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Inorganic Chemistry of High Dynamic Pressures

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The causes and history of the appearance of a new field in the physical chemistry of high pressures, namely the chemistry of shock compression, are examined. Cases of phase transitions under the influence of high dynamic pressures which in principle cannot occur on static compression, namely transformations involving a decrease of density, are also described. Various types of chemical reactions, mainly syntheses, in condensed inorganic substances under the influence of shock waves are examined. Attention is concentrated on the mechanisms of chemical reactions and on the synthesis of new compounds and solid solutions, including those with atoms in unusual oxidation states. The prospects for the further development of the inorganic chemistry of shock compression are assessed.
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I. INTRODUCTION

Together with variation of temperature, the nature of solvents, and the state of aggregation of the reactants, the high pressure technique has come to be used on an increasingly wide scale in recent years in synthetic methods of modern chemistry in order to influence specifically the structure and composition of the given substance. By varying the pressure, it is possible to influence various levels of the organisation of matter. It has been established experimentally that plastic deformation of the majority of materials is observed in the pressure range 1–10 kbar, polymorphic transformations take place in the range 10–100 kbar, while in the range 100–1000 kbar the outer electronic structure of atoms changes. Although the van der Waals, atomic, and electronic interactions can be separated only to a first approximation, it is evident that an increase of the level of pressures gives rise to new possibilities for influencing matter.

It is known that the technique employed in generating high static pressures suffers from two important limitations. Firstly, the pressure attained in presses is limited by the mechanical strength of the working material of the apparatus; record static pressures (1–2 Mbar) have now been obtained using diamond anvils. Secondly, an increase of pressure is accompanied by a decrease of the working space within the presses. As a result, in laboratory diamond presses the useful volume is now reckoned in microns and experiment makes it possible to obtain only new information about the given substance and not to synthesise materials with new properties.

The above limitations led to the need for a fundamentally new method of generating high pressures which would be free from the above disadvantages. Such an alternative procedure proved to be the dynamic methods for compressing matter with the aid of shock waves. It is noteworthy that the general theoretical questions of the physics of shock waves have been inadequately developed. The gas-dynamic principles of the theory of shock waves have been described in familiar monographs[1-3] and we shall therefore confine ourselves merely to a description of the principal terminology of this branch of physics.

Shock waves are formed as a result of the collision of molecules and particles travelling at an ultrasonic velocity with a stationary or moving barrier. The shock waves formed in the barrier are propagated at a rate D and cause the migration of the bulk of the substance at a rate u. The dynamic pressure developed in the given body is

$$p=\rho_0 Du \ , \qquad (1)$$

where ρ_0 is the initial density of the compressed substance.

The energy source of shock waves may be provided by the detonation of explosives, an electric discharge, the work of the evaporation of solids on irradiation with a powerful light source, an electron beam, etc. The period of the increase of pressure from the normal value (1 atm) to the maximum value is 10^{-10}–10^{-12} s, the period of the high pressure is of the order of 10^{-6} s, and the period of the decrease of the pressure (relaxation) is 10^{-5}–10^{-6} s. The region in which the pressure increases is called the shock wave front and extends from tens to thousands of angstroms depending on the state of aggregation of the substance of the specimen.

Precisely because of the concentration of energy in space and time, it is possible to increase greatly the pressure by the dynamic method. However, the brevity of the duration of the dynamic pressure has posed new questions—is there sufficient time during such a brief period for the atoms in the structure of the solid to undergo a rearrangement and, even more so, is there sufficient time for a chemical reaction to occur in a mixture of the substances compressed by the shock wave. Only when these questions are resolved in a positive sense, will it be possible to claim that chemists have acquired a new instrument for influencing matter.

Evidently, the above problem can be solved only provided that the specimen subjected to the action of powerful shock waves is preserved (in a mechanical sense) so that is can be investigated by traditional physicochemical methods. Since the temperature also increases on shock compression, the study of the substance exposed to a shock wave would make it possible to compare its properties with the characteristics of the same substance heated to the corresponding temperatures at the normal pressure. If the results proved to be the same, then, from the chemical standpoint, the shock wave

is simply a means of heating the substance, but, if a difference is observed, then the new physical procedure has novel aspects. The solution of this problem, the protection of specimens against mechanical breakdown, and their careful physicochemical study, were the main topic investigated during the initial stage of the development of the chemistry of shock compression.

We shall consider briefly the sources of the appearance of this new field of study, namely the level of knowledge from which extensive experimental studies began in the 1960's in the field of the chemistry of shock compression. In 1938 to 1949 Michel-Levy and co-workers[4-6] described experiments in which the formation of silicates was noted on detonation of a mixture containing metal silicon oxides. In 1944, when two brass discs were exposed to a detonation pulse, they were found to be joined together (welded).[7] In 1948 Carrington and Gayler[8] described the change in the real structure of iron, duralumin, and silver after pulsed compression, namely an increase in the number of defects and in the strength of the metals was observed.

The next major step was taken in 1954 by Walsh,[9] who suggested, on the basis of the form of the shock adiabat for iron, the possibility of a phase transition under the conditions of dynamic compression. The study of the real structure of iron after its shock compression confirmed this hypothesis.[10,11] In 1956 Bancroft et al.[12] investigated experimentally the dynamic compressibility of iron and observed at 130 kbar a break on the curve relating the volume to pressure and detected ε-iron in the shock compression products, which indicated unambiguously the polymorphic transformation of iron in shock waves.

Non-metallic objects were first investigated in 1956 by Ryabinin,[13,14] who studied chemical compounds subjected to dynamic compression in cylindrical tubes; he observed the appearance of defects and processes involving the total or partial decomposition of organic and inorganic substances. In 1958 a technique for shock pressing, particularly in relation to aluminium and iron oxides, was described.[15] A marked distrotion of the structure, up to the complete conversion into the amorphous form (vitrification) of crystalline quartz was observed by De Carli and Jamieson.[16] Finally in 1961 the same workers[17] observed, after the shock compression of graphite (at $p \cong 300$ kbar), minute crystals of diamond in the specimen, in full agreement with the equation of state for carbon published by Leipunskii[18] in 1939.

In our view, the study of De Carli and Jamieson[17] completed the series of investigations which led to the establishment of the principal elements in the new scinetific discipline—the physical chemistry of shock compression. In the Soviet Union this was formally recognised at the Novosibirsk Scientific Centre of the Siberian Division of the USSR Academy of Sciences by the organisation of the Division of the Physical Chemistry of Pulsed Pressures. The results of the investigations in this Division have been described;[19] an analogous series of physicochemical laboratories have been established in Moscow at the Institute of Chemical Physics of the USSR Academy of Sciences. The combination of the physics of shock waves, the "preservation technique", and the chemistry of the solid state has in fact led to the attainment of very high values of thermodynamic parameters, made it possible to ensure the mechanical preservation of the product of the exposure of the given substance to explosion, and permitted the optimum selection of the objects of study.

An extensive literature on the chemistry of shock compression has already accumulated and it is virtually impossible to consider it in a single review. In the present article we shall therefore summarise the development of only the inorganic chemistry of high dynamic pressures and in our treatment we shall deal consistently with all the deeper levels of the structural changes in matter under the influence of shock waves and the corresponding molecular-physical and chemical consequences of these changes. This approach cannot naturally reflect all the studies on the problems considered. Additional literature may be found in other review articles.[20,21]

II. THE CHANGE IN REAL STRUCTURE

When shock waves are propagated through a crystalline specimen, fragmentation and disorientation of the crystallites take place at the boundary between the compressed and unperturbed substance as a consequence of the steep pressure gradient. This results in an increase of the density of dislocations and of the microhardness of the specimen. This was first observed by Klein and co-workers[22-27] (in relation to MgO).

The present author investigated[28-31] single crystals of alkali metal halides in fluorite, preserved after a dynamic stress, and in a number of instances the dislocation densities and microhardness were determined for different orientations of the crystals. It was observed that, after dynamic compressions up to 60–80 kbar, the dislocation density in alkali metal halide specimens increases by 5–6 orders of magnitude. The increase of the density proved to be minimal for the <110> direction, while during annealing the decrease of the number of dislocations and of the microhardness was faster along the <111> direction. The latter factor can apparently be accounted for by the anisotropy of the plasticity of the crystals. The disorientation of the blocks in the single crystals subjected to shock compression which we investigated varied in the range from 40' to 3°.

The experimental surface dislocation densities (10^{10}–10^{11} cm^{-2} for alkali metal halides and 10^{12} cm^{-2} for MgO) can be accounted for with the aid of the following estimates. The size of the crystal blocks [coherent scattering regions (CSR)] in single crystals subjected to shock compression is ≥100 Å.[30,32] If it is supposed that dislocations constitute the boundaries of these blocks, then the maximum number of surface dislocations per cm^3 is ~10^{18}–10^{19} and the dislocation density is therefore ~10^{12}–10^{13} cm^{-2}. As a consequence of the residual heat, some of the dislocations disappear and the density is reduced by 1–2 orders of magnitude. Thus the residual dislocation density should not exceed 10^{11}–10^{12} cm^{-2}, as has in fact been observed experimentally.

In the study of dislocation structures by the method of etch figures, an interesting feature was observed[30]—the inheritance of the properties of the initial material by the substance subjected to shock compression. Thus, after shock compression, LiF, NaCl, and CsI crystals retain the initial dislocation structure, against the background of which new dislocation networks appear. On the other hand, in the case of KBr, which undergoes a phase transition under the conditions of the dynamic stresses employed, a new dislocation pattern was found after compression, which is apparently due to the breakdown of the initial structures as a consequence of the migration of atoms. It has been suggested[33] that a polymorphic transformation should altogether destroy the crystallinity of the given body, but experiment has shown that a single crystal can be preserved even after phase rearrangement.

At the same time, quartz[16] and silicate crystals undergo a complete or partial conversion into the amorphous form under the influence of shock waves. The latter phenomenon has been studied in greatest detail[34,35] by optical and X-ray

methods. It has been shown that sections (submicroscopic inclusions) of a disordered amorphous phase arise in the bulk of the crystals; as a result, the anisotropy of the properties of the shock-compressed crystal diminishes and its parameters approach those of isotropic bodies.

X-Ray studies of the dynamic compression of single crystals have shown that crystalline order is immediately established behind the shock wave front in LiF,[36-38,41,44,45] Al,[39,43] and BN[40,42] and that the shock compression at a high pressure is isotropic at the level of the unit cell. After the phase transition, the X-ray reflections for KCl[43] were appreciably weakened and broadened, which indicated the fragmentation of the blocks to dimensions of ~100 Å. After the shock compression of NaCl,[44] a monoaxial deformation was observed and the existence of crystalline order in the course of a microsecond behind the shock wave front was noted. The lines on the X-ray diffraction patterns for NaCl and KCl proved to be broader than for the initial single crystal and the intensity of the reflections was lower; however, the lines were more distinct than for a typical powder. The boradening of the lines can be accounted for by the fragmentation of the grains and the increase of the dislocation density. The reflections on the X-ray diffraction patterns of specimens of shock-compressed NaCl disappear 0.8 μs after the pressure peak as a consequence of the distortion of the crystal by plastic deformation.

Thus, according to X-ray diffraction data, the shock compression of single crystals at high pressures takes place isotropically, at moderate pressures deviations from the isotropic behaviour are observed, while at low pressure monoaxial compression takes place. In the region where a high pressure operates ordering of the material is observed and relaxation is accompanied by its deformation and disordering. This factor enabled American[36,40] and German[44] investigators to suggest that the fragmentation of the grains and in general the change in the real structure take place as a consequence of extensive stresses in the decompression wave and not at the front of the shock wave.

At the same time, the present authors' first experiments on the real structure of single crystals[28,30] showed that, with increase of the weight of the explosive charge, i.e. with increase of the smoothness of the decompression, and with decrease of the effects of the extensive stresses, the dislocation density either does not change or actually increases somewhat. Hence it follows that the shock wave front plays an important role in the formation of defects, while during decompression the material either becomes more defective owing to plastic deformations or less so as under the influence of temperature (see below).

Simultaneously with the study of single crystals, much attention has also been devoted to the investigation of the real structure of polycrystalaline materials subjected to the action of dynamic stresses. The pattern of the distribution of shock waves in powders is more complex than in single crystals, since in the former case the effects on the surfaces of crystalline grains are also manifested—repeated reflections, splits, contact fusion, surface evaporation, etc. Table 1 presents the minimal dimensions of the CSR of shock-compressed polycrystalline materials according to the present authors' data;[46] the substances are arranged in order of decreasing degree of dispersion of the material attained in a single step on shock compression.

The minimum CSR cannot be reduced by subjecting the same material to repeated shock compression. Thus single compression of CaF_2 and BaF_2 resulted in the appearance of anisotropic (in conformity with the different strengths in different directions) crystalline blocks whose size was 180–600 and 220–380 Å in the <110> and <111> directions respectively.[47] As a result of repeated compression, the crystallites became fragmented only along the major axes; the dimensions of the maximum axes of the ellipsoidal CSR in the CdF_2 and BaF_2 specimens diminished to 380 and 260 Å respectively, while the lengths of the minimum axes did not change on repeated compression. An analogous picture was obtained also in the shock compression of magnesium and aluminium oxides. This approach to isometric CSR corresponds to the enhancement of the isotropic nature of the properties on shock compression observed in relation to single crystal silicates (see above).

Table 1. Dimensions of the crystallites in shock-compressed powders.

Substance	CSR, Å	Substance	CSR, Å
C, TiO_2	100	UO_2	230
Al_2O_3	130	Al_2SiO_5	250
BN, AlN, Mo	150	Ni, LaB_6	270
LiF, MgO	160	Cu	350
CdF_2	180	ZrC	370
CaF_2	190	NaF	440
BaF_2	220		

The results of the determination of the distribution of grain sizes in powders are also consistent with X-ray diffraction data for the degree of dispersion of polycrystalline materials: it has also been observed that large crystalline grains are fragmented more intensely than small ones.[48,49]

The above findings suggest that the "fragmenting effect" of shock waves has a definite limit (as if the crystalline powder were forced through the openings in a "sieve" of specific size). We shall consider the mechanism of the operation of this "sieve" and the factors which determine the size of the openings in it. If we turn back to the pattern in the propagation of a shock wave in a crystalline specimen, then it is easily seen that the crystals experience the maximum stresses (pressure gradient) only in the shock wave front, since ahead of the latter the unperturbed substance is present, while the region behind it contains the compressed substance. The depth of the front is usually estimated as equal to approximately ten unit cell parameters, i.e. ~100 Å.[50] Thus the minimum opening in the "sieve" is determined simply by the structure of the shock wave front. It has been shown[51] that, under the influence of shock waves, the crystalline grains in various types of steel assume a form close to an ellipsoid with the minor axis perpendicular to the shock wave front.

Generally speaking, the mechanism of the fragmentation of crystals can be various. If the size of the crystallites l is much greater than the depth of the shock wave front h, the situation is favourable for the appearance of pronounced distortions (deformations) of the blocks, which promotes further (in the relaxation wave) cleavage of the crystal along the "weakened" directions. If the size l is comparable to h, then deformations or even microsplits of the grain boundaries appear under the influence of the high pressure. For $l \leq h$, the high pressure region does not distort or fragment the crystal blocks.

Consequently the crystalline grains are deformed mainly during the compression or decompression of the substance and that, after the crystal has been exposed to the high

pressure zone, the defects acquired previously do not disappear. The mechanism of such memory is apparently associated with the disorientation of the crystallites caused by the intense vibrational movements in the shock wave front and observed from the asterism of the X-ray reflections from the preserved crystals.

In fact the contraction of the polycrystalline specimens in the high compression region can abolish micropores and cracks and can increase the apparent size of the grains, i.e. can improve the crystallinity of the material but cannot bring the disoriented crystallites into contact to form a single crystal. All the defects and distortions which had arisen in a crystal during the shock wave stress or which had been present in the initial material, therefore reappear after the decrease of pressure. One may expect that, as a result, microstresses are more likely to arise in large grains than in small crystallites and the dislocation density will correspondingly increase in direct proportion to the size of the CSR and not in inverse proportion, as always happens in the usual grinding of powders. An analogous picture of this type of unusual dependence of the concentration of microstresses on the size of crystallites has been observed in the study of the influence of radiation on crystals.[52] An analogy between the effects of shock waves and radiation has been observed also in other cases, as will be seen from further exposition. Annealing of defects induced by shock waves and radiation restores the real structure of the substance to the state of equilibrium.

Table 2. Dependence of the microstresses on the dimensions of crystallites.

Substance	CSR, Å	$10^3\langle\varepsilon^2\rangle^{1/2}$	Substance	CSR, Å	$10^3\langle\varepsilon^2\rangle^{1/2}$
CaF_2	330	1.2	Al_2O_3	810	3.3
CaF_2	370	1.4	Al_2O_3	1500	3.6
CdF_2	180	1.6	Mo	145	1.8
CdF_2	380	1.8	Mo	185	2.5
CdF_2	650	1.9	Mo	265	3.4
Al_2O_3	660	2.4			

Table 2 presents the results of the study of real structures for a series of shock compressed polycrystalline substances by the present author and his co-workers[47] (the size of the microstresses is $\langle\varepsilon^2\rangle^{3/2} = \Delta d/d$, where d is the interplanar spacing). Examples of the equilibrium relations between $\langle\varepsilon^2\rangle^{1/2}$ and CSR are not quoted here owing to their trivial nature. Comparison of the products of shock compression extracted, for example, from different parts of the preservation tube and exhibiting different types of dependence of the microstresses on the size of the crystallites makes it possible to obtain additional information about the temperature field in the given tube.

The accumulation of microstresses within large grains leads to their splitting during relaxation. As a result of the decomposition of the crystals, the substance evolves the excess free energy. When the critical dislocation density is exceeded, the crystals undergo brittle breakdown. We shall consider this density subsequently in the description of processes involved in the shock pressing of powders.

The dispersion of particles and the appearance in the latter of considerable microstresses after shock compression leads to an increase of the free energy and therefore affects the molecular-physical properties of the substance. Thus, in recording heating curves, it was observed that endothermic effects (fusion of powders) are weaker, while exothermic effects (chemical combination of atoms) are more intense than for the same mixtures before exposure to dynamic action.[53] Data obtained from the determination of the energy stored after exposure to shock waves in relation to magnesium and aluminium oxides agree with this result.[49]

The activation of powders by treatment with shock waves is technologically important (see below). The study of the real structure of the powders proved useful in the investigation of the topography and characteristics of the strengthening of solids, in the determination of the mechanisms of phase transitions, and even in the solution of problems concerning the construction of preservation systems. The procedure followed nowadays in the study of the real structure on the basis of the analysis of the form of X-ray lines constitute an extremely important stage in the investigation of the processes involved in dynamic action on a substance and in the analysis of the results.

III. THE CHANGE IN ATOMIC STRUCTURE

The change in the atomic structure of a substance in the course of a long period has been the main aim of high pressure physics (for example, the conversion of graphite into diamond). At the present time, the aims and possibilities of the technique of high dynamic pressures have expanded, but polymorphic transformations still constitute a very important field with which investigators are concerned.

In the first stage of the study of the physical chemistry of shock compression attention was concentrated on the very fact of the presence or absence of phase transitions and then on the stage involving the determination of the pressures of these transformations—the results of dynamic and static experiments began to be compared, and finally the time came to discover the characteristics of the polymorphic transformations in the course of dynamic stress. Accordingly, we shall divide all the dynamic phase transitions investigated into three groups: transitions whose parameters are close to those of static transitions; transitions differing in the character or properties of products; extremely specific phenomena manifested only in shock wave processes.

We shall consider initially a qualitative picture of the compression of a solid. This process is known to begin with the compaction of the substance at the macroscopic level: air is forced out of pores, cracks are healed, and vacancies and dislocations are abolished. Next begins the compaction process involving the shortening of interatomic distances, first within the framework of the initial structure, giving rise to isomorphic compression. With decrease of the distances, the structure of the substance departs to an increasing extent from the region of thermodynamic stability. Finally the time comes when the given substance with the initial structure can no longer exist under the new thermodynamic conditions and its structure undergoes an abrupt rearrangement, i.e. a first-order phase transition takes place. If the compression process continues then at the next level of pressures a new phase transition can occur, etc. The sequence of polymorphic transformations under pressure, leading to an increase of density, i.e. to the coordination of atoms, has been studied in greatest detail in relation to dioxides (MO_2): the quartz (SiO_2) structural type, which has the coordination number C.N. = 4, is followed, in terms of increasing density, by the TiO_2 structural type, which has C.N. = 6; then we have the ZrO_2 structural type (C.N. = 7), which is converted into the

CaF_2 structural type (C.N. = 8), and finally we have the $PbCl_2$ structural type (C.N. = 9).[54]

Thus there is a series of minima on the potential surface of the crystal corresponding to different packing densities of atoms in space.

Apart from the principal minima, there is a possibility of the presence of subsidiary additional minima on the potential curves in the region of the thermodynamic stability of the main structures. Under the conditions of static compression, where the stress and its relaxation take place comparatively slowly, it is not possible to detect these states. A sharp decrease of the dynamic pressure and temperature makes it possible to "quench" and preserve the compressed state of the substance (without altering the symmetry of the crystal), which was first observed by the present author.[55,56] We call this type of structural change an isomorphic transition. It is noteworthy that, generally speaking, isomorphic transitions have been known also in the physics of static pressures.[57] Thus the imposition of static pressures on lanthanide compounds entailed an increase of the oxidation state of the metal and the corresponding reduction of the unit cell parameters without alteration of their symmetry. However, in dynamic compression a decrease in cell size has been observed also for compounds of metals which do not have higher oxidation states (naturally together with the classical cases of isomorphic compression accompanied by a change in valence).

Table 3. The isomorphic decrease of unit cell parameters.

Substance	C.N.	Unit cell parameters, Å		Δa, Å
		initial	after compression	
BN	3	6.66	6.56	0.1000
CuBr	4	5.690	5.643	0.0470
$MnCr_2O_4$	6	8.422	8.414	0.0080
CaF_2	8	5.4620	5.4592	0.0028
CdF_2	8	5.3839	5.3819	0.0020

Table 3 presents the results of the determination of the unit cell parameters of isomorphic decompressed polycrystalline materials.[55] Evidently the degree of isomorphic compression increases with the looseness of the structure, which is as a rule inversely proportional to the coordination number. It is of interest that the observed isomorphic transitions precede the usual phase transitions, i.e. constitute, as it were, a preparatory stage for the geometrical rearrangement of the crystal structure. At any rate, we have never been able to detect in the preserved substance changes in the unit cell parameters in the pressure ranges where polymorphic transformations of the test substances are not manifested. Analogous isomorphic changes in parameters were found later also by other investigators.[58,59]

Although the changes in the unit cell parameters are small, nevertheless they have a marked influence on the physical properties of substances. Thus the decrease of the unit cell parameter of fluorite was only 0.01% of the bond length, while the dielectric constant of the substance increased under these conditions from 7.1 to 7.9, i.e. by more than 10%. In the case of CuBr the dielectric constant of the initial specimen, which was 10.0, increased after isomorphic compression to 17.8, i.e. by 80%, while the unit cell parameter decreased by only 0.8%. Such a sharp increase in the polarisability of the crystals of isomorphically compressed substances is due to the overlap of the electron shells of the atoms approaching one another.

When the state of the system under conditions of increasing pressure corresponds to the principal minimum on the potential surface, the usual phase transition with a total change in the structure of the substance takes place. If the compressed body does not then have defects (or their number is small), then the transition pressures in the static and dynamic experiments are found to be very close (Table 4).

Table 4. The phase transition pressures.[60]

Substance	Pressure, kbar		Substance	Pressure, kbar	
	static	dynamic		static	dynamic
Fe	130	130	Ge	120	125
P	90	100	GdS	27	28
Bi	25	27	KCl	20	19
I	240	270	Si	115	130
Sb	85	88	CaF_2	100	120
Se	130	150	GaAs	193	203

The observed difference between the phase transition pressures (in Table 4) is caused not only by the possible experimental errors, including the chemical and structural differences between the test materials, but also by the dynamic compression temperature factor. In fact, in static compression it is possible to influence independently the temperature of the compressed specimen, cooling or heating it to a specific temperature (unless otherwise stipulated, this means that the compression was carried out at room temperature). On the other hand, in shock compression the stressed substance is simultaneously heated and the "dynamic" transition compression is therefore found to be higher than the "static" value. If the dynamic and static compression of the test substance are carried out at the same temperature, one may expect even better agreement between the pressures of the phase transitions carried out by the different methods.

The substances listed in Table 4 have one common feature—it is impossible to generate in them a sufficiently high concentration of defects. By applying various influences, the densities of these substances can be reduced only slightly, at most by 10%, while the densities of graphite and boron nitride can be reduced by 50%, for example by creating structural defects. The cause of this difference is the homodesmic character of the structures and in many instances (for P, Bi, I, and KCl) also the high plasticity of the crystals, which promotes the rapid drift of dislocations during the deformation and baring of the specimen even at room temperature.

In many substances with a heterodesmic structure, in particular a structure of the layer type (graphite, boron nitride), the phase transformation pressure under the conditions of dynamic compression can greatly exceed the "static" value, when the initial material has a sufficiently high concentration of defects.[61,62] As will be shown below, at a very high concentration of defects the break in the

shock compressibility curve can be altogher absent[63,64] and the shock compression products do not contain the high-pressure phase.

The thermodynamic cause of the increase of the phase transition pressure in the dynamic compression of a defective crystal is then reduced density, which leads to an increase of the effective porosity of the specimen (at the atomic level) and hence to an increase of the shock compression temperature, which makes it essential to increase the pressure in the system. At a very high concentration of defects, i.e. for substances close to the amorphous state, the spreading of the phase transition boundary owing to the structural inhomogeneity of the specimen is observed, a classical example being provided by the softening temperatures of glasses.

Defects also influence the kinetics of the transformation. Evidently vacancies, dislocations, and disorientations of the blocks in the crystal structure lead to the breakdown of the coherence of the rearrangement and to the retardation of the transformation. In order to eliminate defects, it is necessary to perform work, which is executed under high pressure conditions by increasing the duration and intensity of the stress. Since on exposure to shock waves the duration of the dynamic pressure is limited, only the second procedure remains—one involving the increase of the pressure corresponding to the onset of the phase transition.

This effect obtains also in static compression. Thus in a study of the polymorphism of potassium and rubidium halides, we observed[65] that consecutive compression of the same specimen (accompanied by an increase of the concentration of defects) entails a constant growth of the pressure corresponding to the onset of the transformation, which can exceed the standard value almost by 100%. Thus, when the specimen is enriched in defects, the phase transition may not be observed at the standard pressure, for example, in the shock compression of certain kinds of graphite and boron nitride.[63,64]

It is noteworthy that the increase of the pressure of the onset of the transition is always accompanied by a decrease of the pressure of the end of the transformation, as a result of which the average phase transition pressure remains approximately constant. Thus, when the specimen is enriched in defects up to a certain critical value, the lower branch of the hysteresis loop reaches the normal pressure region. In other words, at the normal pressure it is possible to preserve the high pressure phase. This is in fact the reason for the existence over a specific period of structures of the CsCl type in alkali metal halides forced through draw plates at high pressures.[66]

Presumably, under the conditions of shock compression, where the increase and decrease of pressure take place over a very short time (i.e. the most favourable conditions are created for maximum hysteresis), the high-pressure phases are retained to an extent which is impossible under static conditions. This factor is extremely important for experiments with preservation of shock-compressed specimens, where it is possible to achieve not only the usual polymorphic transformations, which occur also under static compression, but also unusual transformations characteristic only of high dynamic pressures.

We shall begin the examination of the experimental results with the usual first-order phase transitions. The study of lanthanide and actinide compounds subjected to the action of explosion has occupied a significant place in Soviet research into the chemistry of shock compression. Thus in 1965 we carried out a physicochemical investigation of the products of the shock compression of the *C*-forms of lanthanide oxides and in 1966 evidence was obtained for the $C \rightarrow B$ transformations of all Ln_2O_3 for which such modifications had been unknown under normal conditions.[19] It is noteworthy that in 1964 the *B*-forms of a number of lanthanide oxides were obtained in static experiments,[67] but the physical properties of these substances were not investigated. In our communication[68] we therefore quoted the X-ray parameters, densities, refractive indices, and infrared spectra of *B*-Ln_2O_3 and also the temperatures at which these modifications are annealed (in the range 350–500 °C) with reformation of the *C*-form, which indicates unambiguously the physical nature of this transformation. The comparatively low annealing temperature of the *B*-forms necessitated special measures to reduce the influence of the thermal factor in dynamic compression: in order to achieve polymorphic transformations, cylindrical tubes with a central metallic rod were used.[68] Subsequently the transitions of lanthanide oxides from a *C*-type structure to the *B*-form were confirmed in other investigations.[69,70]

In 1966 phase transitions were observed in the compounds MF_4, where M = Ce, Th, or U, and were subsequently investigated in detail.[19,71–74] Whereas the initial tetrafluorides had a structure of the type of ZrF_4, after shock compression structures of the type of LaF_3 were obtained, where 25% of the sites in the cationic sublattice are vacant (for this reason, the formulae of the new modification should be more correctly written as $M_{0.75}F_3$). Refractometric studies confirmed the increase of the coordination number of the atoms in the crystal structures of these compounds under the influence of shock waves. The structure where together with the compaction of the substance atoms are "subtracted" from the metallic sublattice is also apparently formed as a consequence of the quenching of the shock-compressed substance. The absence of an analogous phase transition under static compression agrees with this hypothesis,[75] although the author[75] does not rule out the possibility that the required pressure may not have been attained in this instance. A phenomenon which is in essence analogous was subsequently observed in other studies[76,77] where the shock compression of Nb_2O_5 and Ta_2O_5 led to the formation of a structure of the TiO_2 type with a very slight change in composition.

Classical polymorphic transformations involving an increase of density as a result of the application of high dynamic pressures were achieved in our studies for lanthanide sulphides Ln_2S_3.[78] Like the oxides, the sulphides of light and heavy lanthanides differed in their structures and before dynamic experiments phase transformations involving an increase of density were achieved under the conditions of static compression.[79] Dynamic compression of terbium, dysprosium, holmium, erbium, and yttrium sulphides also led to a transition from the monoclinic form (of the type of Ho_2S_3) to a denser cubic form (of the type of Th_3P_4).

Transitions resulting from the shock compression of the hexagonal (quartz-like) GeO_2 also belong to classical polymorphic transformations involving an increase in the coordination numbers of the atoms.[80,81] It is known that under normal pressure GeO_2 exists in two forms—the low-temperature form of the type of rutile (C.N. = 6) and the high-temperature form of the type of quartz (C.N. = 4). At temperatures above 1000 °C a transformation of the $6 \rightarrow 4$ type takes place, while below 1000 °C there is a $4 \rightarrow 6$ transformation and static pressure does not exert a significant influence on the limits of the thermal transition.[82] Furthermore, in the absence of heating, solely under the influence of a moderate static pressure, the transformation of the $4 \rightarrow 6$ type in pure GeO_2 proceeds extremely slowly owing to the low rate of diffusion.[83] On the other hand, under the influence of dynamic pressures, the transition involving an

increase of the C.N. in GeO_2 proceeds very readily. If an intense shock wave is employed, then polymorphic transformations in the crystalline phase are accompanied by the formation of the yellow vitreous GeO_2. When the compression conditions were altered, a dense glass was obtained in which both four- and six-coordination of the germanium atom was observed by infrared spectroscopy. Such a rutile-like structure in vitreous germanium dioxide was obtained for the first time by ourselves.[81]

When the usual vitreous GeO_2 was exposed to an intense shock wave, not only the rutile phase but also a still denser (by 5%) crystalline modification was subsequently found.[84] It is of interest that the static compression of vitreous GeO_2 also entails the formation of a new, denser phase.[85] According to Ahrens,[86] the vitreous phase is the most convenient source of stishovite (for further details, see below).

As already stated, the vitrification of silicon dioxide under the influence of shock compression was first observed by De Carli and Jamieson.[16] The phase transformations in silicon dioxide involving an increase of density have been investigated in two studies;[87,88] the first study led to the detection of stishovite and the second revealed the presence of coesite. Subsequently this system was investigated by Dremin and Breusov.[89–91] We may also note a study[92] whose authors concluded that a phase transition of the 4 → 6 type in quartz occurs at such a high temperature that it involves the formation of a dense glass with the SiO_6 group in the first coordination sphere. In this connection we shall note the results of investigations of meteorites from craters in which both coesite and stishovite were discovered,[93,94] and dense forms have been frequently detected as inclusions in a mixture of crystalline and vitreous silicon dioxide.[95] This finding assisted us in selecting a natural method for the synthesis of dense forms of SiO_2, namely intense shock compression of quartz and subsequent separation of the products of the dynamic treatment with the aid of heavy liquids. Coesite and stishovite can be readily obtained by this procedure as a result of the shock compression of α-quartz.[96]

The question of the stabilisation of shock phase transitions is of fundamental importance but is still far from being solved. Even in those cases where it is possible to preserve the new phase after the explosion, there is no certainty that this is the precise phase formed under the conditions of high dynamic pressures. For example, a break at 330 kbar has been observed[97] on the compressibility curve for TiO_2 and the change in the volume of the specimen in the phase transition was by 21%. However, in the preserved specimen, the new modification having a distorted fluorite structure proved to be significantly less dense. The authors suggested that, at the instant when the substance was acted upon by the shock wave, a structure of the $PbCl_2$ type was formed and that the degree of coordination of the atoms and the density of the substance decreased during decompression; the dense modification decomposed under the influence of the residual heat. The rapid annealing of the dense modification at 550 °C has been noted.[98]

Various procedures are used to diminish the effect of annealing under the influence of residual heat. The most obvious method is to reduce the degree of filling of the tubes or one can even proceed to the shock compression of single crystals, which has been successfully demonstrated in two investigations.[58,99] The "chemical" procedure involving the wetting of the powder in the preservation tube with water, which by filling the pores displaces air and because of its higher heat capacity induces a sharp decrease of the residual temperature of the evolved heat, also proved extremely useful. The degree of decomposition of PbO_2 in the phase transition has been reduced in this way[100] and transitions known from static experiments for CdS and $CaCO_3$ were observed. After the shock compression of an aqueous suspension of HgO, a new (brown) modification of mercury(II) oxide was obtained,[101,102] differing appreciably in its properties from the known red and yellow forms. Despite the significant differences in the molecular-optical properties and in the density of the brown form of HgO, the X-ray characteristics of this phase proved to be virtually indistinguishable from those of the known modifications. The X-ray absorption spectrum and the L_{III} absorption edge of the brown form has undergone a bathochromic shift.[103,104] On this basis, the authors[101,102] suggested the occurrence of local changes in the coordination of the oxygen atoms in the brown modification although the large difference between the atomic numbers of mercury and oxygen precluded the detection of an inclusion of the new phase by X-ray methods. A neutron diffraction study of the brown modification of HgO yielded some evidence in support of this hypothesis.[105]

As already stated above, in layer structures such as those of graphite and boron nitride, the transition to the diamond structure in specimens with a high content of defects under the influence of shock waves is hindered ("smeared") or is even altogether absent. Shock wave experiments with graphite have been carried out since 1961 (see above and also Trueb[106] and Gust[107]), while boron nitride was first subjected to shock compression and was preserved for subsequent study as late at 1965 in our laboratory.[108]

The shock compression with the aid of a cylindrical scheme of pyrolytic low-density BN led only to a slight increase of the density of the specimen, although small transparent crystals with a density of 2.5–2.6 g cm^{-3} were observed along the axis of the cylindrical tube; their X-ray diffraction pattern contains, among others, lines due to the wurtzite modification of BN: 2.20 (m.), 2.08 (m.), 1.95 (m.), 1.54 (w.), 1.26 (v.w.), and 1.17 (v.w.) Å. The presence of reflections from other interplanar spacings did not allow us to claim that the new phase (we called it the "E-phase") contains a diamond-like modification as a component, although the lines quoted above undoubtedly indicate a geometrical relationship between the E-phase and the dense forms of boron nitride. In 1976 this modification was produced by Japanese investigators in the shock compression of BN (using a planar scheme) to 600 kbar, the initial materials being subjected to two (in succession) dynamic compressions.[109] This factor is extremely significant, since, after the first shock compression, a multiplicity of defects arise in the material and the structure of the latter approaches that of the pyrolytic state, i.e. conditions very close to those in our experiments are realised. The E-phase has also been obtained[110] in a pulsed discharge between boron rods in a nitrogen atmosphere, being detected after a short exposure to these conditions, whereas an increase of the duration of the exposure (of the number of pulses) led to the formation of the classical diamond modification. Hence it was concluded that the formation of the E-phase is the first stage in the transformation of the graphite structure into the diamond structure. Finally, the E-phase has been recently obtained when the graphite-like boron nitride was subjected to laser irradiation and an increase of the duration or the intensity of the irradiation again led to the formation of the wurtzite-like modification of BN.[111]

The simplest explanation of the nature of the E-phase would involve the hypothesis that a mixture or a solid solution (for example, the type of block isomorphism) of the graphite and diamond phases of BN is formed. However, the identity of the properties of the E-phase specimens obtained by different procedures and also the change of

only its concentration and not of its characteristics when the applied dose of the given influence is changed indicate the individuality of the product. Unfortunately, owing to the low quality of the crystals, only the unit cell parameters could be determined: $a = 7.2$, $b = 8.1$, and $c = 18.9$ Å.[112]

Later Kurdyumov and Pilyankevich[113] obtained a polycrystalline carbon with similar properties, which they regard as an analogue of the E-phase. Although the above phase was called simply the dense modification (of the diamond type) in a well known review,[114] we believe it to be useful to differentiate it as an intermediate structure in which the graphite networks may be connected by diamond bridges in a specific sequence (see Noda and Inagaki[115]).

The diamond forms of BN have been obtained by the shock method[116,117] and it has been shown[117] that the yield of the dense forms increases in parallel with the increase of the density (i.e. of the degree of perfection of the crystals) of the initial graphite-like boron nitride. At the same time we demonstrated independently[80] that the structural perfection of the hexagonal BN is essential for the success of the phase transition. Next we obtained dense forms of BN by the shock compression of a fairly perfect initial material.[118] The crystallographic aspect of the transition of the hexagonal boron nitride to the tetragonal or cubic modifications has been examined in detail.[119] The mechanism of the phase transformation of the graphite-like modification to the diamond modification was later investigated[113] from the standpoint of the real structure of the initial and shock-treated boron nitride.

In conclusion of the description of the polymorphic transformations on shock compression, we shall consider certain unusual phase transitions, which cannot occur on static compression of the test substance. We have in mind the phase transitions involving a decrease of density. Generally speaking, the annealing of the dense modifications under the influence of the residual heat, which was already discussed above, can be regarded as the formal outcome of the dynamic compression of the given body. However, for substances which undergo phase transformations with compaction of the structure after heating under normal pressure (AgI, PbO, MnS, Ln_2O_3, etc.), the temperature and even more so a high pressure can no longer promote a decrease of density. In other words, the dense modifications of substances of this class cannot be converted into the loose modifications for any kind of change in the thermodynamic parameters. The study of precisely such substances in our laboratory, starting from 1965, revealed phase transitions involving a decrease of density, i.e. the exposure to shock waves led to a change from irreversible to reversible transitions. The first review of the literature devoted to this topic was written by the present author[19] and more detailed information can be found in other communications.[60,112]

After the discovery of phase transitions involving a decrease of density on shock compression, analogous transformations were achieved in experiments involving the irradiation of substances,[120] in the comminution of crystals in a ball mill,[121] and on static compression with shear.[122] In all these processes the generation of a large number of defects entails partial or total conversion of the substance into the amorphous form, which leads to the activation of the powder and the creation of conditions for the appearance and rapid growth of the nuclei of a new phase which is stable under the given thermodynamic conditions†. Thus, under the influence of shock waves, the initial structure breaks down and the residual heat induces the crystallisation of a new phase, which is initially less dense, while further heating leads to the formation of the densest phase.

According to the model developed above, the physical cause of the decrease of density is the decrease of the coordination number of the atoms as the crystalline grains are fragmented. Since the fragmentation of crystals entails an increase of the fraction of surface atoms, which have smaller coordination numbers than in the bulk of the crystal, comminution is always accompanied by a decrease of the static (effective) coordination number of the atoms. Estimates have shown that, when account is taken of the decrease of the coordination numbers owing to the formation of vacancies and dislocations, fragmentation to a size of 50–100 Å is sufficient to reduce the effective coordination number by 1–2. In this case the energy of the comminution (which appears as an increase of surface energy) is comparable to the heat of the phase transition.

It is of interest to analyse the polymorphic transformations in steels from the standpoint described. It is known that the heating of iron is accompanied by the $\alpha \rightarrow \gamma$ (or $\beta \rightarrow \gamma$) transition involving an increase of density. The reverse transition takes place under the influence of various kinds of deformations, including those induced by the dynamic compression.[123] It is significant that the polymorphism of pure iron is of the reverse character and only after the introduction of carbon or other "hard" additives does the phase transition under the influence of any kinds of deforming forces become possible. Leaving to one side the possible (slight) change in the composition of steels in the polymorphic transformation, the role of alloying additives can be naturally accounted for by a decrease of the rate of elimination of defects as a consequence of the decrease of the plasticity of the material. As soon as this rate becomes lower than the rate of deformation of the material, conditions are immediately generated for the accumulation of defects, i.e. for the conversion of the substance into an amorphous form.

In the first stages the unusual phase transformations were investigated mainly by optical methods and also by measuring the density and by recording heating curves. In all cases the loose modifications were converted after annealing into dense modifications with an exothermic effect, which indicated the absence of a change in the chemical composition on exposure to shock waves. Table 6 presents the structures and densities ρ of certain lanthanide compounds which have undergone a phase transition with decrease of density under the influence of dynamic pressures.

Apart from polymorphic transformations, it was possible to obtain as a result of exposure to shock waves modifications which differed from the initial forms only in the size but not the symmetry of the unit cell.[55] Such transformations were called isomorphic by analogy with the physics of static pressures, where appreciable changes in the parameters without a change in the structural type have been observed in relation to lanthanide metals and their compounds.[57] Whereas such transformations have been induced under static conditions by a change in the oxidation state of the lanthanides, with the aid of the dynamic method the isomorphic transitions have been achieved for compounds of a wide variety of metals, including those which have only one oxidation state. Furthermore, phases involving an increase in the unit cell parameters, caused by a weakening of the chemical bonds as a result of the dynamic pressure, have been obtained on exposure to shock waves.

If account is taken of the fact that, with increase of the density, isomorphic compression precedes the polymorphic transformation, the isomorphic expansion of the parameters

†In the case of α-spodumene, the intermediate amorphous phase was detected experimentally.[124]

can be naturally correlated with the phase transitions involving a decrease of density which have just been discussed. Table 5 presents the X-ray diffraction data for the isomorphically expanded materials. The average differences of the unit cell parameters (Δa) are quoted for anisotropic substances.

Table 5. The increase of unit cell parameters in isomorphic transitions.

Substance	Δa, Å	Refs.
SiO_2	0.013	[125]
SiO_2	0.067	[125]
Ni	0.04	[126]
NdF_3	0.027	[127]

Table 6. The properties of polymorphic modifications.

Substance	Initial phase		After shock compression	
	structure	ρ, g cm^{-3}	structure	ρ, g cm^{-3}
SmF_2	LaF_3 type	6.93	YF_3 type	6.64
HoF_2	LaF_3 type	7.83	YF_3 type	7.64
Tm_2S_3	Ho_2S_3 type	6.27	new phase	6.06
Nd_2S_3	A-form	7.42	C-form	6.29

In conclusion of this Section, we shall attempt to answer the question how the phase transitions occur under shock compression. One should apparently consider separately two types of transformations—those in which there is a possibility of a coherent shift of all the lattice atoms over a short distance (the so-called martensite transitions) and transformations which require the preliminary rupture of the initial structure. Since the changes in bond lengths associated with the usual changes in coordination numbers are within the limits of the vibration amplitudes, the martensite transition can be readily accounted for in terms of a vibrational mechanism, i.e. it should occur at the velocity of sound. The presence of an amorphous phase as an intermediate state is essential for transitions of the second type. In this state the atoms are probably extremely mobile, since they are not linked to their neighbours and resemble free radicals. Thermodynamically, the state corresponds to the disappearance of the potential barrier between the two modifications.

The conversion into the amorphous form gives rise to the possibility of the formation of a phase with a reduced density. Furthermore, in the amorphous (vitreous) initial material the phase transition should take place more readily. Indeed, in many instances the phase traosformation of glasses has been observed at lower pressures than in the corresponding single crystals.[84,85,86,128] It is shown below that the reconstructive phase transitions and the active intermediate state involved in them play an important role also for chemical processes.

IV. CHEMICAL REACTIONS

Processes involving the synthesis and decomposition of chemical compounds have been investigated from the very beginning of the development of the new scientific discipline; furthermore, the very name, shock compression chemistry, presupposes the preservation of the specimen exposed to shock waves for further study.

The chemical investigations have been carried out in terms of two aspects—in order to solve problems of practical importance and to obtain specific substances, on the one hand, and in order to develop the method itself and to elucidate the mechanism and the characteristics of the chemical reactions under the conditions of shock compression, on the other.

We shall consider initially the second question, which is in essence fundamental for the entire chemical component of the dynamic method. The most important task is to determine the period of the reaction, i.e. to determine the possibility of the completion of the reaction under the conditions of a high pressure during 10^{-6}–10^{-5} s.

There is as yet no evidence that the compounds produced under the conditions of shock compression and preserved for further experiments were obtained in the high pressure zones; this can be inferred only from indirect features. However, our present day knowledge about the processes occurring on shock compression of powders permits the conclusion that the character of the chemical processes under these conditions is non-trivial.

A specific feature of the chemical interaction under shock compression is that, under the influence of the shock wave, the crystalline grains are fragmented and a multiplicity of structural defects, namely vacancies, dislocations, and atoms with altered oxidation states, are generated in the particles; the particles of the mixture components interpenetrate one another during migration behind the shock wave front (owing to the differences between the mass velocities of the components), are deformed, and are pressed into a monolithic form. After the establishment of a uniform pressure in a mixture of fairly small particles, the components of the shock-compressed specimens can be compressed in different ways (owing to the differences between the mechanical properties of the reactants) and hence can be heated in different ways. Estimates have shown[129] that the difference between the temperatures of the "hot" and "cold" points in a shock-compressed mixture reaches hundereds of degrees.

If one takes into account further the fact that the plastic deformations occurring on pressing the powders will also cause unequal heating of different mixture components and even different parts of the grains,[130] then it becomes evident that the additional effect may amount to a further several hundred degrees.[131] Thus the overall temperature difference between adjoining sections of the mixture can exceed 1000° and can lead to diffusion and even the evaporation of individual particles. This factor constitutes a fundamental difference between the heating of the reaction mixture by the shock wave and the homogeneous heating of the same composition in the usual furnaces.

Finally, the rapid migration of the shock wave front promotes the rapid propagation of the chemical reaction zone. For highly exothermic reactions, this process can be analogous to high-speed combustion or even detonation.

The characteristic features of the shock compression method gave rise to the hope that unusual results might be obtained. Certain conclusions from the investigations made can now be reached.

The first shock syntheses of substances from the elements were performed by Japanese workers. Thus in 1963 Horiguchi and Nomura[132] reported the synthesis of TiC (see also Ref.133). The same investigators subsequently obtained WC[134] and Al_4C_3.[135] Suzuki et al.[136] synthesised TiC, ZrC, and SiC; all these substances are of interest for the preparation of ultrahard materials. Simultaneously with the solution of practical problems, studies were made of the characteristics and mechanism of the reactions. Thus Horiguchi and Nomura[133] suggested that the shock wave leads to te mechanochemical activation of the reactants and compresses the mixture in which "hot" points, initiating the chemical reactions, are distributed. The subsequent development of the chemical process takes place as a consequence of the liberation of heat at the active centres. Suzuki et al.[136] noted the dependence of the thermodynamic parameters in the cylindrical preservation tube on the location of the specimen and showed that the reactions proceed with the maximum intensity in the axial region of the cylinder.

Adadurov et al.[137] synthesised by the shock compression method a number of silicides from the elements—FeSi, $FeSi_2$, and V_3Si. Otto and co-workers[138,139] obtained the intermetallic compounds Nb_3Sn and Al_3Nb, which are of interest for the study of superconductivity. These workers used copper tubes to improve (as a result of the high plasticity of copper) the compression of the materials; in addition, they employed evacuated preservation tubes before the dynamic experiment. According to these workers, the mechanism of the formation of the intermetallic compounds involves the shock fusion of one of the components, for example, tin, and the dissolution of the other component in it.

The shock compression of Nb–Ge, Nb–Sn, and Nb–Pb mixtures has been described.[140] The syntheses of Nb_3Si and Ta_3Si have been reported.[141,142] Savitskii et al.[143] carried out the shock compression of 3Nb + Y (Y = Si, Ge, Sn, Pb, or In) mixtures and observed that the synthesis occurred only in the axial region of the cylindrical tube.

Elementary syntheses in our laboratory have been carried out in order to investigate mainly the characteristic features of the duration of the shock synthesis of transition metal chalcogenides. In the synthesis of chromium chalcogenides the influence of fine shock dispersion of the powders on the endothermic effects of the fusion process and the exothermic effects of the chemical reactions was observed.[53] Modifications of chromium monochalcogenides with reduced density and with retention of the type of crystal structure were obtained in the same study (see above).

Batsanov et al.[144] determined the temperature of the Sn + S reaction mixture 0.05–0.1 s after dynamic compression, which proved to be 1100 °C. The residual temperature in the case of SnS, synthesised beforehand by the usual method and then shock-compressed under the same conditions, was only 130 °C. Bearing in mind that the residual temperature during the measurement (after 0.05–0.1 s) only decrease, one can conclude that the reactons have been completed by this time. The same paper describes an interesting instance of the influence of particle size on the degree of reaction and even on the direction of the reaction in shock synthesis. An equimolar Sn + S mixture consisted of powders with particle sizes ranging from 0.06 to 0.4 mm; all the experiments were performed with the tube filled to the same extent and with all other conditions kept the same. It was found that, in the range 0.06–0.2 mm, the yield of SnS increased with decrease of the particle size. The grain diameter increased to 0.2–0.4 mm and the degree of conversion of sulphur rose from 45 to 80%. This was caused by the change in the composition of the product: the reaction product proved to be SnS_2. This unusual fact can be explained by taking into account the thermal instability of tin disulphide at temperatures above 600 °C. Since the amount of heat evolved increases with increase of the surface energy of the powder (see the synthesis of chromium chalcogenides described above[53]), there exists a critical particle size above which SnS_2 is stable.

The interaction of the chalcogens sputtered in the form of thin films on the surfaces of plates, under the influence of shock waves directed at right angles to the plane of the plate, has also been studied.[145] The chemical compound is formed as a result of the mutual diffusion of the tin and chalcogen atoms. An increase in the duration of the shock pulse entails the growth of the diffusion zones: for example, for a 3.2 km s^{-1} pulse, the thickness of a tin sulphide layer is 1 μm whereas for a 7.8 km s^{-1} pulse it increases to 3 μm. It is significant that treatment with shock waves promotes also the usual thermal diffusion. Thus, when specimens compressed by a 3.2 km s^{-1} pulse for 50 h are heated, the diffusion zone is 9 μm thick, whereas for the non-compressed specimens the diffusion zone is only 4 μm thick in such heat treatment.

The characteristic features of the diffusion of atoms in a solid subjected to shock compression have been investigated.[146] The authors showed that, in the pulsed compression of a metal, the rate of diffusion can be actually higher than in its melt. It is also of interest that the rate of diffusion was higher in the dense γ-iron lattice (of the face-centred type) than in the less dense α-iron (of the body-centred type), which the authors explained by the sharp increase of the number of point defects in the case of the face-centred lattice. The acceleration of the movement of atoms in the shock-compressed materials has been explained[147] by the decrease of the activation energy for diffusion owing to the decrease in size of the particles and the corresponding decrease of their melting point.

A sharp increase of the rate of the chemical reaction of the elements can be achieved by employing the method of detonation synthesis.[148,149] The absence of metallic tubes leads to close contact between the energy carrier and the material being treated, as a result of which very high temperatures and pressures are generated by this method. Calorimetric and X-ray studies have shown that, during a period of ~10^{-5} s, the synthesis of zinc chalcogenides takes place quantitatively.[149]

Compounds in known structural forms were obtained in all the studies enumerated above. On the other hand, compounds in new crystalline forms were produced in the synthesis of lanthanide sesquichalcogenides, for example, those of holmium and erbium.[78] The shock synthesis of neodymium and samarium monochalcogenides[150] yielded a series of new solid solutions with an intermediate (between 2 and 3) oxidation state of the metal.

Reactions of the type metal + the oxide form of the compound have also been achieved under the conditions of shock compression. The first publication on this topic concerned the reactwon Cu + $CuBr_2$ → 2CuBr[55] with reduction of the unit cell parameters (Table 3). A decrease of the oxidation state of titanium via the reaction Ti + TiO_2 → 2TiO has been achieved by Ruchkin et al.,[151] while a decrease of the oxidation state of indium in InF_3 in the interaction of the latter with metallic indium has been carried out by Batsanov et al.[152] The interaction of lanthanide trifluorides with various lanthanides, which yielded both pure[153] and mixed[154] fluorite

phases, has been studied in detail. The doubly charged state of the lanthanide in these compounds has bee confirmed by optical and magnetic data.[155,156] The oxidation state of the metal could be reduced only in copper[157] and chromium[158] oxides and in the latter case a chromium(II) compound was detected by means of a special system in which two reactants were separated in space within the tube and only one was subjected to shock compression, as a result of which one reactant was swept onto the other by the Mach wave. The reaction mixture is very rapidly cooled in such a system, which promotes the quenching of the metastable compound. We recently synthesised neodymium monoxide by the reaction $Nd + Nd_2O_3 \rightarrow 3NdO$, the mixture of components being initially repeatedly subjected to the action of shock waves and then heated at 600 °C for 100 h;[159] this compound has a structure of the NaCl type, but its unit cell parameter proved to be 5.096 Å, i.e. greater than that for NdO obtained on static compression of the same mixture,[160] which suggests the formation in our case of a compound of neodymium in an oxidation state less than 3.

Apart from the processes involving a decrease of the oxidation state of the metal by some other metal in a free state, the reactions involving the reduction of oxides by other elements have been investigated. Thus the shock interaction of Ln_2O_3 with B yielded[69] LnB_6. The authors[69] believe that the reaction proceeds after the completion of the shock compression due to the residual heat in the preservation tube. The shock reduction of SnO_2 by carbon, silicon, and aluminium, accompanied by the mechanochemical treatment of the mixtures in ball mills, has been described.[161] The importance of the area of the contact surface and of the local temperature ("hot" spots) has been noted.

The shock reactions of metals with Teflon, which proceed in accordance with one of the two equations

$$M + (CF_2)_n \rightarrow MF_x + C,$$
$$M + (CF_2)_n \rightarrow MF_y + MC$$

have been investigated recently.[162] Fluorite phases have been obtained with the aid of these reactions for scandium and yttrium. The reaction of metals with water led to the synthesis of a number of metal oxides, hydroxides, and peroxides.[163,164] The aim of these studies was to elucidate the question of the possible completion of the chemical reaction during the period of shock compression. These experiments were based on the following reasoning. Since water at high pressures has the properties of an acid, the shock compression of the metal + water mixture can lead to the displacement of hydrogen, provided that the metal is electrochemically more active than water (or when the water remains chemically "inert" if the metal is more passive). It is important that the reaction should proceed only in the high pressure zone where water has acid properties. Experiment fully confirmed these hypotheses, but the question of the residual temperature in such a suspension remains open, since in the case of heating to a high temperature there is a possibility of simple pyrolytic decomposition of water by the metal.

We shall now proceed to the description of the results of studies of the reactions of oxides and compounds with one another. In 1963 the shock compression of an equimolar mixture of zinc and iron oxides yielded zinc ferrite[165] (see also Adadurov et al.[166]), while in 1966 zinc orthosilicate was synthesised from a mixture of zinc oxide and silica.[167]

Lanthanide mono- and tri-hydroxides, LnOOH and $Ln(OH)_3$ were synthesised in 1967 by the reaction of lanthanide sesquioxides with water.[168] Tubes with a reduced strength, which remained integral during the experiment if all the water combined with the oxide and were ruptured if water was taken in excess, were used in the above study. Thus the stoichiometry of the chemical reaction can be inferred even from the mechanical behaviour of the tubes. Dremin and Breusov[89] described the syntheses of silicates, double fluorides, and garnets. Subsequently barium titanate was synthesised by the shock compression of a mixture of $BaCO_3$ and TiO_2.[169] Data on the shock synthesis of magnesium and calcium metasilicates as a result of the compression of mixtures of the corresponding oxides and silica have been published.[170]

Lanthanide oxides or chalcogen fluorides have been obtained in our laboratory[171] as a result of the dynamic compression of mixtures of fluorides with lanthanide oxides or chalcogenides. It has been shown for samarium oxide fluorides that, in the presence of a slight excess of the fluoride in the initial mixture, a tetragonal oxide fluoride is produced, whereas in the presence of an excess of the oxide the product is the rhombohedral modification, the cubic SmOF phase being formed only on compression of a stoichiometric mixture. As a result of the movement of masses in the course of shock compression, for example, in a cylindrical tube, there is a possibility of the local breakdown of the reaction stoichiometry as a consequence of the distillation of the mixture components, i.e. the "polymorphic transformation" of complex compounds becomes possible. The $PbO + TiO_2$, $PbO + ZrO_2$, and $2PbO + TiO_2 + ZrO_2$ interactions have been investigated under the conditions of shock compression.[172] The stoichiometry of lead zirconate-titanate (LZT), which is an extremely important piezoceramic material, is infringed in its usual thermal synthesis owing to the unequal volatilities of the components. On the other hand, in the shock compression of the initial mixture of oxides, synthesis, pressing, and shaping of the compound produced take place simultaneously.

Complex formation in accordance with the equations $2KX + PtY_2 \rightarrow K_2PtX_2Y_2$, where X and Y are halogens of different kinds, has been described.[173] We believe this reaction to be promising from the standpoint of the synthesis of inner sphere complexes of coexisting ligands, which cannot be combined [in the same coordination shell] by the usual methods of synthesis. We synthesised by the reaction $SmO + TiO_2 \rightarrow SmTiO_3$ a compound in which there is a definite competition between the Sm(II) and Ti(IV) oxidation states.[129] Evidently analogous compounds can be obtained also by the reaction of titanium monoxide with lanthanide sesquioxides. It is entirely likely that a kind of valence isomerism can occur in this instance. We obtained compounds of the type $Ln_2O_3.MO_2$ and $Ln_2O_3.2MO_2$ by the reaction of lanthanide sesquioxides with TiO_2, ZrO_2, and HfO_2 [59,174] and investigated the dependence of their structure on composition. We recently studied the shock reaction occurring via the mechanism $Ln_2O_3 + Ln + 3/2I_2 \rightarrow 3LnOI$, the Ce, Gd, Ho, and Lu compounds having been obtained and investigated for the first time.

In conclusion of this Section, we shall consider the formation of substitutional solid solutions as a result of shock compression. The feature of the majority of substitutional solid solutions is that their densities are lower than those of the initial mixtures and is of methodological interest. The formation of stable solutions should therefore be caused by the temperature factor and, conversely, phase transitions or other structural changes in the solid solutions formed should take place under the influence of pressure. Indeed the synthesis of KCl–KBr solid solutions yielded[80] a substance with an increased density and the annealing of the product was accompanied by a decrease of density with the simultaneous evolution of heat (exothermic effect on the thermogram).[80] The shock compression of the RbCl–CsCl mixture

leads to the formation of solid solutions with a structure of the NaCl type, but their density again proved to be higher than the standard values.[175] It is significant that the composition of the solid solution did not depend on the component ratio in the initial mixture: the shock compression of a wide variety of compositions yielded a solid solution of the same composition.

The corresponding solid solutions were synthesised for the first time from NH_4X–CsX mixtures by dynamic compression of the latter.[176,177] Solid solutionsof the NH_4X–KX and NH_4Br–NH_4I systems have also been obtained by the dynamic method, their compressibility increasing with the atomic number of the halogen.[178] A change in the intensity of the shock wave entails a change in the compositions of the solid solutions formed, which is characteristic of the chemistry of berthollides. Finally, shock compression of the KCl–CsCl mixture led to a decrease of the phase transformation temperature of CsCl from 469° to 305 °C, while the X-ray diffraction pattern of the mixture remained unaltered. A detailed study showed that the solid solution formed in this system remains in the X-ray-amorphous state at room temperature.[179]

Solid solutions of another type have been investigated in a series of studies. Thus Gryaznov et al.[180] investigated the saturation of iron by carbon under the influence of pressure pulses and showed that at 425 kbar carbon penetrates to a depth of 0.05 mm as a result of dissolution in a layer of melt on the surface and subsequent crystallisation. Kozorezov et al.[181] observed a considerable miscibility (greater by a factor of 7 than in the usual thermal synthesis) of tungsten and iron. Adadurov et al.[76] obtained a continuous series of solid solutions with compositions ranging from Nb_2O_5 to NbO_2 on the basis of the rutile structure. Such solid solutions were formed only for high intensities of the shock waves where the specimens were known to be in a fused state. A solution of gallium in copper with a concentration greatly exceeding the "thermal" value has been obtained by shock compression.[182] Finally, the ZnS + Se shock interaction led to the formation of a continuous series of ZnS–ZnSe solid solutions which have the sphalerite structure in the presence of ZnS contents from 0 to 50% and the wurtzite structure for higher ZnS contents.[183]

In conclusion of the description of shock syntheses, we shall now turn to the question of the duration of the chemical reactions. The usual objection against the possibility of the occurrence of reactions during such short periods arises from the relatively low rate of diffusion in solids, especially under high pressure conditions. However, experiments carried out in the authors laboratory, involving the measurements of the electrical conductivities of powders under pressure, have shown that the conductivity of ionic polycrystalline substances is fairly high under these conditions and does not increase with increase of pressure but increases until the attainment of the monolithic state. Furthermore, it increases sharply at the instant of the phase transformation of the chemical compound.[184] We believe the latter factor to be extremely important because it has been suggested[195] that the chemical reaction can take place during the period of high dynamic pressure, provided that at least one of the reactants undergoes a reconstructive phase transition under the given thermodynamic conditions. A direct experimental test of this hypothesis by investigating the phase transformations in the reacting systems is of interest.

Apart from syntheses under conditions of high dynamic pressures, studies have also been made of chemical decomposition reactions of substances and these had begun earlier than the synthetic experiments. Thus the appearance of metallic sodium as a result of the shock compression of NaCl has been noted.[14] Subsequently Nicholls et al.[186] observed a disproportionation under dynamic pressure into iron and lead oxides.

Batsanov et al.[187] undertook a systematic study of the possibility of the shock decomposition of complex oxygen compounds. A thermodynamic criterion was established, namely the enthalpy of formation of the compound above which the crystal structure is improved under the influence of a specific shock influence, while below it the substance decomposes.

The shock decomposition of alkali metal bromates and nitrates has been described.[188] In the former case an analogy has been observed between shock and radiation decompositions, while for nitrates the process is more complex. The formation of defects as a consequence of the action of an explosion on nitrates has been studied in detail in the present authors' laboratory and a definite analogy has been observed between the formation of shock and radiation defects.[19,189] Symons[190] studied by EPR the formation of radicals when binary oxides and sulphides and complex oxygen compounds are exposed to shock waves; a correlation with radiation defects (produced by γ- and n-irradiation) was not observed. An analogous study has been carried out by Nelson and Hartley.[191]

Lapshin et al.[192] investigated the chemical properties of $K_2S_2O_8$ subjected to dynamic compression and observed that the compression leads to the formation of the same paramagnetic centres as those produced during irradiation.

The decomposition of sillimanite into Al_2O_3 and SiO_2 has been observed.[193] Here an interesting result is the isolation of stishovite when intense shock waves are applied. This justifies the hypothesis that the compound decomposes under the conditions of high pressure.

It has been shown[194] that the CO and CH_4 shock adiabats can be described satisfactorily only if it is assumed that these molecules decompose at high pressures (in excess of 200 kbar) into diamond particles and gaseous O_2, CO_2, H_2, CH_n, and C_2H_2 molecules. We may note that the decomposition of CO_2 into diamond and O_2 has been observed at high pressures under the conditions of the static compression of CO_2.[195] Hence it follows that finely dispersed diamond can be obtained by the dynamic compression of hydrocarbons and carbonates.

Together with the usual decomposition of compounds as a consequence of shock compression, shock structure-breaking in substances exposed beforehand to hard radiation has been investigated.[192,196,197] Thus $K_2S_2O_8$ powder has been subjected to the influence of detonation[192] after its preliminary treatment with γ-radiation (from a ^{60}Co source). The F centres were retained in the test substance after the shock compression, although the absorption spectrum changed appreciably compared with the substance which was simply irradiated. After the irradiation of alkali metal halide crystals and also CaF_2, SiO_2, and $(NH_4)_2S_2O_8$, the appearance of colloidal intralattice metal was observed.[196] Single crystal and polycrystalline NaCl specimens have been studied in greatest detail,[197] the intensity of irradiation and of the dynamic compression being varied within fairly wide limits. It has been established that the formation of a colloidal metal is characteristic of the single crystals, the size of the colloidal particles varying in parallel with the degree of distortion of the specimens; the F centres are retained in the polycrystalline specimens. The latter fact is apparently caused by the higher rate of diffusion of atoms and the higher temperature in the shock compression of powders

compared with single crystals, which leads to the decomposition of colloidal particles on relaxation with formation of *F* centres. It is significant that the concentration of free sodium in the shock-compressed NaCl specimens proved to be higher than that of the *F* centres, which is probably caused by the additional injection of electrons in the course of the shock compression from the material of the preservation tube and from the impurities in the initial specimen. One should note further that the *F* centres in shock-compressed materials are unstable at room temperature—crystals can be decolorised by natural light in the course of several minutes or even seconds.

The first stage of any decomposition is accompanied by a decrease of the oxidation state of the metal owing to the dissociation of chemical bonds. The increase of the magnetic susceptibility of zinc sulphide on shock compression as a consequence of the Zn(II) → Zn(I) transition has been observed by Nomura and Tobisawa.[198] In 1967 the present author and his co-workers studied the Ti(IV) → Ti(III) transition[199] and then the Eu(III) → Eu(II) transition.[200,201] The change in the oxidation state of other lanthanides on shock compression was dealt with above.

The practical application of the shock method for the generation of structural defects, in particular the decrease of the oxidation state of the metal, involves the modification of catalysts by exposure to shock waves. Thus the influence of dynamic compression on the catalytic properties of transition metal oxides has been studied;[199] shock treatment led to an increase of the catalytic activities of ZnO, TiO_2, and $BaTiO_3$ by 2–3 orders of magnitude. This result was confirmed in another study.[202] We established that the increase of the catalytic activity of TiO_2 and other titanium compounds took place as a result of the formation of electronic defects, especially Ti^{3+} centres. The shock compression has been used[203] to activate pyrites catalysts used in the liquefaction of coals. It has been shown[204] that, after the shock-wave treatment of CaF_2, which catalyses the dehydration and dehydrogenation of isopropyl alcohol, the temperature of the onset of the reaction diminished and the selectivity of the catalyst action increased. Increase of selectivity carried by dynamic influence has now been observed also for other catalysts.

Finally, we shall indicate yet another, analytical aspect of the shock compression chemistry. Since the substance treated is enclosed in a strong metallic tube and, generally speaking, there should be no loss of material in the course of the dynamic experiment, there is no need for the usual chemical analysis. The physical methods for the determination of the phase composition and the possible structural changes play an analytical role in this instance. However, the compressed substance may be contaminated by the material of the walls of the tube, which has been investigated.[205,206] It has been found that, when the substance is contaminated by iron in a cylindrical tube, the bulk of the impurities enter the compressed substance from the lower stopper at the centre of which a crater is usually formed as a consequence of the effect of the reflected shock wave.[206] The overall concentration of the impurities is correlated with the packing density of the powder before the experiment, the parameters of the shock wave entering the substance, and the presence or absence of phase transformations involving a change in the volume and compressibility of the given body.[207]

Thus spectroscopic analysis of a shock-compressed substance can serve as an indication of the physicochemical transformations which have occurred as a result of dynamic compression (including reversible transformations which cannot be observed in the preserved specimen).

V. CONCLUSION

The new method whereby the composition and structure of a given substance can be actively influenced, namely shock compression, has immediately found extensive practical application. The fundamental studies and technical applications developed in parallel. Below we shall consider briefly the practical aspects.

We shall begin with the physical and mechanical manifestations of the changes in the real structure. The hardness of the material increases as a result of the fragmentation of the crystalline grains and the increase of the dislocation density under the influence of the dynamic compression, which has already been dealt with at the beginning of the review. Naturally the increase of hardness and hence in the strength of metals is of practical importance. The first review devoted to the metallurgical effect of shock waves is that of Appleton.[208] Subsequently monographs were devoted to this topic.[209–211]

The technical problems of the dynamic strengthening of metals are extremely varied and even a simple list of the results obtained would occupy far too much space. New data concerning different mechanisms of the thermal and shock strengthening of metals, which may lead to new prospects in this field of materials science, are noteworthy (see also Bekrenev and Naumov[212]).

The second major field in which the shock wave techniques are used is that of the pressing of powders. The advantages of the dynamic method compared with static pressing consists in the easier attainment of high pressures and the absence of limitations as regards the size of the treated articles. Several international conferences have been devoted to the application of dynamic pressures in the pressing of powders[213–215] and such pressures have also been considered at the All-Union Symposia on Pulsed Pressures.[216–221] In addition, shock pressing has been described in the above reviews[208,209] and in the original articles by foreign[48,49] and Soviet[222–224] workers.

At the same time, dynamic pressing suffers from serious limitations at the present time due to the specific features of the shock compression itself. We have in mind the phenomenon of "overpressing", which leads to the saturation of specimens by cracks and pores or even its fragmentation into small pieces. This phenomenon is due to the fact that the dynamic compression of the crystal increases the dislocation density of the latter and under certain experimental conditions the concentration of the defects can exceed the critical value for the given substance, after which the crystalline grain disintegrates into smaller particles. In order to prevent disintegration, one either heats the specimen between dynamic treatments in order to increase its plasticity or the maximum plastic deformation of the material is ensured.

The most important practical application of polymorphic transformations under the influence of dynamic pressures is the shock synthesis of diamond and borazone [boron nitride]. The main task here is the rapid removal of heat during (or after) decompression, since diamond and borazone are annealed to the graphite modification at $T \geq 1000$ °C. It is difficult to solve this problem, which has led to the following paradoxical situation: transformations of the graphite → diamond type take place quantitatively in the shock wave, but in the decompressed system the concentration of diamond is only several per cent. Numerous methods and patents have been devoted to the development of various procedures for the solution of this problem.

The application of synthetic methods involves in practice mainly the pulsed welding of metals, which leads to the formation (in the region of the join) of intermetallic compounds, including those which are not obtained in the traditional methods of synthesis. The pulsed welding of metals has found applications in various branches of industry for the large-scale manufacture of bimetallic plates and coatings for tubes and the flat surfaces of machines and mechanisms.[210,225] At the present time the manufacture of welded and strengthened constructions in our country has reached a rate of 100 tonnes annually and shows a tendency to increase.

The methods for the shock synthesis and modification of materials with the aid of a dynamic treatment have also found practical applications in a new branch of science and engineering—the synthesis of superconductors. Apart from the studies quoted above,[138-143] the newest investigations should be mentioned.[226-231] Dynamic experiments make it possible to include in this vigorously developing field methodological features such as high-speed deformation, rapid thermal quenching, and instantaneous increase and relaxation of pressure. In many instances these procedures can be used in technology.

Apart from the direct applications of the dynamic pressure techniques, the latter are used also for the preliminary treatment of materials in the usual technology—for the activation of powders or sintering, pressing, catalytic processes, etc.

Thus we have outlined the most general limits to the applications of the chemistry of shock compression. As regards the prospects for the employment of this method, the unusual nature of the temperature pattern of shock compression, deformation, electrical phenomena, and the enormous pressure gradients create a unique set of physical influences on matter. By varying the energy carriers, the duration of the pulse, the density, and the temperature of the ambient medium and by the joint or consecutive operation of various factors, it is possible to widen significantly the horizons in the application of the shock-wave techniques in chemistry. At the very beginning of the development of shock wave chemistry, its prospects seemed to be limitless; however, in the present author's view, even now the peak in the development of this field has not been passed.

We may note certain problems which have not found a practical solution. This concerns in the first place the synthesis of high pressure phases. Hitherto it has not been possible to obtain such phases chemically; the reason is that the reaction of solids takes place over period $\geq 10^{-6}$ s, i.e. when the high pressure has ceased to operate. The rate-limiting stage is naturally diffusion processes. However, if special measures are taken and the mixture components are comminuted to give a particle size of 0.1–1 μm, then the diffusion time is reduced by 1–2 orders of magnitude and there is sufficient time for the reaction to occur in the high pressure zone. By varying the sizes of the particles of individual components, it is possible, in principle, to "involve" wholly the various parts of the reaction in the chemical process. The successive employment of various pulsed influences—self-perpetuating high-temperature synthesis, electric discharge, shock waves, and radiation can be used for the same purpose. Additional possibilities arise in the inorganic synthesis of high pressure phases under the conditions of the technical application of ultrafast quenching (detonation synthesis "into space") or following the instantaneous imposition of a static pressure after shock compression (for example, in hermetically sealed tubes with water or other gas evolving substance).

The problem of the synthesis of complex and organometallic compounds by-passing the liquid phase appears to be extremely promising. At the present time many substances (with covalent bonds) cannot be directly involved in a chemical process, since they do not dissolve in the known solvents without decomposition and cannot be congruently fused (for example, NaH, $PtCl_2$, CaC_2, CrO_3, etc.). The chemical interaction under the conditions of shock wave compression in strong containers makes it possible to insert directly into the initial matrix additional atoms and molecules and to obtain new clathrate compounds (for example, silicates with neutral metal atoms incorporated in their vacancies) or complexes with unusual combinations of ligands [for example, PtF_2Br_2, LnF_2I, $K_2Ni(CN)_2Cl_2$, etc.]. The problem of the polymerisation of inorganic gases, which, as it now appears, can be solved on the basis of solid solutions or clathrate compounds, is also of interest.

These are the nearest prospects for the inorganic shock-wave chemistry, but, as this science develops, new even more interesting tasks may arise.

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