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# A Retrospective of Materials Synthesis at the Paul Scherrer Institut (PSI)

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## 1. Establishing Material Synthesis at PSI—A. Furrer

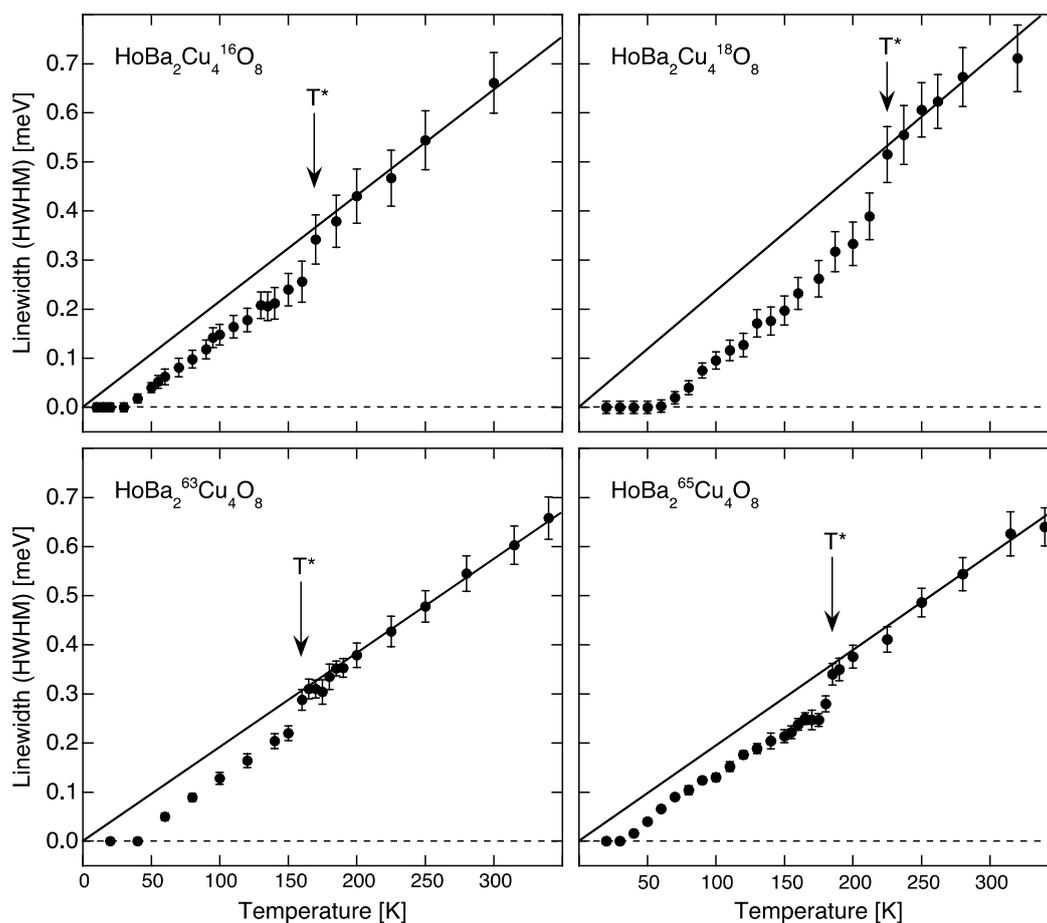
The availability of high-quality and well characterized materials is a key factor for condensed-matter research. The Laboratory for Neutron Scattering at PSI has profited for a long time from extended collaborations with international groups to receive samples for neutron scattering experiments in different fields of science. The situation changed in the year 1986, with the discovery of high-temperature superconductivity in copper-oxide perovskites by Müller and Bednorz [1]. In high- $T_C$  research, the systematic variation of the materials properties is an essential feature, e.g., the variation of the oxygen content. Consequently, the experiments had to be carried out for a large number of systematically varied samples, so that the cooperation with partner groups became rather difficult. It was therefore decided to start in-house efforts for the production of high- $T_C$  materials.

The driving force behind these efforts was Peter Allenspach, who set up a materials synthesis laboratory based on a procedure developed at the Jülich Research Center [2]. In order to obtain sufficient material for neutron scattering experiments, the necessary devices were enlarged up to capacities of 300 g and 30 g for the sintering and oxygen loading furnaces, respectively [3]. Subsequently, the instrumentation of the materials synthesis laboratory was extended to include further devices (e.g., a physical properties measurement system), supported by funds from the Swiss National Science Foundation, the PSI, the ETH Zurich, and the University of Zurich.

Initially, the materials synthesis laboratory operated in a self-service mode. However, this operational mode turned out to be ineffective due to the increasing complexity of the instruments. In the year 1998, Kazimierz Conder took over the responsibility for the materials synthesis laboratory. He further developed the instrumentation, e.g., by crystal-growth devices. Early requests to promote the status of the materials synthesis laboratory to the level of a PSI-group failed, but thanks to the invaluable support by Alex Müller, the group “Materials Synthesis” was installed at PSI in the year 2003 with Kazimierz Conder as group leader. At the same time, Ekaterina Pomjakushina joined the group.

Around the year 2000, the main activities of the materials synthesis laboratory focused on high- $T_C$  superconductors. The concept which led Alex Müller to the discovery of superconductivity in the cuprates was the vibronic property of the Jahn–Teller effect. Therefore, looking for an isotope effect for both oxygen and copper ions was an obvious task. Neutron crystal-field studies provide relevant information on the pseudogap temperature  $T^*$  through the linewidth of the crystal-field transitions. This method was applied to the compound  $\text{HoBa}_2\text{Cu}_4\text{O}_8$  for both oxygen isotope substitution with  $T_c(^{16}\text{O}) = 79.0(1)$  K and  $T_c(^{18}\text{O}) = 78.5(1)$  K [4] and copper isotope substitution with  $T_c(^{63}\text{Cu}) = 79.0$  K and  $T_c(^{65}\text{Cu}) = 78.6(1)$  K [5]. The corresponding samples were synthesized in the materials synthesis laboratory.

Figure 1 shows the temperature dependence of the intrinsic linewidth (HWHM) corresponding to the lowest-lying crystal-field transition at energy 0.6 meV. There is evidence for large isotope shifts  $\Delta T^*(O) \approx 50$  K and  $\Delta T^*(Cu) \approx 25$  K. The corresponding isotope coefficients  $\alpha^*$  defined by the relation  $T^* \propto 1/M^{\alpha^*}$  ( $M$  is the mass of the O or Cu ion) turn out to be  $\alpha^*(O) = -2.2$  and  $\alpha^*(Cu) = -4.9$ . Giorgio Benedek highlighted the latter coefficient in his lecture presented at an international symposium in Zurich in the year 2006 and suggested to call it the Alfa Romeo number, since Alex Müller is an enthusiastic driver of Alfa Romeo cars, such as the model Alfa Romeo Montreal 4.9.



**Figure 1.** Temperature dependence of the intrinsic linewidth  $W$  (HWHM) corresponding to the lowest-lying crystal-field transition in  $\text{HoBa}_2\text{Cu}_4\text{O}_8$  for different oxygen and copper isotopes [4,5]. The lines denote the linewidth in the normal state calculated from the Korringa law.

## 2. Materials Synthesis at PSI from the Past to Nowadays—K. Conder and E. Pomjakushina

### 2.1. HTc and Copper Age at ETH

In 1986, K.A. Müller and G. Bednorz announced discovery of the high-temperature (HTc) superconductivity. Very quickly, many research groups around the world started scientific work on this subject. In the same year one of us (K.C) started an annual scholarship in the group of Professor E. Kaldis in the Laboratory of Solid State Physics (Laboratorium für Festkörperphysik) of the Federal University of Technology (ETH) in Zurich. In addition, also in the group of prof. Kaldis, superconductors quickly displaced other subjects. Among others, a pioneering work of Dr. Karpinski concerning synthesis of superconductors under high oxygen pressure was at the forefront in the field of HTc superconductors. Additionally, in late 1980s, Prof. K.A. Müller proposed a research project concerning studies of oxygen isotope effects in the HTc superconductors. The project was implemented jointly by the University of Zurich (physical property measurements—group of Prof. H. Keller) and

ETH (sample preparation—group of Prof. E. Kaldis). In this project, sample preparation topic was entrusted to one of us (K.C), creating a unique opportunity to work with the Nobel prize laureate. This collaboration lasted for many years, resulting in over 40 publications.

### 2.2. Oxygen Isotope Effect in $YBa_2Cu_3O_{7-x}$

The discovery of the isotope effect in superconductors in the 1950s created an experimental foundation for the BCS (Bardeen, Cooper, and Schrieffer) theory, which is a microscopic theory of superconductivity announced in 1957 (Nobel Prize in 1972). In a classic experiment, a linear relationship between the temperature of the transition to the superconducting state  $T_C$  with the reciprocal square root of the mass of the mercury isotopes was achieved. This pointed out that the appearance of superconductivity is correlated with the energy of the crystal lattice vibrations, which in turn is determined by the masses of atoms creating crystal lattice. This led to the conclusion that the charge carriers in the superconducting state are formed by pairs of electrons (Cooper pairs). Thus, the electrons interact each other through the crystal lattice (electron-phonon interaction). For the HTc superconductors, Prof. K.A. Müller suggested studies of the critical temperature of the “most famous” superconducting material, i.e.,  $YBa_2Cu_3O_{7-x}$  (YBCO) synthesized with oxygen isotopes  $^{16}O$  and  $^{18}O$ . At this time, several papers on the isotope effect in HTc superconductors were already published, but the results presented were inconclusive; either very small or no effect were reported. In addition, Prof. K.A. Müller was interested in the selective isotopic effect, i.e., the effect caused by the substitution of the oxygen isotope at different sites in the unit cell (in the structure of YBCO there are three symmetrically independent oxygen sites). From the beginning, it was clear that the task is very difficult. First of all, the isotope effect was expected to be very small (a fraction of Kelvin). Additionally, it was known that  $T_C$  of YBCO decisively depends on the oxygen stoichiometry in the compound. The key issue was, therefore, to achieve an extremely high reproducibility of the sample preparation procedure. The samples could not differ in any property, besides the oxygen isotope used. Thus, it was necessary to develop a method of extremely accurate determination the oxygen content in YBCO. Apart from that, it was unavoidably to check whether the site-selective isotopic exchange is at all possible. This required comprehensive studies of the kinetics of the oxygen isotope exchange in YBCO. Based on such studies, a series of YBCO samples completely and selectively substituted with the oxygen isotope  $^{18}O$  were made. Magnetization measurements conducted at the University of Zurich (D. Zech in the group of Prof. H. Keller) showed that the overall isotope effect although very small (0.2 K) comes entirely from the  $CuO_2$  planes in the structure. The results were published in *Nature* in 1994 [6]. Following this work, oxygen isotope effect in other high-temperature superconductors and also related materials, e.g., magnetoresistive or exhibiting a metal-insulator transition were performed. This scientifically fruitful period ended in the late nineties with a retirement of Prof. E. Kaldis and a dissolution of his group. It was again initiative and a great commitment of Prof. K.A. Müller to transfer the “superconductivity-isotope” research from ETH to Paul Scherrer Institute (PSI). Fortunately, thanks to the interest and great efforts of Prof. A. Furrer, the head of the Laboratory for Neutron Scattering (LNS) of the time, it became possible. Over the years, we were able to endow our laboratory with equipment for syntheses of ceramic materials, crystal growth (zone melting method using a mirror furnace), as well as characterization instruments (thermal analysis, X-ray diffractometers, micro X-ray fluorescence). The staff of the group also increased over time.

### 2.3. HTc Projects at PSI

One of the first tasks at PSI was inspired by an announcement by Reich and Tsabba [7] about a possible nucleation of superconducting regions with  $T_C = 90$  K on the surface of Na-doped  $WO_3$  crystals. It would be the only superconducting material containing no copper, with  $T_C$  higher than boiling point of liquid nitrogen at normal pressure. Our attempts to examine these materials continued (with many interruptions!) for several years. Unfortunately, due to the possibly filamentary character

of the superconductivity in these materials, we were unable to draw decisive conclusions. A recent work [8] summarizes the results obtained.

The other subjects of the research, carried out at PSI were initially mostly associated with the isotope effect. For example, it was found that oxygen isotope substitution very strongly influences the temperature of the so-called “pseudogap” opening [4]. The isotope effect on pseudogap was also detected by the substitution of natural copper with 63 and 65 copper isotopes [5]. In collaboration with other laboratories (LMS PSI, Physik Institut Universität Zürich), we found that in the case of the HTc-superconductors the isotopic substitution of oxygen also influences other properties, such as magnetic penetration depth, the Néel temperature and the linewidth of the paramagnetic resonance EPR signal.

#### 2.4. Establishing Traveling Solvent Floating Zone Crystal Growth

Later, more and more, the work was concentrated on synthesis, crystal growth and investigating of oxide materials with interesting electrical and magnetic properties. Such materials are, among others, layered cobaltites  $\text{RBaCo}_2\text{O}_{5+x}$  (R = rare earth metal) interesting family of complex oxides with strongly correlated electrons. Layered cobaltites exhibit a number of interesting properties associated with a possibility to adopt different oxidation states by the cobalt cations (II, III, IV) and also different spin states: low, intermediate and high. Thus, these materials exhibit metal-insulator transition at temperatures near room temperature and interesting magnetic properties including giant magnetoresistivity (GMR). All these properties decisively dependent on the oxygen content ( $0 < x < 1$ ), being therefore graceful working subject for chemists. The most interesting were studies of magnetic properties of these compounds. On the basis of the measurements of the spin polarization and the muon spin rotation method ( $\mu\text{SR}$ ), different magnetic phases have been identified characterized by the arrangement of the cobalt in the various spin states. A phase diagram was developed showing temperature ranges of existence of different magnetic phases, as well as ranges of their coexistence [9]. We also reported on oxygen isotope effect on metal-insulator transition temperature in  $\text{RBaCo}_2\text{O}_{5.5}$  (R = Pr, Dy, Ho and Y) [10].

The TSFZ (Traveling Solvent Floating Zone) method of the crystal growth quickly became a specialty of our laboratory. Starting from 2003, we were able to synthesize many materials in a single crystalline form. These were, among others, superconductor  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , frustrated magnet  $\text{YMnO}_3$ ,  $\text{LaCoO}_3$ —showing high, medium and low-spin states of cobalt, multiferroic  $\text{LuFe}_2\text{O}_4$ , two-dimensional antiferromagnetic  $\text{SrCu}_2(\text{BO}_3)_2$  and  $\text{YFeO}_3$  showing magneto-optic Kerr effect. All these crystals and many other materials obtained in the crystalline and polycrystalline forms were often produced on the “order” of physicists from PSI or other research institutions in Switzerland. The materials were used for scientific studies, usually using available at PSI research facilities as large-scale neutron diffraction and synchrotron sources.

It is believed that in cuprates, the two-dimensional square lattice  $\text{CuO}_2$  layers in the structure are responsible for the superconductivity. Therefore, cuprates having in the structure Cu-O layers of different geometry and stoichiometry are of particular interest. Some years ago, great interest was awakened with the cuprate family of the formula  $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$  containing in the structure Cu-O layers of a geometry resembling a ladder (known as “spin ladders”) and stoichiometry  $\text{Cu}_2\text{O}_3$ . These are the only cuprates, besides those containing  $\text{CuO}_2$  layers, which exhibit superconductivity although only at high pressures and large calcium contents ( $x > 10$ ). In these compounds, due to the certain geometry of the Cu-O layers, anisotropy of the transport properties in normal and the superconducting state are particularly important. Together with a partner from India, we performed during 2009–2014 scientific project focused on studies of properties of this compound under uniaxial pressure (i.e., applied along different crystallographic directions). The success of this project was dependent on an availability of single crystals of these compounds. We managed to grow a series of  $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$  crystals by TSFZ method under elevated oxygen pressure [11]. The studies of electrical and magnetic properties, made by our partner, indicate that the mechanical pressure applied along the *c*-direction changes the

nature of the conductivity from one- to the two-dimensional. This increases the critical temperature of superconductivity from previously reported 12 K (using hydrostatic pressure) to 25 K [12]. We also elaborated  $\text{BiCu}_2\text{O}_2\text{PO}_4$ , another compound having in the structure Cu-O layers with a special geometry [13].

### 2.5. Iron Era

The discovery of superconductivity in 2008 in iron compounds (chalcogenides, pnictides and phosphides) was absolutely unexpected, because of the presence in the structure of magnetic iron ions. Iron selenide FeSe has, among these compounds, the simplest structure but also the lowest critical temperature (approx. 8 K). We performed many syntheses experiments [14] and studies of structural, superconducting [15] and magnetic [16] properties. We also synthesized a series of samples with iron isotopes. Here, as in the case of cuprates, reproducibility of preparation was essential for the reliability of the results obtained. It turned out that the isotope effect is very similar to that expected for the conventional superconductors [17].

For iron selenides, substituting half selenium with tellurium increases the critical temperature from 8 to 14 K. In addition, such mixed compounds melt congruently and can be crystallized using the Bridgman method. We have grown a series of crystals of  $\text{Fe}_{1.03}\text{Se}_x\text{Te}_{1-x}$  with  $0 < x < 0.5$ . Based on measurements of magnetization and muon spin rotation, a coexistence of magnetism and superconductivity in these compounds was shown [18].

In 2010, superconductivity with a critical temperature of  $T_C \approx 31$  K in iron chalcogenide intercalated with potassium  $\text{K}_x\text{Fe}_2\text{Se}_2$  was reported. In a short time, we managed to synthesize the next member of this “family”:  $\text{Cs}_{0.8}(\text{FeSe}_{0.98})_2$  [19]. For this family of superconducting compounds, we found that superconductivity coexist with magnetism [20]. Detailed structural studies [21,22], muon spin rotation investigations [23] and microscopic examinations [24] showed a coexistence (at temperatures below 420 K) of two phases with compositions similar to  $\text{AFe}_2\text{Se}_2$  and  $\text{A}_2\text{Fe}_4\text{Se}_5$  ( $A = \text{K, Rb or Cs}$ ). The first one, comprising only approx. 10% of the volume of the sample, becomes superconducting below  $\approx 30$  K, the latter is the antiferromagnetic showing ordered iron vacancy pattern. Our work on alkali metal intercalated iron chalcogenides is presented in a review paper [25].

### 2.6. Stabilization of Transition Metals in High Oxidation States under High Oxygen Pressure

In 2013, our group became a partner in the SNF Sinergia project “Mott Physics Beyond the Heisenberg Model (MPBH)”, which was lasted for seven years and connected researchers across Switzerland in a collective effort to explore new aspects of Mott-physics, such as how a spin-orbit interaction in concert with strong electron correlations can lead to new and exotic quantum materials. The network consisted of researchers hosted by the Ecole Polytechnique Fédérale Lausanne (EPFL), the Paul Scherrer Institute (PSI) and University of Zurich (UniZH). The solid state chemistry group was working in materials discovery part of the project with a focus on iridate compounds. Iridates containing iridium at +VI oxidation state are of great interest in order to reveal the relative contribution of Spin Orbit Coupling effect in 5d compounds. The stabilization of Ir in the high oxidation state often needs high pressure. For the planned studies, a unique oxygen high pressure system relocated from Solid State Physics Laboratory ETH in Zürich [26] was used. The system allows synthesis, crystal growth and thermodynamic measurements at oxygen pressures up to 2000 bars and temperature up to 1200 °C. In contrast to cubic anvil devices, the accessible pressure range is an order of magnitude smaller; however, the possible maximum sample volume is much larger ( $10 \text{ cm}^3$  in comparison with  $\text{mm}^3$  as applicable using the anvil system). This is especially important for a preparation of samples useful for neutron scattering experiments. Additionally, oxygen gas pressure apparatus in the existing form allows precise control of a pressure and temperature during synthesis and can also be used for studies of thermodynamics: e.g., measurements of a chemical stability and oxygen stoichiometry under high oxygen pressure.

One of the results was a successful synthesis of the double perovskite  $\text{Sr}_2\text{BIrO}_6$  ( $\text{B} = \text{Ni}, \text{Cu}$  and  $\text{Zn}$ ) in the high oxygen pressure furnace and determination of a novel magnetic structure with an incommensurate propagation vector along the body diagonal, which has not been seen in double perovskites yet [27]. The incommensurate structure can be explained by the intrinsic frustration between the ferromagnetic coupling of nickel-iridium bonds and the antiferromagnetic iridium-iridium coupling.

With the above-mentioned high-pressure setup, we also have found a new chemical route to synthesize  $\text{Tm}_2\text{Mn}_2\text{O}_7$  pyrochlore, which is thermodynamically unstable at ambient pressure. Differently from the reported in the past high-pressure synthesis of the same compound applying oxides as starting materials, we obtained a pure  $\text{Tm}_2\text{Mn}_2\text{O}_7$  phase by a converting  $\text{TmMnO}_3$  at 1100 °C and an oxygen pressure of 1300 bar [28].

The same year (2015), we started a new project: “High pressure synthesis of iron complex oxides in high oxidation state ( $\text{Fe}^{4+}$ ,  $\text{Fe}^{5+}$ ): mapping between localized and itinerant behavior”. A series of oxygen stoichiometric polycrystalline materials of  $\text{Re}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  ( $\text{Re} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Y}$ ) were synthesized and studied. In this family of compounds iron adopts an average oxidation level higher than  $\text{Fe}^{3+}$ . The preparation of such materials requires high oxidation potential during synthesis, which we obtained using our high-pressure equipment. The aims of this project were to understand crystal and magnetic structure of  $\text{Re}_{1/3}\text{Sr}_{2/3}\text{FeO}_3$  ( $\text{R} = \text{La}, \text{Pr}$ , and  $\text{Nd}$ ), and to provide more information on the metal-insulator transition accompanied by the magnetic transition observed in this system. To disentangle their crystal and magnetic structures we used a combination of neutron powder and single crystal diffraction, neutron spherical polarimetry, and symmetry analysis [29]. One of the main problems when studying these compounds was the fact that two different magnetic structures with possible presence/or absence of iron charge ordering fit equally well neutron diffraction data. Further investigations of doped materials, suppressing possible iron charge ordering are now on the way.

### 2.7. New Techniques for Novel Materials with Topological States

Over time, the limitations of the TSFZ crystal growth system (CSC, Japan), installed in 2003 with a support of the R'EQUIP, were becoming more and more relevant to the further development of our science. First of all, the maximum temperature of growth is limited to 2100 °C. Additionally, many materials, especially oxides, decompose or become oxygen nonstoichiometric at high temperatures. Therefore, to stabilize them, high oxygen pressure during crystal growth is indispensable. In a new R'EQUIP project (2015) we proposed an acquisition of a high temperature crystal growth optical furnace offered by the Scientific Instruments Dresden GmbH (SciDre). This instrument comprises demands of performing crystallization processes at very broad growth temperatures from several hundred up to 2900 °C with simultaneously applied gas pressure up to 150 bars. The project was supported and after the delivery to PSI the HKZ-furnace was assembled and tested on site in 2017 and finally brought into operation in 2018.

Recently discovered new quantum states of matter, such as topological insulators and Weyl semi-metals, attract huge attention from condensed matter physics community, driving a demand for single crystals of these materials. The chemistry of these materials called for new synthesis approaches. Thus, we have implemented two new crystal growth methods into our group: growth from high temperature metal fluxes and chemical transport. Over the past few years, the collaboration established by the group and the large-scale research facilities of PSI has resulted in a good set of scientific publications in very high ranked journals, based on science performed on our single crystals [30]. In a recent work on crystal growth of magnetic Weyl semi-metals, we proved that TSFZ technique is crucial to obtain perfectly stoichiometric  $\text{RAlGe}$  crystals ( $\text{R}$ :rare earth metals) [31]. The availability of large crystals grown with a new TSFZ furnace (HKZ, SciDre) allows the possibility to reveal the interplay between magnetism and the properties of the Weyl state and will result in the discovery of new materials with interesting and potentially applicable electronic and magnetic properties.

Soon after we found the way of crystal growth of  $\text{RAlGe}$ , we reported the discovery of topological magnetism in the candidate magnetic Weyl semimetal  $\text{CeAlGe}$ . Using neutron scattering, we find

this system to host several incommensurate, square-coordinated multi  $\vec{k}$  magnetic phases below  $T_N$ . The topological properties of a phase stable at intermediate magnetic fields parallel to the  $c$ -axis are suggested by observation of a topological Hall effect. Our findings highlight CeAlGe as an exceptional system for exploiting the interplay between the nontrivial topologies of magnetization in real space and Weyl nodes in momentum space [32]. This work is continued with a support of SNF project entitled “Tailoring materials with novel quantum states—exploring magnetic Weyl semimetals”. In this project, we aim to test recent theoretical predictions and search experimentally for materials with novel quantum states. Such ambitious work requires a synergy between different aspects of solid state physics, from theory to experiment linked by material science, requiring elaborate work in the field of synthetic chemistry and crystal growth.

During all these years, the solid state chemistry group at PSI (see Figure A1) was working on the cutting-edge of fundamental science, making our own research in the field of novel materials and providing materials of interest for many groups within and outside PSI. Dozens of PhD students from PSI, ETH, University of Zürich, have made their thesis on materials synthesized in the group. The group was always supported by heads of PSI laboratories, especially LNS, LDM, LMX, and University of Zürich, especially Prof. Hugo Keller. Together with gaining experience in material synthesis, the number of instruments and techniques was incredibly increased, which brings the group to a very high competitive international level.

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## Appendix A

Below are some statistics. Number of group members from 2000 including present (4) and former (13):

- 5 senior researchers—Kazik, Katja, Marisa, Hans, Darek
- 7 PostDocs—Guochu, Anka, Romain, Kathi, Junye, Pascal, Tian
- 5 PhD students—Marian, Ruggero, Shuang, Mickael, Fei
- ~300 papers published



**Figure A1.** Solid State Chemistry Group in April 2016. From left to right: Dariusz Gawryluk, Mickaël Morin, Fei Li, Romain Sibille, Ekaterina Pomjakushina, Marisa Medarde, Kazimierz Conder, Katharina Rolfs.

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