Topological Magnetic Heuslers: Role of Symmetry and the Berry Phase

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Topological materials are a new class of quantum materials where gapless electronic excitations are observed, which are protected by the crystal symmetry and topology of the bulk band structure. It was recently realized that the Berry phase is deeply connected with these topological states of matter and can be easily tuned via the crystal symmetry, band structure, and by engineering the number of valance electrons in topological Heuslers. We synthesized single crystals of these various topological Heuslers and investigate their magnetic, electrical, and thermal transport properties, as well as the electronic band structure with angle-resolved photoemission spectroscopy experiments. We performed topological band theory calculations in order to gain a better understanding of these materials. We found that Co_2MnGa, the first three-dimensional topological magnet, shows one of the highest anomalous Hall conductivities (AHC) ~ (1600 $\Omega^{-1}cm^{-1}$) at 2 K and the highest known anomalous Hall angle (AHA) (up to 12%) of any magnetic Heuslers at room temperature. We observed a remarkably high anomalous Nernst thermopower S_{yx}^{A} of ~6.0 μV K^{-1} at 1 T magnetic field and at room temperature, which is beyond the magnetization-scaling relation in any compound reported so far in literature. We also show how the AHC in topological Heuslers can be tuned from zero to a colossal value that is independent of the sample's magnetization. We also found that the metallic ferrimagnetic compound Mn_2CoGa compensates the AHC to zero due to topological reasons, regardless of its high magnetic moment (~2 μ_B). We illustrate how a metallic magnet can be converted to a topologically trivial semiconductor by symmetry engineering and extend this understanding to a series of compounds like spin-gapless semiconductors.

Topological semimetals have drawn tremendous attention in recent years due to their fascinating properties and promise for potential applications in modern technology. As a highly tunable material, Heusler compounds serve as a fertile playground where various novel topological properties, like the Weyl, Dirac, and nodal line semimetals, and spin-structured topological states like skyrmions can be investigated.

In this collaborative work, we focus to understand the physical properties of various topological magnetic Heuslers. Our investigation led to a deeper understanding of the tunability of these properties, which might result in the discovery of novel phenomenon like topological superconductors, Majorana fermions, or the quantum anomalous Hall effect at room temperature. For this investigation, we employed X-ray and Laue diffraction, magnetization, electrical and thermal transport, angle-resolved photoemission spectroscopy (ARPES) measurements, and we performed electronic band structure calculations using density functional theory.

In our study, we use the Berry curvature as one guiding principle to tune the topological properties of Heusler compounds. Berry curvature is the equivalent of the magnetic field in the parameter space that describes entanglement of the valence and conduction bands in an energy band structure. It resides as a strong value in the case of protected band crossings in topological semimetals.

Giant anomalous Hall effect in Co_2MnGa single crystals

Large anomalous Hall conductivity (AHC) in Co_2MnGa was predicted by Kübler *et al.* [1] via Berry curvature calculations. Here, the intrinsic AHC is calculated by integrating the Berry curvature for all the states up to the Fermi energy (E_F). Thus, for magnetic Weyl semimetals with broken time reversal symmetry, where nodal lines form very close to E_F, the AHC attains a colossal value [2].

Here, we have successfully synthesized Co_2MnGa single crystals with the Bridgman crystal growth technique for the first time (Fig. 1a). An image of a full grown crystal and a corresponding Laue pattern are shown in Figure 1a. The calculated band structure (Fig. 1b) shows the formation of three nodal lines very close to E_F that are protected by mirror symmetry. Co_2MnGa is found to be ferromagnetic with T_C ~ 686.4 K as seen from the field-cooled and zero-field-cooled magnetization in Figure 1c. The saturation magnetization is4 μ_B f.u.$^{-1}$ at 2 K and slightly decreases to 3.8 μ_B f.u.$^{-1}$ at 300 K. The strong Berry curvature from the nodal lines induces a colossal AHC of ~1600 $\Omega^{-1}cm^{-1}$ at 2 K (Fig. 1d), which is the highest know AHC value apart from Co_2MnAl in any magnetic Heuslers [3]. The AHC decreased marginally to 970 $\Omega^{-1}cm^{-1}$ as the

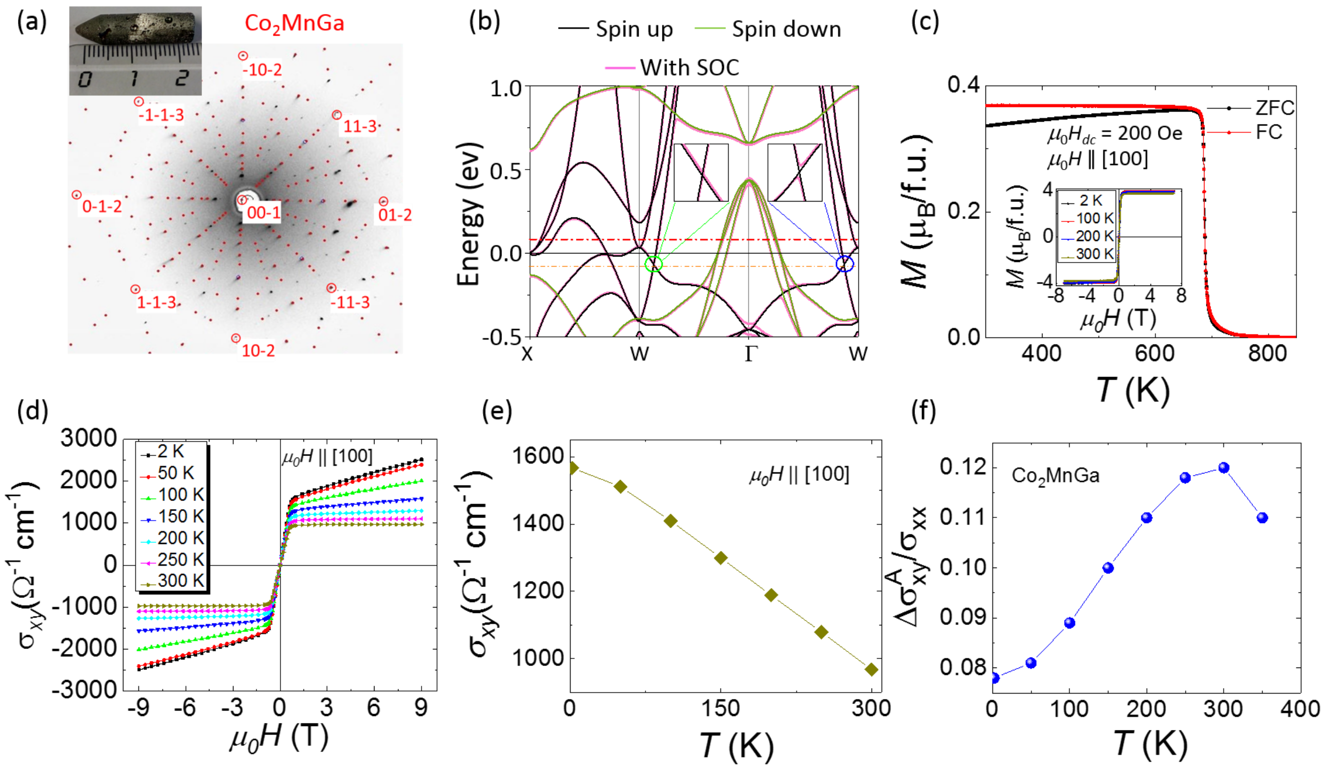

Fig.-1: (a) Bridgman grown single crystal along with the Laue diffraction pattern and (b)calculated band structure in Co_2MnGa with and with-out considering spin-orbit coupling (SOC). The band crossings are marked with the small circle and is zoomed in the inset. SOC lifts the degeneracy and opens the crossing at the blue circle. (c) Field-cooled and zero-field-cooled magnetization, and (inset) magnetic hysteresis at various temperatures in Co_2MnGa single crystals. (d) Field and (e) temperature dependent AHC [σ_{xy}], (f) temperature dependent anomalous Hall angle [$\Delta\sigma_{xy}^{A}/\sigma_{xx}$], in Co_2MnGa single crystals. Here magnetic field is applied along [100].

temperature increased to 300 K (Fig. 1e), but the longitudinal conductivity dropped sharply [3, 4]. As a result, we observed a giant anomalous Hall angle (AHA) up to 12% at room temperature (Fig. 1f), which is maximum observed value in any magnetic Heusler reported so far in the literature [3].

Colossal anomalous Nernst effect beyond the magnetization scaling relation in Co_2MnGa single crystals

The anomalous Nernst effect (ANE) is analogous to the electrical anomalous Hall effect, where a temperature gradient is applied in a magnetic material and a Hall voltage is generated that is perpendicular to both the heat flow and the magnetization of the sample. For a long time it was believed that the value of ANE is proportional to the net magnetic moment of the sample. However, recent investigation shows that the ANE actually originates from a net Berry curvature of all bands near E_F. Conversely, a large anomalous Nernst thermopower (S_{yx}^{A}) can be observed in topological materials with no net magnetization but large net Berry curvature [$\Omega_n(k)$] near E_F. A typical example is non-collinear antiferromagnetic system, such as Mn_3Ge and Mn_3Sn. Clearly this falls outside the scope of the conventional magnetization-model of ANE, but a worthy question remains: Can the value of ANE in topological ferromagnets exceed the highest values observed in conventional ferromagnets? Recently, we observed a remarkably high value of ~6.0 μV K^{-1} at 1 T magnetic field (Fig. 2a) in ferromagnetic topological Heusler Co_2MnGa single crystals at room temperature [4]. This is nearly a factor 7 larger than any anomalous Nernst thermopower value ever reported for any conventional ferromagnet (Fig. 2b). Combined electrical, thermoelectric, and first-principles calculations reveal that this high ANE value arises from a large net Berry curvature near the Fermi level associated with the nodal lines and Weyl points.

Discovery of the first three-dimensional topological ferromagnet

We discovered the first three-dimensional topological magnetic phase in our Co_2MnGa single crystals in collaboration with Prof. M. Zahid Hasan from Princeton [5]. A nodal line is formed when two bands of opposite mirror eigenvalues cross (Fig. 3a). We observe a pair of bulk bands crossing along the curves

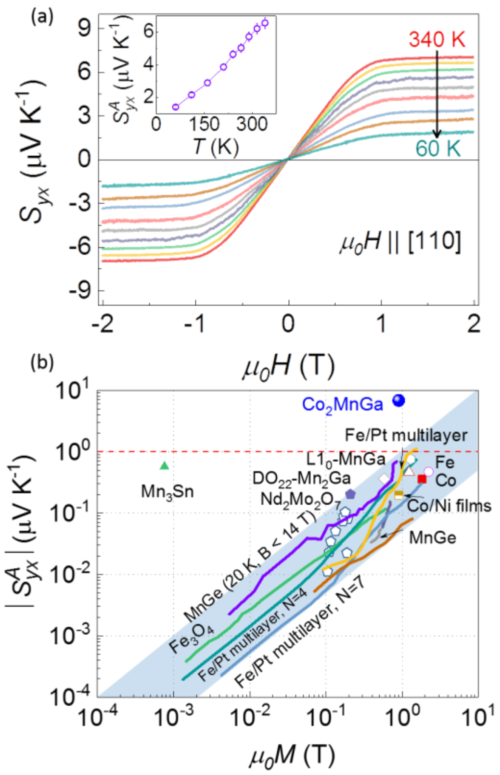

Fig.-2: (a) Magnetic field-dependent Nernst thermopower (S_{yx}) in Co_2MnGa single crystals at temperatures ranging from 340 to 60 K. The inset shows the temperature variation of the extracted anomalous Nernst thermopower (S^A_{yx}) after extrapolation from the data gathered at high field (above 1 T). (b) A comparison plot of the magnetization-dependent anomalous Nernst thermopower (S^A_{yx}) in various ferromagnetic metals. Co_2MnGa single crystals show the highest value beyond any magnetization scaling relation, as highlighted by the blue shaded region.

in the bulk Brillouin zone, which is the topological line nodes associated with π Berry phase and protected by mirror symmetry. All the line node features of the measured Fermi surface (Fig. 3b) matches very well with the *ab initio* constant energy surface (Fig. 3c).

Considering a series of $E_B - k_x$ ARPES cuttings at different k_y values (Fig. 3d-f), we located band crossing over a range of k_y, where E_B is the binding energy. This is the distinctive feature for observation of a line node and hence is different from the conventional Dirac or Weyl semimetals where band crossing occurs at one particular k_y value. To further confirm the line nodes, we plot the constant energy surfaces as a function of E_B. As we move from E_F to a deeper E_B value, we see that the line node feature changes from a '<' shape to a '>' shape (Fig. 3g-i), forming electron and hole pockets accordingly. For

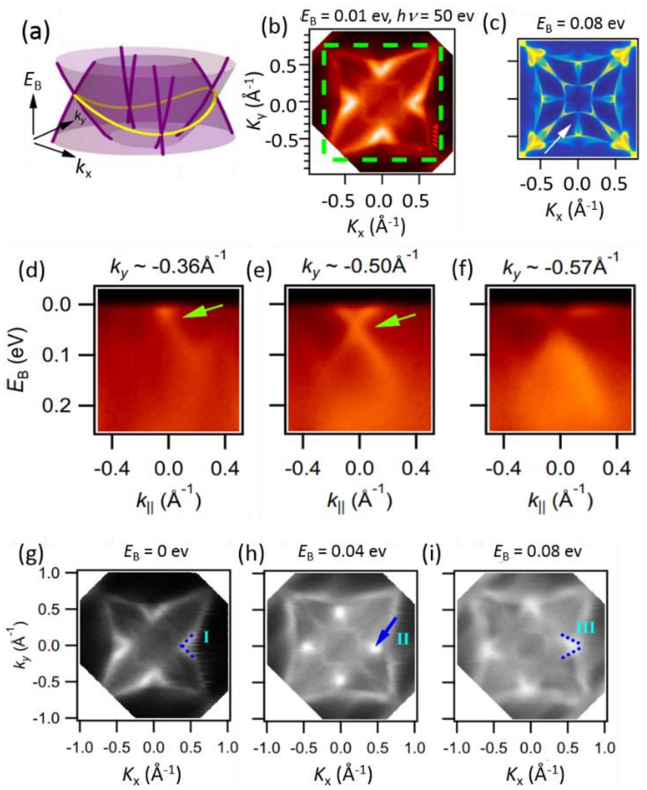

Fig.-3: (a) Band degenerate line node (yellow curve) as a closed curve in the Brillouin zone. (b) The Fermi surface matches very well with (c) the ab initio constant energy surface at E_B = 0.08 eV below E_F, reflecting hole doping in the sample. (d-f) $E_B - k_{||}$ spectra cuttings at different k_y and (g-i) E_F at various E_B values mapping the dispersive evolution of the line node in Co_2MnGa.

energies which cross the line node, we find electron and hole pockets intersecting at a point (Fig. 3h). All of these results clearly demonstrate the first experimental proof for the formation of topological line nodes in Co_2MnGa single crystals [5].

Tuning the anomalous Hall conductivity from colossal to zero in topological magnetic Heuslers

The Hall resistivity is commonly expressed as: $\rho_{xy} = R_0 B + (\alpha\rho_{xx}^2 + \beta\rho_{xx})M + \rho^{Topo}$, where R_0, α, and β are constants. The first term is the linear Hall coefficient due to the Lorentz force, and the last term is the contribution from the Berry curvature in real space (spin texture) due to skyrmion formation, etc. Evidently, the second term gives a finite Hall contribution and AHC ≠ 0 for a ferromagnetic metal (M, $\rho \neq 0$). Interestingly, all the magnetic Heusler compounds we investigated here are metallic in nature. Since the discovery of AHE, it has been considered that AHE is a characteristic feature of finite magnetization in a compound. But is it a universal law? Our recent

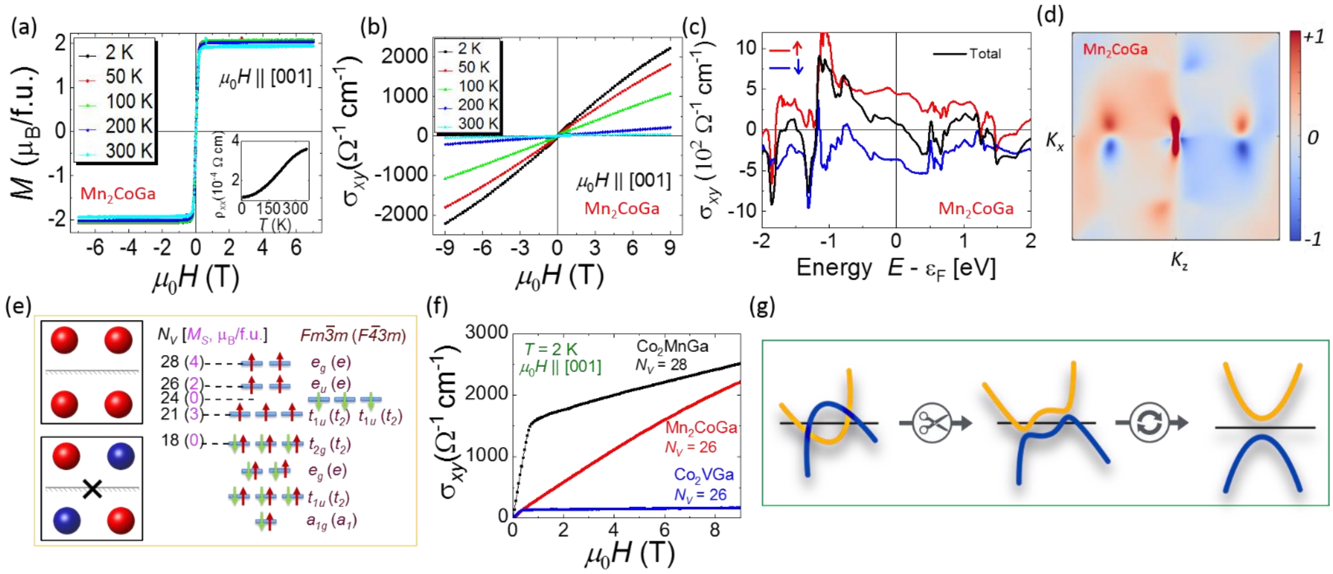

Fig.-4: (a) Magnetic hysteresis at various temperatures, temperature dependent longitudinal resistivity (inset, a), and (b) magnetic field dependence of Hall conductivity at various temperatures of Mn_2CoGa single crystals. Calculated (c) Hall contributions in the majority and minority spin channels and (d) Berry curvature distribution in k-space of Mn_2CoGa. (e) Strategy for tuning the anomalous Hall conductivity via suitable atomic arrangement and doping. NV is the number of valance electrons and M_S is the saturation magnetization. (f) Experimentally observed Hall conductivity in three magnetic Heusler compounds with various N_V, showing the tunability of anomalous Hall conductivity in magnetic Heuslers. (g) Observation of the topologically equivalent state in a trivial semiconducting and topological metal obtained via symmetry-breaking or other perturbations.

investigations on transport measurement in topological Heuslers indicate otherwise.

In topological semimetals like Co_2MnGa, three nodal lines form near the Γ point in the k_x, k_y and k_z planes and are protected by the mirror symmetries M_x, M_y, and M_z in the $Fm\bar{3}m$ space group. Upon incorporating SOC, the crystal symmetry changes depending on the magnetization direction. For example, the M_x and M_y mirror symmetries are broken if a sample is magnetized along the [001] direction. Therefore, the nodal lines will open up unless certain symmetries remain to protect the band crossings away from E_F. As a consequence, at least two Weyl points form along the k_z axis, leading to a finite AHC [2, 3]. Now, what happens if we break this mirror symmetry that protects the nodal line in the k_z plane?

We reduce the crystal symmetry in such a way that the inversion and mirror symmetries are broken. An easy example is to form an inverse-Heusler structure with $F\bar{4}3m$ space group, such as occurs in Mn_2CoGa. Because of the non-centrosymmetric crystal structure, the mirror planes M_x, M_y, and M_z of the full-Heusler no longer exist. Naturally, a gap appears between the nodal lines, and no Weyl points form upon incorporating SOC. Our DFT calculations show that the Berry curvature attains a positive and negative hot spots in *k*-space resulting zero AHC upon integration, which is independent of the sample's magnetization.

We investigated ferromagnetic Mn_2CoGa single crystals (T_C of 687 K with a saturation magnetization of ~2 μ_B and electrically metallic with finite DOS at E_F (Fig. 4a). However, the AHC is zero (Fig. 4b), which breaks the classical law established so far in the literature. From the theoretical calculations, we understand that both spin channels in Mn_2CoGa contribute a finite and opposite Hall contributions due to the special crystalline symmetry and band structure (Fig. 4c) as well as both positive and negative hot spots in the Berry curvature (Fig. 4d). Thus, the overall integration results in a *zero* AHC for Mn_2CoGa [3]. We arrive at a situation where the compound is topologically semiconducting, but electrically metallic (Fig. 4g).

We realize that the classical law governing AHC breaks down in a series of compounds like the spin-gapless semiconductors [3]. Here, the AHC can be compensated, irrespective of finite magnetization in the sample. Our theoretical calculation also predict that the converse effect is also true, i.e., a large AHE can be observed in a compensated ferrimagnet as well. Here, one can break the glide symmetry that prevents any operation to reverse the sign of Berry curvature of the inverse-Heusler structure via atomic substitution, hence resulting in a non-zero AHC. We predict Ti_2MnAl as a candidate compound, which is a compensated ferrimagnetic Weyl semimetal and might show a strong AHE (~500 S/cm) [6]. Therefore, through simple materials engineering via manipulation of the crystal symmetry and N_V, we present a design scheme that allows the the details of band structure to be tuned so as to change the AHC from colossal to *zero*, independent from sample's magnetization, which is suitable for next generation topo-spintronic applications (Fig. 4e,f).

Outlook

This year, we are about to receive a laser based-optical floating zone instrument and a high powder rod casting machine. This extends our flexibility and capacity for growing single crystals of various compounds beyond our halogen-based optical floating zone, Bridgman, or flux-growth techniques. In the future, we are interested to investigate various exotic compounds with multiple-topological order and in exploring how the real space topological effect like skyrmion formation can influence the *k*-space topological effects, such as the Dirac or Weyl points.

External Cooperation Partners

M. Z. Hasan (Princeton University, USA); Y. Chen (Physics Department, Oxford University, Oxford, UK); J. Heremans (The Ohio State University, USA)

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