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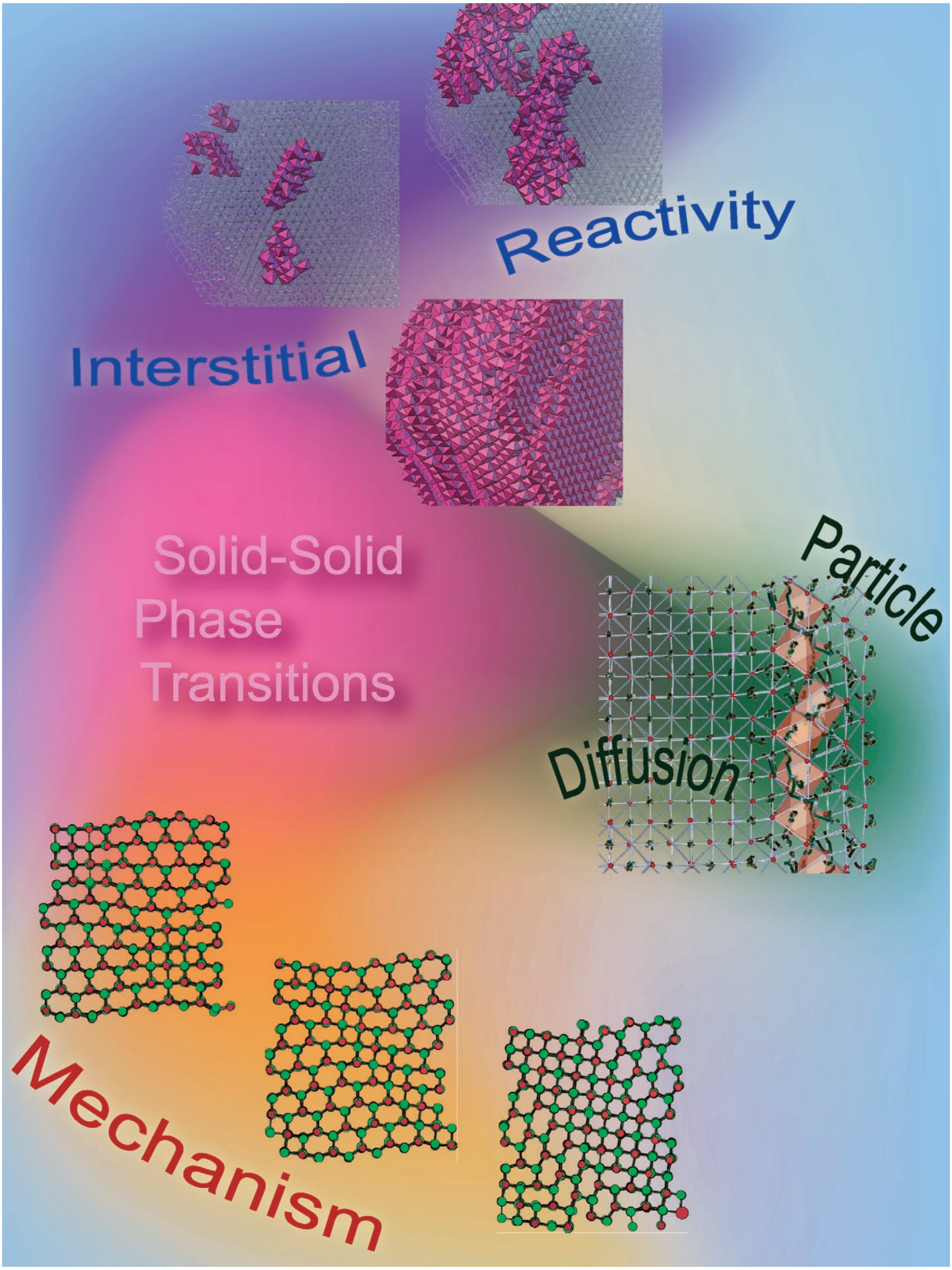

Solid–Solid Phase Transitions: Interface Controlled Reactivity and Formation of Intermediate Structures

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Abstract: Finding new pathways to novel materials is an open challenge in modern solid-state chemistry. Among the reasons that still prevent a rational planning of synthetic routes is the lack of an atomistic understanding at the moment of phase formation. Metastable phases are, in this respect, powerful points of access to new materials. For the synthetic efforts to fully take advantage of such peculiar intermediates, a precise atomistic understanding of critical processes in the solid state in its many facets, that is, nucleation patterns, formation and propagation of interfaces, intermediate structures, and phase growth, is mandatory. Recently we have started a systematic theoretical study of phase transitions, especially of processes with first-order thermodynamics, to reach a firm understanding of the atomistic mechanisms governing polymorphism in the solid state. A clear picture is emerging of the interplay between nucleation patterns, the evolution of domain interfaces and final material morphology. Therein intermediate metastable structural motifs with distinct atomic patterns are identified, which become exciting targets for chemical synthesis. Accordingly, a new way of implementing simulation strategies as a powerful support to the chemical intuition is emerging. Simulations of real materials under conditions corresponding to the experiments are shedding light onto yet elusive aspects of solid–solid transformations. Particularly, sharp insights into local nucleation and growth events allow the formulation of new concepts for rationalizing interfaces formed during phase nucleation and growth. Structurally different and confined in space, metastable interfaces occurring during polymorph transformations bring about distinct diffusion behavior of the chemical species involved. More generally, stable structures emerge as a result of the concurrence of the transformation mechanism and of chemical reactions within the phase-growth fronts.

Keywords: molecular dynamics • particle diffusion • phase transitions • reaction mechanisms • solid-state reactions

Introduction

Today the quest for novel materials with distinct properties for critical technological applications, like power or information storage, energy conversion, or improved mechanical properties, has motivated a consistent effort in better understanding solid-state processes, both experimentally and from theory. The progress of the past decades on nanomaterials have shown that bulk properties break down on crossing lower size limits, unfolding a rich set of new stability rules and opening new synthetic pathways. For solid-state synthesis this means (at least) that bulk materials ruled out by an unfavorable thermodynamics may suddenly become accessible on reducing size. While a wealth of facts and rules on the polymorphism of solids has been collected, finding new pathways to novel materials remains an ongoing challenge in modern solid-state chemistry. Especially an understanding of the rules governing the stability of the (known) phases of a compound, and thus affecting the "metastability" of some configurations, has escaped a full rationalization, although experiments are shedding light on the "rules of metastability" in solids.[1] In a subset of cases, metastable phases can be formed that persist indefinitely, like diamond that does not revert to graphite on releasing pressure, or AlN that stays in the high-pressure rocksalt structure type. In the vast majority of cases, however, compounds obtained under pressure or at high temperature quickly relax towards less dense configurations that are lower in energy. Clearly, the energetic barriers in between are different. However, a firm understanding of what determines such differences is still missing.

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Metastable phases represent a powerful point of access to new materials, so understanding the rules of metastability is not just an investigation on fundamental aspects. It means figuring out which intermediate configurations can be realized during a transformation and how to access them. The new material nucleates within the pristine one, and initially isolated nuclei grow through propagation of phase fronts. Such interfaces may fuse upon domain–domain contacts, or turn into grain boundaries under formation of polycrystalline solids. Understanding the details of such processes means not only a better control of material properties, but primarily a rational approach to material synthesis.

In general terms, it is the nature of the reactivity in solids that has to be unfolded. For this, new theoretical concepts and simulations for direct comparison to the experiments have to be brought into existence. Such integral approaches not only require the availability of improved simulation schemes or the better performance of computers, it is the discovery of the richness of chemical issues beyond the bare thermodynamic classification of phase transitions that has boosted new perspectives.

So far, critical phenomena are accounted for within classical Landau theory,[2] and phase growth is described within classical nucleation theory. Due to the missing relationship of a group and a subgroup between the symmetry groups of the crystal structures surrounding a phase transition, a necessary condition for Landau theory is in general not met by reconstructive phase transitions, with large atomic movements and macroscopic stress. This has probably prevented a general theory of reconstructive phase transitions to develop and the investigation of the *reactivity* of solids has too often been dimmed out by the search of the *mechanism* of a phase transition, which is only part of a much richer chemical picture.

Having realized that phase transitions are extraordinary phenomena of the "ordinary" chemical reactivity of solids, we have recently started a systematic theoretical study of reactions in the solid state,[3–9] with emphasis on phase transformation with phase coexistence, to reach a firm understanding of the rules governing polymorphism.

Solid-State Reactions and Chemical Reactivity

The investigation of reactions in the solid state, especially in case of experiments performed on single crystals, often reveals preferred crystallographic orientation relations between the initial crystal and the final product.[10] The fact that such relations accompany solid-state chemical reactions has often been used to justify the derivation of transformation mechanisms on the basis of geometrical–topological arguments.[11–13] The geometrical argument is supposed to hold on the assumption of shortest atomic displacements and lowest strain, and the derived models are concerted in the atomic moves and develop smoothly, that is, without any interface region of coexisting structural domains. However, the existence of orientation relationships does not imply a second-order type, continuous transformation. It rather hints at a more articulated scenario in which one or several nuclei start growing from the initial atomic pattern. The latter functions as some sort of substrate for the forming nuclei, which may influence their initial relative orientation and the final mutual arrangement of domains. Different from continuous, second-order phase transitions, in which domain orientations are subsumed under group–subgroup relationships, the initial space group does not need to play any active role in determining domain orientations.[14] The latter are determined by the local reactivity alone, which reflects different ways of implementing a global mechanism and energetic preferences rather than group–subgroup patterns. The existence of a more or less extensive topotaxy[15] between initial crystal structure and final product, invites the theoretical oriented chemist to formulate more articulated integral simulation approaches, able to account for both local chemical reactivity and the global mechanism.

This change in the point of view on phase transitions is illustrated in Figure 1. The upper part shows the traditional picture of two structures types, B2 (CsCl type structure) and B1 (rocksalt structure type) transforming into each other under pressure. This type of transformation is undergone by the majority of alkali-metal halogenides, among them NaCl, KF, or RbCl. By means of geometric interpolation structural motifs are transformed, leading to a concerted movement of all atoms within an intrinsically single-crystalline model. The lower part presents the same type of transformation with the details as we have learned them from our simulations. The transformation sets in as an archipelago of nucleation centers, followed by growth resulting in complete transformation into the final structure type. Unlike the concerted ionic movement inherent to the traditional approach, the nucleation and growth scenario implies the coexistence of motifs of both stable structures in separate domains. The many arrows connecting initial and final atomic configurations hint at many intermediate steps of local reactions that

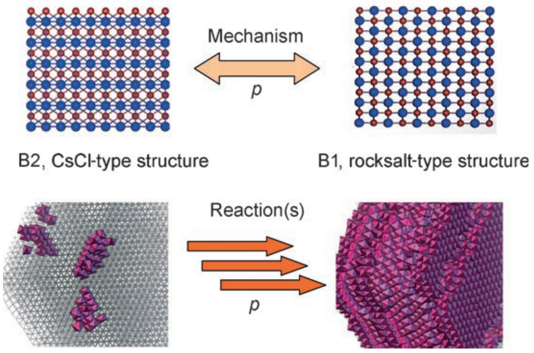

Figure 1. Distinct points of view on reconstructive phase transformations. Upper part: Collective picture of a solid state transition. Lower part: Formation of nucleation centers in a solid-state reaction within an initial structural pattern, followed by domain intergrowth under formation of a complex morphology.

are responsible for the complex final morphology, and for a (more or less extensive) topotaxy. The nucleation and growth pattern is pertinent to the high-pressure reactivity of the compound. Indeed it is a nucleation pattern rather than a single nucleus that destabilizes the system and promotes material transformation. Interestingly, a B1→B2→B1 cycle is better written B1→B2→B1′ as the B2→B1 reaction induces poly-crystallinity.

In the following, example scenarios demonstrating the investigation of phase nucleation and growth,[3–6] phase growth,[3–6] domain morphogenesis,[6–8] metastable interfaces and metastable intermediates,[3–9] and ionic conduction at interfaces[9] are described, and the impact of our simulations on the way of thinking about solid-state reactions is demonstrated. While the computational details are discussed in detail in the given references, some important issues shall be recalled here.

1) The calculations are based on classical molecular dynamics, and address the mechanistic details of transformation among polymorphs. Therein, an initial trajectory is iteratively optimized until a stable regime is reached.[3] The analysis is then performed on the trajectory manifold related to the stable regime.
2) The initial trajectories are derived from geometric models based on transforming periodic nodal surfaces.[4,16] Starting the calculation from different initial paths that code distinct mechanistic models, and verifying their convergence to the same final mechanistic regime represents a strong indication of the preference of a way of transforming. Furthermore, it allows for a direct comparison between mechanisms.
3) For the examples given in the following, (empirical) interatomic pair potentials were used in the calculations. The choice is based on the adequateness of the potential model to the chemical system under investigation. The potential is then required to be portable across the polymorphs in terms of bulk properties, energetic score, and charge separation. An example on how to verify the latter point can be found in reference [7]. Furthermore, the size of the system for a mechanistic investigation is critical (and will be demonstrated in the following) and the computational costs of the calculations can only be overcome with a slim (yet appropriate) potential model. A too small simulation system, in the typical order of ab initio methods, does not allow the observation of nucleation and growth phenomena. For a discussion on static quantum-mechanical calculations with respect to pair potential-based simulations for mechanistic analysis with nucleation and growth phenomena, we refer to our recent work on GaN.[16]

The Example of NaCl

Although NaCl represents a fundamental structure type, the quest for the transformation mechanism of NaCl under pressure has been an outstanding scientific challenge for a long time. NaCl undergoes a high-pressure transition from NaCl type or B1 to CsCl type or B2 at a pressure of approximately 29 GPa and $T = 300$ K. Two main mechanisms for this reconstructive phase transition have been proposed over the years. In the mechanism named after Bürger[18] a concerted distortion occurs as a compression of the unit cell of NaCl along the cell diagonal and an expansion in the perpendicular direction. The second, due to Hyde and O'Keeffe,[19] involves an interplanar movement and an antiparallel displacement of atoms in adjacent (100) NaCl layers. While experimentally difficult to assess, mainly due to the large volume change of the crystal, the elucidation of the mechanism has motivated many theoretical efforts. Traditionally, continuous deformation pathways are derived on the basis of a common cell, which has sufficient degrees of freedom for the atoms to move from one limiting high-symmetry atomic configuration to the other. Therein, the mechanisms are intrinsically concerted. Moreover, artificial intermediate configuration may be enforced by the simulation Ansatz.

In contrast to this, our approach based on a combination of molecular dynamics simulations and topological modeling[3,16,20] does not require assumptions on the way the initial B1 structure is aligned with respect to the final arrangement in the B2 structure. Instead, the general mechanism is iteratively optimized from an initial way of transforming B1 into B2, which can thus simply be a (more or less good) guessed one.[4] On this basis many mechanistic models can be compared, by choosing distinct starting routes and verifying the convergence of independent calculation runs towards the same mechanistic regime. In this way, the mechanism is obtained free from premises. Moreover, besides the global transformation pattern, a nucleation and growth scenario is emerging, underlying the local character of the B1→B2 solid-state reaction. On abandoning the too narrow simulation approach based on unit cell calculations, a much richer and realistic simulation perspective is emerging. Here the term realistic accounts for the emergence of a detailed phase nucleation and growth scenario, for the emphasis on the local character of phase formation and growth, and for the renewed perspective of a simulation approach that is able to fully account for the role of chemistry and chemical reactivity.

Metastable Interfaces

The transformation from B1 to B2 starts locally and rapidly grows within a plane (yellow bars in Figure 2a,b). This initiates a sequence of antiparallel layer displacements along which the reconstruction propagates (red bars in Figure 2b). At each stage, B1 motifs coexist beside B2 motifs, separated by an interface. The interface arises already from the first-

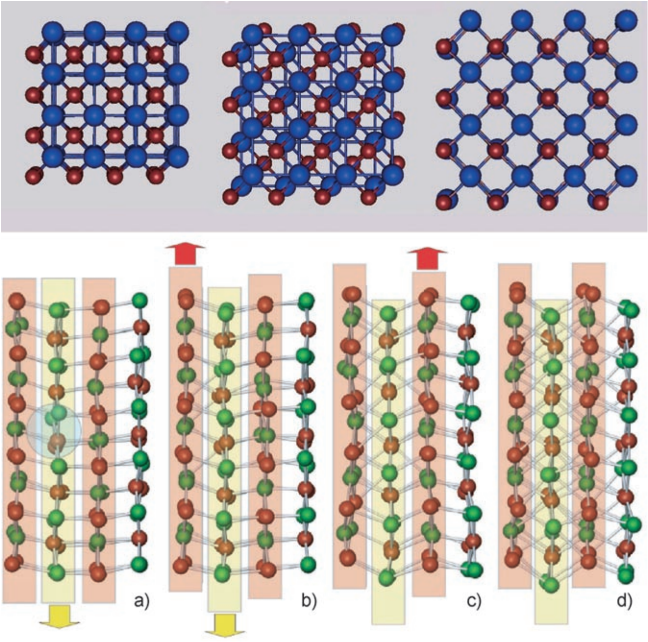

Figure 2. B1→B2 transformation in NaCl. Upper part: a geometric intermediate (middle) bridging two atomic configurations (B2 (CsCl type) left & B1 (NaCl type right)). Lower part: local nucleation event (blue circle) initiating the lattice reconstruction, followed by phase growth in form of layer shuffling (yellow & red arrows).

layer displacement that follows the nucleation event, and is progressively shifted in a perpendicular direction to the one of the initial displacement. It reaches out over three layers, and is thus strictly local. The average coordination number of the atoms in the interfacial region amounts to seven, halfway between six (B1) and eight (B2). The atomic pattern in the interface corresponds (locally) to the α-TlI structure (B33). This is not simply a curiosity or a didactic way of rationalizing the transformation in terms of symmetries. It reflects the reactivity of alkaline halogenides under pressure. In fact, while the B33 structure appears in form of a metastable interface for NaF or NaCl, already with the bromides the B2 structure no longer reflects the high-pressure phase anymore, but the B33 structure is formed instead. It is thus the chemistry and the smooth reactivity changes across the groups that favor transformation routes in which the B33 forms as an interface rather than a stable structure. This is probably a chemically more consistent reason to rule out other B1→B2 mechanistic models than just mechanical arguments. Accordingly, to better highlight reactivity trends and the existence of intermediate structural motifs, the reactions can be written as Equations (1) and (2).

$$\mathrm{NaCl_s(B1,\,B33)} \rightarrow \mathrm{NaCl_s(B33,\,B2)} \tag{1}$$

$$\mathrm{NaBr_s(B1,\,B33)} \rightarrow \mathrm{NaBr_s(B33)} \xrightarrow{?} \mathrm{NaBr_s(B33,\,B2)} \tag{2}$$

A fundamental assumption of classical nucleation theory is the growth of a predefined (often assumed to be spherical!) nucleus of the building phase within the transforming one. The detailed atomistic pictures emerging from the simulations provide realistic scenarios of nuclei shapes (typically not spherical) and domain formation. In NaCl the initial nucleus represents a slab (Figure 2), while in KF it takes the form of sticks (orange in Figure 3). This is again connected to the distinct local chemical reactivity and was recently demonstrated to result from different relative ionic hardness/softness ratios.[8]

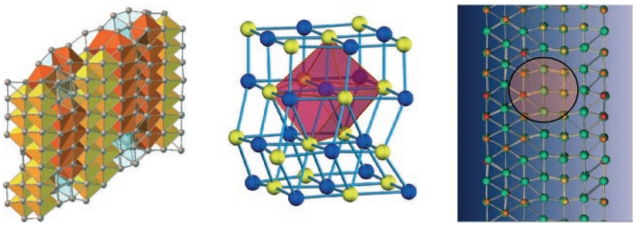

Figure 3. Different forms of metastable interfaces. Left: B33 motifs in KF forming “sticks” colored in orange. Right B1–B2 interface of B33 structure, extending over three layers (red circle), as it appears in NaCl or KCl. Center: close-up of a B33 structure type motif with the characteristic sevenfold coordination polyhedron.

The existence of a metastable phases of α-TlI structure (B33, space group *Cmcm*) has been repeatedly pointed out in the literature.[11,21–23] Therein, several alternative pathways for the B1→B2 phase transition have also been proposed. While the structural motif found in the interfacial regions corresponds to the one of α-TlI, as pointed out above, it remains strictly local, and stays as an interface until complete consumption of the transforming polymorph. As an important difference with static approaches, the interfacial motif of α-TlI originates in our simulations from a particular way of nucleation and growth, and it is thus an aspect of chemical reactivity. It does not emanate from the space-group symmetries of the polymorphs surrounding the B1→B2 phase transitions.

Interfaces and Domains

The formation of domains in solid materials is also a consequence of chemical reactions that take place locally. KF exhibits an enhanced nucleation density with respect to NaCl. The nucleation sets in as columnar displacement of fluoride ions only. This is remarkably different from the scenario that emerged in NaCl. First, the interface is much more localized and cylindrical instead of planar. Second, cations and anions behave asymmetrically, since fluoride ions displace first eventually followed by potassium ions. This different behavior is rooted in the different ionic softness/hardness ratio of KF with respect to NaCl. Fluoride ions are harder, and respond to local changes by rapidly displacing. Potassium ions are on the contrary softer and may accommodate local changes by deforming their electron clouds, and initially do not need to be displaced as an entity. In NaCl, the ionic species are similar in this respect, and in the nucleation event and propagation steps they are exchangeable. Due to the cylindrical shape of the initial nuclei, even small simulation models may involve several nucleation centers. The way the nuclei grow may be compatible or not: the growth direction may be along the same direction, or along different crystallographic directions. In the latter case, the fronts of domain growth meet under formation of grain boundaries. In case of parallel columnar displacement of fluoride ions, and different growth directions, the domains are separated by a mirror plane (Figure 4).

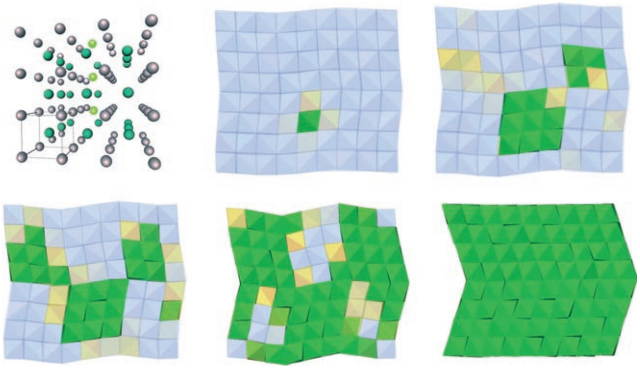

Figure 4. Consequences of a nucleation and growth scenario originating from two nucleation centers. The contact of two growth fronts with different reconstruction patterns accounts for domain formation in the transformed material, here KF in a polycrystalline B1 type structure.

If available the nucleation starts at the domain boundaries. Different domain morphologies result from different ways of connecting initially coexisting nuclei. The way nuclei are locally formed depends in turn on local changes due to different responses to local fluctuations. So a precise knowledge of microstructure reactivity is mandatory for influencing the final morphology of the material.

Reactions at Interfaces

To better capture the role of ionic hardness and softness on local reactivity pattern, an investigation of the reactivity trend along the respective main groups can be performed in silico. The evolution of the final morphology of potassium halogenides was investigated on varying the halogenide moiety, from fluoride to chloride to bromide.[8] With respect to the ionic hardness/softness ratio, potassium represents the softer species in KF, whereby in KBr the roles are inverted, potassium being relatively hard with respect to bromide. KCl occupies an intermediate position. As a consequence, domains are formed for the combinations with the largest difference in ionic hardness/softness, KF and KBr.[8] KCl does not show any pronounced tendency to form domains within a given volume, like the case for NaCl. KF and KBr break down into domains instead. While their morphology appears similar at first sight, as in both cases domains are separated by mirror planes, there is an important difference that shows up upon closer inspection. The chemical species that is occupying the interface—the energetically most problematic place in the structure—is always the softer one. So in KF potassium is sitting at the interface, on the geometric place of the mirror plane separating the domains (Figure 5). In KBr the analogous site is occupied by the softer bromide ions.

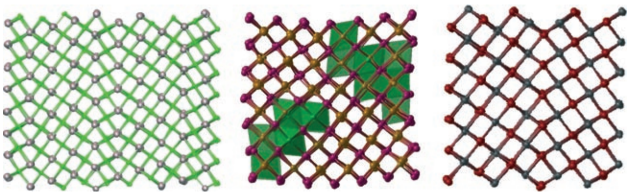

Figure 5. Different final morphologies as a consequence of a different ionic hardness/softness ratio. Right: In KF domains are separated by mirror planes and potassium atoms occupy the interface sites. Center: Distinct growing regions that may merge "in phase" or "out of phase", in which case domains result. Left: Domains in KBr. In this case, the softer species, bromide ions, are placed at the interface.

Cadmium Selenide (CdSe)

CdSe has found extensive use in quantum dot nanocrystals, and recently in nanocrystal-based solar cells. The visible absorption and photoluminescence of cadmium selenide depends on the size of the particle, which can be tuned by chemical synthesis. Size effects also control the high-pressure behavior of CdSe. The activation volume, that is the volume deformation necessary to induce a phase transition, is namely different, depending on the reaction direction, from wurtzite type (normal pressure phase) to rocksalt type (high-pressure phase), or vice versa. This is reflected in a large hysteresis loop, and in an "equilibrium" transition pressure offset from the center of the loop. This in turn reflects different activation energies that arise from locally rearranging the bonds. An investigation from molecular dynamics simulations[7] reveals the details of the reconstruction process, shown in Figure 6. Six-membered rings are initially deformed in axial direction under formation of small islands, which do not directly grow into rocksalt but bring the system into an intermediate configuration, similar to the initial wurtzite structure, but distinct. Under pressure, the system builds an intermediate metastable configuration first, of intermediate volume between the normal- and high-pressure phase, before the transformation into rocksalt continues. The latter involve a shearing of skew layers (Figure 6, bottom left), which can take place along two equivalent directions, the occurrence of which is weighted by strain minimization.

In high-pressure experiments on nanocrystalline and bulk CdSe the layer stacking sequence of hexagonal wurtzite is modified, and lamellar insets of ZnS structure type emerge on releasing pressure. While the energetic difference between Wurtzite and ZnS type is tiny, this is not the main reason for the appearance of stacking variations. Instead,

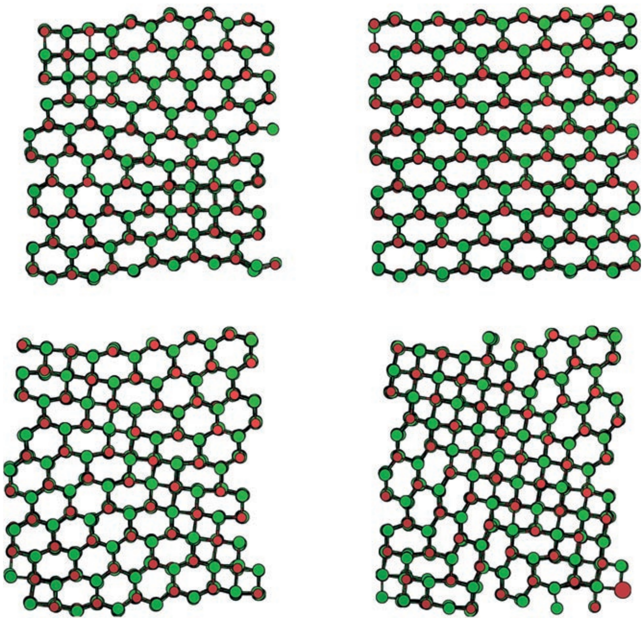

Figure 6. Reconstruction of CdSe from Wurtzite (B4) type to Rocksalt (B1) type. Top left: insets of nucleation in the B4 structure. Top right: Intermediate configuration close to B4. Bottom left: Growth of NaCl by skew layer shearing. Bottom right: B4 and B1 motifs coexisting during reconstruction.

both ZnS and Wurtzite nucleate from the NaCl type. Distinct reaction patterns set in locally, and domain boundaries results from the contact of different growth fronts. Essentially, the product of the high-pressure experiments is a "nanocomposite". Understanding the local reactivity rules and the chemical means for promoting or inhibiting nucleation events (by chemical substitution, for example) represents a different way of engineering interfaces between domains with different electronic properties, such as optical band gaps.[24]

Size Effects at Interfaces

Transformation phenomena that link liquid and solid states are of central importance in natural processes. Crystallization from the melt is often used as synthetic pathway in solid-state chemistry. While in most solidification or fusion processes the two-phase domains coexist next to each other, a different way of solid/liquid coexistence is represented by superionic conductors. The latter are a fascinating blend of liquid and solid states and arises when only part of the structure liquefies on raising the temperature. In CaF_2, the fluoride sublattice becomes liquid at higher temperature, while calcium ions maintain a configuration as in the solid. In CaF_2 mass diffusion is initiated by a local change of the chemical potential obtained by creation of Frenkel defects (Figure 7). A more spectacular way of enhancing mass diffusion is the formation of less ideal structures than the perfect crystal, for example, by creation of a structural discontinuity in form of an interface, in which the "rules of the bulk" can locally be violated.[25] An interface for example does not need to strictly fulfill charge neutrality. In CaF_2 grain boundaries represent such special places as therein ionic diffusion in enhanced. Another way of introducing abrupt changes in the structure is by means of pressure-induced lattice reconstruction. Therein the controlling thermodynamic parameter is not temperature anymore, but pressure. Fluorite CaF_2 transforms into cotunnite above 9.5 GPa. At the onset of the transition an enhanced mobility of fluoride ions appears, that is promoted by Frenkel defects. The local accumulation of vacancies initiates the reconstruction, which manifest itself in the formation of a narrow interface. This abrupt discontinuity in the lattice brings fluoride ions to locally melt (Figure 8).

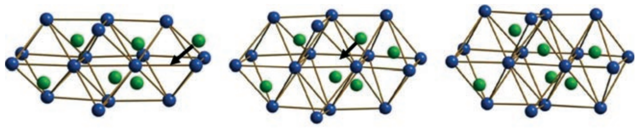

Figure 7. Accumulation of Frenkel defects (black arrows, left and middle) by occupation of octahedral voids (right) initiates the lattice reconstruction in CaF_2. Three snapshots of a portion of the reconstructing fluorite structure are shown. Ca^{2+} and F^- ions are colored in blue and green, respectively.

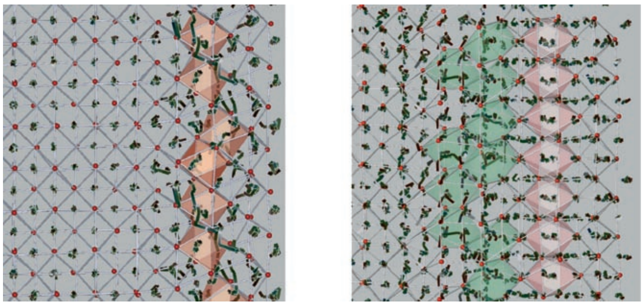

Figure 8. Sublattice melting by pressure. Left: Enhanced mobility of fluoride ions (black stripes) along a two-dimensional interface (red polyhedra). Right: Shift of the phase growth front, freezing of the fluoride ions (red polyhedra) and melting in the new interfacial region (green polyhedra).

Propagation of the transformation front corresponds to the "recrystallization" of the liquid sublattice in the cotunnite structure. The existence of an interface with liquid characteristics is also reflected in the tendency towards incomplete reverse transformation to the normal pressure fluorite structure. The distinct mobility at interfaces reflects size effects in the nanometer regime, and suggests a different way of modifying materials, based on local (structural, chemical) changes.

Outlook

The few examples shown above are part of an ongoing effort to elucidate fundamental details of polymorphism in the solid state that are experimentally not accessible or are difficult to rationalize. Initially, the simulations moved from the need to depart from a too limited point of view on reconstructive phase transitions, which was to a large extent affected by second-order phase transition models. The nucleation and growth scenario emerging represents a definitive departure from that point of view, as non-concerted movements are accounted for in detail by simulating systems larger than a few unit cells only. Therein the focus is shifted on local reactions that are taking place at interstitial sites and interfaces, which are distinct places in the solid material. The role of symmetry is recast into more appropriate boundaries, and the need to abandon group–subgroup relationships for this class of solid–solid reactions is emphasized. Instead, the role of chemistry in driving patterns of nucleation, domain formation, and the evolution of metastable interfaces and intermediates is clearly emerging. Therein the phase-formation sequences and its interplay with chemical reactivity controlling the final material morphologies become firmly rooted from premise-free model studies. All in all, a perspective is emerging of bringing together computer simulation and high-pressure chemical synthesis, in a way that the chemical intuition is supported by the atomistic resolution of the computer models.

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