Single crystal growth for topology and beyond

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Single crystals are the pillars for many technological advancements, which begin with acquiring the material. Since different compounds have different physical and chemical properties, different techniques are needed to obtain their single crystals. New classes of quantum materials, from insulators to semimetals, that exhibit non-trivial topologies, have been found. They display a plethora of novel phenomena, including topological surface states, new fermions such as Weyl, Dirac, or Majorana, and non-collinear spin textures such as antiskyrmions. To obtain the crystals and explore the properties of these families of compounds, it is necessary to employ different crystal growth techniques such as the chemical vapour transport method, Bridgman technique, flux growth method, and floating-zone method. For the last four years, we have grown more than 150 compounds in single crystal form by employing these methods. We sometimes go beyond these techniques if the phase diagram of a particular material allows it; e.g., we choose the Bridgman technique as a flux growth method. Before measuring the properties, we fully characterize the grown crystals using different characterization tools. Our TaAs family of crystals have, for the first time, been proven experimentally to exhibit Weyl semimetal properties. They exhibit extremely high magnetoresistance and mobility of charge carriers, which is indicative of the Weyl fermion properties. Moreover, a very large value of intrinsic anomalous Hall and Weyl physics with broken time-reversal symmetry is found in the full-Heuslers, while the half-Heuslers exhibit topological surface states. Among our grown crystals of topological compounds, WP_2, MoP_2, and MoP crystals show an anomalously very low resistivity of up to 3 nΩ cm. These excellent properties of the different crystals of topological materials validate the quality of crystals grown by us.

A single crystal is a repeating arrangement of atoms, ions, or molecules in three dimensions throughout the volume. Without crystals, the electronics and photonics industry, and fibre-optic communications would not have been imagined; crystals are the unacknowledged pillars of technology. It is clearly more difficult to grow single crystals, and it requires extra attention. This extra effort is justified in terms of their outstanding advantages over polycrystalline materials, such as uniformity, anisotropy, and the absence of grain boundaries. Many physical properties of materials are complicated by the effect of grain boundaries, and single crystals are necessary to determine the actual physical properties. Particularly, our transport experiments for realizing surface states in topological insulators, visualizing quantum oscillations for establishing the fermiology, etc. require high-quality single crystals. Obtaining a high-quality crystal is a very challenging task, and depending on the physical properties of the crystal and its constituent elements, a suitable growth route can be chosen. We mainly grow the crystals using the flux growth method, Bridgman technique, chemical vapor transport, and optical floating-zone method. Single crystals can be directly obtained, or cut from ingots, depending on the crystal growth technique.

Many different alloying techniques for metals, and methods for the synthesis of inorganic materials, are commonly used. Radio-frequency melting, arc melting, and suction and tilt casting are used to prepare ingots, whereas ball milling and melt spinning are used to obtain nano- and micro-textured powders. Many glove box systems, that protect all the materials against the reaction with oxygen and moisture, are available. One laboratory is especially designed for the synthesis of extremely air-sensitive materials using Schlenk-line techniques. High-pressure high-temperature synthesis (autoclave technique and high hydrostatic pressure setup) is also available, as well as the ability to handle toxic materials such as Hg, As, Cd, etc. For heat treatment furnaces operating at different temperature regimes, vacuum or reactive/non-reactive gases are used. Different types of zone-wise temperature-controlled furnaces and different temperature ranges are used to obtain single crystals.

Chemical vapor transport method

Chemical vapor transport (CVT) reactions are a versatile method for the synthesis and crystal growth of a wide variety of inorganic compounds. A condensed phase is volatilized by the reaction with a gaseous transport agent, and deposits elsewhere in the form of crystals, owing to a mass transfer achieved by a temperature gradient.

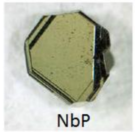
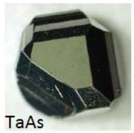
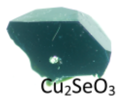
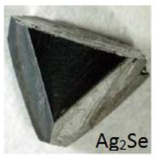
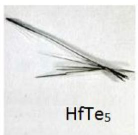
Compound type		**Composition**	**Optical image of the crystal**
Intermetallic		CrGe, FeSi, FeGe, CoSi	
Pnictide	Phosphide	CrP, NbP, MoP, MoP_2, TaP, WP_2	 
	Arsenide	CrAs, NbAs, $NbAs_2$, $MoAs_2$, Cd_3As_2, TaAs, $TaAs_2$, WAs_2	 
Antimonide		$CoSb_3$, $NbSb_2$, $TaSb_2$	
Oxide		Rh_2O_3, ReO_2, RuO_2, OsO_2, IrO_2, Cu_2OSeO_3, $SrPd_2O_4$, $PtCoO_2$	 
Chalcogenide	Sulfide	MnS, CoS_2, PdS_2, TaS_2, HfSiS, $BiSbTe_2S$	
	Selenide	$TiSe_2$, MnSe, FeSe, $FeSe_2$, $CoSe_2$, $NiSe_2$, $CuSe_2$, $ZrSe_2$, $NbSe_2$, $MoSe_2$, $RuSe_2$, $RhSe_2$, $PdSe_2$, Ag_2Se, $TaSe_2$, WSe_2, $ReSe_2$, $OsSe_2$, $IrSe_2$, $PtSe_2$, Bi_2Se_3	
	Telluride	MnTe, FeTe, $NiTe_2$, GeTe, ZrTe, $ZrTe_3$, $ZrTe_5$, $NbTe_2$, $MoTe_2$, Ag_2Te, SnTe, Sb_2Te_3, $HfTe_2$, $HfTe_5$, $TaTe_2$, WTe_2, $OsTe_2$, Bi_2Te_3	
	Halide	CrI_3, $RuCl_3$, Ta_2Se_8I	

Table -1: Optical images of chemical vapour transport growth crystals. At least one dimension of the crystal is 0.5 mm.

Over the last 3 years, many compounds of different classes, e.g., intermetallics, pnictides, oxides, antimonides, and chalcogenides, have successfully been grown using CVT reactions. The crystals that have been grown by this method are given in Table 1, and their growth facets can be seen in the optical images. These high-quality crystals exhibit topological characteristics in physical property measurements. The selection of the CVT reaction is based on the following conditions:

- One or more components of the compounds have a high vapor pressure at the melting temperature.
- The compounds have high melting temperature.
- The formation of the compounds is peritectic or peritectoid.
- The compounds merely have small phases in the subsolidus region.
- The compounds are not crystallizable from the melt (low-temperature modifications; e.g., FeGe).
- The compounds differ only slightly in their chemical composition.

Chemical transport is characterized by the reaction of a solid material which volatilizes in the presence of a

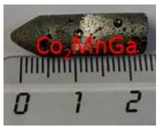
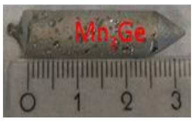
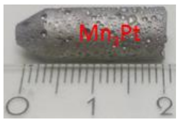
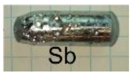
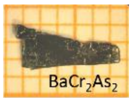
Compound type	**Composition**	**Optical image of the crystal**
Heusler	Co_2MnGa, Co_2VGa, Co_2FeGa, Co_2CrGa, Mn_2CoGa, Mn_2CrGa, Mn_2FeGa, CoFeMnSi, $Co_2V_{0.8}Mn_{0.2}Ga$	 
Non-collinear AFM	Mn_3Ge, Mn_3Sn, Mn_3Ir, Mn_3Pt, Mn_3Rh, Mn_3IrGe, MnPtGa	 
Chiral	RhSi, AlPt	
Elemental	Bi, Sb, Te	 
Pnictide	$BaCr_2As_2$, $BaCrFeAs_2$, MnP	

Table -2: Optical images of Bridgeman growth crystals on an mm scale.

gaseous reactant and deposits elsewhere in the form of crystals. The driving force for the mass transfer between the dissolution and deposition zones is a potential gradient which is usually achieved by temperature differences. The deposition will take place if the volatilization and crystallization zones have different temperatures. According to the mass transport, the back reaction takes place with the separation of a solid from the gas phase. Different models have been developed to describe chemical transport and its theoretical principles. Because chemical transport reactions can be described by thermodynamic laws, efficient transport agents can be used to accelerate the transport reaction conditions. The choice of agents and control of the growth parameters are very important. The composition of the crystals mainly depends on the starting composition, temperatures of the source and sink, pressure inside the transport ampoule, as well as the quantity of the source material.

These crystals demonstrate excellent properties, and achieve the criteria of the theoretical predictions. The TaAs family (NbP, TaP, NbAs and TaAs) of crystals is grown by CVT in the 800–1000 °C temperature range, and this family is the first experimentally proven Weyl semimetal family in which the Weyl nodes and Fermi arc have been observed by angle-resolved photo-emission spectroscopy (ARPES) [1, 2] and scanning tunneling microscopy (STM) [3]. NbP and TaP show extremely high mobility and magnetoresistance [4, 5], while HfSiS exhibits a massive amplitude in quantum oscillations. The mobility of the charge carrier helps enhance the H_2 evolution reaction through catalytic activity [6]. Interestingly, TaAs shows super-conductivity at 7 K [7]. WP_2, MoP_2, and MoP exhibit an anomalously low resistivity up to 3 nΩ cm, which suggests a hydrodynamic electron fluid [8, 9].

Bridgman technique

The Bridgeman technique is a versatile method to grow crystals, even if the melting point of the compound is high. In this method, a vertical crucible containing the melt moves slowly, relative to a temperature gradient. When the crucible leaves the hot zone, solidification takes place at the bottom. Nucleation of a very small part of the sample is needed to reduce the number of grains. This can be achieved using a pointed-tip-shaped crucible. Bridgeman-grown crystals are rod-shaped ingots and consist ideally of only one grain, but often, a rod consists of different grains. In this case, single grain areas are identified using the Laue technique, and thereafter, a single grain (which is a single crystal) can be cut from the rod. The Bridgeman technique can only be used if the desired compound can exist in equilibrium with the liquid. The method is optimum for congruent melting phases. However, off-stoichiometry is also used to obtain an equilibrium phase in particular

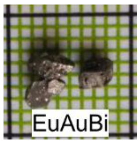
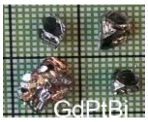
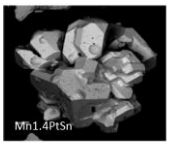
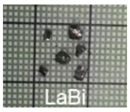
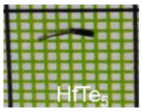
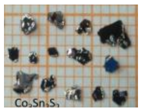
Compound type	**Composition**	**Optical image of the crystal**
Heusler and related structure	$YbMnBi_2$, CuMnAs, VAl_3, MnAs, EuAuBi,	 
Half-Heusler	YPtBi, NdPtBi, GdPtBi, ErPtBi, YbPtBi, ScPdBi, YPdBi, ErPdBi, GdAuPb, HoPdBi, TbPdBi, TbPtBi, DyPtBi	 
Antiskyrmion	$Mn_{1.4}PtSn$	
Chalcogenides and Pnictides, Antimonide, Shandite etc.	Bi_2Te_2Se, Bi_2Te_3, Bi_2Se_3, KHgSb, KHgBi, LaBi, LaSb, GdBi, GdSb, $HfTe_5$, CaAgAs, $PtSe_2$, $PtTe_2$, KMgSb, KMgBi, $PdSb_2$, Bi_4I_4, $Co_3Sn_2S_2$	  

Table -3: Optical images of flux growth crystals on an mm scale.

cases, and an extra amount of component is segregated at the side of the rod.

By employing the Bridgeman technique, we have grown a series of crystals of different materials as shown in Table 2, which contains Heuslers, silicides, Ge, Ga, Mn, and Pt element-containing binary compounds, etc. Co_2MnGa, the first three-dimensional topological magnet, shows one of the highest anomalous Hall conductivities (AHC) (~1600 Ω^{-1} cm^{-1}) at 2 K and the highest known anomalous Hall angle (AHA) (up to 12%) of any magnetic Heuslers at room temperature [10]. We observed a remarkably high anomalous Nernst thermopower S_{yx}^{A} of ~6.0 µV K^{-1} at a 1 T magnetic field.

Flux growth method

Another crystal growth method is solution growth. A melt of appropriate composition is slowly cooled down in a suitable crucible placed in a furnace with a homogenous temperature distribution and a highly precise temperature regulation. If the solvent provides atoms to the compound being formed, the technique is also known as reactive flux or self-flux. The starting composition has to be chosen according to the phase diagram or is based on the information obtained from thermal analysis. After homogenization of the melt, well above the liquidus, the temperature is almost isothermally decreased. The crystals are then obtained by decanting the liquid through a centrifuge at an appropriate temperature chosen according to the phase diagram. Decanting is an important step in which the flux is separated from the crystals. The grains are often well faceted; hence, crystal orientation can be done manually. If seeding or nucleation is not possible, several crystals grow together as a result of intergrowth. In such cases, a single grain material is then obtained by manual selection. Solution growth is

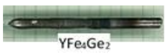
Compound type	**Composition**	**Optical image of the crystal**
Heusler	$Ni_2Mn_{1.4}In_{0.6}$ $Ma_{1.4}PtSn$	 
Antiferromagnet	YFe_4Ge_2	

Table -4: Optical images of optical floating zone growth crystals on mm scale.

generally used when at least one of the constituting elements has a low melting point (< 500 °C) in self-flux, or another low-melting-point foreign element is chosen as a flux, according to the phase diagram of the desired crystal. The whole solution of the compound exists in equilibrium with the flux.

We have grown half-Heusler compounds containing the elements Bi and Sb, chalcogenide series of topological insulators, shandites, and many other Dirac and Weyl semimetals by the flux method; they are listed in Table 3. Our ARPES investigations of the half-Heusler compounds YPtBi and LuPtBi show metallic topological surface states [11], while the chalcogenide topological insulator exhibits evidence of surface transport in resistivity measurements. Very recently, we have grown the shandite $Co_3Sn_2S_2$, which is expected to show a high anomalous Hall parameter value due to the presence of a Kagome lattice of spin structure.

Floating zone method

The optical floating-zone is a very powerful and highly efficient technique to grow high-quality single crystals of various metal oxides as well as intermetallic compounds. This is a crucible-free method where the crystals are grown from the melt, for both conducting and non-conducting materials. This optical heating shows a major advantage over other induction- or electron-beam-type heating, where only conducting samples can be grown. Furthermore, the single crystals of various congruently and incongruently melting compounds can be easily grown using this method.

We employed a four-mirror optical floating-zone furnace (FZ-T-10000-H-HR-I-VPM-PC, procured from Crystal Systems Inc., Japan) with halogen lamps having a maximum power of 6 kW. The four ellipsoidal mirrors focus the light from the halogen lamps onto a vertically held feed rod. The feed rod is made of the same target compound to grow the single crystal. A seed rod, which can be polycrystalline or a previously grown single crystal of the same compound, is also used. Then, a molten zone is formed and held between the seed and feed rods by the material surface tension. After stabilization, the molten zone is moved along the length of the feed rod to grow the single crystal. The growth rate can be up to 300 mm h^{-1}, and the maximum temperature that can be reached is up to 2200 °C. The rotation of the upper and lower shafts can be independently controlled between 5 and 100 rpm, while the total length of the grown crystal can be as long as 150 mm. The stability of the molten zone is monitored by visualizing the growth through an attached CCD camera. The crystals can be grown under different atmospheres such as O_2, Ar, and air with the maximum pressure up to 10 bar. A magnetic liquid sealing helps to maintain the high-quality atmospheric state in high-vacuum as well as high-pressure conditions. We have grown various Heusler-based intermetallic alloys using this optical floating-zone technique, as presented in Table 4.

After a successful growth of the crystals, we employed a large variety of characterization techniques, and each crystal was characterized with regard to its bulk chemical composition, phase composition and fractions, crystal structures, disorder, defects, and microstructure. ICP-OES and MS were used for the chemical analysis of majority of the components and of impurities, respectively. Light-weight elements like hydrogen, carbon, nitrogen, and oxygen were determined by combustion analysis or hot-gas extraction. Single crystal X-ray and powder X-ray diffraction (in-house, and synchrotron at ESRF, Grenoble) were used for crystal structure determination and phase analysis. Neutron diffraction (neutron sources: FRM II (Garching, Germany), ILL (Grenoble, France), LLB (Saclay, France), and BER II (Berlin, Germany)) was typically used to determine the magnetic structures.

Outlook

Recently, two groups of scientists developed a database of topological materials comprising thousands of compounds from extant databases of materials. To enable the growth of crystals from distinct families of materials, we have extended our single crystal growth facilities to include a floating zone instrument and a rod casting machine. These new crystal growth capabilities will allow us to grow more challenging chiral crystals in the future. One of our main ambitions is to design materials that will allow us to achieve the quantum anomalous Hall effect in a layers of magnetic Weyl semimetals and previously undiscovered quantum effects.

External Cooperation Partners

Y. Chen (Physics Department, Oxford University, Oxford, UK); H. Beidenkopf (Weizmann Institute of Science, Israel); C. N. R. Rao (JNCASR, Bangalore, India); P. Werner (MPI Halle, Germany); G. Sheet (IISER, Mohali, India)

References

[1]* *Weyl semimetal phase in the non-centrosymmetric compound TaAs, L. X. Yang, Z. K. Liu, Y. Sun, H. Peng, H. F. Yang, T. Zhang, B. Zhou, Y. Zhang, Y. F. Guo, M. Rahn, D. Prabhakaran, Z. Hussain, S.-K. Mo, C. Felser, B. Yan and Y. L. Chen, Nat. Phys.* ***11*** *(2015) 728.*

[2]* *Evolution of the Fermi surface of Weyl semimetals in the transition metal pnictide, Z. K. Liu, L. X. Yang, Y. Sun, T. Zhang, H. Peng, H. F. Yang, C. Chen, Y. Zhang, Y. F. Guo, D. Prabhakaran, M. Schmidt, Z. Hussain, S.- K. Mo, C. Felser, B. Yan and Y. L. Chen, Nat. Mater.* ***15*** *(2016) 27.*

[3]* *Visualizing weakly bound surface Fermi arcs and their correspondence to bulk Weyl fermions, R. Batabyal, N. Morali, N. Avraham, Y. Sun, M. Schmidt, C. Felser, A. Stern, B. Yan and H. Beidenkopf, Sci. Adv.* ***2*** *(2016) e1600709.*

[4]* *Extremely large magnetoresistance and ultrahigh mobility in the topological Weyl semimetal candidate NbP, C. Shekhar, A. K. Nayak, Y. Sun, M. Schmidt, M. Nicklas, I. Leermakers, U. Zeitler, Y. Skourski, J. Wosnitza, Z. Liu, Y. Chen, W. Schnelle, H. Borrmann, Y. Grin, C. Felser and B. Yan, Nat. Phys.* ***11*** *(2015) 645.*

[5]* *Negative magnetoresistance without well-defined chirality in the Weyl semimetal TaP, F. Arnold, C. Shekhar, S.- C. Wu, Y. Sun, R. D. d. Reis, N. Kumar, M. Naumann, M. O. Ajeesh, M. Schmidt, A. G. Grushin, J. H. Bardarson, M. Baenitz, D. Sokolov, H. Borrmann, M. Nicklas, C. Felser, E. Hassinger and B. Yan, Nat. Commun.* ***7*** *(2016) 11615.*

[6]* *Weyl Semimetals as Hydrogen Evolution Catalysts, C. R. Rajamathi, U. Gupta, N. Kumar, H. Yang, Y. Sun, V. Süß, C. Shekhar, M. Schmidt, B. Yan, S. S. P. Parkin, C. Felser and C. N. R. Rao, Adv. Mater.* ***29*** *(2017) 1606202.*

[7]* *Mesoscopic superconductivity and high spin polarization coexisting at metallic point contacts on Weyl semimetal TaAs, L. Aggarwal, S. Gayen, S. Das, R. Kumar, V. Süß, C. Felser, C. Shekhar and G. Sheet, Nat. Commun.* ***8*** *(2017) 13974.*

[8]* *Extremely high magnetoresistance and conductivity in the type-II Weyl semimetals WP_2 and MoP_2, N. Kumar, Y. Sun, N. Xu, K. Manna, M. Yao, V. Süß, I. Leermakers, O. Young, T. Förster, M. Schmidt, H. Borrmann, B. Yan, U. Zeitler, M. Shi, C. Felser and C. Shekhar, Nat. Commun.* ***8*** *(2017) 1642.*

[9]* *Extremely high conductivity observed in the unconventional triple point fermion material MoP, C. Shekhar, Y. Sun, N. Kumar, M. Nicklas, K. Manna, V. Süß, O. Young, I. Leermakers, T. Foerster, M. Schmidt, L. Muechler, P. Werner, W. Schnelle, U. Zeitler, B. Yan, S. S. P. Parkin and C. Felser, arXiv:1703.03736 (2017).*

[10]* *From colossal to zero: Controlling the Anomalous Hall Effect in Magnetic Heusler Compounds via Berry Curvature Design, K. Manna, L. Muechler, T. H. Kao, R. Stinshoff, Y. Zhang, N. Kumar, G. Kreiner, K. Koepernik, R. Car, J. Kübler, G. H. Fecher, C. Shekhar, Y. Sun and C. Felser, Nature Materials, under review, arXiv:1712.10174 (2018).*

[11]* *Observation of unusual topological surface states in half-Heusler compounds LnPtBi (Ln=Lu, Y), Z. K. Liu, L. X. Yang, S.-C. Wu, C. Shekhar, J. Jiang, H. F. Yang, Y. Zhang, S.-K. Mo, Z. Hussain, B. Yan, C. Felser and Y. L. Chen, Nat. Commun.* ***7*** *(2016) 12924.*

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