omega_z(\underline{k}) = \sum_n f_n(\underline{k})\,\Omega_{n,z}(\underline{k})$$

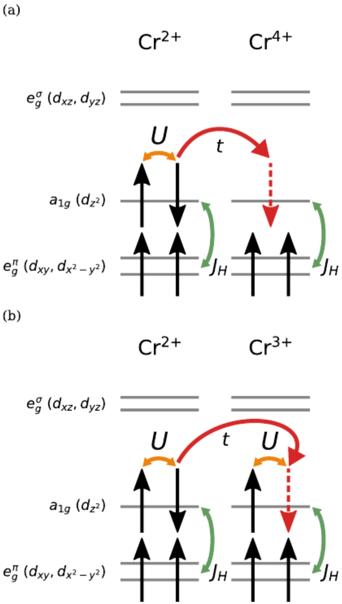
- Anomalous Hall conductivity is the integral of the total Berry curvature $\Omega_z(\underline{k})$ over the entire Brillouin zone (PRB **74**, 195118 (2007)):

$$\sigma_{xy} = -\frac{e^2}{\hbar} \int_{BZ} \frac{d\underline{k}}{(2\pi)^3}\,\Omega_z(\underline{k})$$

- Total Berry curvature from FPLO Wannier interpolation
- BZ integration with adaptive Monte Carlo

Appendix: Minority spins and Coulomb repulsion

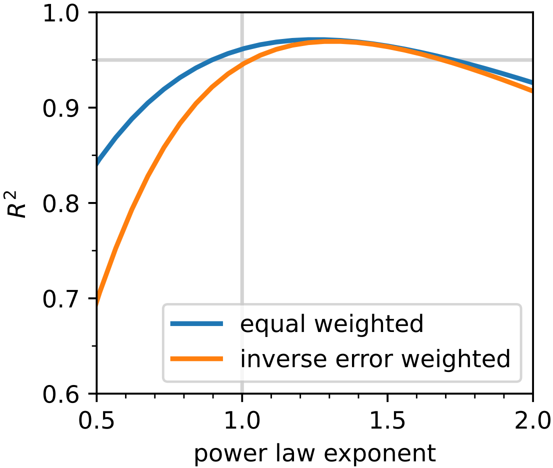
- Minority spins feel strong unfavorable Coulomb repulsion
- Slightly less unfavorable Hund's rule interaction
- Minority Cr $3d_{z^2}$ electrons have lowest QP weight, i.e. most strongly localized
- Localization around holes in the majority Cr $3d_{z^2}$ orbital?



Figures: arXiv:2410.02522

Appendix: Double-exchange model with general power law

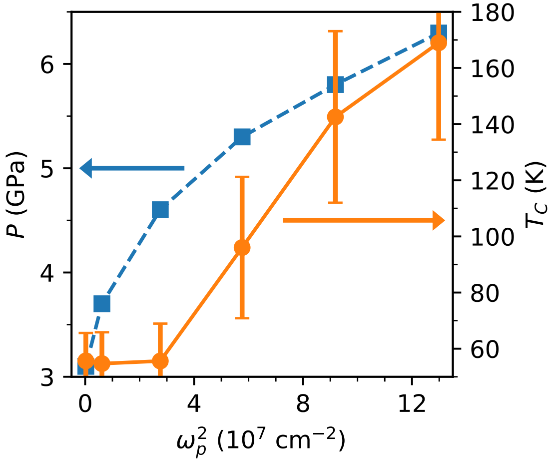
- Fit general power law $T_C = a \cdot (\omega_p^2)^k + b$
- Not enough data to directly determine exponent k
- Sample model space instead and calculate coefficient of determination R^2
- Whole range of power laws fits data very well $R^2 \geqslant 0.95$
- Linear model clearly consistent with data, as predicted by mean-field theory (PRL **93**, 147202 (2004))



Figures: arXiv:2410.02522

Appendix: Plasma frequency as a function of pressure

- Linear relationship between T_c and ω_p^2
- But non-linear relation between ω_p^2 and pressure
- Non-linear mapping back to physical pressure
- Hence slightly nonlinar T_C as function of pressure



Figures: arXiv:2410.02522