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# FROM SOLID to solid

Mechanics of chemical transformations



*Chemistry like any other field of science is so diverse that the knowledge accumulated in this field has to be classified into "branches": organic chemistry, inorganic chemistry, physical chemistry, etc. Even a high school student is familiar with the first two of them, while many college graduates do not know what solid state chemistry is. However, many problems of this field of science positioned at the intersection of chemistry, physics and even mechanics are interesting not only for specialists; they are of interest to any person who wants to know how the world around us is arranged*

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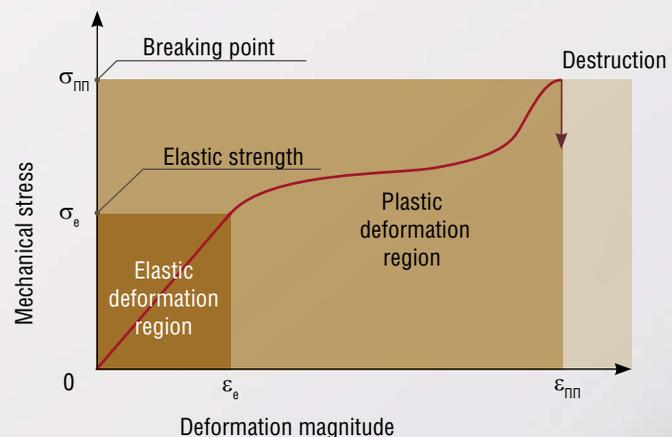
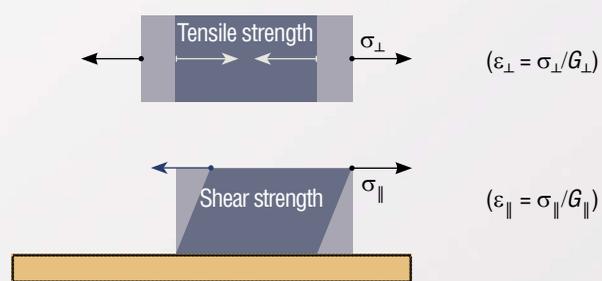
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*Key words:* solid state chemistry, elastic strains, plastic deformation, kinetics, reactivity, phase transformations, basaltic colonnades

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When a weak tensile or shear force is applied to any solid, it experiences elastic deformation. According to Hooke's law, its magnitude  $\epsilon$  (relative extension, shear angle) will be proportional to the external force (created stress)  $\sigma$ . Such deformation is reversible. After the elasticity limit  $\sigma_e$  is exceeded, the deformation becomes irreversible (plastic). When the breaking point is reached, the solid is destroyed. The type of relationship between the applied stress and the value of relative deformation beyond the elasticity limit is specific for each substance

Academician V. V. Boldyrev, founder of the Siberian school of solid-state chemists, formulates three main constituents of this science in his first lecture on solid state chemistry (SSC) as follows: "defects + transfer processes + phase transformations."

Using these concepts, it is possible to describe all SSC specific features and the area of its applications. *Defects* are arbitrary inhomogeneities in an object; they are characteristic only of solids in contrast to liquids and gases. In solids migrating atoms have to "squeeze" through a densely packed network of atoms bonded to each other. Therefore, *transfer of matter* requires substantial energy consumption. As for phase transformations, these phenomena do not exist in gases or liquids. These three phenomena significantly affect the reactivity of solids.

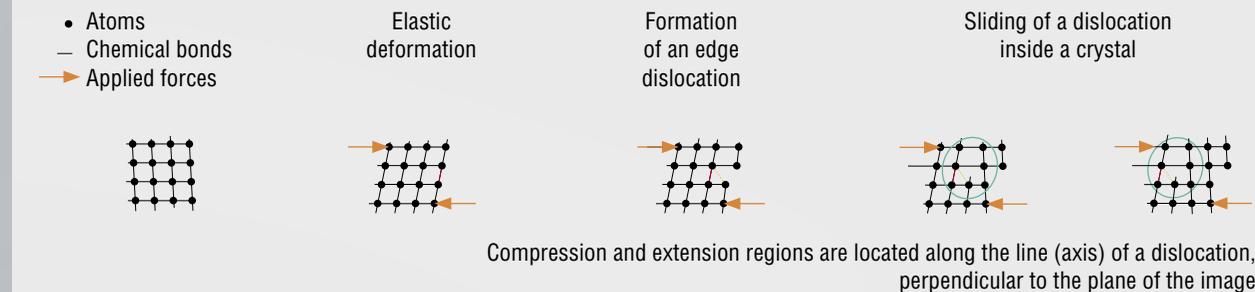
As Russians say, "One cannot embrace the unembraceable." Still, is it possible to single out one main specific feature of chemical reactions in solids? What is the foremost property that distinguishes "solids" from "non solids"?

Of course, this is *solidity*. According to the high-school physics textbooks, it is the ability of solid bodies to retain their shape by resisting the action of deforming forces. The university physics calls this phenomenon existence of *elastic properties*.

### Beyond the elasticity limit

Any reaction of substances where at least one of the reactants and one of the products are solid and contact each other (we shall call such transformations *solid state*, SST) usually results in the change of the substance atomic structure accompanied by an increase or decrease of its volume. Expansion (or contraction) of the reacting material leads to the appearance of elastic mechanical stresses in the area of contact between the reacting substance and the newly formed substance. Obviously, the emerging stresses directly influence the reaction conditions by changing the local pressure. Furthermore, relaxation of these stresses generates defects in the crystalline structure, i.e. disruptions of the ordered structure, which, in turn, may also affect the conditions of the substance conversion.

Although no systematic experimental studies of the dynamics of elastic stresses during solid-phase transformations have been carried out, their relaxation has been extensively studied by a related field of science – *solid state physics*. Of course, physicists do not use a chemical reaction to create such stresses. Instead, they use physical methods, such as extension, compression, shear, non-uniform heating, etc.



Edge dislocation is a linear crystal defect that appears when the shear load on a crystal exceeds its elasticity limit. *On the scheme:* shear deformation of a solid is carried out by dislocation sliding. Unlike destruction (cracking) this process does not require much energy because the number of broken bonds between atoms is almost equal to the number of newly formed bonds

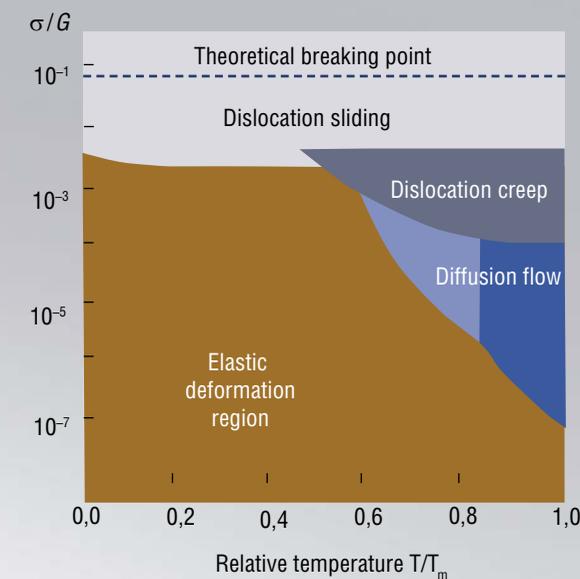
### DISLOCATION AS AN INSTRUMENT OF RECONSTRUCTION

One of the simple models of a crystalline solid is an ideal crystal where atoms are arranged in strict order in all directions. However, "the world is not perfect." The world of crystals is no exception to this rule: their perfection is disrupted by *defects*. There are three types of defects: surface defects such as crystal faces, grain boundaries, interface boundaries; linear defects (dislocations); and point defects (interstitial atoms, etc.).

Plastic deformation of solids is caused by the movement of dislocations, which can be imagined as a broken edge of an atomic half-plane inside a crystal. The most efficient movement mechanism is dislocation sliding i.e. movement in the direction perpendicular to the half-plane. When a dislocation travels another interatomic distance, atoms adjoining the dislocation axis are subject to a collective shift.

As soon as the dislocation reaches the opposite face of the crystal, the stress is released; and the two faces of the crystal become "ideal" again. However, they are now shifted by one interatomic distance – a "step" is formed. This process results in the mass transfer of a large amount of substance because the dislocation axis penetrates the crystal all the way through. It is similar to turning over pages in a thick book: after the turning over is completed, the book will be located adjacently.

Another type of dislocation movement, climb, goes parallel to the broken atomic half-plane due to the one-by-one movement of atoms located on the dislocation line. In the end, atoms forming the excess half-plane go to vacancies or to the crystal surface, and the dislocation, as well as the stress, vanishes. Such a mechanism of mass transfer is called *dislocation creep*. Its implementation requires high diffusion mobility of atoms, which is reached at temperatures close to the melting point



The map of plastic deformation mechanisms in relative coordinates temperature vs. pressure has features common to all substances and can be used to predict the mechanism of stress relaxation under given conditions. For instance, fragile substances with directed covalent bonds (diamond, glass) are destroyed without plastic deformation. Salts with ionic bonds (e.g. NaCl) are plastically deformed, like metals, when temperature increases via the diffusion creep mechanism. Near the melting temperature  $T_m$  all substances begin to "flow", i.e. they experience plastic deformation following the diffusion flow mechanism

So, what will happen if the stress applied to a body exceeds the elasticity limit of the material? This will lead to a *plastic deformation* of the body characterized by an irreversible shift of its one part relative to the other. Deformations of this type are caused by the movement of *dislocations* – linear crystal defects.

Several types of dislocation movements are distinguished. The first one is *sliding*. It can be compared to the movement of a caterpillar, when it successively moves the parts of its body. Sliding of dislocations is characterized by the collective movement of atoms. This is different from other mechanisms of mass transfer such as *creep*, *diffusion flow*, which take place when the temperature approaches the melting point of the material.

It is interesting that mechanical properties of all solid materials have common features despite the variety of crystalline structures and types of bonds between atoms.

Furthermore, regions corresponding to different types of deformations practically match for different substances in the diagrams built in the coordinates “temperature/melting temperature” vs. “mechanical stress/shear modulus.” This similarity allows one to predict the most probable mechanisms of stress relaxation under certain conditions.

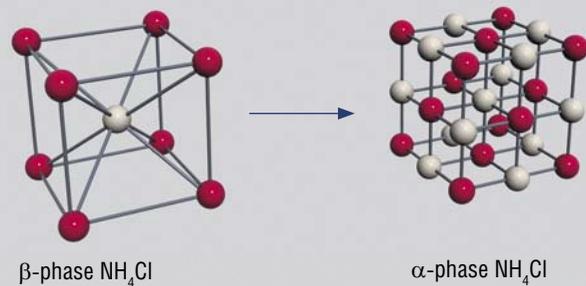
Thus, internal mechanical stresses, which are generated during various solid-phase processes (phase transformations, chemical reactions of decomposition or exchange with participation of metals, ionic or ionic-covalent compounds), relax either by variants of plastic deformation, or by destruction, or by change of the shape.

For certain model transformations we managed to discover and describe quantitatively the mechanisms of how structural changes and stresses induced by them influence each other.

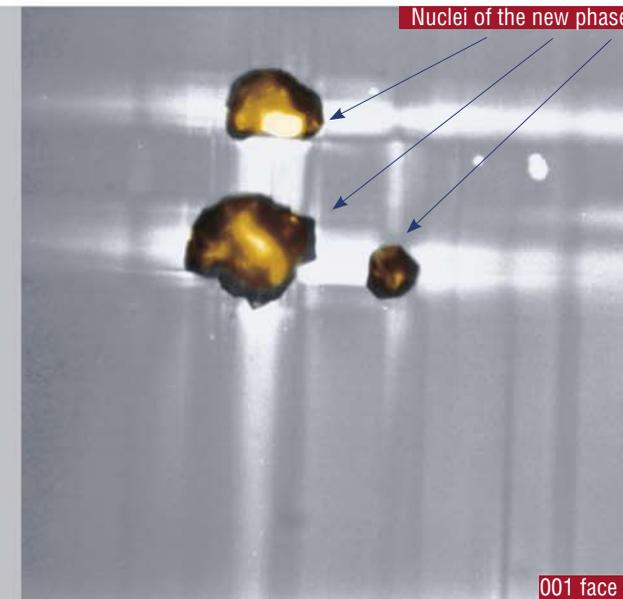
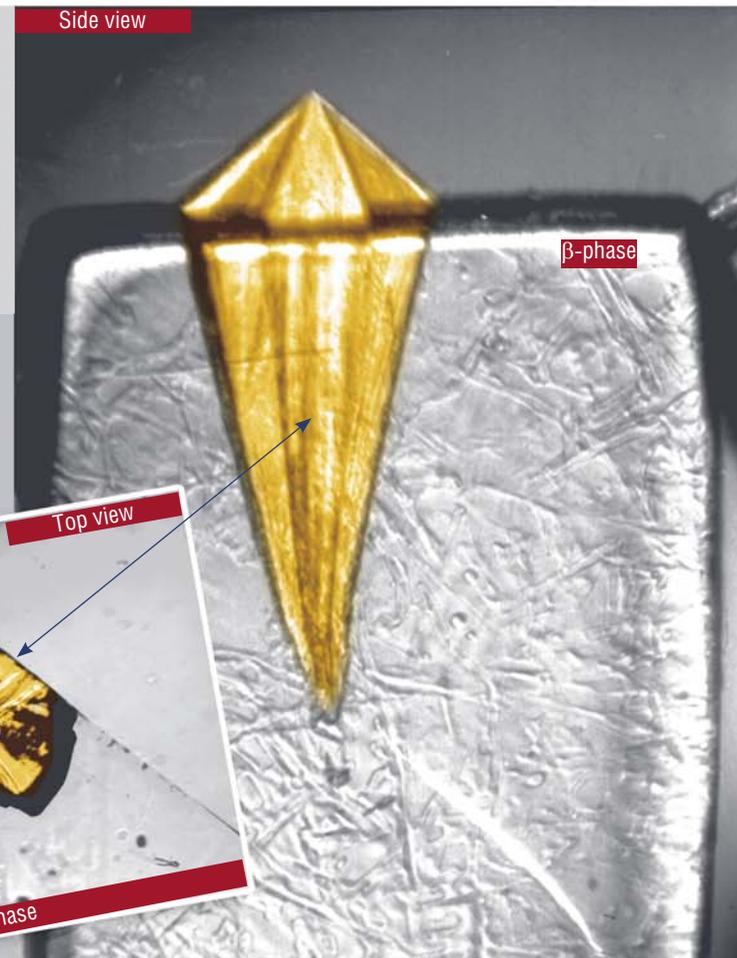
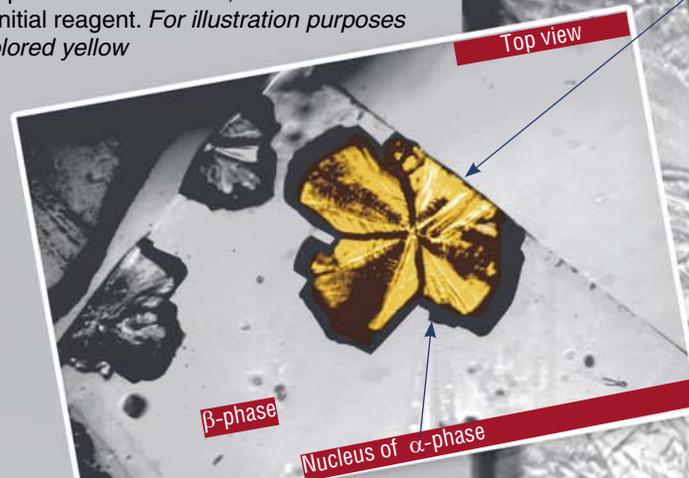
## Self strain-hardening as a result of creep

Chemical reactions of solid substances include, at least, two stages: the chemical reaction proper, i.e. formation of a new substance, and structural stage, i.e. formation of a new solid phase. This complicates their investigation. Transformation of one chemical phase into another – polymorphous transformation of a substance without changing its chemical composition – can be analyzed as a model of the structural stage, not complicated by any “chemical specifics.”

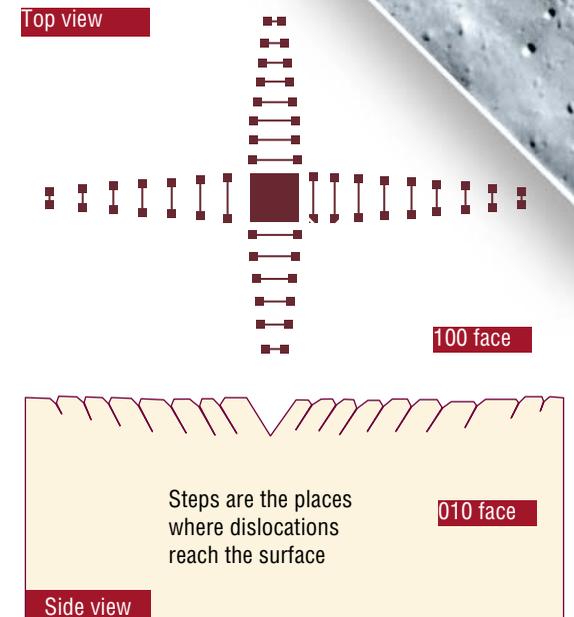
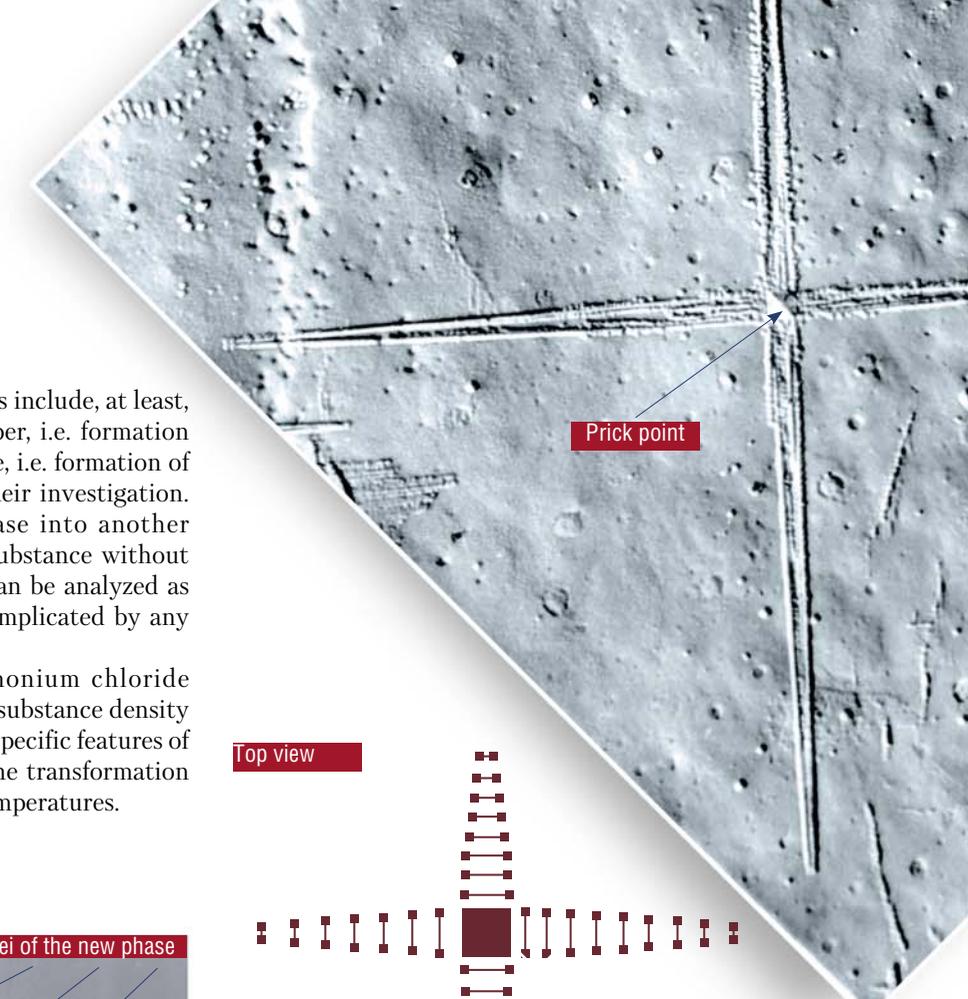
The phase transformation in ammonium chloride  $\beta \rightarrow \alpha$  accompanied by a decrease of the substance density is a good model for investigation of the specific features of crystalline structure reconstruction. The transformation begins at 457 K (184°C) or at higher temperatures.



$\text{NH}_4\text{Cl}$  transformation from the  $\beta$ -phase to the  $\alpha$ -phase is accompanied by the 16% density decrease: correspondingly, the molar volume grows by 19%. At the first stage of the transformation there appear tiny particles of the product called nuclei, formed on the surface of the initial reagent. For illustration purposes some nuclei are colored yellow



Elastic stresses around the nucleus of the  $\alpha\text{-NH}_4\text{Cl}$  phase are observed in polarized light as double-reflective areas. For illustration purposes some nuclei are colored yellow



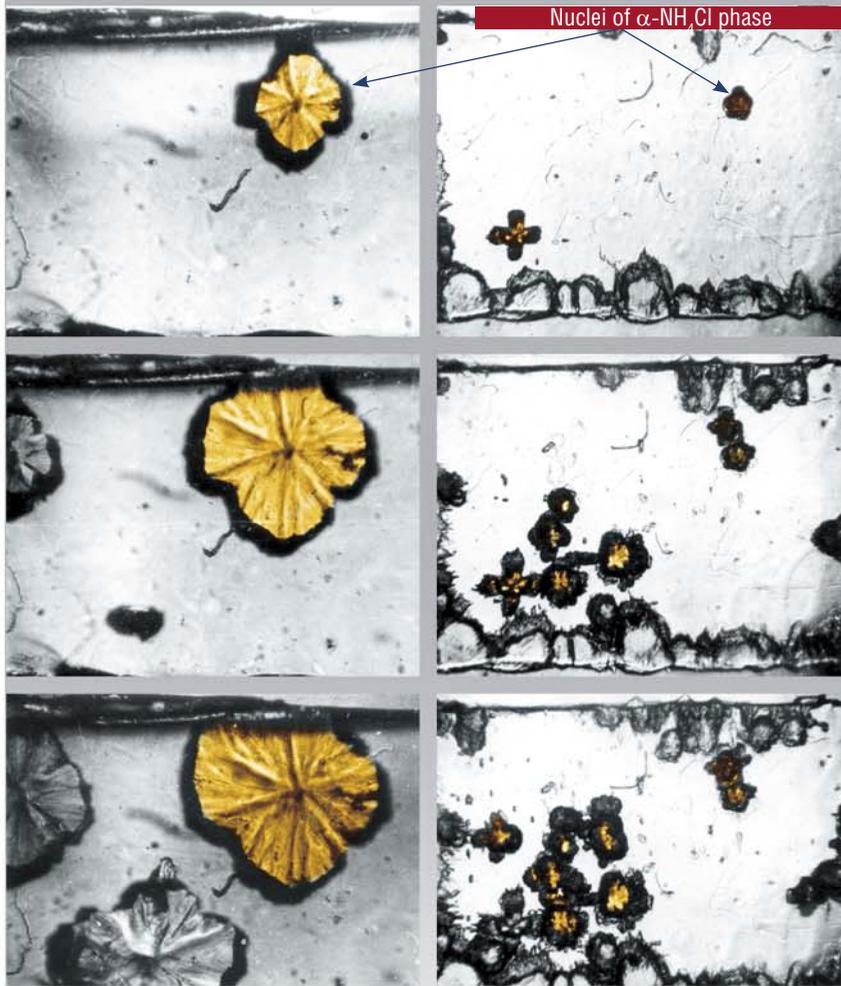
When it is necessary to detect the direction of the dislocation movement in a crystal, it is pricked with a hard spike, e.g. with a diamond pyramid. Then, its surface is treated with a solvent. Defects shaped like etching pits will “run” from the “prick” point along the directions matching those of stresses around a growing nucleus. This experiment proves that relaxation of stresses from a nucleus is accomplished by generation and sliding of edge dislocations. In other words, the extra volume appearing during a solid-phase transformation is squeezed out by sliding of dislocations from the newly formed phase through the initial one.

Above: photo of an indented (pricked) and etched ammonium chloride crystal. Optical microscopy

The hydrostatic pressure created at the interface boundary by the nucleus of the  $\alpha$ -phase estimated by the order of magnitude from the known shear modulus of  $\beta$ - $\text{NH}_4\text{Cl}$  is about several thousand atmospheres. However, according to the  $\text{NH}_4\text{Cl}$  phase diagram, the minimum temperature necessary to begin the polymorphous transformation at such pressure has to exceed the actually observed value by hundreds of degrees.

In practice, phase transformation in thin lamellar  $\beta$ - $\text{NH}_4\text{Cl}$  crystals occurs when crystals are overheated by just one degree. Such discrepancy is explained by the fact that the calculated pressure substantially exceeds the elasticity limit of this material. Relaxation of stresses takes place, the pressure decreases, and overheating becomes not necessary for the reaction to occur (Chupakhin *et al.*, 1987). The ionic character of the crystal suggests that mechanical stresses caused by the volume increase are likely to relax via the dislocation sliding mechanism.

With time, the nuclei growth slows down until a complete stop. The deceleration results from the fact that dislocations form a thick “forest” where they start impeding each other’s movement. As a result, the stress relaxation by sliding becomes more and more difficult. Finally, the deformation mechanism changes to less efficient diffusion-dislocation creep (due to alternating diffusion of atoms along the dislocation axis). Essentially, this phenomenon is similar to *strain-hardening* (mechanical strengthening of a material due to plastic deformation). The only difference is that here it occurs due to internal rather than external forces. Therefore, it is called *self strain-hardening* (Sidelnikov *et al.*, 1985).



Pure crystal.  
Heating for several minutes

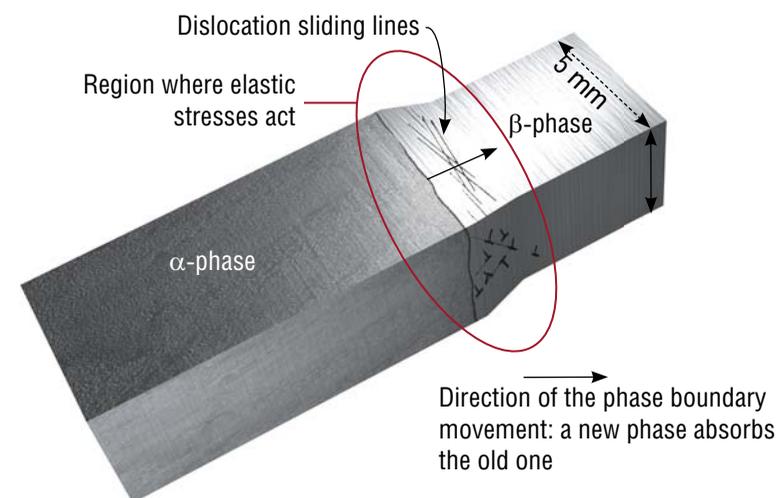
Crystal doped with copper at a ratio 1 : 800.  
Heating for several hours

$\text{Cu}^{2+}$  ions are efficient stoppers of the dislocation sliding during deformation of ammonium salt crystals. If only 0.1 mol.%  $\text{CuCl}_2$  is added to the mother liquor during the growth of a  $\text{NH}_4\text{Cl}$  crystal, temperature required to begin the phase transformation increases by almost  $40^\circ\text{C}$ . The general picture of the phase transformation is changed as well. Pure crystals (*left*) experience fast phase transformation through the formation and future growth of a small number of nuclei. Doped crystals form many small nuclei. An increase of the  $\text{Cu}^{2+}$  concentration in the crystal leads to a linear growth of the microhardness of the doped material and of temperature when the phase transformation begins. For illustration purposes some nuclei are colored yellow

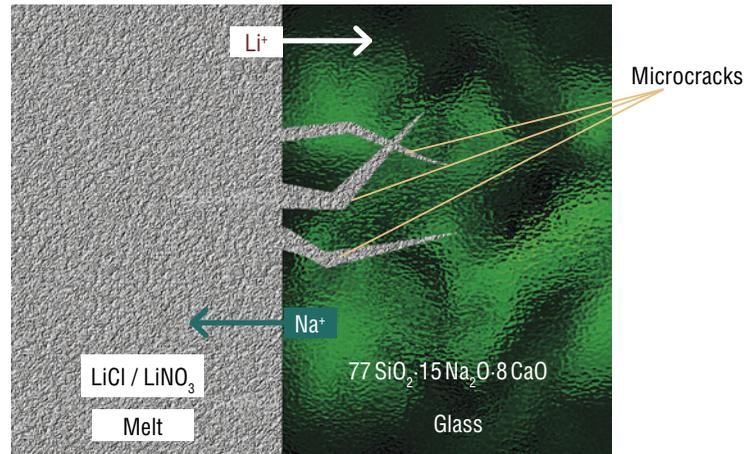
### SIZE MATTERS

Doping is not the only method that is used to regulate the properties of materials. According to *Saint-Venant's principle* the size of the region where elastic stresses act in a plate-shaped object is comparable with its thickness. Therefore, it is possible to affect the way in which stresses appearing in a solid relax by changing its geometry. The validity of this idea was demonstrated for the so-called *tin plague*, i. e. phase transformation of the metal white tin to the semiconductor grey tin that takes place at low (below 276 K) temperatures. (There is a hypothesis that tin buttons on the uniform of French soldiers disintegrated in severe frosts, which played an important role in Napoleon's defeat in Russia. Indeed, it is hardly possible to wage war without buttons on pants...)

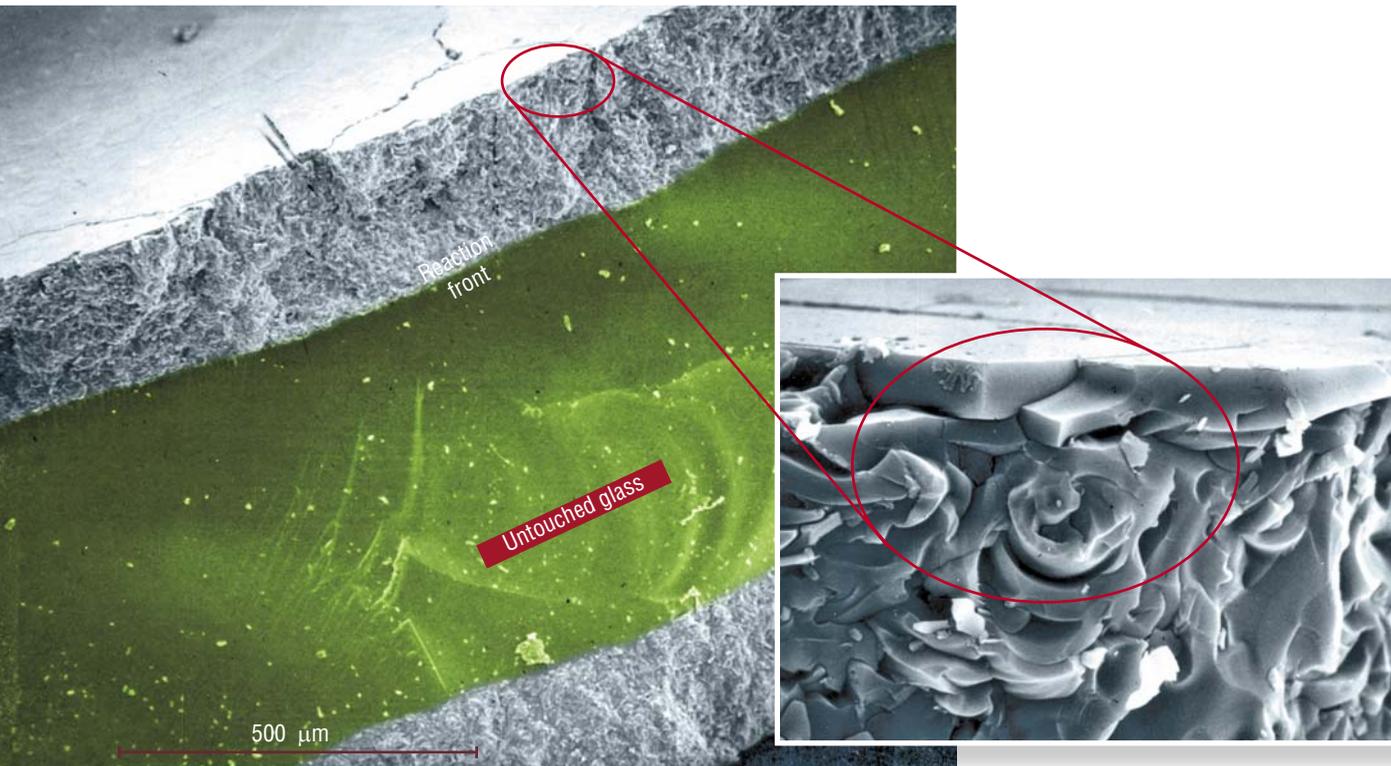
Common practice shows that a decrease of the particle size usually leads to an increase of their reactivity. However, the phase transformation of tin, produced an opposite effect: the transformation rate was found to decrease with the decrease of its thickness (Matvienko *et al.*, 1997). Why does it happen? The decrease of the sample thickness shortens the zone where stresses act and, consequently, the zone of plastic deformation. This was proven by visual observations. The size of the zone, where sliding lines are observed, decreases when the plate gets thinner. Since the number of dislocations generated per unit volume remains the same, in thin samples they have to “crowd” in a shorter zone, which increases their average density in front of the boundary. As a result, sliding of dislocations is hampered due to their intersecting and elastic interacting with the other dislocations. Hence, the movement rate of the phase boundary decreases as well



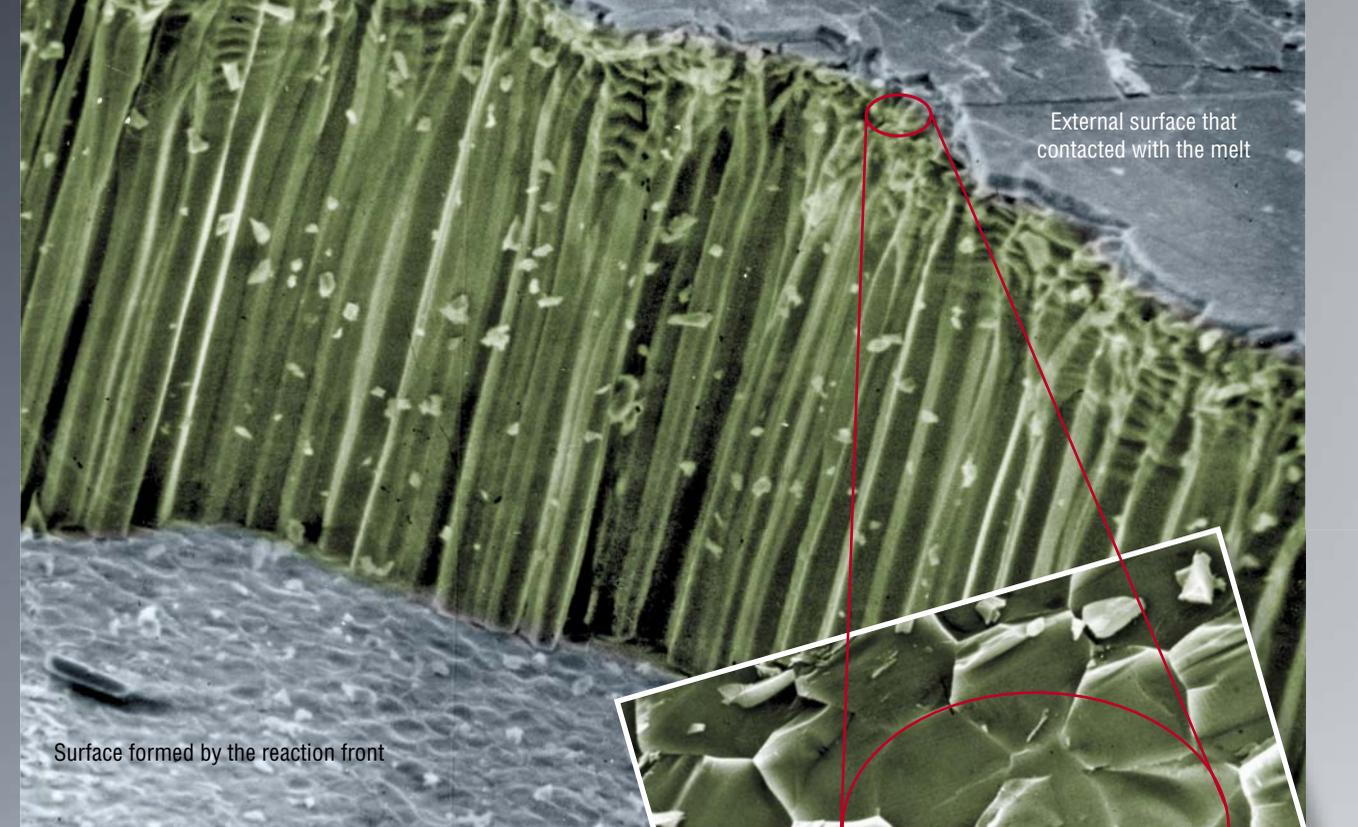
As the tin plate gets thinner, the rate of the phase boundary movement decreases, the effect becoming visible only when the sample is less than 0.5 mm thick. Thicker samples undergo the phase transformation at the same rate. Thus, the size of the region where elastic stresses act in a thin lamellar crystal is comparable to its thickness



Ion exchange of sodium ions for lithium ones in silicate glass is a good model of a solid state chemical process. When a glass plate is lowered into a melt containing lithium ions, they substitute for sodium ions on the glass surface. Then they penetrate inside following the mechanism of diffusion reciprocal to that of sodium ions. The reaction is characterized by a decrease of the sample volume due to the smaller size of the lithium ion, the volume difference leading to tensile mechanical stresses. Plastic deformation in glass, which is an amorphous material, is impossible. So, the stresses relax through destruction: the glass cracks and loses transparency (Chizhik, 2007)



If nitrate melts are used as a source of lithium ions, the glass destruction resulting from ion exchange occurs via a layer-by-layer chipping of thin plates parallel to the reaction front. The plates are split off as soon as the critical stress state is reached. Mechanical energy accumulated due to the stresses is used to form a new crack. After splitting, the reaction melt flows in, through the cracks, to the fresh surface of the glass, where lithium substitutes for sodium. So, the cycle is closed. The repeating cycles of reaction and destruction result in the formation of a transformation front that moves at an almost constant rate. *In the photo the color of the glass is different*



The contact of sodium glass with a lithium chloride melt leads to the breaking of the glass into columns with almost perfect hexagonal faceting. During the reaction these columns uniformly “grow” deep into the glass plate. Such ordered destruction occurs due to the fact that crystallites of high-melting NaCl are formed at the tips of the cracks. They displace the melt, thus decreasing the local reaction rate and altering the processes of stress accumulation and relaxation. *In the photo the color of the glass is different*

The doped surface layer, though, does not experience the transformation even after overheating by 70 K. This is how changes in a mechanical property of a crystal, namely of its hardness, made it possible to increase the temperature of its phase transformation and alter its kinetics.

### Glass metamorphosis

Phase transformations are an interesting and important subject that helps to understand how the “solid-state” world is arranged. Still, chemistry primarily deals with chemical reactions and the formation of new substances. The enormous effect of stresses on the kinetics of solid-state chemical transformations can be demonstrated with conventional glass where an ion-exchange reaction takes place.

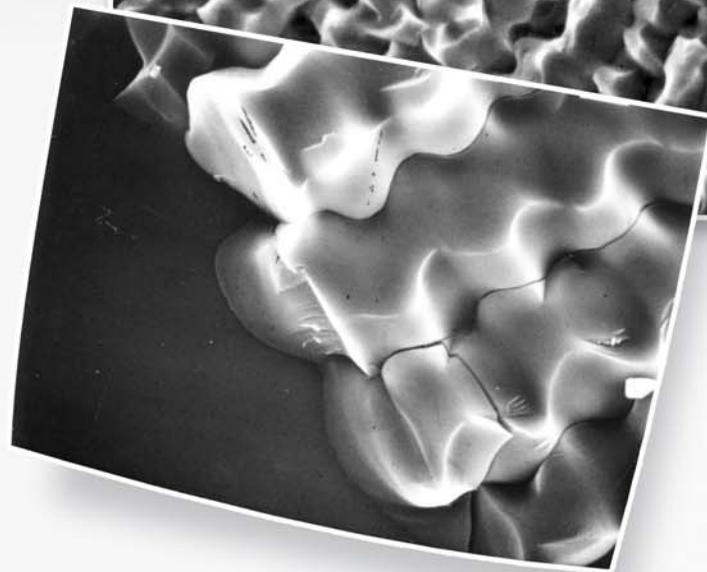
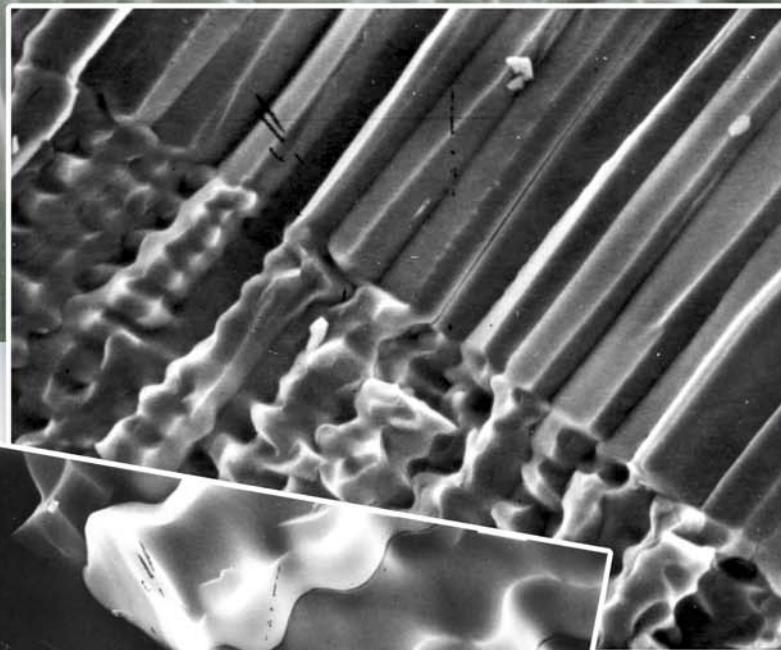
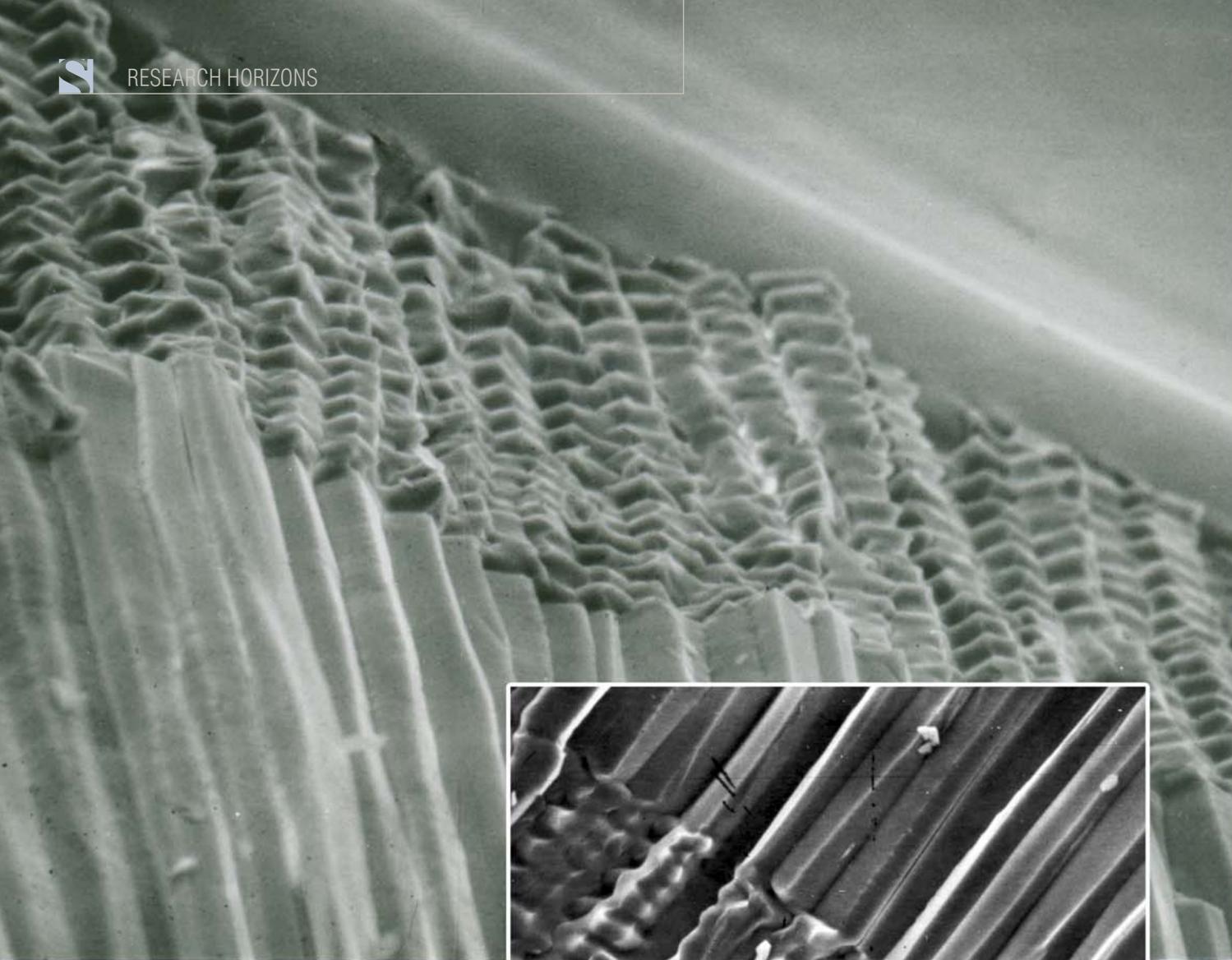
The change of the volume after smaller lithium ions have substituted for sodium ions is not large – about 5%. However, unlike crystalline ammonium chloride and tin, glass is an amorphous material. The orientation of chemical

bonds and the lack of order in the location of ions make the formation of dislocations in it impossible. Hence, stresses must result in destruction. That is why glass is fragile! No wonder that glass substantially changes its appearance in the course of the reaction. After the reaction is completed, the material preserves its integrity but loses transparency, i.e. becomes opaque (Chizhik *et al.*, 2007).

It is interesting to note that in this case the shape and typical size of the fragments resulted from destruction depend far more on the melt composition than on the reaction temperature.

For instance, when glass reacts with a nitrate melt, fragments shaped as irregular platelets are chipped off. Glass reacting with a chloride melt, the cracks assemble into a network of almost regular hexagons. The movement of this network inside the glass, following the reaction front, results in the fragmentation of the glass into faceted columns (Chizhik *et al.*, 2008).

The main reason for these differences is related to different phase diagrams of the systems “LiNO<sub>3</sub> – NaNO<sub>3</sub>” and “LiCl – NaCl” or in other words, it is caused by the



In lithium chloride-nitrate melts we managed to implement mixed modes, both chaotic and ordered, of the ion exchange in silicate glass. The character of this solid-phase reaction depends on the ratio of chlorides and nitrates in the solution. *In the photo:* a cut of a glass plate that was first placed into a chloride melt which was subsequently replaced with a mixed one (with 1: 4 molar ratio of chlorides to nitrates). It is clearly visible that regular hexagonal columns are replaced with a ribbed structure after the melt composition was changed

fact that the melting temperature of sodium chloride is significantly higher than that of nitrate. That is why solid inclusions are formed in chloride, rather than in nitrate, melts. The inclusions block the cracks used by the melt to reach the reaction zone. As a result, stresses in the reaction zone acquire a certain spatial configuration, in which cracks can steadily move only perpendicular to the front and get arranged into a regular hexagonal network. Stresses emerging during reaction in the nitrate melt do not allow the cracks to move so steadily – they constantly turn parallel to the reaction front.

These hypotheses were proven by an indirect experiment in mixed chloride-nitrate melts, which made it possible to realize intermediate modes between the ordered and the chaotic.

It should be noted that the phenomenon of spatial organization (*self-organization*) of a substance in physicochemical processes has been known for a long time. It includes hexagonal *Benard cells* formed by heating thin liquid films due to ordered convection; and *Liesegang rings*, which are a regular structure observed in products of some reactions. However, the formation of colonnades during ion exchange in glass, which that is initially an isotropic material, belongs to a new class of such processes.

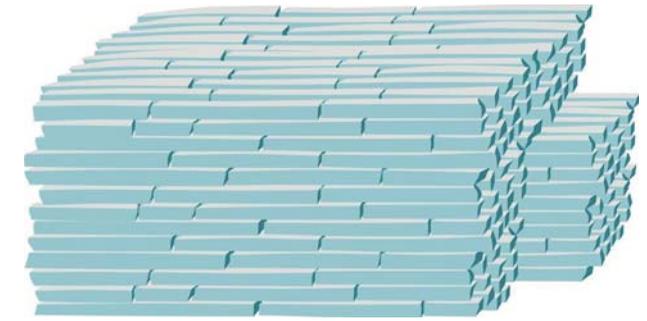
### Kuril Giant's Causeway

Of course, it is funny and instructive to examine images of different types of cracking in chemically reacting glass. Still, is there any benefit to the national economy from such an occupation?

Actually, there is! A macrokinetic model was constructed on the basis of the concept of feedback between a chemical reaction and destruction of a solid. The most important parameter of this model is the characteristic that reflects the scale of minimum possible destruction. (Chizhik *et al.*, 2007; 2008). This parameter appears as a result of the energy conservation law: work expended to form a new surface must be equal to the energy of mechanical stresses released during the formation of a crack (as in the above problem on the destruction of glass).

This model is applicable to describing of a wide range of thermal decomposition reactions  $AB_s = A_s + B_g$  (e.g. dehydration of crystalline hydrates or hydroxides, conversion of carbonates to oxides, etc.). The solid-state product of such reactions A is generated as the so-called *pseudomorphosis* reproducing the shape of the initial crystal, which consists of separate fragments and contains voids.

The magnitude of mechanical stresses and, consequently, the size of fragments of the formed product are primarily determined by the magnitude of shrinkage, which is usually known. Despite the existing limitations, the model makes



This is a picture of a product of thermal decomposition reactions. This body, which reproduces the shape of the initial crystal, contains voids whose volume fraction is equal to the decrease of the volume during the reaction

it possible to estimate the minimum possible fragmentation unit, i.e. to predict the size of fragments into which the crystal will be broken during the chemical reaction. This is important for predicting the properties of substances formed in such reactions (Sidelnikov, 2011).

And this is not all. This model appeared successful in describing the formation mechanism of a natural phenomenon many million years old. We are talking about one of natural wonders the "Giant's Causeway" in Northern Ireland. This structure consists of basaltic columns reaching a meter in diameter and tens of meters in length. There are many similar colonnades in the world. There is even a special term for them: columnar joints. There also exist basaltic joints with chaotic cracks.

An adequate model that could quantitatively describe the formation of an ordered colonnade from a melt has not been developed yet, although there were many attempts to make it. If we use the above-described model of glass dispersion during ion exchange, heat dissipation will act as an analog of the diffusion of ions to the reaction front. Basalt solidification is accompanied by heat release. So, the more intense the heat dissipation, the faster the solidification front will move inside the melted basalt layer.

Mathematical equations used to describe diffusion and heat dissipation are similar. The specific volume of basalt is lower than that of its melt (as the volume of lithium glass is lower than that of the initial sodium glass). So, tensile stresses appear during solidification. The application of the model developed for describing the ion exchange in glass allowed us to predict the size of the basaltic columns and describe the kinetics of their growth depending on the conditions of heat dissipation during the lava solidification.



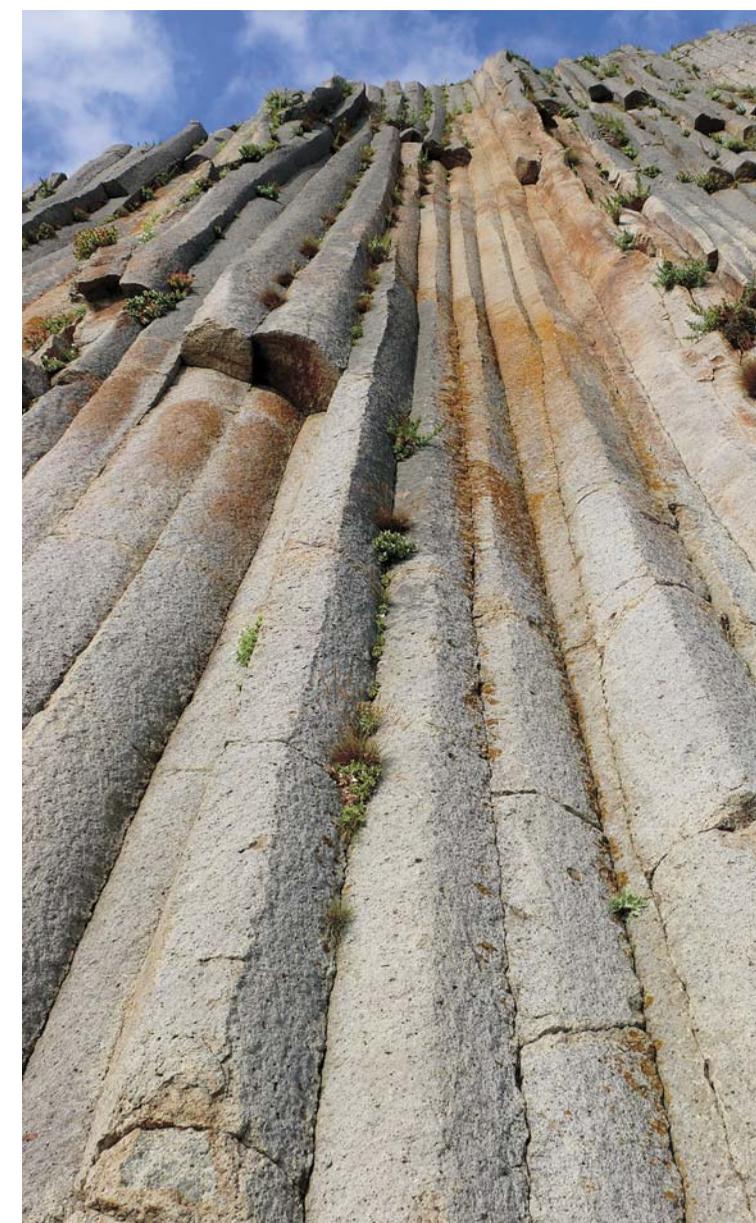
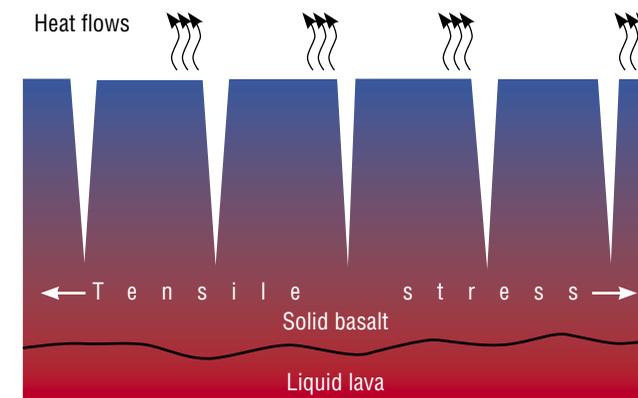
Chemistry of the 21st century favors a microscopic approach since chemical reactions are changes of the state of valence electrons. The studies of reactivity go into such “details” as specific features of femtosecond processes, positions of vibrational and rotational energy levels of molecules, etc. So, doesn't it seem an anachronism to use a phenomenological approach where substances and reactions are distinguished not by their chemical nature but rather by purely macroscopic parameters, such as differences in specific volume, surface energy and other not chemical properties.

The progress in the theory of chemical kinetics in gases and liquids was supported by easy and direct control over the conditions of such reactions: it is always possible to set or measure temperature, pressure, and reactant concentrations in a reactor or reaction vessel. However,

a solid-state reaction does not simply occur in a vessel; instead it takes place in the zone formed due to the reaction itself. It is this zone that is the “reactor” of a solid-state reaction, which exists as long as the reaction itself continues. Such structures are usually called *dissipative structures*. Their most interesting feature is the capacity for self-organization.

Before proceeding to describe the kinetics of solid-state reactions on a microscopic level, it is necessary to study the principles of self-organization in such a reactor. Naturally, the investigation of the reaction zone structure is hampered by its small size, usually of the order of nanometers, and by a multitude of interconnected physicochemical processes taking place in it. However, without this, it is impossible to develop the understanding of the mechanism of solid-state reactions.

The macrokinetic model describing connections between a chemical reaction and the destruction of a solid can be used to describe a particular natural phenomenon: formation of ordered colonnades during solidification of a basaltic melt. In this case, heat dissipation acts as an analog of ion diffusion to the reaction front. According to the model, specific volume of basalt is lower than that of its melt. That is why tensile stresses are formed during its solidification (*right*). The heat exchange conditions during lava solidification affect the size of the formed columns. Such huge basaltic columns, which are tens of meters in length, form, for example, a unique geological phenomenon, the Giant's Causeway in Northern Ireland, recognized as a UNESCO World Heritage Site. However, in Russia there is an equally interesting similar object, namely Cape Stolbchaty in the east of Kunashir Island (Sakhalin Region). It consists of vertical cliffs up to 40 m high and it juts out into the Kunashir Strait (*left*).  
Photo by D. Kulakov (Papanin Institute for Biology of Inland Waters, Russian Academy of Sciences, Borok)



#### References

- Sidel'nikov A.A., Chupakhin A.P., Boldyrev V.V. Vliyanie vznikajushih pri tverdogaznyh prevrashhenijah mehanicheskikh naprjazhenij na ih kinetiku. II. Regulirovanie temperatury polimornogo prevrashhenija  $\text{NH}_4\text{Cl}$  gomofaznym i poverhnostnym uprochnenijem // Izv. SO AN SSSR. Ser. him. nauk. 1985. № 17, vyp. 6. S. 39–49.
- Chizhik S.A., Sidelnikov A.A. The kinetics of solid state reactions accompanied by fracture: I. Reaction of ion exchange in lime-soda glass; II. Model of stationary front with disordered fracture morphology; III. Model of stationary front with spatially ordered fracture morphology // *Solid State Ionics*. 2007. V. 178. P. 1344–1352; P. 1487–1492; 2008. V. 179. P. 1823–1834.
- Chupakhin A.P., Sidelnikov A.A., Boldyrev V.V. Control of the Reactivity of Solids by Changing their Mechanical Properties // *Reactivity of Solids*. 1987. V. 3, № 1. P. 1–19.
- Matvienko A.A., Sidelnikov A.A. The influence of relaxation of stresses occurring during the  $\beta \rightarrow \alpha$  transformation of tin on the kinetics of the transformation // *Solid State Ionics*. 1997. V. 101–103. P. 641–646.

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