Pressure-enhanced ferromagnetism in Cs_2CrCl_4 studied by optical spectroscopy

Luis GÓMEZ (University of Cantabria, Santander, SPAIN),
Fernando RODRÍGUEZ (University of Cantabria, Santander, SPAIN),
Alfonso MUÑOZ (University of La Laguna, Tenerife, SPAIN),
Daniel R. GAMELIN (University of Washington, Seattle, USA),
Rachel T. SMITH (University of Washington, Seattle, USA),
Rafael VALIENTE (University of Cantabria, Santander, SPAIN).

Abstract

Cs_2CrCl_4 is a rare transparent ferromagnet (T_C = 52 K)[1] whose magnetic ordering arises from a cooperative Jahn-Teller (JT) effect. This effect stabilizes an in-plane antiferrodistortive (AFD) Ruddlesden−Popper-type perovskite structure (*Cmca*)[2]. Within this structure, Cr^{2+} ($3d^4$) ions exhibit a strong JT distortion, forming $CrCl_6^{4-}$ octahedra with alternating short (R_s = 2.39 Å) and long (R_l = 2.79 Å) Cr-Cl bonds in the plane (Figure 1). This configuration leads to orbital ordering that maximizes ferromagnetic (FM) Cr^{2+}–Cr^{2+} superexchange coupling by directing the half-occupied dz^2 orbitals of each ion toward the empty dx^2-y^2 orbitals of its neighboring Cr^{2+} ions.

Despite early optical studies on A_2CrCl_4 (*A*: K, Rb), their pressure-dependent behavior remains entirely unexplored. Pressure offers a clean tuning parameter to modify the in-plane JT distortion or to induce octahedral tilting–the former favoring FM coupling, the latter AFM coupling.[3,4] We present the first high-pressure optical absorption study on Cs_2CrCl_4.

Two spin-flip transitions ($^5B_{1g}(^5D) \rightarrow {}^3B_{1g}(^3G)$ and $^3A_{1g}(^3H)$), both parity- and spin-forbidden electric dipole transitions in the isolated ion, become weakly allowed via spin-dependent exchange mechanism[5], making their intensity a sensitive probe of magnetic exchange. These transitions show a strong temperature dependence with associated oscillator strengths increasing from $f \sim 10^{-8}$ at 4.2 K to $f \sim 10^{-5}$ at room temperature. In Cs_2CrCl_4, pressure increases the intensity of these peaks, consistent with DFT simulations showing enhanced exchange interaction upon compression. This behavior **contrasts sharply** with isostructural Mn^{3+} layered perovskites ($AMnF_4$, *A*: Na, Cs), where analogous spin-flip peaks decrease in intensity with pressure due to pressure-induced tilting of the JT-distorted MnF_6^{3-} octahedra reducing the exchange mechanism.

Our results establish a direct magneto-optical correlation under high pressure and highlight optical spectroscopy as a powerful tool for probing pressure-driven magnetic transitions in JT-distorted layered perovskites. A full account will be presented at the EHPRG Meeting.

We acknowledge financial support from Contrato Programa Gobierno de Cantabria-UC under project VQ17 and support from the U.S. National Science Foundation (DMR-2404703).

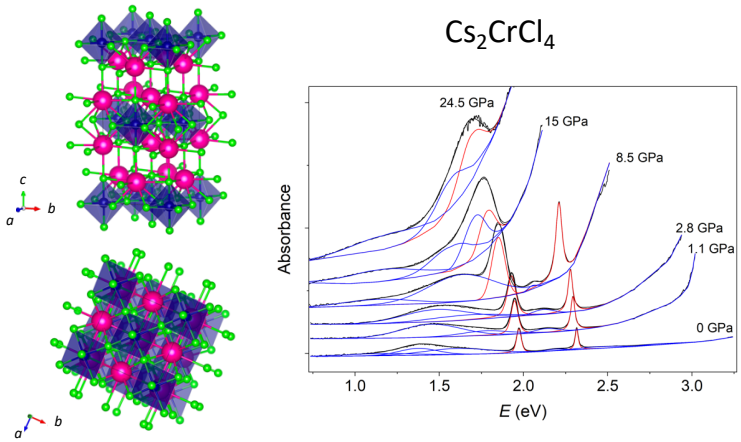

Figure 1.
(Left side) Orthorhombic crystal structure of the layered perovskite Cs_2CrCl_4 (*Pbca*) showing the antiferrodistortive Jahn-Teller-distorted $CrCl_6^{4-}$ octahedra.
(Right side) Pressure dependence of the optical absorption spectrum at room temperature. The spin-flip peaks (in red) increase their intensity with pressure, together with the progressive reduction in charge-transfer band gap energy.

1. M. T. Hutchings, A. K. Gregson, P. Day, D.H. Leech, *Solid State Commun. 15*, 313-316 (1974).
2. R.T. Smith *et al.*, *Chem. Mater.*, 36, 1571−1578 (2024).
3. F. Aguado, *et al.*, *J. Phys.: Condens. Matter* 16, 1927–1938 (2004)
4. D. Pérez-Francés, F. Rodríguez, R. Valiente, *Opt. Mater.*, 160, 116965 (2025).
5. P. Day, A. K. Gregson, D. H. Leech, *Phys. Rev. Lett. 30*, 3 (1973)