

## Confined Metals and Low Temperature Syntheses

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Within the next decades, modern information and communication technology will approach the length scale of a few nanometers. Besides the limitations of the lithographic process also fundamental problems such as a poor signal-to-noise ratio or unexpected quantum effects will appear. Still a suitable materials basis and a lot of basic knowledge about the physics of such surface-dominated materials are lacking, especially when they are embedded into other materials or exposed to air. Current research just started to look on quantum effects on the surface of nanostructured materials, such as Majorana electrons in topological insulators.

Being chemists, our task is to create new materials suitable for subsequent research on properties and to develop innovative routes of processing. In close cooperation with physicists we are presently exploring the properties of so-called *confined metals* [1]. While most of the synthetic methods out of the wide variety of classical solid state chemistry are not suited for processing metals on the nanoscale, soft chemistry routes must be adopted.

### Confined Metals: Limiting the Mobility of Conduction Electrons

The boundaries between the material classes of metals, semiconductors, and insulators are more vague than often recognized. This becomes apparent when the mobility of the conduction electrons is massively restricted by at least one of the following circumstances: (a) Partial electronic localization in covalent bonds, on ions or in lone-pairs; (b) contrast of bonding interactions in adjacent parts of the structure, i.e. separation of metallic and non-metallic domains; (c) reduced size or dimensionality of metallic domains; (d) real structure effects like impurities, dislocations or grain boundaries. For such cases the terms of *poor metals* or *confined metals* have been coined [1].

Confined metals proved to have particular physical properties, e.g., coexistence of ferromagnetism and superconductivity in the same phase. The latter was found in nanostructured Bi<sub>3</sub>Ni (see below).

Generally, low-valent bismuth compounds are a fertile field for the investigation of the properties of matter at the limit of the metallic state [2]. They comprise metallic nanorods and nanotubes, crystalline metal/salt hybrids, low-dimensional metals, complex intermetallics and unique clusters. Most of these compounds have been obtained by typical high temperature methods, generally crystallization from melts or deposition from the gas phase. The adoption and development of low temperature synthetic routes to inorganic materials, however, did not only reproduce previous results but opened new perspectives.

### Room Temperature Ionic Liquids: A Mighty Tool for the Synthesis of Metal-Rich Compounds

Room temperature ionic liquids (RTIL) are molten salts of only weakly interacting (organic) ions. They have distinct physical properties, such as high thermal stability, wide liquid range, negligible vapor pressure, good ionic conductivity, wide electrochemical window, and high solubility of both organic and inorganic substances. The inherent thermal stability of RTIL permits access to low and moderate temperatures, at which kinetically stabilized phases can be obtained. This soft-chemical approach is common in organic synthesis, catalysis, polymer science, nanotechnology, and in the synthesis of clathrates, and zeolites, but widely unexplored for the preparation of metal-rich compounds.

We succeeded in expanding the span of this technique towards the preparation of cluster compounds by demonstrating that main-group elements (e.g. Ga, In, Sn, Sb, Bi, Se, or Te) and transition elements (e.g. Mo or W) as well as their halogenides are high soluble in Lewis-acidic RTIL [3]. After overcoming the issue of kinetic hindrance of crystallization from such highly viscous media, a wide variety of well-crystallized compounds could be isolated with high yields in uncomplicated one-pot syntheses within only two days [4]. Some examples are Sn[SnCl][W<sub>3</sub>Cl<sub>13</sub>] [5], Bi[Mo<sub>5</sub>Cl<sub>13</sub>]Cl [6,7], [Mo<sub>2</sub>Te<sub>12</sub>]I<sub>6</sub> [8], Te<sub>6</sub>[WOC<sub>4</sub>]<sub>2</sub> [4] and

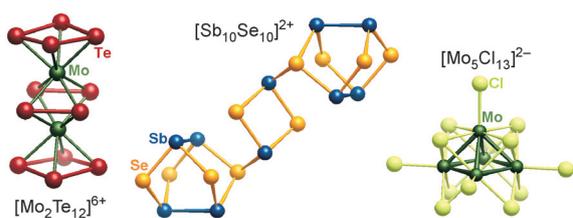


Fig. 1: Clusters from Ionic Liquids.

$[\text{Sb}_{10}\text{Se}_{10}][\text{AlCl}_4]_2$  [9] (Fig. 1). The mild reaction conditions in RTIL minimize the risk of product decomposition, which is a major drawback of high temperature routes. The control of reaction parameters, such as solvent acidity, oxidizing/reducing agent, or halide acceptor, allows optimization of the synthesis and improves reproducibility.

### Microwave-Assisted Polyol Process: Nanoscale Intermetallics at Hand

In addition we established an alternative synthetic strategy, the microwave-assisted solvent-mediated precipitation of intermetallic phases. Chemical reduction of metal atom containing precursors in ethylene glycol is known as the polyol process. Reduction, seed formation, and crystal growth take place in solution at a temperature ( $T \approx 240^\circ\text{C}$ ) far below that necessary for crystallization from melt. The polyol serves as both solvent and reducing agent, and it acts as a protecting agent, avoiding agglomeration or sintering of the dispersed metallic (nano)-particles. The use of microwaves instead of conventional heating proved to be highly beneficial with regard to yield, purity and uniform morphology of the product.

In the case of  $\text{Bi}_3\text{Ni}$  highly dispersed sub-micrometer crystals were obtained [10]. The faceted particles have the same shape and almost the same size (Fig. 2). For comparison: Crystallization from melt needs more than  $500^\circ\text{C}$  and always results in a heterogeneous regulus due to the peritectic formation of  $\text{Bi}_3\text{Ni}$  at  $469^\circ\text{C}$ .

Another instructive example is the preparation of  $\text{Bi}_2\text{Ir}$  nano-particles by this method. Direct reaction between the elements is hampered by the inevitable fact that iridium melts at  $2410^\circ\text{C}$ , a temperature at which bismuth is already in the gas phase (boiling point  $1560^\circ\text{C}$ ).



Fig. 2: Submicron  $\text{Bi}_3\text{Ni}$  by microwave-assisted polyol process.

### Reductive Pseudomorphosis: An Access to Metastable Metals

Metastable metallic phases are rarely isolated due to the lack of directed covalent interactions, which hinder further phase transitions into thermodynamically stable states. The conventional approach, a very rapid quenching of melts, usually produces metallic glasses instead of quasicrystalline or periodic structures. We succeeded in the synthesis of the metastable intermetallic compound  $\text{Bi}_{28}\text{Ni}_{25}$  via the low temperature reduction of the subiodide  $\text{Bi}_{28}\text{Ni}_{25}\text{I}_5$  with  $n\text{BuLi}$  [11]. In a pseudomorphosis, the iodine was completely extracted while the needle shaped crystals were preserved. Even the intermetallic structure fragments of the precursor survived the procedure and rearranged themselves into a unique crystal structure (Fig. 3). These fragments are decagonal rods of about 1 nm in diameter, which consist of an outer Bi tube and an inner Ni tube. As in  $\text{Bi}_{28}\text{Ni}_{25}\text{I}_5$ , the additional Bi atoms on the central axis follow another periodicity than the rest of the structure.  $\text{Bi}_{28}\text{Ni}_{25}$  decomposes exothermically into  $\text{BiNi}$  and some  $\text{Bi}_3\text{Ni}$  upon heating to about  $140^\circ\text{C}$ . Thus, the compound is metastable (probably under all conditions) and not part of the binary phase diagram.

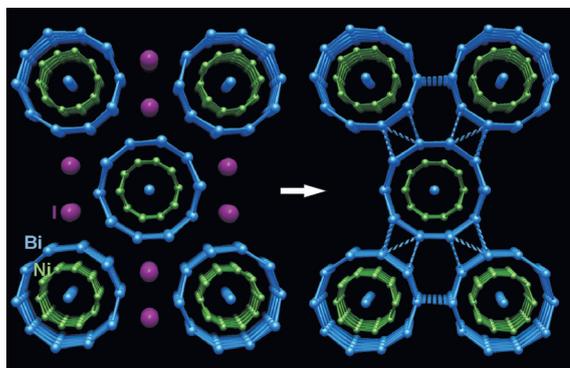


Fig. 3:  $\text{Bi}_{28}\text{Ni}_{25}\text{I}_5$  transformed into  $\text{Bi}_{28}\text{Ni}_{25}$ .

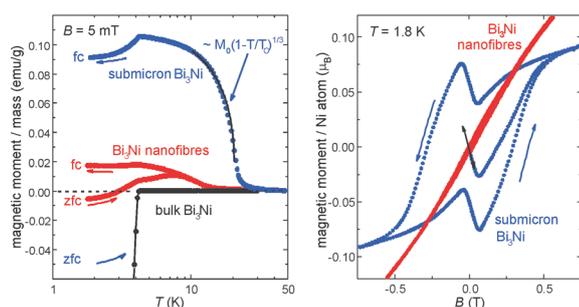


Fig. 4: Superconducting transition and broadened ferromagnetic hysteresis of nanostructured  $\text{Bi}_3\text{Ni}$ .

In a similar heterogeneous reaction  $\text{Bi}_{12}\text{Ni}_4\text{I}_3$  was transformed into bundles of parallel  $\text{Bi}_3\text{Ni}$  nanofibres [10]. While the bulk is diamagnetic and shows conventional type-II superconductivity, the nanofiber bundles as well as the submicron nanoparticles from polyol synthesis undergo ferromagnetic ordering below 20 K [12]. Type-II superconductivity emerges in all samples at the same critical temperature, slightly above 4 K. Furthermore, we observe that superconductivity coexists with ferromagnetism while the latter's order has already been established. Below  $T_c$  the superconductivity broadens the ferromagnetic hysteresis due the mutual interplay of both ground states (Fig. 4). The morphology of the  $\text{Bi}_3\text{Ni}$  samples influences Curie temperature, coercive field, remnant magnetization, saturation moment, diamagnetic screening, and critical fields. The maximum upper critical field  $\mu_0 H_{c2}$  of the nanofiber bundles reaches remarkable 11 T (bulk: 0.4 T), which indicates a stabilization of the Cooper pairs.

Finally, the room-temperature reduction of  $\text{BiI}$  resulted in the formation of double-walled bismuth nanotubes (DWBiNT), i.e. in a structural motif distinct from the precursor (Fig. 5) [13]. Although no template was used, the tubes are uniform with an outer diameter of 6 nm. The two coaxial cylinders consist of six-membered rings with chair conformation resembling the bulk structure of bismuth. According to quantum theoretical calculations, DWBiNT should show superior thermoelectric performance ( $ZT$  up to 10), which now has to be tested.

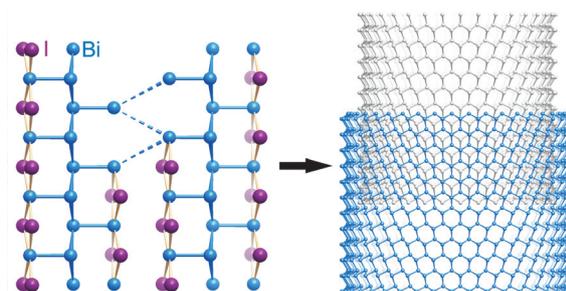


Fig. 5: Bismuth nanotubes by reduction of  $\text{BiI}$ .

## Conclusion and Outlook

The above selection of recent results demonstrates the unbroken aptitude of inorganic chemistry to generate interesting materials. Adequate characterization and theoretical analysis, however, lie in the hand of experts from experimental and theoretical physics, who are willing to accept the challenge.

## References

- [1] M. Ruck, *Z. Kristallogr.* **225** (2010) 167.
- [2] M. Ruck, in L. Schröder, R. Kniep (Eds.): *Dresdner Abhandlungen zur Chemischen Physik fester Stoffe*, Vol. 6, 2008; ISBN 978-3-00-021356-4.
- [3] E. Ahmed, D. Köhler, and M. Ruck, *Z. Anorg. Allg. Chem.* **635** (2009) 297.
- [4] E. Ahmed and M. Ruck, *Coord. Chem. Rev.*, submitted.
- [5] E. Ahmed, M. Groh, and M. Ruck, *Eur. J. Inorg. Chem.* **2010** (2010) 5294.
- [6] E. Ahmed, E. Ahrens, M. Heise, and M. Ruck, *Z. Anorg. Allg. Chem.* **636** (2010) 2053.
- [7] E. Ahmed, E. Ahrens, M. Heise, and M. Ruck, *Z. Anorg. Allg. Chem.* **637** (2011), in print.
- [8] E. Ahmed, E. Ahrens, M. Heise, and M. Ruck, *Z. Anorg. Allg. Chem.* **636** (2010) 2601.
- [9] E. Ahmed, A. Isaeva, A. Fiedler, M. Haft, and M. Ruck, *Chem. Eur. J.* **2011** (2011), in print.
- [10] D. Köhler, A. Grigas, R. Boldt, R. Skrotzki, Th. Herrmannsdörfer, J. Wosnitza, S. Kaskel, and M. Ruck, submitted.
- [11] M. Kaiser, A. Isaeva, and M. Ruck, *Angew. Chem.* 123 (2011); *Angew. Chem. Int. Ed.* **50** (2011) in print.
- [12] T. Herrmannsdörfer, R. Skrotzki, J. Wosnitza, D. Köhler, R. Boldt, and M. Ruck, *Phys. Rev. B* **83** (2011) 140501.
- [13] R. Boldt, M. Kaiser, D. Köhler, F. Krumeich, and M. Ruck, *Nano Lett.* **10** (2010) 208.

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