Topological Chiral Crystals

Kakali Santra[#], Vicky Hasse, Changjiang Yi, Patrick Merz, Chandra Shekhar[##] and Claudia Felser

Chirality represents a fundamental property of nature relevant across various disciplines, including physics, chemistry, and biology. Topological chiral materials have attracted significant attention from several researchers owing to their potential to host chiral charges. The combination of the topology of chiral materials, which arises from their spin, orbit, and momentum coupling, creates a plethora of possibilities for discovering new science. These phenomena include the emergence of new fermions, giant topological surface states, chiral charge transfer, chiral charge density wave, and chiral phonon. Numerous topological homochiral crystals have been grown through dedicated growth methods to achieve these promising properties. Nevertheless, the question of how to alter the one-handedness to another of a homochiral material during its growth process remains unresolved.

Two objects that are mirror images cannot be superimposed on each other; this is because chiral objects possess a specific handedness. The most common example of a chiral object is our own hands. Similarly, crystals are formed from periodic arrays of unit cells with distinct symmetries such as inversion, mirrors, or roto-inversion. Crystals that lack these symmetrical elements may also be chiral, which is a vital link between structural symmetry and exotic quantum physical properties. Among the 230 space groups, 22 are enantiomeric and 43 are non-enantiomeric but can host enantiomorphic crystals [1]. The classification of solid-state materials has recently been reevaluated through the lens of topology, which goes far beyond the simple sum of their symmetry elements. There is a direct connection between real space (atoms, valence electrons, bonds, and orbitals) and reciprocal space (bands and Fermi surfaces) through symmetry and topology. In some aspects, chiral materials extend the concept of topology beyond Dirac and Weyl semimetals, in which chiral electrons have no corresponding analogs in high-energy physics and are therefore described as *new Fermions*. However, a combination of the topologies of chiral materials, which arises from their spin, orbit, and momentum coupling, creates a plethora of possibilities. These phenomena include new fermions, giant topological surface states, chiral charge transfer, chiral charge density waves, and chiral phonons (Figure 1). Moreover, the chiral structure is an example of a real-space manifestation of chirality, which refers to the properties of these crystals, in which their atoms follow a spiral. Notably, both handedness values are energetically equivalent and have an equal propensity to grow, which leads to the formation of a racemic mixture during synthesis. Suppressing such mixed reactions and obtaining homochiral materials are challenging tasks. In this study, we employed several methods to facilitate the growth of numerous homochiral materials.

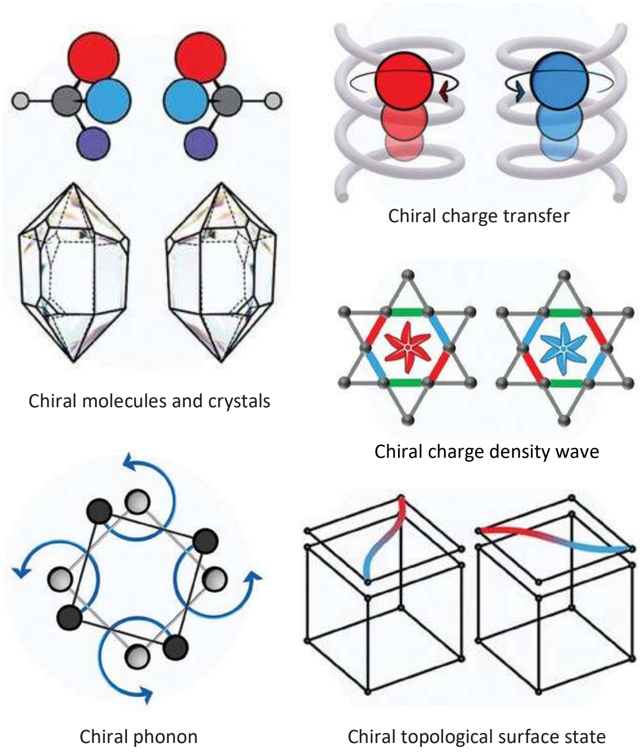

Fig. 1: Chiral objects in physics and chemistry.

Flux growth

The successful growth of single crystals generally requires a considerably high temperature for sufficient diffusion of atoms. A metal flux capable of dissolving constituent elements at relatively low temperatures can be an effective method for growing single crystals from a solution. Once a supersaturated solution is formed at a high temperature, controlled cooling forms single crystals with the desired composition. A self-flux method has been employed to produce multiple batches of PdGa single crystals from a stoichiometric melt. Initially, a polycrystalline ingot was produced through an arc melting technique by employing a stoichiometric mixture of high-purity Pd and Ga. The crushed pieces were then placed in a bottom-cone-shaped alumina crucible and sealed in a quartz tube.

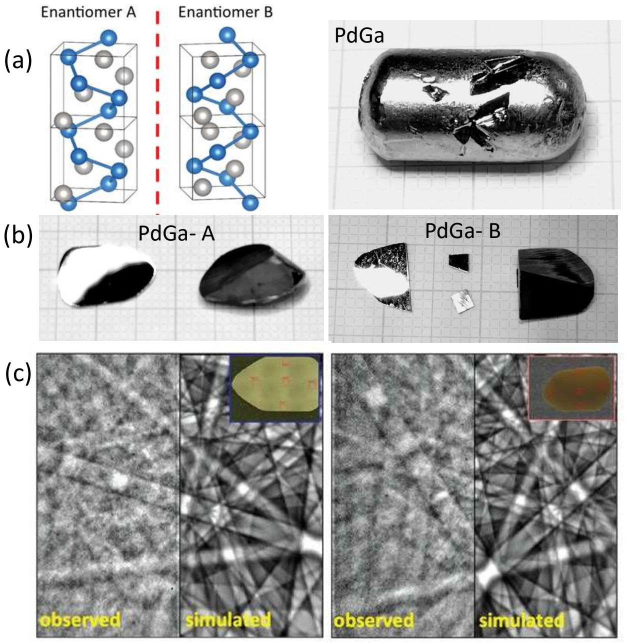

Fig. 2: (a) *Schematic illustration of chiral PdGa enantiomers (A and B form) crystal structure. (b) Few centimeters long PdGa crystal grown from self-flux method. (c) observed and simulated Kikuchi pattern of the PdGa crystals cut along (111) orientation confirming the chirality.*

The entire quartz ampoule was heated to 1100°C, maintained at this temperature for 12 h, and then cooled to 900°C at a rate of 1.5 °C/h. Subsequently, the sample was cooled to 800°C at a rate of 50°C/h, annealed for 120 h, and cooled to 500°C at a rate of 5°C/h. This heating profile resulted in the formation of a homochiral phase throughout the ingot. One of the principal disadvantages of the flux method is that it is not straightforward to control the handedness. Given that each ingot was homochiral, there was a high probability of obtaining handedness from multiple batch trials without using seeds (Figure 2). Surface-sensitive electron backscatter diffraction (EBSD) was employed to ascertain the chirality, which revealed a fundamental distinction between the two. In this method, the experimental backscattered Kikuchi diffraction patterns were acquired using an EBSD system and matched to the simulated Kikuchi pattern of the reference structure (Figure 2).

Laser floating zone growth

The laser floating zone (LFZ) is a highly effective technique for growing large single crystals of materials with extremely high melting temperatures. Contrary to other methods, the LFZ process does not necessitate the use of a crucible throughout the growth phase. The LFZ system was equipped with five diode lasers of 200 W power and 878 nm wavelength. The five lasers were arranged in a circle, with the laser beam focused at the center of the circle, which was the contact point between the seed and feed rods. This method offers several possibilities for controlling the crystal growth process, including the manipulation of chirality and directional growth of the crystal using a suitable seed rod. A polycrystalline rod was prepared in a levitation-melting facility using an arc-melted button. For homogeneous growth, the seed and feed rods rotated in opposite directions with a growth rate typically ranging from 1–10 mm/h. Several large-size, high-quality chiral crystals have been successfully grown. The sizes of the grown CoSi and PtGa crystals were ~ 7 and ~ 4 cm, respectively. The materials were crystallized in the $P2_13$ space group (structure type: B20). These materials exhibit left- and right-handed enantiomorphs, both belonging to the same space group. EBSD analysis showed no change in chirality between the growth stages, with the crystals exhibiting homochirality throughout (Figure 3).

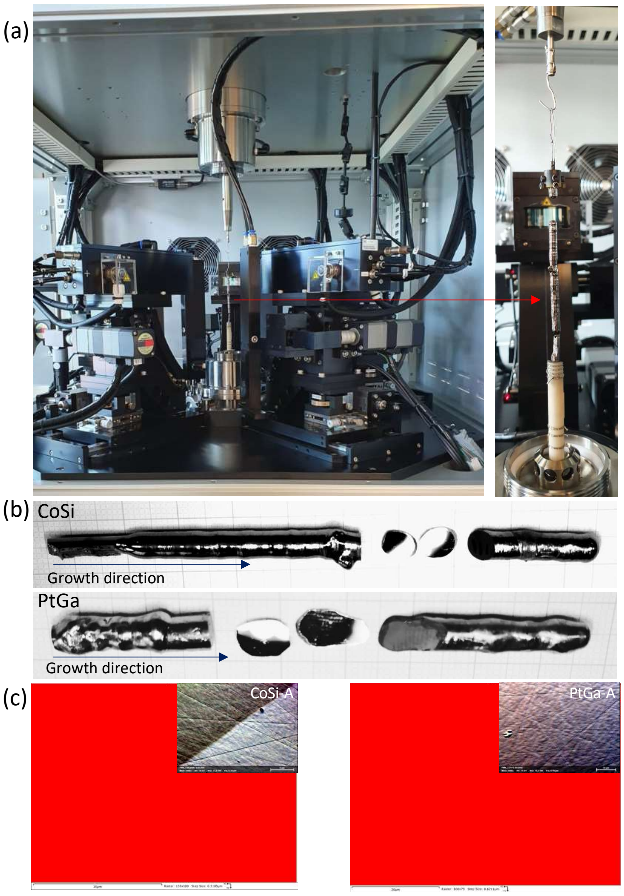

Fig. 3: (a) Image of the 1000 W laser floating zone instrument set up its zoom-in view of seed and feed rods. (b) As grown rods and polished (111) surfaces of CoSi and PtGa. (c) Measured EBSD patterns showing a large area of only enantiomer-A of both crystals.

Table 1: List of chiral crystals grown using various crystal growth methods, corresponding space group and properties.

Name	Space Group	Method	Property
CoSi	$P2_13$ (198)	LFZ	New fermion
FeGe	$P2_13$ (198)	CVT	Helical AFM, T_N~ 280 K
PdGa	$P2_13$ (198)	Flux/LFZ	New fermion
PtGa	$P2_13$ (198)	LFZ	New fermion
RhSi	$P2_13$ (198)	Bridgman	New fermion
RhSn	$P2_13$ (198)	Flux	New fermion
MnSi	$P2_13$ (198)	CVT	Skyrmion
FeSi	Fm/3m (225)	CVT	New fermion
PtAl	$P2_13$ (198)	Bridgman	New fermion
Te	$P3_121$ (152)/ $P3_221$ (154)	CVT	Semimetal
$FeNb_3S_6$	$P6_322$ (182)	CVT	Helical AFM, T_N ~ 47 K
$CoNb_3S_6$	$P6_322$ (182)	CVT	Helical AFM, T_N ~ 27.5 K
$CrNb_3S_6$	$P6_322$ (182)	CVT	Helical AFM, T_N ~ 127 K
Mn3IrSi	$P2_13$ (198)	LFZ	AFM, T_N ~ 220 K
Mn_3IrGe	$P2_13$ (198)	LFZ	AFM, T_N ~ 220 K
RhBiS	$P2_13$ (198)	Flux	Low gap semi-metal
PdBiSe	$P2_13$ (198)	Bridgman	Low gap semi-metal
NiSbS	$P2_13$ (198)	Flux	Low gap semi-metal
$NbGe_2$	P6222 (180)	Flux	Chiral super-conductor
Mn_3CoSi	$P2_13$ (198)	Bridgman	New Fermion
$NbSi_2$	P6222 (180)/ $P6_422$(181)	CVT	High conductivity
$TaSi_2$	$P6_222$ (180)/ $P6_422$(181)	CVT	High conductivity
$SrSi_2$	$P4_3\,32$ (212)	LFZ	Double Weyl Fermion
Ta_2Se_8I	I422(97)	CVT	Axion, Weyl, CDW ~ 280 K

Czochralski growth method

The Czochralski method is an effective technique for the congruent melting of materials, allowing the growth of high-quality, large single crystals. This method begins by inserting a small seed from the top into the surface of a fully molten material contained in a crucible. The seed is then slowly pulled with rotation, allowing crystals to form at the interface. In general, the crystal grows in a cylindrical shape, the diameter of which can be controlled by tuning the heating power of the melt, and the rotation and pulling rates of the seed crystal. Although this method can be employed to grow high-quality single crystals of materials that melt congruently, it is particularly useful for chirality control when growing chiral single crystals, such as topologically chiral materials, for example CoSi (Figure 4). The Czochralski technique allows for the straightforward control of the structural chirality and selective growth of left-handed or right-handed crystals. The efficacy of this method depends on the proper selection of the seeding material, which can transfer its structural chirality to the grown material.

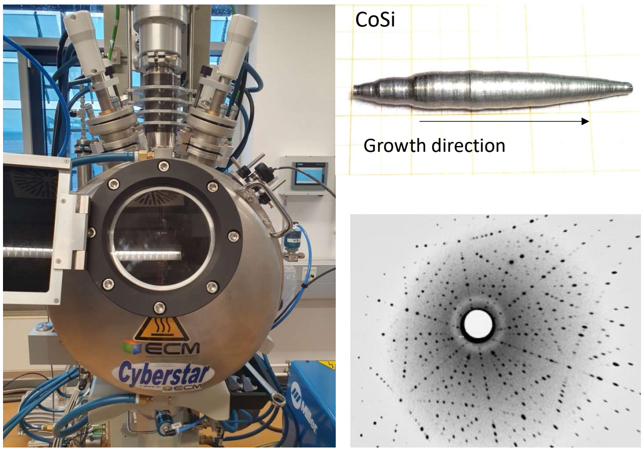

Fig. 4: Image of the Czochralski instrument, CoSi crystals grown from the method, and Laue diffraction pattern of a grown CoSi crystal.

Chemical vapor transport

In chemical vapor transport (CVT), all components of the material are transformed into gaseous species and transferred to different locations where they form single crystals. In the typical growth of a binary or more complex compound, a mixture of individual elemental powders or a pre-reacted polycrystalline powder of the compound was sealed in a quartz tube under vacuum along with a transport agent. The reaction mixture was then placed in a horizontal tubular furnace and heated independently to maintain the temperature gradient. The temperature gradient provided a pathway for the diffusion of gaseous species, with the direction of diffusion controlled by the reaction being either endothermic or exothermic. Transport agents were typically employed to accelerate the kinetics of single crystal formation. In a typical process, there was no control over the chirality of the compound, and crystals were formed with handedness. Consequently, each crystal

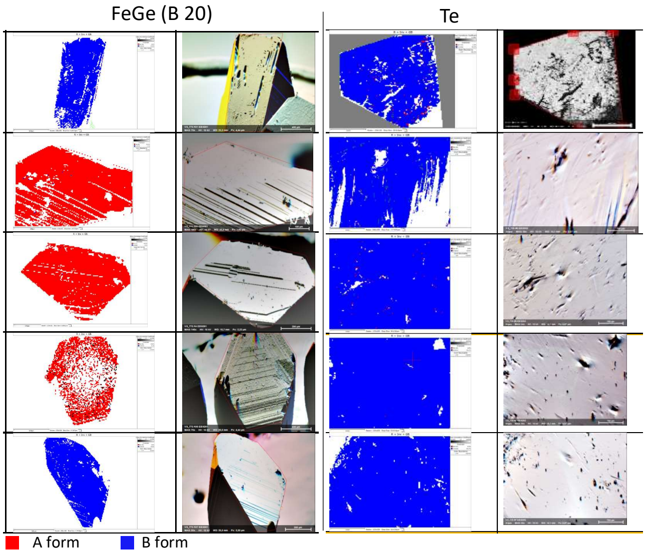

Fig. 5: Measured EBSD patterns of several crystals of cubic FeGe and Te.

was analyzed based on its chirality, which was fundamentally distinct from the LFZ and Czochralski processes, in which the entire piece was homochiral. For example, cubic FeGe and Te crystals were grown, and their handedness was investigated. Both types of chiral crystals were obtained in a batch of syntheses (Figure 5). Te crystals were synthesized in a mixture of Te and S in a 1:1 ratio at temperatures ranging from 300 to 275°C for 4 days. During this process, S served as a transport agent. However, cubic FeGe crystals were grown from a mixture of Fe and Ge in a Fe 50.5:Ge 49.5 ratio at a temperature ranging between 560–540°C for three months, with iodine acting as a transport agent. Notably, the cubic FeGe phase existed below 750°C and lacked a liquid phase, rendering the LFZ and Czochralski methods unsuitable.

Organic chiral molecule on chiral substrate

The achievement of an absolute homochiral state from a racemic mixture necessitates the introduction of an initial bias through the action of a symmetry-breaking agent such as circularly polarized light, spin-polarized electrons, or muons. This initial imbalance is then autocatalytically amplified to attain a homochiral state. We examined the influence of homochiral topological intermetallic PdGa crystals on the crystallization of organic chiral molecules, e. g. amino acids and sugars. The results demonstrate that chiral PdGa, when used as a substrate, directs the spontaneous crystallization of these chiral compounds in an enantioselective manner. This interaction was followed by charge polarization, resulting in a spin-selective interaction that leads to preferential crystallization of the enantiomer with the favored spin–spin interaction. The intrinsic chirality of PdGa simplifies the experimental conditions compared to previous reports and reduces the complexity of the underlying mechanism governing this enantioselectivity. Before commencing the crystallization experiment, we performed a confirmation procedure to ascertain that the mixture of the chiral was fully racemic. This involved the measurement of the circular dichroism (CD) spectra. In a typical crystallization experiment, the PdGa substrates were placed in a petri dish containing a supersaturated aqueous racemic mixture of Hexagonal crystals were obtained in few hours to few days depending on the growth, collected, dissolved in water, and subjected to CD spectroscopy measurements (Figure 6). The crystals collected from the entire surface exhibited optically active CD spectra with opposite directions of the spectra for the crystals collected from the PdGa substrate with opposite handedness. Our findings indicate that electron spin is strongly coupled with molecular chirality, independent of other factors, such as the magnetochiral effect.

As in the preceding three years, the growth of chiral crystals exhibiting homochirality was successfully achieved using the LFZ and Czochralski methods, in which a seed crystal of intended handedness is always required. Once growth is initiated, it is no longer possible to exert control over the handedness of the resulting piece, which is formed in a single handedness. It would be beneficial to ascertain whether it is possible to control the chirality or change the handedness during the growth process. It seems reasonable to posit that the use of chiral light may prove an effective means of controlling the handedness of a chiral crystal, given the sensitivity to such radiation. Therefore, one potential method for modifying the handedness of a homochiral crystal during its growth is through the use of a circularly polarized laser light. Such experiment will be conducted in collaboration with Prof. Stephen Wilson,

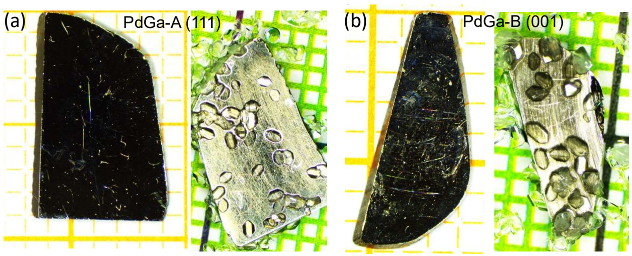

Fig. 6: (a) Bare PdGa-A (111) substrates and enantioselective growth of organic chiral crystals on the corresponding substrate. (b) The same enantioselective growth of organic chiral crystals on (001) substrate.

UC Santa Barbara, USA. Contrarily, the CVT and flux techniques resulted in the formation of crystals exhibiting handedness within the same batch of growth. This limitation can be circumvented by using chiral transport agents, magnetic fields, and chiral fluxes. The impact of an external magnetic field on crystal growth will be examined in future studies. Experiments on the deposition of crystals on substrates have also been initiated to systematically investigate the influence of the substrate on crystal growth. The crystal growth of selected chemical transport reactions will be investigated in situ using optical methods to enhance comprehension and control of crystal growth and to determine the optimal time for crystallization.

References

[1]* *Chirality in the Solid State: Chiral Crystal Structures in Chiral and Achiral Space Groups, G. H. Fecher, J. Kübler, C. Felser, Materials* ***15*** *(2022) 5812,* *https://doi.org/10.3390/ma15175812*

[2]* *Topology and Chirality, C. Felser, J. Gooth, Chiral Matter: Proceedings of the Nobel Symposium 167 (2023) 115,* *https://doi.org/10.1142/9789811265068_0010*

[3]* *Chiral Quantum Materials: When Chemistry Meets Physics, X. Wang, C. Yi, C. Felsr, Adv. Mater.* ***36*** *(2024) 2308746,* *https://doi.org/10.1002/adma.202308746*

[4]* *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, C. Felser, Angew. Chem. Int. Ed.* ***62*** *(2023) e20230329,* *https://doi.org/10.1002/anie.202303296*

[5] *Enantioseparation by crystallization using magnetic substrates, F. Tassinari, J. Steidel, S. Paltiel, C. Fontanesi, M. Lahav, Y. Paltiel, R. Naaman, Chem. Sci.* ***10*** *(2019) 5246,* *https://doi.org/10.1039/C9SC00663J*

[#] kakali.santra@cpfs.mpg.de

[##] chandra.shekhar@cpfs.mpg.de