

# Quantum Materials in Reduced Dimensions: Thin Films & Exfoliated Crystals

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**Quantum materials are materials whose ground states, as well as some low-energy excitations, can only be captured by a truly quantum description, beyond semiclassical approximations. This includes all magnetic systems, as well as superconducting or topologically nontrivial electronic phases. The electrodynamics of such materials require consideration of the geometrical Berry phase of the electronic wave packet, while the topology of their electronic band structures has emerged as a powerful classifier of their ground states. Concentrations of Berry curvature in momentum-space act as emergent fictitious magnetic fields, generating an anomalous transverse velocity of quasiparticles and giving rise to the intrinsic anomalous Hall and spin Hall effects. In this context, we report on a number of crystalline quantum materials in relation to their superconducting or anomalous transport properties and magnetic ground states, with an emphasis on epitaxial Heusler thin films grown by physical vapor deposition.**

## Noncollinear magnetic Heusler compounds

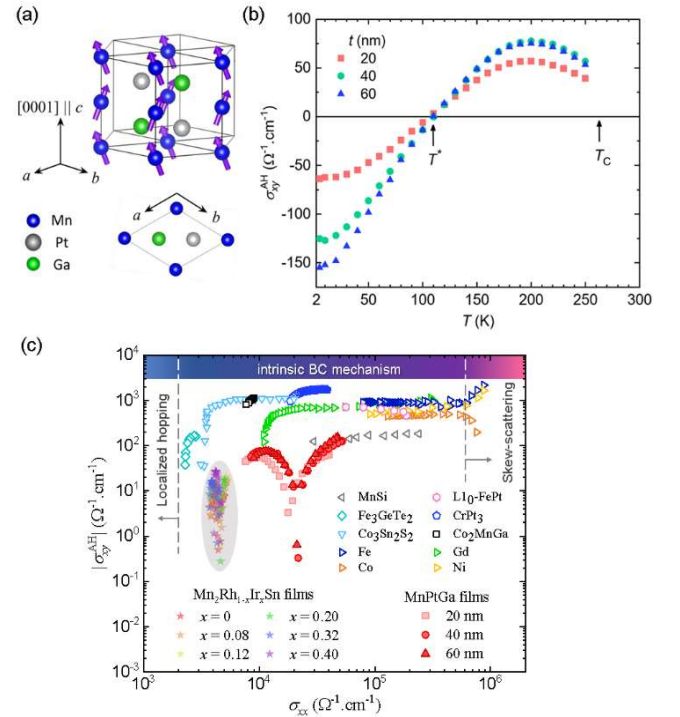
Heusler compounds belong to a remarkable class of intermetallic ternary materials that host a variety of ground states, including superconducting and half-metallic compounds, topological Dirac and (magnetic) Weyl semimetals. They exhibit exotic magnetism with noncollinear ferro-, ferri-, and antiferro-magnetic orderings and topologically nontrivial magnetic textures dubbed (anti)skyrmions.

The experimental discovery in acentric tetragonal inverse Heusler compounds (with  $D_{2d}$  symmetry) of (i) a noncollinear ferrimagnetic ground state in  $Mn_2RhSn$ , followed by (ii) the observation of magnetic antiskyrmions in  $Mn_{1.4}Pt_{1-x}Pd_xSn$  [1] and  $Mn_2Rh_{1-x}Ir_xSn$  [2], in collaboration with Stuart Parkin, has triggered the search for new emergent phenomena in this family of materials. One such material is the half-Heusler compound  $MnPtGa$ , which exhibits rich temperature- and field-driven magnetic phase diagrams, and hosts a noncollinear spin-canted magnetic ground state.

In crystalline thin-film form,  $MnPtGa$  grown on  $Al_2O_3(0001)$  stabilizes in its centrosymmetric hexagonal structure with a preferred  $c$ -axis (0001) out-of-plane crystal orientation, and exhibits a perpendicular magnetic anisotropy below its Curie temperature ( $T_C \approx 260$  K). In addition, the  $MnPtGa$  system undergoes a thermally induced spin-reorientation transition below  $T_{sr} \approx 160$  K, which marks the onset of a noncollinear spin-canted state (Figure 1a). We have confirmed these transitions by single-crystal neutron diffraction and quantified the Mn spin canting angle ( $20^\circ$  from the  $c$ -axis) [3] in collaboration with Dmytro Inosov's group.

We have also studied the magnetic phase diagram of another Heusler system, the tetragonal inverse Heusler  $Mn_2Rh_{1-x}Ir_xSn$ , grown epitaxially on  $MgO(001)$ . We tuned the content of Ir ( $0 \leq x \leq 0.4$ ), which (isovalently)

substitutes Rh. The films exhibit a thermally driven transition from a collinear ferromagnetic state (below  $T_C \approx 280$  K) to a noncollinear ferrimagnetic state (at  $T_{sr} \approx 170$  K), similar to that of the parent compound,  $Mn_2RhSn$ .



*Fig. 1: (a) Spin-canted magnetic ground state of hexagonal  $MnPtGa$  crystalline thin films [3]. (b) Anomalous Hall conductivity (AHC) of  $MnPtGa$  films of various thicknesses as a function of temperature, displaying a cancellation of the AHC at a thickness-independent temperature  $T^* = 110$  K [4]. (c) Experimentally reported  $|AHC|$  vs.  $\sigma_{xx}$  for various magnetic systems for whom the AHE originates from intrinsic Berry curvature, compared to those for our  $MnPtGa$  and 60 nm-thick  $Mn_2Rh_{1-x}Ir_xSn$  crystalline thin films. Adapted from Ref. [4].*

We also turned to the anomalous transport properties of the MnPtGa and Mn<sub>2</sub>Rh<sub>1-x</sub>Ir<sub>x</sub>Sn systems. Relatively recent theoretical and experimental developments in condensed matter physics have cemented the understanding that the anomalous Hall effect (AHE), which is a consequence of spin-orbit coupling in materials with broken time-reversal symmetry, can originate from extrinsic (skew scattering and side-jump) and/or intrinsic (Berry curvature) mechanisms. The intrinsic mechanism is grounded in the topology of the Fermi surface and the geometric Berry phase of the electronic wave packet, which generates finite accumulations of Berry curvature (in reciprocal space). For an intermediate conductivity regime (given by the values of  $\sigma_{xx}$ ), the anomalous Hall conductivity (AHC) is expected to be independent of the longitudinal conductivity.

By contrast, we found that the AHC of MnPtGa thin films exhibits nonmonotonic behavior as a function of temperature, which notably changes sign at a thickness-independent temperature  $T^* = 110$  K (Figure 1b) [4], and at first sight is not correlated to the spin-reorientation temperature. A similar behavior is observed for all Mn<sub>2</sub>Rh<sub>1-x</sub>Ir<sub>x</sub>Sn ( $0 \leq x \leq 0.4$ ) crystalline films. Thus, our observations constitute remarkable realizations of zero AHC in systems with finite magnetization. While first-principles calculations agree with the magnitude and sign of the reported AHC at low temperatures – which suggests the intrinsic Berry curvature mechanism is the dominant source of the AHE in both systems (Figure 1c) – further theoretical investigations (combining density functional theory, model Hamiltonians, and mean-field theory) are underway to clarify the mechanism(s) underlying the temperature-driven sign change of the AHC.

### Time-reversal symmetry breaking Weyl semimetals

In condensed matter systems, Weyl fermionic quasiparticles exist as low-energy excitations of Weyl semimetals, in which electronic bands disperse linearly in three-dimensional momentum space and cross at symmetry-protected nodes called Weyl points, which systematically come in pairs. The Berry curvature becomes singular at the Weyl points, which in turn act as monopoles in momentum space with opposite handedness and sign of the Berry curvature. Consequently, they govern a number of intrinsic electronic transport and optical responses of Weyl semimetals.

The coexistence of band inversion and magnetic ordering in a given material provides a method for designing time-reversal symmetry breaking Weyl semimetals.

We have used several optical and spectroscopic (pump-)probe methods, in close collaboration with a number of international research teams, to study the ultrafast dynamics and/or optical conductivities of two canonical systems – noncollinear antiferromagnetically ordered Weyl semimetal Mn<sub>3</sub>Sn [5] and ferromagnetic Weyl semimetal Co<sub>2</sub>MnGa [6–11] – in the terahertz regime. Hereinafter, we focus on ferromagnetic Weyl semimetal Co<sub>2</sub>MnGa.

In collaboration with Tobias Kampfrath and Henri Jaffrès’ groups, we studied the ultrafast optically driven spin injection from Co<sub>2</sub>MnGa thin films into an adjacent Pt layer by means of terahertz emission spectroscopy [6,7]. We found that Co<sub>2</sub>MnGa is an efficient terahertz spin current generator, reaching efficiencies of typical 3*d*-transition-metal ferromagnets such as Fe. Further experiments by Stefano Lupi’s group suggest the existence of multiple terahertz generation mechanisms originating from both the bulk and surface states of Co<sub>2</sub>MnGa [8]. The bulk emission mechanism is explained in terms of a photon-drag effect, whereas the surface emission mechanism relates to the photovoltaic effect originating from the topological surface state [8]. We also found evidence of photoinduced polaronic formation in Co<sub>2</sub>MnGa [9]. With Liang Wu’s group, we reported a thickness-independent AHC of Co<sub>2</sub>MnGa of  $\sim 600 \Omega^{-1} \text{cm}^{-1}$  ( $0.2 \leq \omega \leq 1.5$  THz) at room temperature. The longitudinal and Hall conductivities, weak spin-orbit coupling, and proximity of the Weyl points to the Fermi level satisfy the criteria for intrinsic terahertz AHC. We further established that Co<sub>2</sub>MnGa exhibits a sizeable Hall angle (8%), and thickness-independent Faraday rotation 56 mrad at room temperature, which are attributed to the intrinsic Berry curvature contribution [10].

Altogether, these results highlight the potential of Co<sub>2</sub>MnGa as a spin-sink material for efficient spin-charge interconversion and as a spin current source in spintronics terahertz emitters. In addition, direct manipulation of the spin and magnetization via light irradiation may provide a path toward ultrafast energy-efficient devices. However, distinguishing the microscopic processes that occur during ultrafast laser excitation in magnetic alloys is challenging. In collaboration with Margaret Murnane’s group, we combined the element specificity of extreme ultraviolet high-harmonic probes – which sense light-induced spin transfers across the entire M-edge of Co<sub>2</sub>MnGa – with time-dependent density functional theory. In doing so, we disentangled the competition between three ultrafast light-induced processes in Co<sub>2</sub>MnGa: same-site

Co–Co spin transfer, intersite Co–Mn spin transfer, and ultrafast spin flips mediated by spin–orbit coupling. This combined approach facilitates a comprehensive microscopic interpretation of laser-induced magnetization dynamics on timescales of less than 100 femtoseconds [11].

### Superconducting half-Heusler topological insulator candidate material

The emergence of topological states of matter introduced new possibilities for both the understanding and application of superconductivity. A fascinating idea involves combining topological and superconducting properties to create topological superconductors with zero-energy modes suitable for applications in fault-tolerant quantum computing. One candidate family of materials expected to provide these conditions are the heavy-element-containing half-Heusler compounds (with general formula XYZ). Relativistic corrections in these materials lead to band inversion with the fourfold degenerate  $p$ -like  $\Gamma_8$  band having higher energy than the twofold degenerate  $s$ -like  $\Gamma_6$  band, as observed in topological insulators.

YPtBi is a particularly promising half-Heusler compound. The  $j = 3/2$  character of the  $\Gamma_8$  band, which derives from the Bi  $p$  orbitals, is predicted to lead to higher-order pairing and thus to a topological superconducting state. However, experiments have thus far been limited to bulk single crystals, which drastically limits the scope of available probes. To reveal any exotic superconducting nature, it is typically necessary to examine lithographically patterned devices, where the details of the superconducting wave function play a tangible role in the transport properties. Examples of such structures include superconducting quantum interference devices (SQUIDS) and Josephson junctions. However, the fabrication of such devices requires advanced nanofabrication techniques, typically starting from thin film materials; it is not really feasible to use bulk crystals.

In collaboration with Laurens Molenkamp’s group, we have successfully grown high-quality crystalline epitaxial thin films of YPtBi(111) on  $\text{Al}_2\text{O}_3(0001)$ , resorting to molecular beam epitaxy [12]. A robust superconducting state was observed, with the critical temperature ( $T_c = 0.67$  K) and critical field ( $H_c(0) = 1.4$  T) being consistent with those previously reported for bulk crystals. Furthermore, we estimated the out-of-plane superconducting coherence length to be 15 nm. Notably, we found that  $\text{AlO}_x$  capping protected the sample surface from oxidation or degradation, facilitating fur-

ther lithographic processing and *ex situ* investigations. Our results pave the way toward the development of elaborate device architectures, which will benefit the exploration of the potentially topological nature of superconductivity in YPtBi, and to tentatively realize the quantum spin Hall insulator regime in a wider bandgap material than the canonical HgTe/CdTe quantum wells.

### Superconducting misfit compounds: from bulk crystals to mesoscopic devices

Over the past two decades, the exploration of truly two-dimensional (2D) materials, as exemplified by monolayer graphene, has become an exciting frontier in materials science and condensed matter physics. The recent discovery of correlated electronic phases and superconductivity in twisted bilayer graphene, a superstructure that forms a Moiré pattern, has triggered the discovery of further 2D compounds and heterostructures. A myriad of van der Waals-layered and transition metal dichalcogenide heterostructures have been extensively explored owing to their novel electronic and magnetic properties at the ultrathin/atomic limit.

Among 2D materials, misfit layer compounds (MLCs) have attracted considerable attention owing to their distinctive structure, crystallographic diversity, and chemical tunability. Similar to twisted bilayer graphene, MLCs feature lattice mismatch between the layers, leading to the formation of Moiré patterns or strain-induced modifications in their electronic structure. MLCs are

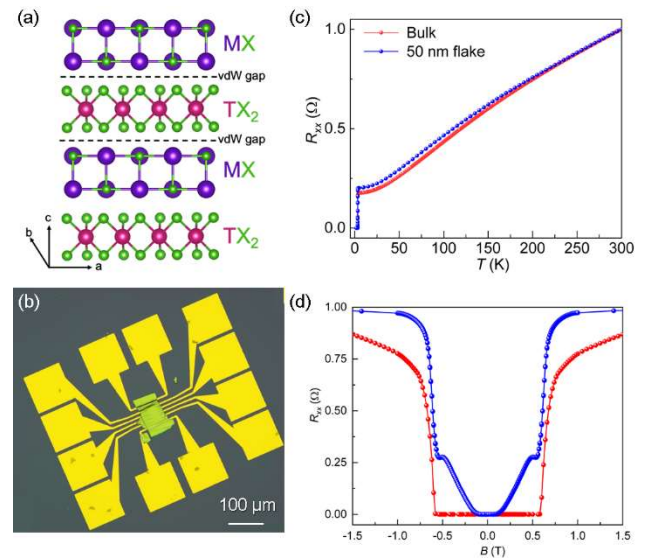


Fig. 2: (a) Schematic of a misfit crystal  $[(MX)_{(1+\delta)}]_m[(TX_2)_n]$  ( $m = n = 1$ ). (b) Hall bar device of  $(\text{SnSe})_{1.16}(\text{NbSe}_2)$  MLC. (c) Critical temperature and (d) longitudinal resistivity of the bulk crystal and 50 nm flake of  $(\text{SnSe})_{1.16}(\text{NbSe}_2)$ .

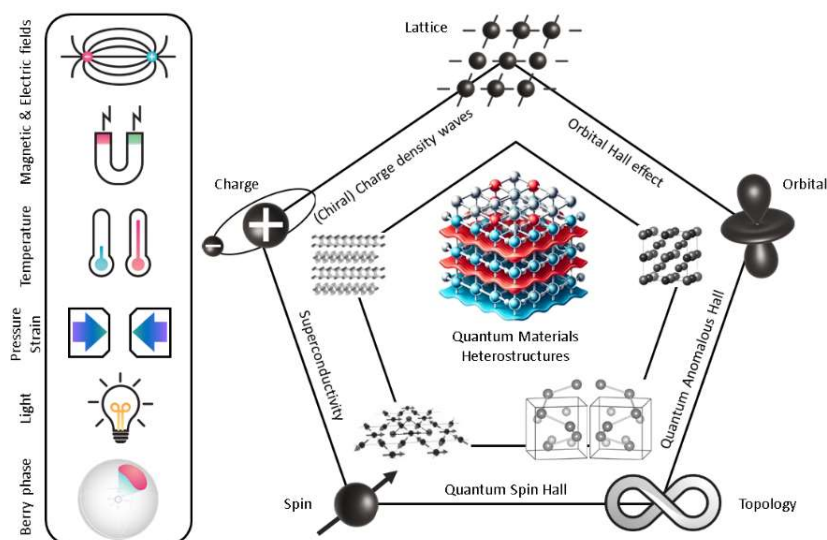


Fig. 3: New opportunities of quantum materials in reduced dimension by tuning charge, spin, orbital, and lattice degrees of freedom.

typically represented by the general formula  $[(MX)_{(1+\delta)}]_m[(TX_2)_n]$ , where  $m$  and  $n$  equal 1, 2, or 3;  $T$  denotes a transition metal element;  $M$  represents a post-transition metal or rare-earth element; and  $X$  represents a chalcogen (Figure 2a). These compounds mimic natural van der Waals heterostructures, comprising alternating stacked layers of distorted rock salt  $MX$  and hexagonal  $TX_2$  structural units. Notably, effective charge transfer occurs from the  $MX$  layers of MLCs to the  $TX_2$  layers, resulting in a variety of intriguing physical phenomena. To date, MLCs have been extensively studied for their potential applications in optoelectronics, catalysis, energy storage systems, and thermoelectrics. However, the fabrication of nanodevices to manipulate the electronic properties using mono- or multilayered misfit crystals remains a challenging and underexplored area.

With this motivation, we have grown high-quality single crystals of  $(\text{SnSe})_{1.16}(\text{NbSe}_2)$  and  $(\text{PbSe})_{1.14}(\text{NbSe}_2)$  MLCs by chemical vapor transport and characterized the crystals using Laue diffraction and energy-dispersive X-ray spectroscopy. In collaboration with Nicola Poccia's group at IFW, Dresden, we exfoliated the misfit  $(\text{SnSe})_{1.16}(\text{NbSe}_2)$  using a simple scotch tape technique and dry-transferred the few-layered exfoliated flakes (thickness  $\approx 50$  nm) onto prepatterned Cr/Au electrodes to form well-defined Hall-bar microdevices (Figure 2b). The entire process was performed inside an Ar-filled glove box, with the samples transferred using a cryogenic transfer stage to mitigate oxidation and defect formation or migration. In such Hall-bar microdevices, we observed that the superconducting transition temperature of the flakes remained similar to those of the bulk MLCs, however, the Hall resistance of the

flake exhibited interesting features, indicating unique electronic properties at the nanoscale (Figure 2c-d). These studies provide a first step toward exploring the low-dimensional emergent electrodynamics of MLCs.

### Toward engineered chiral structural, electronic and magnetic degrees of freedom with topology

Over the past few years, chiral crystals have emerged as a promising research direction in condensed matter physics owing to their symmetry-related exotic physical properties. Among chiral crystals, topological chiral semimetals with noncentrosymmetric cubic B20-type structures (space group  $P2_13$ , No. 198) are of particular interest because they display chirality in their crystal, electronic, and magnetic structures (with B20-MnSi as the canonical skyrmion lattice system). Although the synthesis of chiral single crystals with noncentrosymmetric cubic B20 structures is well established, their heteroepitaxial growth into crystalline thin films remains a notable challenge. In this regard, our group has recently made progress in stabilizing the B20 structure in a prototypical CoSi nonmagnetic chiral semimetal using crystalline seed-layer epitaxial engineering.

Studies in the crystalline thin films of chiral B20 topological metals are expected to provide fundamental insight into their intertwined electronic, chemical, and physical properties. Compared with bulk crystals, heteroepitaxial thin films offer additional tuning parameters, such as film thickness and biaxial (tensile or compressive) strain, in addition to composition/doping control. Moreover, the larger area-to-volume ratio in thin films versus bulk crystals facilitates the study of

surface-dependent phenomena such as interfacial spin transport and catalytic reactions [13], which are difficult to explore in bulk crystals.

Along these lines, epitaxial thin films and exfoliated layered compounds generally offer new opportunities to study topologically nontrivial systems and their intertwined degrees of freedom (charge, spin, orbital, and lattice) in reduced dimensions. Heterostructures of magnetic Weyl and nonmagnetic topological materials with other quantum materials, such as noncollinear (anti)ferromagnets and (topological) superconductors, lithographically patterned into mesoscale devices, are expected to enable vast studies (Figure 3), including superconducting and magnetic proximity effects, quantum anomalous Hall and quantum spin Hall insulator states, Ising superconductivity, chiral charge density wave, Josephson diode effects in noncentrosymmetric superconductors, (inverse) spin and orbital (Rashba) Hall effects, current-induced spin selectivity, and electrical magnetochiral anisotropy.

The realization of high-quality crystalline thin films by physical vapor deposition (e.g., magnetron sputtering and molecular beam epitaxy) is a worthwhile challenge to undertake to enable the integration of entirely new classes of topological materials into functional quantum hardware architectures and next-generation spintronic and electro-optical devices, and promises to both challenge and further our understanding of topology in condensed matter systems.

### External Cooperation Partners

Stuart Parkin (Max Planck Institute Halle, Germany); Laurens Molenkamp (Universität Würzburg, Germany); Nicola Poccia (IFW Dresden, Germany); Tobias Kampfrath (Freie Universität Berlin, Germany); Stefano Lupi (Sapienza Università di Roma, Italy); Henri Jaffrès (Albert Fert Laboratory/CNRS, France); Liang Wu (University of Pennsylvania, USA); and Margaret Murnane (University of Colorado Boulder, USA).

### References

- [1] *Magnetic antiskyrmions above room temperature in tetragonal Heusler materials*, A. K. Nayak, V. Kumar, T. Ma, P. Werner, E. Pippel, R. Sahoo, F. Damay, U. K. Rößler, C. Felser, and S. S. P. Parkin, *Nature* **548** (2017) 561-566, <https://doi.org/10.1038/nature23466>
- [2]\* *Nanoscale Noncollinear Spin Textures in Thin Films of a D2d Heusler Compound*, A. K. Sharma, J. Jena, K. G. Rana, A. Markou, H. L. Meyerheim, K. Mohseni, A. K. Srivastava, I. Kostanoskiy, C. Felser, and S. S. P. Parkin, *Adv. Mater.* **33** (2021) 2101323, <https://doi.org/10.1002/adma.202101323>
- [3]\* *Noncollinear magnetic order in epitaxial thin films of the centrosymmetric MnPtGa hard magnet*, R. Ibarra, E. Lesne, B. Ouladdiaf, K. Beauvois, A. S. Sukhanov, R. Wawrzynczak, W. Schnelle, A. Devishvili, D. S. Inosov, C. Felser, and A. Markou, *Appl. Phys. Lett.* **120** (2022) 172403, <https://doi.org/10.1063/5.0090009>
- [4]\* *Anomalous Hall Effect in Epitaxial Thin Films of the Hexagonal Heusler MnPtGa Noncollinear Hard Magnet*, R. Ibarra, E. Lesne, B. Sabir, J. Gayles, C. Felser, and A. Markou, *Adv. Mater. Interfaces* **9**, 2201562 (2022), <https://doi.org/10.1002/admi.202201562>
- [5]\* *Ultrafast helicity-dependent photocurrents in Weyl Magnet Mn<sub>3</sub>Sn*, D. Hamara G. F. Lange, F. N. Kholid, A. Markou, C. Felser, R.-J. Slager, and C. Ciccarelli, *Communications Physics* **6** (2022) 320, <https://doi.org/10.1038/s42005-023-01440-5>
- [6]\* *Spin-voltage-driven efficient terahertz spin currents from the magnetic Weyl semimetals Co<sub>2</sub>MnGa and Co<sub>2</sub>MnAl*, G. Bierhance, A. Markou, O. Gueckstock, R. Rouzegar, Y. Behovits, A. L. Chekhov, M. Wolf, T. S. Seifert, C. Felser, and T. Kampfrath, *Appl. Phys. Lett.* **120** (2022) 082401, <https://doi.org/10.1063/5.0080308>
- [7]\* *Spintronic THz emitters based on transition metals and semi-metals/Pt multilayers*, J. Hawecker, E. Roncione, A. Markou, S. Krishnia, F. Godel, S. Collin, R. Lebrun, J. Tignon, J. Mangeney, T. Boulier, J.-M. George, C. Felser, H. Jaffrès, and S. Dhillon, *Appl. Phys. Lett.* **120** (2022) 122406, <https://doi.org/10.1063/5.0079955>
- [8]\* *THz Generation from the Topological Nodal Line Semimetal Co<sub>2</sub>MnGa*, L. Tomarchio, S. Mou, L. Mosesso, A. Markou, E. Lesne, C. Felser, and S. Lupi, *ACS Appl. Electron. Mater.* **5** (2023) 1437-1443, <https://doi.org/10.1021/acsaelm.2c01376>
- [9]\* *Optical Conductivity and Photo-induced Polaronic Formation in Co<sub>2</sub>MnGa Topological Semimetal*, L. Tomarchio, S. Mou, L. Mosesso, A. Markou, E. Lesne, C. Felser, and S. Lupi, *Adv. Sci preprint* (2024), <https://doi.org/10.1002/adv.202400247>
- [10]\* *Giant intrinsic anomalous terahertz Faraday rotation in the magnetic Weyl semimetal Co<sub>2</sub>MnGa at room temperature*, X. Han, A. Markou, J. Stensberg, Y. Sun, C. Felser, and L. Wu, *Phys. Rev. B* **105** (2022) 174406, <https://doi.org/10.1103/PhysRevB.105.174406>

- [11]\* *Optically controlling the competition between spin flips and intersite spin transfer in a Heusler half-metal on sub-100-fs time scales*, S. A. Ryan, P. C. Johnsen, M. F. Elhanoty, A. Grafov, N. Li, A. Delin, A. Markou, E. Lesne, C. Felser, O. Eriksson, H. C. Kapteyn, O. Grånäs, and M. M. Murnane, *Sci. Adv.* **9** (2023) eadi1428, <https://doi.org/10.1126/sciadv.adi1428>
- [12]\* *Molecular beam epitaxy of a half-Heusler topological superconductor candidate YPtBi*, J. Kim, K. M. Fijalkowski, J. Kleinlein, C. Schumacher, A. Markou, C. Gould, S. Schreyeck, C. Felser, and L. W. Molenkamp, *Phys. Rev. Materials* **7** (2023) 024802, <https://doi.org/10.1103/PhysRevMaterials.7.024802>
- [13]\* *Observation of Asymmetric Oxidation Catalysis with B20 Chiral Crystals*, G. Li, Q. Yang, K. Manna, Y. Zhang, P. Merz, C. Shekhar, Y. Zhang, H. Lv, A. Markou, Y. Sun, and C. Felser, *Angew. Chem. Int. Ed.* **62** (2023) e202303296, <https://doi.org/10.1002/anie.202303296>

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