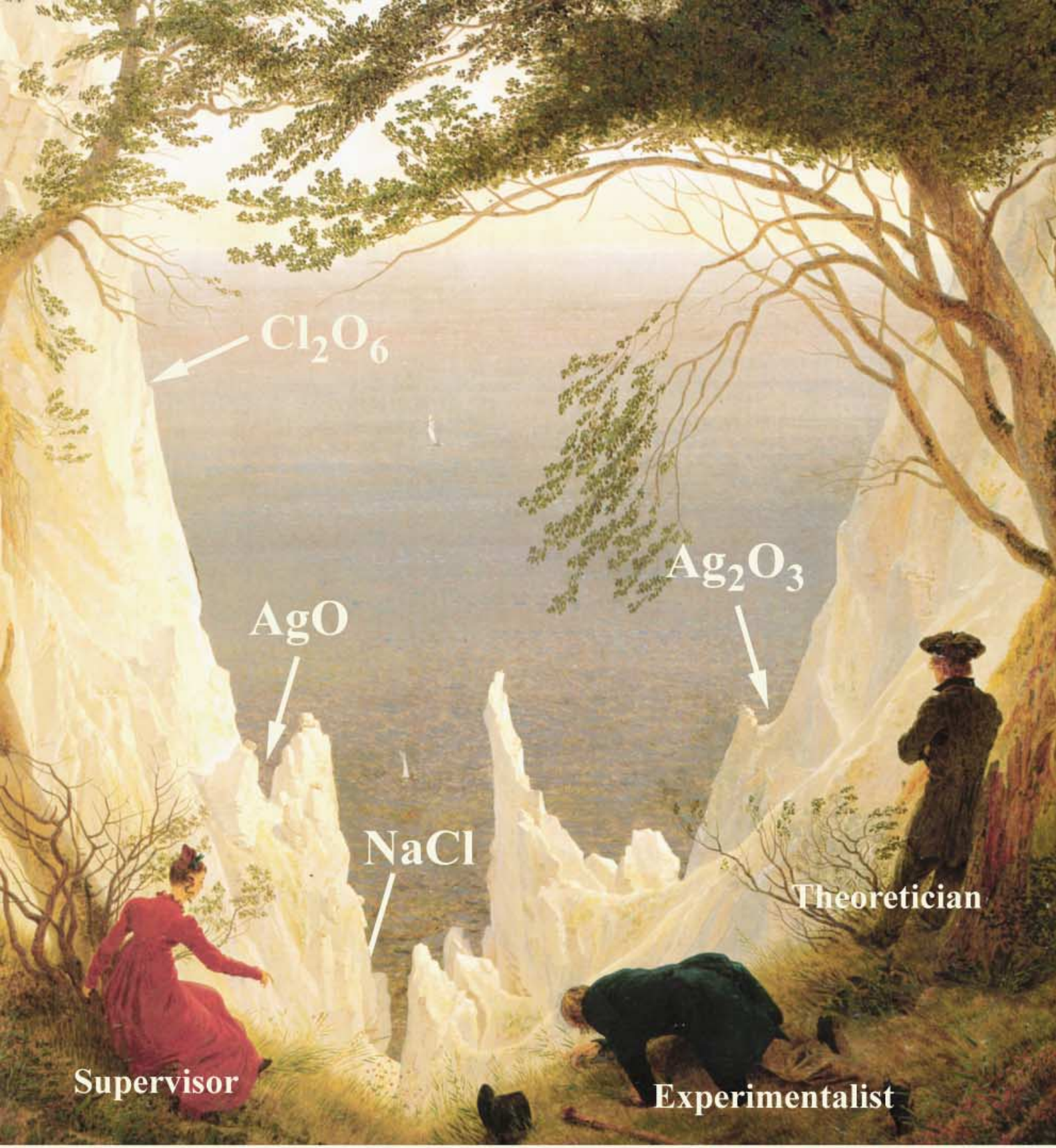

Caspar David Friedrich [about 1818]

An early, allegoric representation of the energy landscape of chemical systems, and of people exploring it.

ANGEWANDTE CHEMIE

A Concept for Synthesis Planning in Solid-State Chemistry

Martin Jansen*

Dedicated to Professor Rudolf Hoppe on the occasion of his 80th birthday

There is a widely-held belief that the preparation of new solid-state compounds based on rational design is not possible. Herein, we present a concept that points the way towards a rational design of syntheses in solid-state chemistry. The foundation of our approach is the representation of the whole material world, that is, the known and not-yet-known compounds, on an energy landscape, which gives information about the free energies of these compounds. From this it follows that all chemical compounds capable of existence are present on this landscape. Thus the chemical synthesis always corresponds to the discovery of compounds, not their creation. Consequently, the first step in planning a synthesis can and must be to identify a synthesizable compound. Up to now, materials capable of existence are discovered in the course of an experimental exploration of the energy landscape; however, an a priori identification of a synthesis goal requires an exploration using theoretical methods. In contrast to those computational approaches currently employed for structure determination for fixed composition and already known unit cells, our aims clash with such restrictions and full global optimizations have to be performed on the landscape. Although for reasons of computational feasibility the accuracy of the energy calculations is not yet as high as one would wish, our approach proves to be surprisingly robust. One always finds the already known compounds of a given chemical system, and, in addition, further plausible structure candidates are discovered. The second step of a rational planning of syntheses is the design of feasible synthesis routes. Modeling such routes requires highly accurate computations for realistic thermodynamic conditions, however this is usually beyond our current capabilities. Thus, we have not seriously pursued such a deductive approach; instead we have attempted, to reproduce the "computational annealing" employed during our structure predictions in the experiment. Educts, generated by vapor deposition methods, that are disperse on an atomic level are found to react with surprisingly low activation energies to give highly crystallized products. However, even this technique does not yet provide the possibility to selectively synthesize a specific solid compound. For this final step, modeling and experimental control of nucleation processes will be the key ingredient. Only when viewed superficially, our goal of a "rational design" of solid-state syntheses and the "high-throughput" syntheses are in contradiction. But an exhaustive exploration of the unimaginably large combinatorial diversity of chemistry remains beyond our capabilities, even with an exceedingly high throughput. The future of solid-state synthesis will be found in a union of these two conceptual approaches.

Keywords: solid-state chemistry · synthesis planning · solid-state reactions · structure prediction

1. Introduction

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The alchemist's saying "solve et coagula" describes in a nearly paradigmatic way the basic goals of modern chemistry, which provide it with genuine and distinct characteristics in a time of increasing overlap among the various disciplines of natural science. This special feature is the sometimes seemingly playful disintegration and recombination of matter in ever new combinations and their characterization, that is, the synergetic interplay of synthesis and analysis. For example, a current focus of (solid-state) chemistry is the construction of ordered structures just above the atomic length scale.[2, 3] Clearly, such solids structured on a nanoscopic or mesoscopic scale fill a true gap in sizes between the atomic and macroscopic, and they are of a not-to-be-underestimated importance because of their very special chemical and physical properties caused by various size and boundary effects.[4]

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However, the new nomenclature should not fool us into thinking that either the problems encountered or the ideas proposed for their solutions are truly new. In particular, one needs to counter the impression that the synthesis of traditional (atomically structured) solid compounds has been mastered. In fact, the lack of control and selectivity encountered in attempts to construct materials structured on the nanometer-level (chemical interactions as the order principle, bottom-up approach[5]) is a well-known phenomenon in classical solid-state synthesis. It is still impossible to synthesize an up-to-now unknown solid compound with a prescribed composition, structure, or even properties, intentionally and in a reproducible generalizable fashion. This fact, which has been referred to many times already since the beginnings of solid-state chemistry,[6, 7] has led to the widely accepted, and often somewhat resigned, attitude that experimental solid-state chemistry is not amenable to detailed design and thus is intrinsically of an explorative nature.[8–12] Obviously, the state of matter, in which the chemical reaction takes place, plays a decisive role. The contrast to molecular syntheses,[13] in particular in organic chemistry, which are predominantly performed in liquid or gaseous solutions, could not be more extreme. In molecular chemistry it has for a long time been possible, to design molecules capable of existence and then prepare them. And even more importantly, an extensive toolbox of chemical reactions is available to prepare the intended molecule by following a sequence of predictable and often highly selective synthesis steps.[14]

A comparison of the different boundary conditions (and their consequences) in solid-state and molecular synthesis, lets us view the nearly antagonistic situation regarding the relevant features of these two sub-fields of synthetic chemistry.[15, 16] Ignoring some minor details, the difference in success can be reduced to one fundamental issue, the difficulty in solid-state chemistry to bring the reaction partners sufficiently close together, that is, close on an atomic level, over macroscopic distances. In traditional solid-state reactions, this macroscopic diffusive transport usually requires a high thermal activation, which ruins any hope for subtle control of the reaction, and in addition often closes off the routes to thermally labile and metastable solids. Because of this mainly thermodynamic control of the reaction processes, the possibilities for a rational design of a synthesis towards a prescribed compound appear to be severely limited. Nevertheless the scientific imperative remains, to continue developing and improving preparative solid-state chemistry until a goal-oriented rational approach becomes feasible. Only then will it be possible to reach the, also economically crucial, efficiency in the development of new solid compounds that constitutes the first step in materials research.

Thus, about ten years ago, we began to develop an approach for the rational synthesis in solid-state chemistry.[15–20] Such a concept has to consist of at least two steps:

1) Prediction of compounds capable of existence,[21] and their structures,
2) Development of a synthesis route towards these compounds.

In this Review the current state of the enterprise is presented.[24] From the point of view of efficiency, the so-called "combinatorial", or better: "high-throughput", methods[25] constitute a possible alternative to our method based on rational design. Thus, at the end of this article a comparison of these rather opposite approaches is attempted.

2. Heuristic Aspects of Design in Solid-State Chemistry

The fascinating, yet sometimes confusing, multitude of structures, valence states, and properties of solid matter have early on nudged, if not pushed, the workers in the field to assess and classify this plethora of experimental data. Always one has chosen the inductive approach, so successful throughout chemistry, where generalizable connections and rules are derived from individual observations. At the beginning, the focus was on structural aspects. Not even twenty years after the discovery of X-ray diffraction on crystals and the first successful structure determinations, V. M. Goldschmidt recognized the composition, the ratios of the radii of the constituting particles, and the polarization (type of chemical bonds) as the three most crucial factors determining the observed structure.[26] During this early period, W. Biltz conceived his "Raumchemie der festen Stoffe" (spatial increment chemistry of solids), too.[27] Later, F. Laves added the principles of maximal space filling and highest possible symmetry.[28, 29] Side to side with these classical criteria one has to place L. Pauling's crystal-chemical rules,[30] which are the origin of the bond-length bond-strength relations.[31–34]

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These approaches only take local interactions into account, clearly a defect considering the importance of long-range interactions in crystalline solids. For ionic crystals, R. Hoppe's MAPLE[35–37] and concepts such as CHARDI,[38] derived from MAPLE, which are based on the Coulomb contribution to the (lattice) energy and the partial, that is, referring to a particular crystallographic site, Madelung energies, address this problem by providing data for correlating different crystal structures and structure elements. Quite generally, the often noticeable multi-facetedness of crystal structures requires an analysis from as many diverse points of view as possible.

In addition to the methods mentioned, the calculation of minimal- and equipotential surfaces[39] yields many insights, just as the recognition of hierarchical structural connections[40] and the description of structure elements as virtual displacements, such as shear motions[41, 42] and twinning operations.[43] Inherent to all these approaches is the classification according to symmetry properties. Quite often, crystal system, crystal class, or even the space group of a compound are mentioned in one breath with its formula. Here, the generation of group–subgroup relations has proven to be a particularly efficient tool in the analysis of structural relations.[44] Beyond their applicability to classifications, symmetry considerations are of fundamental importance, for example, for the understanding of phase transitions and solid-state properties.[45]

The two most common ways to describe newly discovered crystal structures are based on the analysis of the anion substructure complemented by the cations occupying the various holes in the anion packing, and/or the description of the coordination polyhedra and their connectivity. Both approaches are also employed for the purpose of systematic classification. Concerning the analysis of atom packings, it has turned out to be a surprisingly successful alternative to read the structures starting with the arrangements of the cations, instead.[46–49] The polyhedra and their topological connectivity and spatial arrangements have become the foundation of, for example, a comprehensive structure systematics of the silicates and related classes of compounds following F. Liebau,[50] or A. Simon's concept of condensed clusters.[51]

In the case of intermetallic phases, the valence electron concentration[52, 53] takes on a similarly controlling role as the formula for ionic or covalent compounds. In particular for this class of compounds structure field diagrams serve a valuable role when trying to structure the experimental data.[54–58] Surprisingly widely applicable consistent structure systematics can be developed on the basis of the Zintl–Klemm concept[59–61] and following the ideas developed by Hume-Rothery and co-workers;[62] in contrast the Laves phases are classified only following geometric considerations.[28, 29]

This strongly abbreviated review of the crystal chemical repertoire predominantly serves for the description and classification of the otherwise overwhelming plethora of experimental information.[63] Beyond this primary task, these tools offer qualitative ways to tentatively judge the plausibility and correctness of newly found crystal structures. Turning this line of reasoning around, these concepts can also be used as a guide for the imagination when conceiving of chemically reasonable but not-yet-observed atomic arrangements. In particular, one can strongly restrict the nearly infinite multitude of imaginable structures just by considering the formula, the type of chemical bond, and the effective sizes of the building units (usually atoms or ions). Already the number of possible motives of mutual coordination of the different atomic species, which can been formulated in a compact way by the Niggli notation,[69] can be greatly reduced using the above assumptions.[70, 71] Taking furthermore the connection between the chemical formula and the multiplicity of the Wyckoff-sites into account, one can significantly reduce the number of possible space-group types.[71–74] In particular, structures of simply constituted solids sometimes appear to follow from these assumptions alone.[75, 76] Similarly, systematic permutations of the occupation of the holes in close anion packings while taking the space-group symmetries into account generate both the known structures and also plausible but so far unknown variants.[77, 78]

However, one quickly reaches insurmountable limits when employing only these recipes that are purely based on geometric and topological structural properties, unless general heuristic rules based on experience or metaphysical expectations, such as "striving for the highest symmetry"[28] or "employing a minimal number of structure elements" (Gott ist ein Gerechter! (God is a just one!)[79]), are used as additional criteria.

Yet the goals of solid-state chemistry are not limited to the realization of certain well-defined crystal structures. Primarily, the issue is the synthesis of new compounds and their characterization, also with an eye on possible applications, that is, the trinity of mutually interconnected aspects: structure, bonding, and property. The conscious tuning of material properties,[9, 16, 80] which goes beyond the sheer optimization of an already well-known material, is without doubt the final goal, currently, however, barely more than a dream.

Of course, those approaches that have the greatest hope for success, are where the causal connection between microscopic basis and desired macroscopic physical property is known in detail. Such a situation pertains for ionic conduction, as long as the mechanism can be described as a random walk in a concentration gradient.[81] For example, the discoverers of the fast ionic conductor NASICON make the claim to have developed this material in a consciously planned fashion.[82] However, in general the successful route to a new material has been based on a mixture of analogies, intuition, and empirical knowledge. Examples of this latter approach abound, these include, the many instances of successful syntheses of compounds with unusual valence states, such as paramagnetic Ag^{3+}[83] or high oxidation states of transition metals.[84–91] Similarly, one could mention the adjustment of band gaps in semiconductors,[92, 93] the optimization of ferro-electric compounds,[94, 95] superconductors,[96, 97] or GMR-materials (GMR = giant magneto-resistance)[98, 99] belonging to the extended structure family of perovskites. Often, the "models" behind those results constitute just extra- or interpolations of known compounds, and/or the more accidental improvement of some property is only afterwards explained in terms of structure and chemical bonding. Nevertheless, these indisputable successes have encouraged the appearance of optimistic essays[100] with titles such as "Predictive Character of Solid-State Chemistry".[101, 102]

On its own, the rational development of goals for solid-state synthesis, the subject of our discussion so far, is not sufficient. A second hurdle is the development of feasible synthetic routes leading to the desired compound.[13] Although quantitative verifiable models for chemical reactions among solids[103–108] are usually only available for model systems, the results of such investigations have long been taken into consideration in preparative solid-state chemistry, at least on a qualitative level. The most influential guiding mottoes have been "increase of mobility in the solid state" and "achieving as good as possible a mixture of the educts". Pioneers in this field are G. Tammann,[109] A. Hedvall,[6] and R. Fricke;[110] their ideas are still being felt today, and employing specially prepared ("activated") starting compounds belongs to the elementary tools of every experimental solid-state chemist.

A large number of methods are being employed today to provide such highly activated educts, both by mixing the components as intimately as possible and by creating a very high defect concentration.[6, 10, 110, 111] Among the most important ones are co-precipitation, thermal decomposition of precursors (for example, of nitrates, carbonates, oxalates and carboxalates[112–114]), freeze drying,[115] mechano-chemical procedures,[116] sol–gel methods,[117–119] or polymer routes.[120, 121] The activation required for the solid-state synthesis can be reduced most effectively by using chemical transport reactions,[122–125] melting reactions,[126–130] solvothermal syntheses,[131] or topotactic reactions (intercalation, de-intercalation).[132–137] This progress in the development of preparative techniques has continued unabated until the present, clearly proving that the creativity of chemists has not yet reached its limits.[138–140] For completeness, one should also mention the efforts to increase the range of temperatures and pressures accessible to solid-state syntheses.[141–145] Besides modifying the reactivity of the materials, this extension also changes the equilibrium structures one can reach and enlarges the accessible part of the thermodynamic phase space spanned by the thermodynamic variables.

Even this highly abbreviated sketch of the conceptual foundations of classical preparative solid-state chemistry gives an idea of the fruitfulness of these basic concepts, as one also realizes by considering the seemingly inexhaustible productivity of this branch of chemistry. Nevertheless, all these successes cannot hide fundamental deficiencies on the conceptual level. Perhaps the most grave ones are the lack of coherence and consistency of the models employed, and their often unclear or insufficient physical basis. While the strengths of the current models can be found in the systematic classification and subsequent validation and/or explanation of experimental data, they only exhibit a very limited predictive power. Up to now, they have not been sufficient to significantly decrease the inherent unpredictability of syntheses in the solid state.

3. Multi-Minima Energy Landscapes as Representations of Material Systems

For an n-component material system in thermodynamic equilibrium, chemical thermodynamics produces a unique relation between the state of the system and the prevailing thermodynamic conditions, the values of the state variables p, T, $x_1, \ldots, x_{n-1}$ (x_i: molar fractions). Here, the thermodynamic state of the system is completely described by the knowledge of the co-existing phases, their mole fractions, and their compositions. This information can be encoded in a compact and elegant way in the guise of phase diagrams. If one were to assume that solid-state synthesis is fully controlled thermodynamically, a rational prior determination of realizable synthetic goals would necessitate the computation of the phase diagram for the chemical system under investigation.

Long-term efforts to determine phase diagrams as completely as possible because of their great importance in solid-state and materials science have been underway for many years, with quite impressive results. Thus, in the context of the CALPHAD-project,[146] algorithms and computer programs have been developed that allow us to employ caloric data of a system drawn from a variety of sources to optimize and supplement experimentally determined phase diagrams. In addition, attempts are made to derive the basic structure of the phase diagram of multi-component systems from information about the few-component boundary systems. Going beyond these extra- and interpolations, a few largely ab initio based computations have been performed[147–149] of, among others, excess enthalpies[150] or phase separations, for example, through spinodal mechanisms.[151] With respect to rational synthesis design, the predictive value of these or the other methods mentioned above is rather limited, since we are interested in the determination of new compounds, which of course cannot be part of known phase diagrams. Within the context of the CALPHAD approach, only experimentally known data can be employed, and in general one cannot recognize and eliminate a fatal defect such as a missing thermodynamically stable phase. A second restriction is of a fundamental nature. When pursuing the goal of predicting all compounds capable of existence, and thus also capable of being synthesized, in principle, a restriction to thermodynamically stable compounds is unacceptable. In fact, the overwhelming part of the accessible solid matter is found to be in a metastable, only kinetically stable state. And this applies even more strongly to the combinations of compounds that are employed in technological applications.

If one's goal is the determination of all compounds capable of existence, including those that are only kinetically stable, one has to leave the usual depiction of a chemical systems at equilibrium in the form of phase diagrams behind, and analyze the full function of the free energy F for all locally equilibrated states in the system. This idea can be visualized using a one-component system (Figure 1). For every state of matter, F can be plotted as a function of p and T. The intersections of these surfaces characterize the thermodynamic conditions for co-existence of the different states. For given p and T conditions, the state with the lowest value of the free energy is the thermodynamically stable one. The corresponding sections of the free-energy surfaces are projected onto the (p,T)-plane in the usual representation of phase diagrams. In general, one expects that in the liquid and gaseous states of matter, usually only one phase is going to be

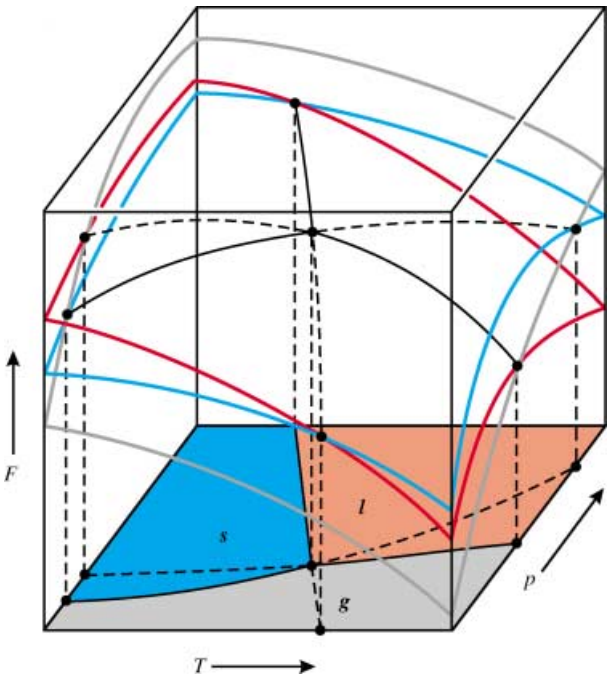

Figure 1. Phase diagram for a single-component system (schematic). The free energies for the solid, liquid, and gaseous state, respectively are shown, and their projections onto the surface spanned by the state variables p and T.

present, while in the solid-state polymorphism can occur, that is, several modifications might be formed. The corresponding surfaces of the free energy can, but need not cross. In contrast, there always exist intersections with the surfaces belonging to the liquid and gaseous state, defining respectively, the vapor-pressure and melting-pressure curves of the corresponding solid modification.[152] However, with respect to their realizability it does not matter, whether we are dealing with thermodynamically stable or metastable compounds.[153]

The claim that by fixing a full set of state variables (here: p and T) the state of matter and at the same time the thermodynamic state functions are uniquely determined, only refers to a system in thermodynamic equilibrium and is a purely phenomenological and descriptive statement. Usually, the state of the system (type, number, and composition of the phases present in equilibrium) is determined experimentally. When trying to include non-equilibrium-states, the uniqueness of the relation between thermodynamic state and state variables is lost, and the phase content of a system can vary for the same values of the state variables, depending on the experimental path taken.

A crucial difference to equilibrium systems is that now the macroscopic thermodynamic state must be treated as potentially variable in time, that is, time needs to be taken into account as an additional "coordinate".[154] The resulting complex interplay of the variables may be visualized using a thought experiment. For this we consider all states that can be realized for an arbitrary (n-component) system at $T = 0$ K and fixed atom positions (i.e. with time frozen, $\Delta t = 0$ s). For all combinations of compositions and spatial arrangements of atoms (configurations)[19, 155, 156] one can then assign, formally, a value of the free energy, which, for $\Delta t = 0$ s exactly corresponds to the potential energy of the particular configuration. Using these hypothetical assumptions, one can formally construct a connected hypersurface of the free energy. In the classical picture one can distinguish unstable, metastable, and stable regions. If one now lifts the restriction $\Delta t = 0$ s while keeping $T = 0$ K, this allows the system to slide from the unstable points into the nearest local minimum. Adding the zero-point vibrations, and choosing Δt large compared with the inverse frequencies of the vibrations around the minima, one needs to average over the regions in configuration space corresponding to the vibrational amplitudes, and one can only speak of the value of the free energy referring to this set of atomic configurations. Although some relaxation processes resulting from quantum tunneling will occur, transport by diffusion is not possible under these thermodynamic conditions ($T = 0$ K).

Moving to finite temperatures, the atomic positions are going to change continually, accompanied by a minimization of the free energy of the system, until finally thermodynamic equilibrium has been reached. During this process, many metastable intermediate states with various life times will be passed through. Which among these intermediary "compounds" or structures can be considered as "capable of existence" is a matter of judgment. A minimal requirement is surely that the metastable states must be detectable within the resolution of the available measurement probes.[16, 19, 157] Thus, one would treat a molecule as capable of existence in molecular chemistry, if it survives for at least one vibrational period. In the case of solids one usually deals with time periods ranging from human experience to geological times.[158] This is a result, less to the time resolution, which is essentially independent of the state of matter for spectroscopic probes, but reflects the transformation and reaction speeds of solid matter, which are on the order of seconds even for non-diffusive processes.

It follows from our considerations that at finite temperatures only subregions of the "virtual hypersurface" of the free energy, generated in the thought experiment, are going to be populated. These usually correspond to minimum regions in configuration space, which represent regions of locally equilibrated configurations with finite (in the case of the global minimum essentially infinite) life times.[19] A chemical interpretation of these regions is not always trivial. In a simple case, a minimum can be associated with a well-defined crystalline compound without higher-dimensional defects. For fixed activities of the components and constant pressure, which takes on the character of an external variable for metastable compounds, the "width" of the minimum is then given by the vibrational amplitudes of the constituent atoms about their equilibrium positions and the concentration of point defects. The degree to which the resulting states are populated, is determined by the temperature. The value of the free energy (the macroscopic observable) follows from the summation over the corresponding densities of states.

Other examples from the multitude of possible constellations are metastable mixtures, for example, of annealed MgO and α-Al_2O_3, the polytypes of SiC,[159, 160] which are close neighbors in configuration space but separated by high barriers, or a ferroelastic compound, such as As_2O_5,[161, 162]

near the phase transition into the paraelastic high-temperature form (vanishing barrier).

When documenting metastable and stable solid states in form of phase diagrams, one can only reach those regions on the "virtual hypersurface" of the free energy described above, which can be assigned a value of the macroscopic parameter F under realistic conditions, that is, where a locally equilibrated region (around a minimum) in configuration space can be identified. Which piece of such a region associated, for example, with a minimum should be taken into account, depends on the prescribed temperature.

The above description may be visualized in Figure 2 again using a one-component system. Here, the surfaces of the free energy of three (solid) polymorphs are depicted as a function of pressure and temperature. The point ($p = 0$ Pa, $T = 0$ K) is assigned to the hypothetical surface of the free energy schematically described above. Clearly the transitions among the three modifications considered take place by shifting the atoms in position space. For finite pressures and temperatures the corresponding macroscopic thermodynamic state function (here: F) is computed by averaging over the populated microstates belonging to a locally equilibrated (minimum) region, and their temperature and pressure dependence can be represented in the usual fashion (Figure 2, right). If one restricts the considerations to ideally crystalline, chemically similar modifications, for example, S_8, S_{10}, and S_{12} (three allotropes of sulfur),[163] the vibrations of the atoms about their equilibrium positions is the most important aspect to be included. Since this contribution is nearly the same for each polymorph, taking it into account will only lead to minor modifications of the shape of the corresponding free-energy landscape. Thus, for temperatures far below the melting point, it is not at all unrealistic, to picture known (or still-unknown) compounds capable of existence as being represented on landscapes that essentially reflect the shape of the potential-energy surface over the corresponding configuration spaces. The move, required in principle, to the free-energy landscape leads, because of the averaging process mentioned above, to a more discrete energy landscape, where the locally equilibrated (minimum) regions represent the stable or metastable chemical compounds capable of existence.

The one-component system discussed above can be a single-element compound or a multi-element compound with fixed component activities, that is, fixed composition. Chemical reactions assume an exchange of material. An exemplary phase diagram allowing such an exchange, a two-component system, is shown in Figure 3. The free energy (F function) is now a function of three thermodynamic variables, and its dependence on these can be depicted graphically only in form of cuts through thermodynamic space. For equilibrium, the phase content for given thermodynamic conditions can be

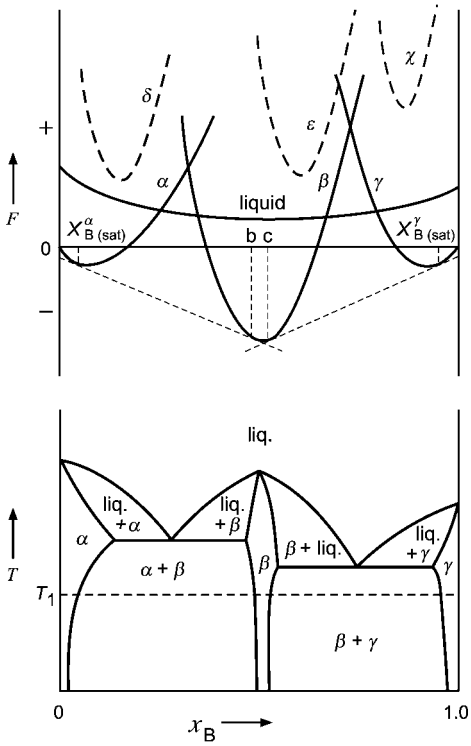

Figure 3. Phase diagram for a two-component system at constant pressure (bottom) and the free energy functions including metastable states (top), schematic representation for fixed pressure and temperature T_1.

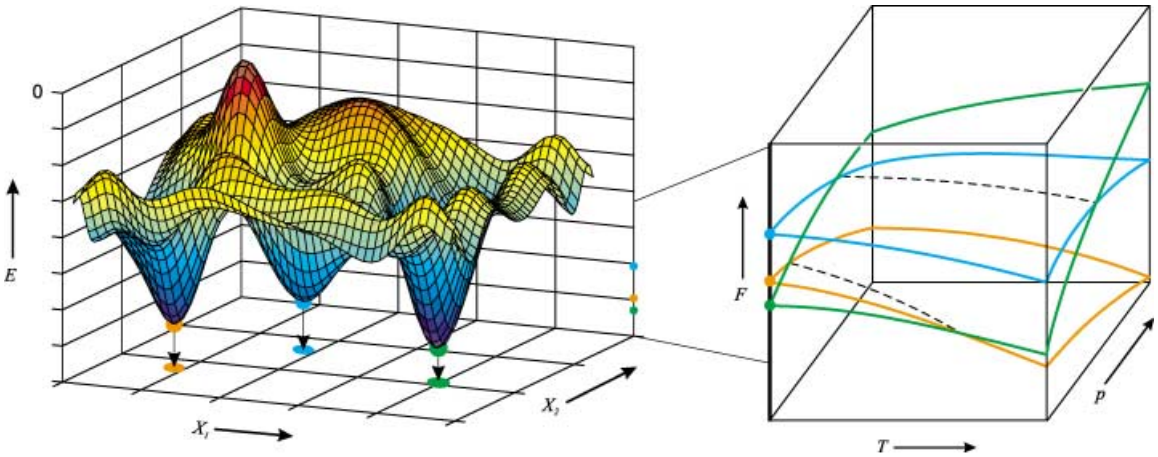

Figure 2. Schematic representation of a cut through a configuration space for a single-component system with fictive coordinates X_1 and X_2 (left) and the correlation with the usual representation of the free energy as function of pressure and temperature for three solid (metastable and stable) modifications (right).

derived from the equality of the chemical potentials of all co-existing phases. In an elegant and easily visualized fashion this can be done by constructing the common tangents to the F function in the representation $F_{p,T}(x_1)$. Such methods cannot be used, of course, to determine metastable phases that can co-exist with each other, since in general they exhibit different chemical potentials. The connecting element among all compounds capable of existence is again the configuration space. These compounds can all be found on the energy landscape, from which free energies can be computed for distinct locally equilibrated (minimum) regions.

A certain charm of these admittedly qualitative and partly abstract considerations, still far away from the compromises and approximations that will be necessary when moving to real implementations, is found in their universal validity. Even keeping in mind all the foreseeable difficulties (see next Section) involved with the development of a methodological route to the synthesis planning in solid-state chemistry, which today still appear insurmountable, this general approach, that is, to visualize the material world as being represented on energy landscapes, opens the window to important insights:

- All compounds capable of existence are already present on such energy landscapes (a picture that exhibits strong analogies to Plato's theory of forms). Thus the synthetic chemist is always the discoverer, not the creator of new materials,[15, 16] and this holds without exception for all fields of synthetic chemistry.
- General precondition for a compound to be capable of existence is that it can be associated with a locally equilibrated region, for example, a local minimum, in its configuration space. The sign and amount of the free enthalpy of formation, and with this the question of thermodynamic stability, are not decisive as far as the feasibility of synthesizing a compound is concerned.
- These general considerations appear to open the door leading to a deductive approach to chemistry.

The approach presented removes a number of preconceptions widely held in the past and to some extent still held. The over-emphasis on the aspect of thermodynamic stability when discussing the existence of hypothetical compounds has definitely impeded the development of preparative chemistry, and, in particular, of solid-state chemistry. Claims such as "MgCl cannot be synthesized since it would be thermodynamically unstable against a disproportionation into $MgCl_2$ and Mg", or an analogous justification of the lack of success up to now to synthesize CuF, are even part of the canonical teachings in chemistry.[164] How deeply rooted such a point of view is becomes obvious when reading the, in principle, very inspiring monograph by W. E. Dasent "Nonexistent Compounds",[165] where in a number of instances the thermodynamic stability is presented as the only criterion for the feasibility of synthesizing a hypothetical compound. We feel that compounds such as MgCl or CuF can definitely be synthesized, and consider it to be much more fruitful to work on realizing such compounds than to justify their supposed nonexistence.

The energy landscape discussed is the foundation of the whole material world, and its investigation unites all of natural science. Of course, this very satisfying conclusion does not exclude the fact, that, for pragmatic reasons, answering different classes of questions, and in particular the analysis of various specific sub-systems, will require the use of quite different techniques and methods. But at least fruitless polarizations and artificial distinctions, such as between natural and unnatural materials[166] or static and dynamic solid-state chemistry,[167] should lose their purpose.

4. Rational Planning and Performing of Solid-State Syntheses

4.1. Prefatory Remarks

Starting from the realization that the full set of both already known and up-to-now unknown chemical compounds capable of existence in some chemical system are represented on an energy landscape, one recognizes that "doing chemistry" just corresponds to exploring this landscape. Traditionally, this exploration is done by chemical synthesis, where each synthesized compound marks a locally equilibrated region of configuration space, for which one can determine, for example, a value of the free energy. This exploration by experiment can proceed by relying to a varying degree on "conceptional" input and purely explorative testing of a set of reaction parameters, depending on the class of chemical systems and the "maturity" of the field investigated.

A particularly noticeable current development is the gain of importance of an alternative option, the theoretical treatment of chemical issues. The great improvements both regarding the computational power available and the efficiency of the algorithms employed allow an ever increasing accuracy in the computations and the analysis of increasingly larger (number of atoms) systems.[168] However, in most instances these tools are currently applied to a prescribed compound or element,[169–175] and not used for the exploration of a chemical system as a whole with an eye on the identification of possible goals for syntheses. While for the case of experimental exploration the synthesis route is a necessary by-product of reaching a desired compound, finding an experimentally feasible synthesis route after theoretically identifying a promising not-yet-synthesized compound (for example as a local minimum on the energy landscape) constitutes a second, independent step. Thus, this chapter dealing with "rational solid-state synthesis" has been split into two parts, where the identification of compounds and the development of appropriate synthesis routes are discussed separately.

4.2. Exploration of Energy Landscapes of Chemical Systems by Using Theoretical Methods

As easy as it has been to state the task in general terms, so difficult it is to reach a practical solution. This applies in particular to the ambitious general goal: to compute a distribution of the expectation values of the free energy for the chemical system under consideration over regions on the microscopic landscape, for all p, T, x_i values. This aim requires,

in principle, quantum-mechanical energy calculations, and the derivation of the macroscopic state functions from these results based on the rules of statistical mechanics. Currently, it is well-recognized that a completely rigorous treatment of systems of realistic sizes is not yet possible. Among the necessary simplifications, the restriction to ideal crystalline solids and their properties at $T = 0$ K are probably the least problematic within the context of this discussion. Using this assumption, one can compute the energy E_0 as the sum of the energy of cohesion U of the participating atoms at their (equilibrium) positions on the lattice and the energy of the zero-point vibrations[45] [Eq. (1)].

$$E_0 = U + \tfrac{1}{2}\sum_{i=1}^{3N} h\nu \quad (1)$$

The amount of cohesive energy depends on the constituent particles, of course.[176] In the case of quantum-mechanical calculations, these particles are all the atomic nuclei and electrons, while, for example, for noble-gas crystals it makes sense to treat whole atoms as the elementary building block.[17] For ionic crystals, one can refer to ions or neutral atoms, where the cohesive energy would correspond to the lattice energy (consisting of long-range Coulomb plus short-range repulsive terms) for the ions, or the enthalpy of formation ΔU, from the neutral atoms, respectively.

The number of calculations that need to be performed depends on the number of components in the system under consideration and the steps in the thermodynamic variables p, T, and x_i. Similarly, the computational effort, for example, for an individual energy calculation is determined by the maximal number of atoms allowed and the (effective) charge of the nuclei or ion cores. Since the development of a set of tools for the planning of solid-state syntheses which can be of practical use, needs to take systems with three, four, and more components into account, one realizes right away that the number of computations necessary for a sensible scanning density of the space of thermodynamic parameters grows exceedingly large very quickly. Thus, a rigorous quantum-mechanical treatment, however desirable, is beyond our capabilities even when employing the usual approximations. These facts clearly show the limits of our capabilities, and decisively influence the approach chosen by us for the exploration of the energy landscape of solids.

Our concept has been discussed in great detail elsewhere; thus here we only give the most pertinent aspects.[16–20, 177–184] Going beyond the restrictions of $T = 0$ K, we neglect the zero-point vibrations, and consider the life times of the metastable states only in a rather qualitative fashion. This simplification results in a configuration space spanned by $3N$ position coordinates for a N-atom system.[19] Of course, when using simplified potential-energy functions instead of quantum mechanical ones, the resulting energy landscape can only be a rough representation of the true (free) energy function. Quite generally, one needs to check carefully, whether employing such approximations might not put the desired goal in jeopardy. We are not necessarily interested in the absolute value of the energy of a hypothetical compound but whether it can be associated with a local potential-energy minimum (at low temperatures). Thus, the assumption of an ideal crystalline solid and the neglect of zero-point vibrations are clearly acceptable simplifications. Similarly, the temperature dependence of the energy of cohesion that is associated with the thermal expansion, should leave the general structure of the (free) energy landscape unchanged when going to finite but low temperatures.

Indubitably, neglecting entropy is more problematic in our approach that focuses on local minima of the potential energy, since in this fashion entropy-stabilized[185] compounds cannot be taken into account. However, if one restricts oneself to crystalline solids, this lack is not quite as critical, since the entropy term ($T\Delta S$) typically only contributes about 10% to the standard free-energy of formation. Thus, the number of local minima of the free energy, which are destroyed or newly created when taking entropy into consideration, should be limited. Of course, this justification only applies to low temperatures.

After constructing this multi-minima energy landscape employing the simplifications and approximations described above, it is now explored using global optimization methods.[186] Here, periodic boundary conditions are applied, and the starting configurations are generated by randomly placing atoms belonging to the system under consideration into a simulation cell. The potential energy, which, for the noble-gas compounds[17, 187] and ionic crystals,[177] is usually computed using two-body potentials with Lennard-Jones and Coulomb terms, serves as the cost function of the global optimization. The weighted random walk (Monte Carlo method) in configuration space during the global optimization proceeds mainly by stepwise changes of both atomic positions and the shape and size of the simulation cell, and by transfer of charges between atoms or ions. In addition, we also exchange atoms, and, in principle, can add and remove atoms from the system. The route in configuration space mapped out by these changes that are accepted or rejected based on certain acceptance criteria,[188] ends in some local minimum. A representative view of the energy landscape can be gained from the accumulation of the results of many such optimization runs.

Here, too, we want to discuss the limits of our approach, as implied by our choice of boundary conditions and method:

- The choice of periodic boundary conditions leads to crystalline structures; amorphous or quasi-crystalline solids are not included. One should note, however, that neither the symmetry of the translational lattice nor the basis vectors are fixed. They are freely varied during the exploration runs. Fixing only one of these aspects would strongly restrict the configuration space and make it impossible from the outset to determine all the structures imaginable.
- There exists an upper limit regarding the number of atoms in the simulation cell; this limit is essentially determined by the computational power available. A structure that exists or is at least capable of existence, but contains more atoms in the smallest unit cell than given by this limit cannot be found. The probability of the occurrence of such an event can be estimated based on the distribution of the number of formula units in already known crystal structures.[189]
- An issue open to concern in our current implementation is surely the use of simple two-body potentials when calcu-

lating the energy, that is, the cost function for the global optimization. This approach is forced upon us by the very high number of energy calculations required. To really reach a significant fraction of all the minima on the energy landscape, thousands of "simulated annealing" runs are necessary, with each implying millions of energy evaluations. If one were to use more accurate methods for the energy calculation, one would only be able to explore very small regions of configuration space. But in this way, we would clearly miss our goal of predicting as many compounds as possible that are capable of existence in a chemical system. Of course, one would be able to reach a higher accuracy concerning, for example, the lattice constants, by employing empirical interaction potentials between the atoms or ions that have been optimized based on known structures.[190] However, in this case one can easily, unwittingly restrict the general applicability of the energy function, since, all regions of the landscape must be explored with comparable weight.[177, 180, 191] As a result of the simplifications in the potentials employed, the lattice constants of the structure candidates do not agree exactly with the experimentally determined ones. Similarly, structure distortions (spontaneous ferroic polarizations, Peierls-instabilities) resulting from electronic effects or phonon instabilities cannot be identified. However, we do not regard these latter restrictions as very worrisome, since we are primarily interested in identifying compounds and structures capable of existence, and not in these structural details.

To deal with this currently not resolved contradiction between the goal of employing an energy function as unbiased as possible that is suitable for global optimization and the desire to produce structures with accurate parameters, we use a two-step approach. In the first phase, we globally explore the configuration space using simple general potentials, while in the second step we perform local optimizations on an ab initio level for the seemingly most relevant minima (usually lying very low in energy).[16, 19, 183] At this stage of the calculations one can, in principle, investigate the structure candidates with respect to, for example, structural instabilities caused by electronic effects.

The degree to which the approximations and simplifications discussed influence the results of the global optimizations is difficult to estimate. A first impression of the robustness of the approximation can be gained by checking, within what range, parameters in the interaction potential can be varied without producing qualitative changes in the energy landscape under consideration.[177] A much more significant benchmark is whether, when performing an "unbiased" global optimization of the chemical system, one observes the structures already known from experiment. A final judgment about the, in principle, conclusiveness of our concept and the capabilities of our current implementation can only be made, once an unknown compound is first predicted, subsequently synthesized, and finally shown to exhibit the predicted structure. A very encouraging step in this direction has been the analysis of the landscape of sodium and chlorine. Here, a new structure type for ionic AB compounds has been found, where cations (A) and anions (B) coordinate each other in a very regular arrangement with coordination number five.[15, 16, 177] Only much later an order variant of this structure type has been experimentally observed in form of Li_4SeO_5.[192, 193] And additional structure candidates that are quite unusual for monohalogenide compounds have been identified during the global optimization, such as the NiAs- and the Wurtzite-type, that have been realized in the systems LaI[194] and LiI,[195] respectively.

In practice, the system under consideration is intensively explored using global optimization methods such that statistically robust claims can be made. For the structure candidates found, an analysis with respect to their symmetry is performed, within defined tolerances, the corresponding space group is determined, and the structure is transformed to a conventional crystallographic setting.[196, 197]

But the exploration of the energy landscape of a chemical system produces far more information than just a list of local minima. Using appropriate algorithms,[178, 198–202] one can analyze the barrier structure, from which neighborhoods of structure candidates in configuration space can be recognized, and first indications of the kinetic stability (height of the lowest saddle point) of the corresponding modification can be obtained.[178, 182, 184, 200, 201, 203] Since the configuration is very high-dimensional even when restricted to a fixed composition, it is very difficult to visualize and present these insights into the structure of the corresponding energy landscape. Among the various methods available to compress the information we have chosen the representation by means of a tree graph,[182, 184, 204] which yields a fast overview over the lowest-lying minima and their connections.

As representatives of the many systems that have been investigated to date, we want to discuss here Na_3N[183, 205] and MgF_2.[179, 182, 184] Both systems were analyzed without variation in the composition. For MgF_2 (Figure 4), the energetically

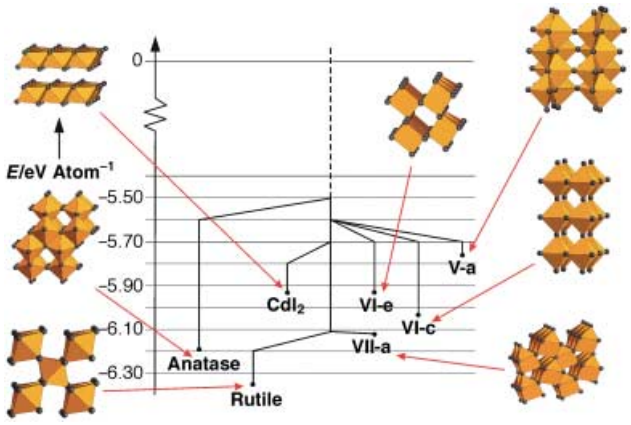

Figure 4. Results of a theoretical exploration of the energy landscape of MgF_2.[182, 184] Structure candidates with low energy are shown, together with the barrier structure in form of a tree graph.

most favorable structure found corresponds to the rutile-type, in agreement with the experiment. Remarkably, the second-lowest minimum found shows the anatase-structure, with a realistic barrier height between this and the rutile-type structure—a result that is very plausible bearing in mind that this is one of the well-known modifications of TiO_2. Thus it would appear to be quite promising to attempt to synthesize

MgF_2 in this structure type. Similarly, the other structure candidates observed obey the standard criteria for crystallochemical plausibility without any problems.

At the time when our theoretical investigations of Na_3N were performed, this compound had not yet been synthesized. It is quite remarkable, how it was possible to generate convincing structure candidates with our method (Figure 5).

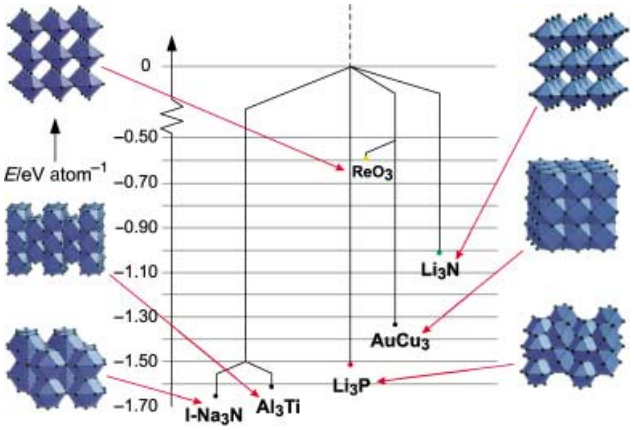

Figure 5. Structure candidates for Na_3N,[183, 205] determined by global optimization, together with the barrier structure depicted as a tree graph.

Even scientists well-versed in structural chemistry might have some trouble designing these model structures, in spite of the relatively high simplicity of the composition. For some of these structure types for Na_3N local optimizations were performed with ab initio methods (Crystal 95;[206] Figure 6). In this process, the set of low-lying minima is preserved, but the absolute values of the cohesive energies per atom can change quite significantly.

Taken as a whole, our approach has proved to be surprisingly powerful, even in the boundary region to covalently bonded solids,[16] and in the application to structures that contain complex building units.[181]

It is natural that there are going to be various connections between our concept and both earlier and current work in the

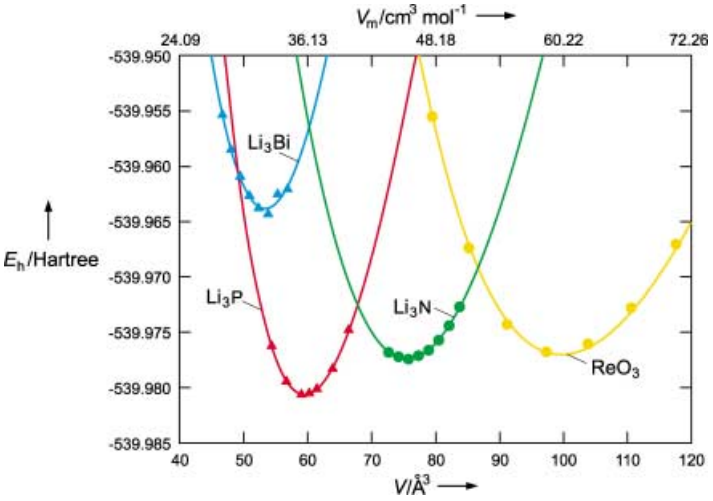

Figure 6. Results of the refinement optimization of selected structure candidates for Na_3N at Hartree–Fock level as a function of volume.[238]

field of solid-state theory. In particular the interest in computing cohesive energies goes back to the beginnings of theoretical solid-state physics.[207, 208] In addition to the computed binding energies further quantities such as lattice-constants values were often compared with experimental. In this fashion the quality of the calculations and, in particular, the empirical potentials employed could be evaluated. Furthermore, the motivation behind much work in proposing structures of solids has come from the field of X-ray crystallography of solids, where models of the structure under investigation were checked in a "trial-and-error" fashion, regarding their ability to reproduce the measured X-ray intensities.

With the increased availability of powerful computers, the call for an as unbiased as possible prediction of the structures of solids became more prominent.[209] For the first successful modeling of crystal structures sometimes unphysical cost functions were employed,[210] which in subsequent years were replaced by the cohesive energy as the only relevant quantity. In particular, researchers belonging to or being connected to Harwell in Great Britain prepared the ground for these developments. Among other work, they performed many structure determinations, where they usually employed empirically derived (effective) potentials.[211] These, and subsequent semi-empirical quantum-mechanical approaches,[212] allowed a rather impressively accurate calculation of various quantities, such as lattice constants, thermal expansion, or dielectric properties.[213] Among the favorite materials investigated were oxides,[214] halogenides,[215] and zeolites.[216] All these investigations have in common that they explore a greatly restricted energy landscape, that is, the size of the allowed configuration space is much reduced by fixing certain boundary conditions. As a consequence, often only relatively few structure candidates are present, perhaps even only one structure, usually of an already synthesized compound. One of the most common applications has been the determination of the crystal structure of a new compound, where the crystal system and the lattice constants have already been determined from a powder diffractogram and are prescribed during the optimization phase.[216]

Although our approach[16] exhibits some similarities to some of the earlier work, it is fundamentally different with regard to the basic concepts and the implementation. From the outset, our primary intention has been the identification of rewarding and realistic synthesis goals, constituting the first step in the rational planning of solid-state syntheses. The goal has always been the determination of all compounds (of not-yet-known composition), which are capable of existence in a chemical system. Taking this as the basic guideline, we reach the necessary conditions for a successful implementation: We need to perform global explorations on an unrestricted energy landscape, where, while using periodic boundary conditions, one must not fix symmetry or shape and size of the unit cell. Recently, work has appeared, which is based on the same motivation, although the implementation is different. In these studies, G. Férey and co-workers have presented a computational procedure for the automated generation of framework-structures from complex building units,[217] where the resulting structures are also meant to serve as goals for synthetic efforts.

4.3. Musings About the Rational Development of Synthetic Routes

Within the context of the concept of energy landscapes as the representations of material systems, a chemical synthesis corresponds to the transition from a set of initial configurations, located somewhere in a locally equilibrated (minimum) region of configuration space, to an analogous set of final (minimum) configurations, where both are characterized by their corresponding values of the free energy. Since such a process requires some activation and some processing time, the simplifications discussed in Section 4.1 ($T = 0$ K, $\Delta t = 0$ s) are clearly not appropriate. Thus, the modeling of a synthesis route towards an as-yet-unknown solid compound has to take place taking all external and internal influences into account, and be based on the correct physical microscopic mechanisms. Up to now, it is not possible to fulfill these requirements.

As a reasonable first step, one can try to classify the reactions that are suitable for the generation of solid compounds according to various phenomenological aspects. In Table 1, such a classification scheme is given, which appears to encompass all types of solid-state syntheses currently known. At this point, we would like to refer to the completely different situation encountered in molecular chemistry, where, at least in simple cases, one can follow reactions among individual molecules along one-dimensional reaction coordinates or, in more general situations, on still visualizable potential surfaces.

Table 1. Classification of solid-state syntheses.[a]

A) Closed systems (compositions of the sums of the educts and products are identical)
Without additives
$A(s) + B(s) = AB(s)$
$A(s) + B(l) = AB(s)$ [b]
With activating additives
$A(s) + B(s) + \text{solvent} = AB(s) + \text{solvent}$
$A(s) + B(s) + \text{transport agent} = AB(s) + \text{transport agent}$
B) Open system (formation of gaseous by-products)
Molecular precursors (s,l,g) $\rightarrow$ AB(s) + by-products
Polymer precursors (s,l) $\rightarrow$ AB(s) + by-products

[a] As examples only binary compounds are listed, ones with more components can be included in an analogous fashion. [b] For all combinations of states of the system.

For some of the reaction types listed, methods for their quantitative description have already been developed. This applies in particular to the probably most intensively studied classical solid-state reactions, that is, the ones proceeding by interdiffusion. In this instance, one can perform quite reliable calculations for given thermodynamic conditions, based on the thermodynamic data of educts and products and the diffusion coefficients for the main participants in the transport processes.[103, 104, 106–108, 122, 123, 125] This applies not only to the reaction rates, but also to the morphological changes of the interfaces between educts and products.[218, 219]

Figure 7 shows a schematic representation of an example, the formation of a spinel ($MgAl_2O_4$) from the binary components in the phase diagram. The cut shown is reached by fixing p and T, while at the same time focusing on two minima in configuration space of the components Mg, Al, and O. For the same composition, and the same amount of material, one minimum corresponds to a metastable mixture of educts MgO/Al_2O_3, the other to the spinel $MgAl_2O_4$, which probably corresponds to the global minimum. Upon thermal activation, the product is formed by interdiffusion. As a rule, the high thermal activation necessary for this reaction type, leads to the establishment of the thermodynamic equilibrium. This situation also holds for reactions between metals or intermetallic phases, which can, in principle, be performed in an analogous fashion (by interdiffusion). In most cases, one actually chooses the route by the melt for this class of substances, from which the thermodynamically stable phase crystallizes. It appears that such reaction paths (Figure 8) should in principle be capable of being modeled.

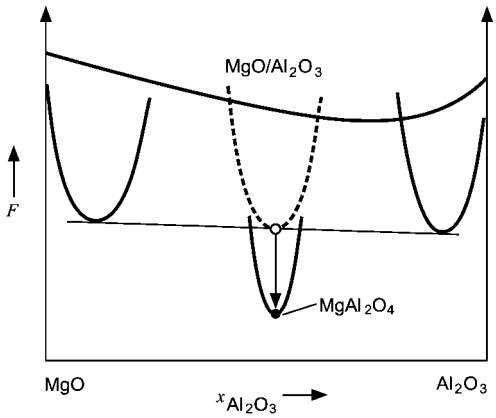

Figure 7. Synthesis of $MgAl_2O_4$ by interdiffusion of the binary components.

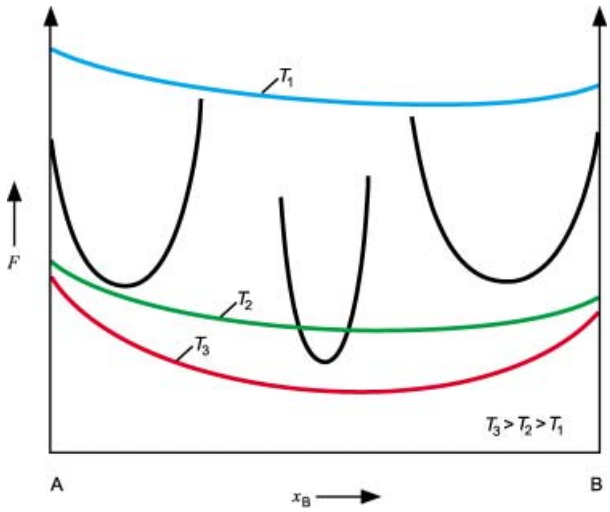

Figure 8. Schematic depiction of the synthesis of an intermetallic phase from the melt. Initial state (mixture of A and B) at T_1 (blue line shows the free energy of the melt), heating to a temperature above the melting point (T_3, red line), and cooling to a temperature below the melting point of the product phase AB (T_2, green line).

However, there exist numerous examples of solid-state syntheses by interdiffusion that proceed via non-equilibrium states. This process is always possible, once the mobility of one type of atoms exceeds those of the other components by several orders of magnitude. This group of reactions is commonly summarized under the heading of "topochemical reactions".[132, 134] Among these one counts the (reversible) incorporation of hydrogen in metallic glasses,[220] ion exchange in zeolites, and intercalations in graphite[133] or clay materials.[221, 222] Over the years, this concept has led to the development of a broad field of synthetic chemistry.[136, 223] In attempting to maintain elements or parts of the structure while only allowing specific regio-selective changes, the basic principles of this approach are close to those that hold sway in molecular chemistry. If one is willing to accept the structural framework as essentially unchangeable, one really can, within the limits this assumption imposes, perform purposeful goal-oriented syntheses. In this context, first interesting steps towards the development of theoretical models have been taken, where the preferred locations within the framework for certain reactions have been predicted based on the quantification of the chemical hardness or softness of the constitutents.[224, 225]

A very effective method to reduce the thermal activation required for a solid-state synthesis, and, at the same time, gain a higher degree of control about the reaction process, is the increase in mobility of the reactants by transferring them into a mobile gaseous or liquid phase (Table 1, A). Here, one has to recall one of the oldest techniques in chemistry, the dissolution of the educts in appropriate solvents, followed by the precipitation of the products. Another related approach is the chemical transport in the gas phase, which, after first having been described phenomenologically, has been systematically analyzed by H. Schäfer and has been made amenable to a quantitative description.[13, 122] The developments to date now allow, even for complex chemical systems, a rational choice of transport media, the computation of the direction of transport and of the optimal temperatures for source and sink, and finally an estimate of the transport rates.[226–228] However, if one wants to apply chemical transport not simply in an experimental fashion, one needs to know both the composition in the gas phase, which is often a very critical aspect, and the enthalpies and entropies of formation of all participating species at the temperature of the experiment. One should note that compared to the conditions in a classical solid-state reaction, the input of thermal energy is reduced. One of the strengths of this synthesis method is the possibility to synthesize solids, which are only stable at low temperatures (subsolidus-region). As another (often desired) consequence of the high mobility, the processes during chemical transport are close to equilibrium, and they can be used analyzing equilibrium phase diagrams.[229]

There is an increasing tendency in preparative solid-state chemistry to employ compounds as educts ("precursors"), which produce the components of the desired compound in a highly reactive form by thermal degradation.[119, 121] In the special case of single-source precursors, the constituent elements of the final compound are already in the right proportion dispersed on an atomic level, but still bonded chemically.[121, 230] In this instance, the product results from a thermal degradation of all the "volatile" constituents. In particularly fortuitous cases, the initial state of the system is as well defined as the final product. However, the many different heterogeneous, amorphous, and partly crystalline intermediary stages are very difficult to intercept and analyze. Thus, these synthesis methods defy a quantitative description to a large extent.

When designing a solid-state synthesis, as is true for every chemical synthesis, it is important to ensure that the thermodynamic precondition for all spontaneous processes holds, that is, that the free energy of the closed system decreases during each of the steps along the synthesis route. Of course, this issue is not a critical one as long as the final product corresponds to the global minimum of the system under consideration. If the desired compound is metastable, one either needs to employ starting compounds that are rich in excess energy and/or the reaction paths must be designed in such a way that by-products of a very low free enthalpy of formation are evolved. Another option consists in adding energy to the system from the outside, for example by electro- or photochemical methods. The minimal kinetic requirement for a reaction is the availability of a sufficiently efficient material transport. It has already been mentioned several times that as mild (thermal) conditions as possible should to be used to achieve a certain degree of control over the reaction. This catalogue of tasks and issues involved in the planning of a synthesis route is usually addressed by today's solid-state chemist for each problem individually in a mostly intuitive and empirical fashion. This approach is understandable, since all attempts to proceed in a more systematic rational way, which might, for example, include an active steering of the reaction process towards a pre-defined compound, would require a complete knowledge of the intermediate compounds and the barrier structure of the corresponding energy landscape for realistic thermodynamic conditions. Furthermore, a quantitative treatment of the transport processes during the reaction, as discussed above for interdiffusion and chemical transport, is at best feasible for model systems under the assumption that the necessary thermodynamic and kinetic data are available. Although one can reach some degree of insight for such isolated instances, a practical and generally applicable design of synthesis routes in solid-state chemistry is not yet within our reach.

5. High Mobility, Short Transport Distances: Reactions in the Solid-State with Minimal Thermal Activation

As discussed in Section 4.3, the second step necessary for a rational planning of syntheses, that is, the general unbiased development of a reaction path for the synthesis of a predicted compound that is capable of existence, cannot yet be taken with the theoretical methods available today. Thus we have not pursued such deductive approaches any further for the time being. Instead we have attempted to reproduce as closely as possible the "computational annealing" employed during structure prediction in the actual experiment. At the same

time we are trying to avoid the complications which are associated with an only macroscopic mixing of the educts and the subsequent need for a high thermal activation of the material transport. Since one cannot influence the elementary processes contributing to diffusion in solids, that is the local jumps of atoms, to a meaningful degree, we have concluded that one should instead attempt to reduce the distances across which the material has to be moved to a minimum, preferably to atomic distances. This goal can be achieved by generating a mixture of educts that contains the constituting elements randomly distributed on an atomic level.[231, 232] If in addition the starting state exhibits the same composition as the desired crystalline product, one would not expect any large concentration gradients to develop in the course of the reaction that would require increased thermal activation for equilibration by an extended material transport.

The thermodynamic consequences, as in the Born–Haber cycle, of the use of educts that are distributed in an atomically disperse fashion, instead of macroscopic mixtures of the constituting components in their states under standard conditions, are an increase of the reaction energies by an amount that approximately corresponds to the atomization energies of the components. A comparison of the usual tabulated standard enthalpies of formation with such "atomical enthalpies of formation" can be quite instructive, since the latter show the intrinsic thermodynamic stabilities of chemical compounds, independent of the variations in the cohesive energies of the starting materials.[233] Of course, this way of implementing a synthesis route for the realization of metastable solids meets a well-defined limit: If during the reaction no additional energy is added from the outside, only such metastable compounds will be accessible, which have a positive free enthalpy of formation that is smaller than the sum of the free energies of atomization of the components.

To implement this general approach experimentally, we have developed a vapor deposition method, where the desired components are first vaporized separately to form a gas of atoms in an ultra-high vacuum (UHV) chamber (Figure 9).[231] These gas particles are then deposited simultaneously in a statistical distribution on a substrate. The evaporation sources are resistance-heated effusion cells and an electron-beam vaporizer together with a microwave plasma source for the dissociation/activation of the gases employed. One can mount a maximum number of five sources under an angle of 22° or 45° normal to the substrate. The substrate resides on a sample carrier, the temperature of which can be adjusted between 77 and 600 K. The sample carrier is part of a moveable transfer system, which is connected to the preparation chamber by a vacuum hatch. In this way, a transfer of the samples from the preparation chamber to, for example, a diffractometer or an exchange of samples through a glove box is possible while preserving both the cooling and the vacuum. In addition to the adjustment of the various sources the atmosphere in the chamber during the deposition is monitored using a mass spectrometer. The machine possesses a system of cryo-pumps, which creates a basic pressure of $< 1 \times 10^{-8}$ mbar, and allows pressures during processing in the range of $3-6 \times 10^{-5}$ mbar. Furthermore, it is possible to fill the evaporation sources with air- and humidity-sensitive substances through a transfer box.

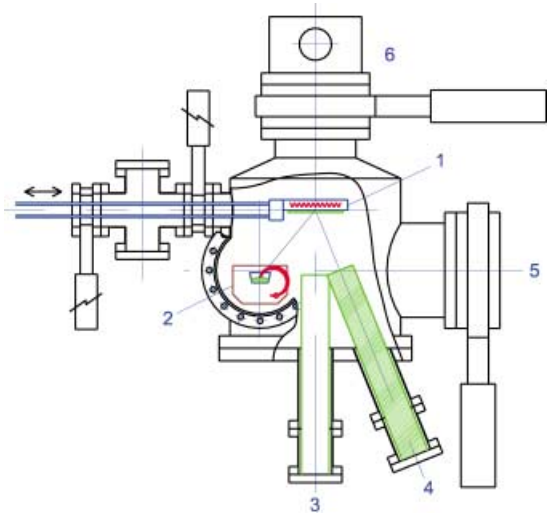

Figure 9. UHV-set up for the synthesis of solids from atomically disperse educt mixtures (preparation chamber including hatch to the movable transfer system). 1) Sample holder with sapphire substrate, integrated heating, and feed for LN_2, 2) electron-beam vaporizer, 3) effusion cell, 4) MW-plasma source, 5) gate valve to the cryo-pumps, 6) transferbox with gate valve.

We have checked the applicability of the basic concept and the functioning of the set-up in a number of case studies. From among these investigations, the results for the systems Ag/N/O, Ag/O, and Na/N are presented. In the first case, silver was deposited simultaneously with nitrogen and oxygen on a sapphire substrate cooled to 77 K.[231] The educt mixture at this temperature is X-ray amorphous (Figure 10). On slowly

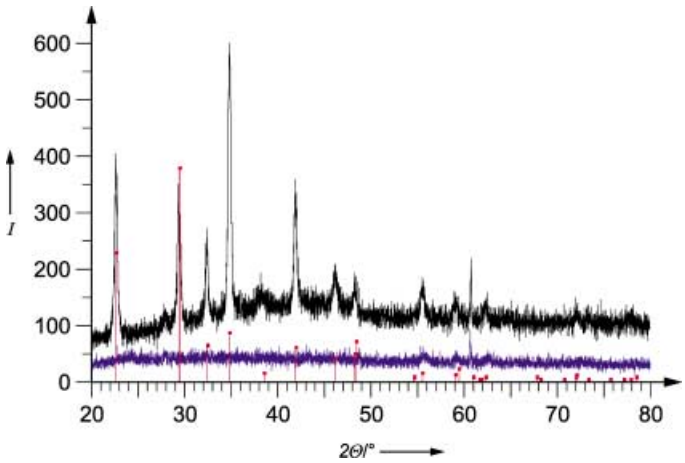

Figure 10. X-ray powder diffraction patterns of the educt mixture consisting of Ag, N, and O at 77 K (blue curve) and the reaction products after heating to room temperature (black), together with computed intensities for HT-$AgNO_3$ (red).

heating the sample to room temperature, reaction and crystallization occur. The diffractogram observed is, considering the temperatures employed, surprisingly well structured, and can clearly be assigned to the high-temperature phase of $AgNO_3$. If silver and oxygen are deposited in an analogous fashion on a sapphire substrate at room temperature, immediately a reaction to AgO occurs.[231] However, in this instance the intensities of the Bragg reflections are

strongly affected by the preferred orientations of the crystallites. Similarly, in the case of sodium and nitrogen the components were transferred to the gas phase and simultaneously deposited in a random distribution on a cooled (77 K) substrate (sapphire).[232] After heating to room temperature, the diffraction pattern shown in Figure 11 was collected. This result demonstrates that the route outlined above has enabled us to synthesize the compound Na_3N for the first time, a material that had been searched for over a long time and had even been claimed to be "not-capable-of-existence". Its structure can clearly be assigned to the anti-ReO_3 type.

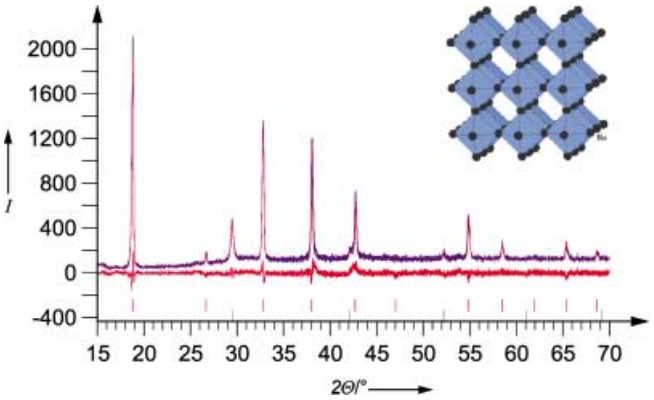

Figure 11. Powder diffraction pattern for Na_3N (Rietveld refinement) and structure candidate (anti-ReO_3 type).[232]

These observations are quite unusual in several ways. In the context of the analysis presented here, one should surely highlight the unparalleled low thermal activation needed to transform the solid mixture of educts by a solid-state reaction into highly crystallized monophase products. Another remarkable fact is the straightforwardness, which is manifest in the synthesis of, for example, $AgNO_3$ from the elements, compared with the traditional synthesis of $AgNO_3$ (synthesis of ammonia, Ostwald-method for the production of nitric acid, dissolution of silver in nitric acid, crystallization). In particular the examples of AgO and Na_3N demonstrate the potential of the method for the synthesis of thermally extremely labile metastable compounds. Up to now, AgO has only been accessible by precipitation from aqueous solution[234, 235] or by electrocrystallization.[236] Of note is that Na_3N decomposes already at 360 K, and thus is unlikely to be accessible by conventional solid-state synthesis.

A crucial element for the ease with which the solid-state reactions described were able to proceed even below room temperature is definitely the extremely homogeneous and smooth distribution of the reactants in the initial mixture. The transport distances have been reduced to atomic length scales, and thus the notorious difficulties of a long-range transport of material in the solid can be circumvented. As a consequence, one can now perform chemical reactions in the solid phase under thermal conditions that are similarly mild as those usually employed in solution chemistry.

This novel set-up for solid-state syntheses appears to be universally applicable. Its particular advantages are reflected in the opportunity to experimentally reach especially high-lying and/or particularly flat minima of the energy landscapes of chemical systems. This is an important partial success in our efforts to develop a rational and efficient solid-state synthesis. However, this approach still misses the mark in one decisive issue, the ability to generate a definite compound with a given structure in a completely intentional and controlled fashion.

Once one analyzes the results of the case studies described above, it becomes clear that the selection of the product phases actually produced from among the multitude of the possible ones is controlled by the speed of nucleation. Thus, following Ostwald's or Vollmer's rule, at high supersaturation first the modifications with the lowest density crystallize,[237] that is, those for which with the smallest number of atoms the critical crystal size has been reached. In this way, one can easily understand, that a synthesis at low temperatures yields the high temperature phase of $AgNO_3$, at first sight a paradoxical result. Similarly, for the case of Na_3N, for which theoretical investigations had predicted the most promising structure candidates,[205] we did not find one of the modifications with the highest energies of cohesion. Instead, Na_3N was found in the anti-ReO_3-type (see Figure 6[238]), the modification with the lowest density. Thus, these observations place the focus on the initial step in the generation of crystalline phases, the formation of a crystal nucleus, when searching for the most important element in the control of a solid-state synthesis of a desired product.

In the widest sense one has to place the route we have taken to generate educt mixtures that are atomically disperse among the traditional PVD (physical vapor deposition) methods.[239] Insights gained from these and the modern MBE (molecular beam epitaxy) methods[240] have been crucial in the design and construction of our UHV-evaporation set-up. In general, PVD is mostly employed to evaporate chemical compounds and to deposit these as more or less thin films on a substrate.[241] Interestingly enough, one had already noticed at the beginning of PVD-applications that the material deposited often was present in metastable modifications, in agreement with Vollmer's rule.[242] The formation of metastable LiI in the Wurtzite type during PVD of LiI also serves as an example within this context.[195]

In the examples discussed so far, the chemical nature of the evaporated and re-deposited materials remains unchanged. Chemical reactions of the substrate appeared during the development of MBE for the generation of semiconductors with well-defined structures. The constituting elements were deposited epitactically, monolayer after monolayer and converted into the desired semiconductor.[243, 244] The synthetic relevance finally stepped into the foreground in the context of the creation of thin films of superconducting chevrel phases from the elements.[245, 246] To achieve this result, UHV-chambers were constructed, in which the constituent metals were evaporated, either in a H_2S atmosphere or together with elementary sulfur, and made to react on a heated substrate ($\sim$800 °C). In similarly constructed evaporation chambers, D. C. Johnson et al. have deposited layers of metallic and non-metallic elements, and then induced a reaction.[247–250] In a series of impressive studies they could show, how in this fashion novel, partly modulated layer structures could be built up,[251, 252] where they paid special attention to the issue of nucleation and growth.[253, 254] However, one should note that

the thickness of their layers approached macroscopic dimensions. This feature might explain, why the reaction temperatures necessary for their experiments were still in the range of 200–700 °C. In any case this difference to our approach cannot be related to the properties of the elements involved, in particular their diffusion coefficients, since these are, for metal ions, typically larger in chalcogenides and pnictides than in oxides.

6. Rational Synthesis Planning or High-Throughput Exploration?

The traditional experimental approach to the exploration of energy landscapes of chemical systems has in recent years been enriched by the addition of an attractive option. The modification consists mainly of the fact that solid-state syntheses are being performed in an automated and parallelized fashion, which results in a much higher throughput.[25, 255] The set of compounds produced in this fashion is often denoted a "library", a term that has been recently and justifiably challenged.[256] The compounds synthesized in parallel can be tested for various structural, bonding, or materials properties of interest, by using appropriate probes. Since an "automated" generation of many different initial mixtures and their traditional reactions (only in parallel and thus more efficient) do not really justify the attribute "combinatorial"; at least in the field of solid-state synthesis, we prefer the alternative name "high-throughput method". This approach has only been used for a few years, but it has already had substantial successes, in particular regarding the optimization of materials properties of already known compound families. Especially impressive applications have been results in the field of inorganic phosphorescent materials,[257] ceramic superconductors,[258] and heterogeneous catalysts.[259, 260] There can be no doubt that a systematic use of high-throughput methods will raise the efficiency of solid-state and materials research. This is a welcome development, no matter whether the original motivation has been of an economic or academic nature. However, one must warn against an uncritical application of these methods. One can very easily overlook compounds capable of existence, while having a false sense of security because one has chosen a very fine resolution in composition space. Already the directing force of nucleus formation and selection will favor certain phases under given reaction conditions and suppress others. In addition, the synthesis of a specific solid compound usually requires individually optimized synthesis parameters (going beyond the composition of the initial mixture). Additional problems can result from using small sample sizes which can result in a non-negligible amount of interface and surface effects. Furthermore, some of the properties cannot be screened easily in parallel, necessitating a rather large screening effort.[261] Finally, if one really wants to know which material is responsible for a certain effect, each sample has to be analyzed in detail (in the case of a new phase, one needs to determine its structure); in particular, its homogeneity has to be verified.

How does this increase in efficiency of exploring the energy landscape of chemical systems with experimental methods face up to the task of identifying all the compounds capable of existence? To answer this question, let us perform some crude estimates regarding the minimum number of syntheses required for such a task. Taking the number of reactive elements with sufficiently long-lived atomic nuclei to be 86, we find the number of chemical systems that need to be investigated (see Figure 12) to be the unimaginably high

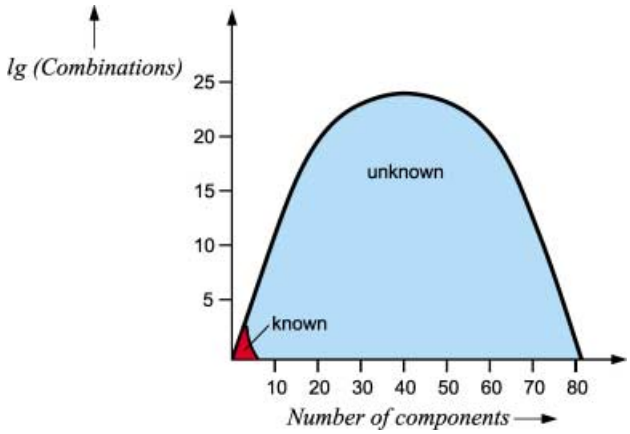

Figure 12. Dependence of the number of possible systems on the number of components; red: systems investigated up to now.

number of 2^{86}.[262] From among these, today only the unary and nearly all binary ones have been investigated, a state of affairs that is not to be confused with "completely explored". Of course, the total number of experiments to be performed depends on the resolution in parameter space one employs. But the number of compounds to be synthesized during a restriction-free exploration of our material world easily reaches 10^{80}–10^{90} (Table 2). These gigantic numbers, comparable to the estimated number of atoms in the universe, do not lose anything of their power, if one were to exclude "obviously unproductive" element combinations. This would at most reduce the number of compounds by ten to perhaps twenty orders of magnitude.

Let us take as a specific example the high-temperature superconductor $YBa_2Cu_3O_{7-x}$, and investigate, how many samples need to be synthesized and tested, to definitely include this compound in the output of a high-throughput method. Even with the highly restrictive information that we are dealing with a quaternary oxide, where oxygen is to be offered in unlimited amounts, one would need to prepare about 10^{12} samples. Using a (today still very optimistic) throughput-rate of 10^5 samples per day, a systematic and unbiased, one might even say "mechanical", search through the parameter space would take about 27000 years.

The numerical examples given above demonstrate the overwhelming chemical variability that grows out of the comparatively small number of available elements. We feel that this is an essential characteristic of chemistry in general. At present, we have gained access only to a minute fraction of the possible chemical compounds, nearly infinitely less than the proverbial "tip of the iceberg". This explains in a natural

Table 2. Considerations concerning the number of experiments needed to explore chemical systems by a high-throughput synthesis.

- Number of systems overall:[a]
  $\sum_{n=0}^{86} \binom{86}{n} = 2^{86}$
- Number of systems with n elements:[a]
  $\binom{86}{n} = \frac{86!}{n!(86-n)!}$
- Number of possible compositions of all elements:
  –without variation of experimental conditions[b]
  $\sum_{n=0}^{86} \binom{86}{n} I^n = (I+1)^{86}$
  –Including experimental conditions[b,c]
  $(I+1)^{86} \cdot n_p \cdot n_T \cdot n_R \cdot n_A$
- As comparison: total number of atoms in the universe: $\approx 10^{80}$

Case study: $YBa_2Cu_3O_{7-x}$
$n = 3$[d], $I = 10$, $n_p = 10$, $n_T = 10$, $n_R = 10$, $n_A = 10$
N_{Exp}: Number of high-throughput experiments that need to be performed.
$N_{\mathrm{Exp}} = \binom{86}{3} \cdot 10^3 \cdot 10 \cdot 10 \cdot 10 \cdot 10 \approx 10^{12}$ experiments

[a] Assumption: 86 elements available. [b] Assumption: Every element A in a system contributes i_A ($i_A = 1,..,I$) atoms to a formula unit. Number of compositions for n components: I^n. [c] Assumptions: n_p pressures, n_T temperatures, n_R reaction pathways, n_A machines available for high-throughput exploration. [d] Oxygen adjusts to the composition and the experimental conditions

way, why newly discovered compounds and unconventional structures are often experienced as "accidental" or "surprising", which in reality means nothing else but that they cannot (yet) be placed into the general context of chemical compounds and structures based on our current level of understanding.

Thus, the answer to the question posed in the heading of this section is quite clear: Trying to rely only on high-throughput methods is clearly not the most efficient way to explore chemical systems. One needs to find reasonable criteria to restrict the parameter space under investigation. This can either occur on the basis of intuition and experience, or with the help of theoretical methods. For example, one might want to use our concept of the exploration of the landscape of chemical systems by global optimization to identify very promising regions in configuration and parameter space, or, subsequently, to check, whether one has overlooked important regions, for example, deep minima, within the space explored using high-throughput methods.

7. Outlook

We have presented a concept for the development of a rational planning of syntheses in solid-state chemistry. The foundation of our approach is the fact that the material world is represented on an energy landscape, which leads to a unified and consistent picture that allows us to include, in principle, all aspects of planning a rational synthesis route. At the current state of development, only parts of this approach have been implemented. Thus, in some ways, it still carries a visionary feeling. However, we do not consider our approach a utopian one, and we feel that each of the separate steps presented can be realized. And even though we are still far away from a routine application of our concepts, wrestling with them yields many insights into conventional explorative solid-state chemistry. The competition between traditional methods and syntheses involving rational design will, in the end, be decided based on their usefulness in practice. But in both cases, this measure will reflect the efficiency in exploring the energy landscape, as seen in the number and novelty of new solid compounds compared to the effort required. Considering the productivity and output of current solid-state chemistry, it is obvious that rational synthesis planning will face a steep climb. However, we are convinced that with the passing of time, the scales will tip in its favor.

Indubitably, the path ahead is still quite long. The most likely goal to be reached in the nearer future appears to be the theoretical exploration of the energy landscape of chemical systems, that is, the prediction of compounds capable of existence. Currently, the most critical issue is the computation of the energy of a given configuration during the global optimization. This is not yet feasible with the desired accuracy and in an acceptable time for the relative large systems investigated. The weak point of the current implementation is the necessity to use simple empirical potentials, which tends to push the system towards a certain type of bonding. Even though this can often be estimated with good accuracy for many element combinations, such an approximation negates the stated purpose of an unbiased exploration of the configuration space. The most straightforward solution would be to employ ab initio quantum-mechanical energy calculations instead. Although there has been much progress in this respect,[174, 263–266] the algorithms developed are still too slow. Their application does not yet allow a global exploration of configuration space of realistic systems within an acceptable length of time. In this respect, our hopes rest with further methodological advances and the not-yet-abating increase in computational power. Possible intermediary solutions might be the use of "learning" empirical potentials or a Pareto-optimization[267] using as cost function a linear combination of energies computed according to different methods (corresponding, for example, to the three most important types of chemical bonding). However, it is doubtful, whether the ratio of computational effort to quality of the results might not be even more unfavorable than the one encountered when employing simplified Hartree–Fock or density-functional approaches. Nevertheless, we feel that our current two-step procedure, the global optimization with a very general two-body potential followed by a local refinement optimization with ab initio methods, is at the moment the most efficient solution to the problem. Of course, the danger of overlooking interesting structure candidates cannot be completely excluded. This aspect might gain in relevance once one tries to determine compounds capable of existence that possess only a very low kinetic stability.

The second step, the rational design of a feasible synthesis route, is not yet possible for most instances. The reason for this can be found to a large extent in the requirement that the modeling needs to take place under realistic p/T conditions and for systems with realistic sizes, which does not allow us to use several of our standard approximations. Furthermore, larger regions on extended configuration spaces need to be

analyzed, which include both the possible educts and the final product.[268, 269] Thus, one still has to rely on procedures that are essentially of an exploratory nature. But here, too, significant improvements are possible as we could show with our approach to solid-state synthesis with minimal thermal activation.[231, 232] In particular these mild reaction conditions open the door towards the synthesis of thermally labile (metastable) solids. If designed as a high-throughput method, this synthesis technique should be capable of being developed into an efficient explorative solid-state-synthesis method.

The progress made to date cannot hide the fact that up to now there does not yet exist an approach to the rational goal-oriented design of a synthetic route to a (predicted) novel solid. As our own results confirm, the route to such a methodology proceeds through a theoretical description and experimental control of formation of crystal nuclei.[270–272] Going beyond the macroscopic, classical phenomenological description, first attempts to model nucleus formation on an atomic level have already been presented.[273–275] Compared to these first steps, the tools available for an experimental control of this process are disappointingly rudimentary. Depending on the external conditions, spontaneous formation of crystal nuclei leads either to the crystallization of the thermodynamically stable phase or, according to Ostwald's rule, first to a modification with low density usually followed by (eventually a cascade of) phase transformations to the phase corresponding to the global minimum.

It is clear that both these routes will only lead to a small fraction of the (predicted) compounds capable of existence. One can influence the formation of nuclei by varying temperature, pressure, and supersaturation. However, with respect to the desired selectivity these are rather blunt instruments. Providing a seed in the most general interpretation can serve as a universal tool for the control of crystallization. In addition to adding a crystal seed of the desired compound—which assumes that such seeds are already available (see below)—using heterogeneous nucleation appears to be most useful. Particularly promising should be epitactic growth on a substrate, the lattice parameters and symmetry of which agree with those of a plane of the desired substance. Such a substrate could be used either as the macroscopic base for the initial mixture of educts during the atomically disperse vapor deposition, or as a very finely ground additive. But a fundamental advance would entail an effective control and steering of the homogeneous nucleation. Solving this problem requires us to set the external parameters (p, T, supersaturation) such that the critical size for nucleation is reached first for those nuclei belonging to the desired product. If one demands a rational approach in this respect, one will have to perform the corresponding modeling of nucleation for the desired compound as a function of the external parameters while including interface and matrix effects. These, and other conceivable approaches, which are based on a systematic building of the nucleus atom by atom with physical or chemical means, are quite reasonable, of course, but are today still far from being realizable.

When dealing with the many issues discussed in this Review, certain conclusions and ramifications are naturally impressed upon us, the discussion of which, however, would exceed the limited range of the topic we have been trying to address. According to our ideas, all chemical compounds capable of existence (with a certain lifetime) are already present on the energy landscape, and are just waiting to be discovered. If one considers the fundamental importance of solid matter in the form of traditional and novel materials for the welfare of mankind, should one not then propose to start a systematic world-wide coordinated effort with the goal of tabulating all the compounds capable of existence? Reminding oneself of Lao-Tse's teachings,[1] the size of such an enterprise should not scare us. It would be comparable to the development of the botanical and zoological classification in classical biology or, even more, the exemplary "Human Genome Project", which has succeeded in fully deciphering the human genetic information.

Our work has been supported by the Deutsche Forschungsgemeinschaft (Gottfried-Wilhelm-Leibniz program) and the Fonds der Chemischen Industrie. My special thanks go to my co-workers Holger Putz, Marcus Wevers, Alexander Hannemann, Zeljko Cancarevic, Dieter Fischer and, in particular, Christian Schön for their highly motivated efforts and their competent contributions. I would also like to thank Jeannette Knapp, Lars Hildebrandt, Zeljko Cancarevic, and Alexander Hannemann for their support in preparing this manuscript.

Received: April 18, 2002 [A 531]

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