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# Processes Occurring in Solids Under the Action of Powerful Shock Waves

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The action of powerful shock waves on condensed materials can lead to a wide variety of physicochemical changes: polymorphic transformations, decomposition and synthetic processes, polymerisation of monomers, and defect-formation or conversely the formation of a more perfect structure. The study of these processes has shown that many of them take place exceptionally rapidly. The development of methods for the recovery of substances after the action of shock waves made it possible to employ high dynamic pressures for preparative purposes. Examination of the mechanism governing the compression of a substance by a shock wave shows that the transition from elastic monoaxial compression to bulk-phase compression may be identified with phase transformations as regards gas dynamics and thermodynamics and suggests that phase transitions in the shock wave cannot take place at pressures below the dynamic yield point of the substance. The presence of vigorous plastic flow in shock waves together with the operation of pressures reaching millions of atmospheres suggests that in many ways dynamic operations of this kind on various substances are comparable to methods combining high static pressures with shear stresses. Plastic flow in shock waves leads to the appearance of a characteristic mass-transfer mechanism which gives rise to diffusion processes during the very short period of shock-wave compression. Comparison of dynamic and static studies at high pressures reveals a very close correlation between them. However, a number of effects observed by shock-wave techniques are so far inconsistent with the phase diagrams of the corresponding substances.

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## I. INTRODUCTION

Numerous experimental data show that, under the action of shock waves due to the detonation of explosives and impact of bodies moving at a high velocity, various chemical and physicochemical transformations take place in condensed substances. In particular, certain substances subjected to the action of shock waves undergo polymorphic transformations. Attention was drawn to this for the first time by Bancroft et al.[1], who investigated the shock compressibility of iron and observed at 130 000 atm a break in the Hugoniot curve†, which they accounted for by polymorphic transformations occurring in iron under these conditions. Subsequently such breaks were observed also in the Hugoniot curves for a number of other substances, for example carbon[2], quartz[3,4], marble[5], potassium bromide and chloride[6-8], and other compounds[9]. Apart from polymorphic transformations, phenomena such as fusion[10,11] and plastic flow on transition from monoaxial elastic compression to bulk compression can also be reflected in breaks in the Hugoniot curves[3,4,12].

An important distinctive feature of these transformations in shock waves is their unusually high rate. Whereas the formation of new phases in static experiments requires times reckoned in seconds, minutes, and sometimes hours and even longer periods, in shock waves these processes are completed in fractions of a microsecond.

The observation of breaks in Hugoniot curves is only a part of the investigation of the transformations in substances under the action of shock waves. Successful studies of this kind permit the determination of the parameters of the shock-wave compression during which the transformation took place, which is itself of scientific interest. On the other hand, in order to determine what transformation is undergone by the substance and whether it is reversible or irreversible under the given conditions, it is desirable to recover the test specimen in the state which obtains at the instant when the shock wave ceases to operate. Such methods have been developed.

† The Russians refer to this as the shock compressibility curve or the adiabatic shock curve (Ed. of Translation).

## 2. RECOVERY OF SUBSTANCES SUBJECTED TO SHOCK-WAVE COMPRESSION

The first data derived from studies of substances recovered after shock-wave compression were published by Ryabinin[13] in 1956. Novosibirsk investigators[14] began their study by a similar method and later applied other procedures also[15]. Designs of cylindrical and flat iron and copper tubes, whereby substances can be recovered after being subjected to the action of detonation of charges consisting of the most powerful standard explosives, were developed in the laboratory of one of the authors[16,17]. The pressure which then arises in the tube depends not only on the power of the explosive charge used and the duration of its operation but also on the initial density and compressibility of the test substance. With dense comparatively compressible substances the pressures reached more than five million atmospheres and yet the test specimens were satisfactorily recovered. Readily compressible substances of low density are recovered with greater difficulty.

Similar studies are being carried out also outside the Soviet Union. For example the Japanese investigator Kimura[18] developed an unusual recovery method, while Israeli scientists[19] use a method similar to that of Ryabinin.

American investigators have also reported studies on the recovery of specimens (see, for example, Wackerle[3] and DeCarli and Jamieson[20]) but little information is available about the recovery methods which they used.

The study of specimens recovered after shock-wave compression confirmed that the breaks in the Hugoniot curves can indeed be caused by phase transformations. For example, the suggestion by Alder and Christian[2] that the break in the Hugoniot curve for graphite corresponds to the transformation of the latter into diamond was confirmed by DeCarli and Jamieson[20], who succeeded in obtaining diamond from graphite, containing regions of rhombohedral structure, after shock-wave compression at a pressure of up to 300 000 atm during 1 ms. The present authors also achieved partial conversion of ordinary graphite into diamond with a yield of 3%.

It has been shown[21] that there is also a break in the Hugoniot curve for hexagonal graphite-like boron nitride. Studies on the recovery of specimens confirmed that the break is due to the polymorphic transformation of boron nitride into a denser modification, namely the hexagonal wurtzite-like modification of borazon. Later it was shown that, together with the hexagonal wurtzite-like borazon, there forms also a certain amount of a cubic sphalerite-like modification of this ultrahard substance.

Batsanov and coworkers[22], who studied the shock-wave compression amorphous boron nitride synthesised in their laboratory, obtained a new form of this compound. Kennedy and Benedick[23] showed that wurtzite-like cadmium sulphide is converted in the shock wave into a modification with a structure of the sodium chloride type during a period not greater than 1 μs. Batsanov and Deribas[14] reported the transformation on shock-wave compression of the usual form of neodymium oxide into a new phase.

Deribas and coworkers[24] studied the effect of shock-wave compression on silica and obtained a number of interesting results. Wackerle[3] also recovered specimens of single-crystal silica subjected to shock-wave compression. Traces of coesite were detected by Deribas et al.[24] and by ourselves in silica subjected to shock-wave compression. Wackerle[3], Deribas et al.[24], and earlier DeCarli and Jamieson[25] showed that, when silica is compressed by sufficiently powerful shock waves, it is converted into a vitreous form although the maximum temperature of the specimens at the instant of shock was much less than the melting point of this compound. Albite underwent a similar transformation in the experiments of DeCarli and Jamieson[25]. Secrist and Mackenzie[26] attribute considerable importance to this method of preparation of substances in the vitreous state.

Shock-wave compression may lead not only to polymorphic transformations but also to chemical changes. For example, Kimura[18] showed that shock-wave compression of a mixture of iron and zinc oxides leads to the formation of ferrites. We achieved certain syntheses as a result of shock-wave compression. For example, a mixture of sodium and magnesium fluorides was almost completely converted into sodium fluoromagnate $NaMgF_3$, and a mixture of metallic indium and phosphorus gave rise to a satisfactory yield of indium phosphide. The shock-wave compression of a mixture of elemental boron and lithium nitride and also of boron oxide and ammonium chloride gave rise to the formation of small amounts of boron nitride, the reaction products containing its dense modifications—cubic and hexagonal borazon.

Ryabinin[13] noted significant defect formation in sodium chloride subjected to shock-wave compression, the decomposition of lead nitrate to the dioxide, the decomposition of magnesium carbonate to a mixture of magnesium oxide and carbon dioxide, and pyrolysis of hydrocarbons.

A large number of chemical reactions were observed by Batsanov and Deribas and coworkers. They noted the decomposition of a number of carbonates[27], sulphates, and nitrates[28]. By analysing their results, these investigators found that the changes occurring in the test substances subjected to shock-wave compression are associated in the first place with their thermodynamic stability. Under constant shock-wave compression conditions, the substances decompose if the heat of their formation is below a limiting value, the extent of decomposition being greater the lower is the heat of formation. If the heat of formation of the compound exceeds the limit, the effect is restricted to the formation of chemical or structural defects. In the most stable compounds, a more perfect structure of the crystal lattice is formed. The same investigators noted a number of interesting phenomena in the study of the effect of shock waves on potassium nitrate.

Our own data[16,29] confirmed the results of Batsanov et al.[28] Substances with high chemical and thermal stability, such as alkaline-earth fluorides, alumina, etc. acquire a more ideal crystal structure on shock-wave compression, approaching in their properties well-formed single crystals. However, since we used more powerful explosive charges, we observed the decomposition even of those substances which remained completely unchanged in the earlier experiments[13,27,28]. For example, copper sulphate was partially decomposed to cupric oxide and partially to metallic copper. Compounds such as PNO, $Li_3N$, $NiF_2 . 2H_2O$ etc. were found to decompose. Partial or complete decomposition of a number of metal oxides was observed (oxides of antimony, nickel, iron, titanium, molybdenum, tungsten, etc.), the free metal formed in the decomposition being sometimes observed in the form of large beads (1–3 mm) in the tubes used to recover the substance.

It has been established that porous substances can be significantly contaminated by the material of the tube wall, and therefore many chemical reactions may be due to the usual high-temperature interaction with the iron in the tube[16,30].

It is interesting that many dispersed substances (for example magnesium, nickel, and calcium fluorides) are converted into materials with much larger crystals after shock-wave compression[16]. Before shock-wave compression magnesium and nickel fluorides consisted of powders of very small particles, which gave rise to distinct powder diffraction patterns even without rotation of the specimens and proved to be optically isotropic on examination in a polarisation microscope. After shock-wave compression the particles of these substances became significantly larger, so that powder diffraction patterns recorded without rotation showed distinct reflections from individual crystals and the anisotropy characteristic of the substances became apparent in polarised light.

Many organic substances were found to polymerise under the action of shock waves[31]. Studies of the shock compressibility of monomeric and polymeric acrylamide showed that the polymerisation process takes place at an enormous rate when the density of the monomer reaches that of the polymer under shock conditions[32]. It was shown that the energy evolved in polymerisation intensifies the shock wave. (The dimerisation of cyclopentadiene under the influence of the detonation of tetryl was achieved by Vereshchagin and coworkers as early as 1945.[35]) Barkalov et al.[33] suggested the possibility of the shock polymerisation of infinitely large monomer blocks (polymerisation detonation).

## 3. ULTRAFAST PROCESSES IN SHOCK WAVES

The above findings show that, when various substances are acted upon by shock waves, the resulting processes do indeed take place at high rates. This applies also to non-diffusion reactions (certain polymorphic transformations) and reactions for which the occurrence of diffusional processes is inevitable (for example, syntheses and decompositions)‡.

At the present time there are no generally accepted hypotheses which would account for the unusually high rates of physicochemical reactions in shock waves. Probably this is caused in the first place by the lack of the necessary experimental data, for example, such as those on the dependence of the degree of conversion and the particle size of the new phase, on the parameters of shock-wave compression (pressure, temperature, time of operation of high pressure) and the initial state of the substance (in particular its degree of dispersion).

Roughly speaking all physicochemical changes occurring under the action of a shock wave (polymorphic transformations, conversion into the vitreous state, formation of a more perfect crystal lattice in relatively weak shock waves and defect formation in powerful shock waves, decompositions, syntheses, and polymerisation) can be divided into two classes. The first class includes those transformations which occur during the period of operation of the high pressure during shock-wave compression. Polymorphic transformations and polymerisation phenomena undoubtedly belong to this class. Indeed, as already stated above, shock-wave compression curves for substances undergoing polymorphic transformation or polymerising under the action of shock waves show breaks demonstrating that the corresponding phenomenon takes place directly in the shock-wave front. The first class also includes synthetic reactions with formation of phases which are thermodynamically stable only at a high pressure. For all other transformations, which belong to the second class, there is unfortunately no proof at present that they occur during the operation of the shock waves and not, say, during a much longer period under the action of high residual temperatures.

The effect of the high pressures generated in the shock wave cannot alone account for the enormous increase in the rate of processes. A series of investigations showed, in agreement with theory [36-40], that, on increasing the pressure, diffusional processes are not only not accelerated but in fact retarded as a rule. A wide variety of explanations have been put forward for this phenomenon. For example, Hilliard and Cahn [41] attribute the decrease of the rate of diffusion at high pressure merely to a decrease of the equilibrium concentrations of vacancies and not a decrease in their mobility. (So far there are no data about diffusion along grain boundaries.) In the same publication the authors write that at high pressures the rate of transformations should decrease mainly due to the decrease of atomic mobility. On the other hand, Pozin et al. [42] believe that the rate of "true" solid-phase reactions should increase on raising the pressure due to the increase of contact between the grains. Then, of course, it may again fall due to the decrease of the diffusion coefficient.

The ultrahigh rates of processes in shock waves have been attracting the attention of an increasing number of scientists, although ten years ago it was generally believed that during shock-wave compression of heterogeneous polycrystalline mixtures "such a wide variety of complex phenomena may be encountered that there are no means for a complete explanation" [43].

Attempts are now being made to investigate non-diffusional processes. Thus, after a long discussion, Anders and Lipschutz [44,45] concluded that diamonds in meteorites are formed by a direct solid-phase transformation under the action of the shock wave produced on impact of the meteorite against the earth. They believe that the usual mechanisms governing the appearance of a new phase (generation and growth of nuclei) cannot operate in shock waves because the process is extremely short-lived. Wentorf and Bovenkerk [46] share this view and note that the growth of nuclei from the melt also cannot play a significant role because the time is too short and the probability of any appreciable extent of diffusional processes during this period is low. Libby [47] likewise supports this view and suggests that polymorphic transformations in a shock wave take place directly over the entire bulk of the substance without the usual requirement of the growth of a new phase from the previously formed crystallisation centre. Another aspect of Libby's views is that the formation of new phases in a shock wave consists of two stages: the formation of "an activated complex" (the substance compressed to the metallic state is usually understood as the activated complex§) and the conversion of this complex, on expansion, into a new phase, which is thermodynamically stable at the temperatures and pressures corresponding to the loss of stability by the activated complex (i.e. the metallic state of substance). It is believed that shock-wave compression of two different modifications of the substance (for example, graphite and diamond) leads to the formation of identical activated complexes.

In an examination of decomposition of synthetic processes in shock waves one must inevitably invoke one or other diffusion mechanism, whereby one can explain how metal and oxygen atoms, for example, which are adjacent in the crystal lattice of the initial oxide, are sorted out after shock-wave compression and separated in space.

At the same time it appears unlikely that the usual diffusion mechanism, involving the motion of individual atoms or ions (or whole groups of atoms) among the surrounding neighbouring species, which are strongly compressed at the high pressures existing behind the shock-wave front, can lead to the formation, in a period of the order of $10^{-5}$–$10^{-7}$ s, of the particles of a new phase, which in practice reach dimensions of 0.1 mm and more. This is contradicted by abundant experimental data showing a decrease of the rate of diffusion with increasing pressure (see, for example, Refs. 36–40).

Probably the key to the solution of the problem of the unusually high rates of reactions of the first class should be sought in experiments on the effect of ultrahigh static pressures in combination with shear of the compressed

‡ In the light of the above findings the view expressed by Dachille and Roy [35] sounds a little odd: ".....it is clear that, in experiments with shock-wave pressures which act upon the specimen during periods of the order of a microsecond, it is difficult to achieve considerable chemical or structural changes in the specimen". In contrast, one may note that Kormer et al. [8] showed by direct experiments that in the compression of potassium chloride and bromide by a powerful shock waves phase transitions (fusion) take place over a period of $10^{-11}$ s.

§ In agreement with theory, numerous experiments show that sufficiently high pressures convert all substances into a metallic state (see, for example, Refs. 48–51).

specimen. Here the idea of the possibility of such an analogy for polymorphic transformations was put forward by Douglas et al.[52]

## 4. ULTRAHIGH PRESSURES AND SHEAR DEFORMATION

Many investigators have shown that at usual pressures shear deformation can have a significant effect on the rates of chemical and phase transformations in solids (see, for example, Refs. 53 and 54). Similar phenomena might have been expected also at ultrahigh pressures. However, it was found that under these conditions shear deformation not only accelerates the processes but also leads to a radical change in their character. For example, Bridgman[55-58] established that bismuth oxide $Bi_2O_3$ subjected to the simultaneous action of a pressure of the order of 25 000–50 000 atm and shear deformation breaks down into metallic bismuth and free oxygen. Under these conditions tin dioxide lost part of its oxygen and was converted into the monoxide, and metallic copper and elemental sulphur interacted with formation of copper monosulphide.

Vereshchagin and coworkers devoted much attention to this technique[59-66]. They showed that pressure combined with shear accelerates certain polymorphic transformations, lowers the temperature of some phase transitions, sometimes gives rise to phase transitions which are not observed in the absence of shear (for example, in metallic lithium), leads to the decomposition of a number of compounds (copper sulphide, lead oxide, molybdenum trioxide, and others), and permits a number of syntheses from the elements (iron, nickel, and cobalt sulphides and magnesium and zinc phosphides).

A general feature of these processes is that high pressures make their occurrence thermodynamically possible but their rates are fairly slow due to diffusion-dependent limitations. On the other hand, when a shear stress is applied to the test specimen during the operation of these pressures¶, the rates become much higher and frequently the process goes to completion during the period of the shear stress. For example, in a study of the effect of high pressures on potassium hexacyanoferrate(III), Larsen and Drickamer[67] showed that shear stresses accelerate the decomposition of this compound into potassium hexacyanoferrate(II), cyanogen, and free iron by a factor of $10^{14}$. Enikolopov et al.[68] observed that at static pressures of tens of thousands of atmospheres many monomers virtually do not polymerise without the artificial creation of polymerisation centres. On the other hand, at the same pressures combined with shear polymerisation takes place at high rates without the introduction of any additional active centres.

Teller[69] believes that shear phenomena at high pressures can play a decisive role in chemical processes, in particular in the conversion of an exothermic reaction into an explosive process. However, he reduces the entire role of shear deformation to the accumulation of energy in the substance, which in turn helps overcome the activation barrier between the initial and final states. Leiserowitz et al.[19] draw a complete analogy between experiments on shock-wave compression and experiments on the effect of pressure combined with shear without taking into account the specific features of the effect of the shock-wave front.

¶ It is useful to note here that the plasticity of most substances increases with pressure[53,54].

## 5. THE MECHANISM OF SHOCK-WAVE COMPRESSION

Let us consider the mechanism of the compression of a substance by a shock wave. When the substance does not undergo any transformations on shock-wave compression, the shock-wave compression curve does not show any unusual features. The width of the shock-wave front (the region between the initial and final states of the substance subjected to shock-wave compression) is then very small: of the order of the free path in gases[70] and probably of the order of the interatomic distances in solids. On the other hand, if the substance does undergo a transformation on shock-wave compression, experiments show that the shock compressibility curve shows a break in one or other direction depending on the nature of the transformation, when the intensity of the shock wave is just below the intensity corresponding to the transformation. As predicted by Zel'dovich[71] and subsequently frequently confirmed experimentally, the shock-wave front then becomes diffuse and broadens, since the transformation requires a finite time.

If the transformation under shock-wave conditions takes place with increase in volume, the shock compressibility curve becomes steeper. The pressure profile in the stationary shock-wave front in such a substance is of the form shown in Fig. 1*b*. In principle, waves with such a profile are capable of steady-state propagation without the supply of energy from outside. A convincing example of the existence of such waves is the detonation waves in explosives.

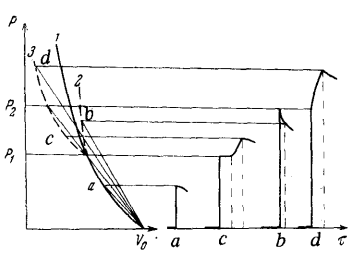



Figure 1. Hugoniot curves for various substances and the corresponding shock-wave profiles:
*1*) without transformations; *2*) transformation with increase in volume; *3*) transformation with decrease in volume;
*a*) pressure profile in the shock wave in the absence of transformations; *b*) transformation with increase in volume; *c*) transformation with decrease in volume; *d*) transformation with decrease in volume at sufficiently high pressures.

A break in the direction of smaller volumes has been observed for the polymorphic transformations investigated hitherto. Then, as shown by experiment, the shock wave loses stability over certain range of pressures. Initially a shock wave with an amplitude corresponding to the pressure of the onset of the phase transformation is propagated through the substance and then a slower second wave, in which the transformation itself occurs. The width of the front of the second wave corresponds to the duration of the transformation (Fig. 1*c*). At a pressure higher than $P_2$ (Fig. 1*d*) a single shock wave with the pressure profile shown in Fig. 1 is propagated in the substance undergoing polymorphic transformation; the width of the shock-wave front corresponds to the duration of the transformation.

Thus the complex form of the shock compressibility curve and the increase in the width of the shock-wave front constitute a direct demonstration of the occurrence of the transformation in the wave front, i.e. during a period less than $10^{-6}$ s.

Probably the unusually high rates of transformations with which we deal in these cases are due to the specific features of the compression of the substance by the shock wave. Shock-wave compression is a non-isentropic process. On the other hand, the flow before and beyond the shock-wave front in the rarefaction wave (in the system of coordinates associated with the front) is an isentropic process. Consequently the increase of entropy occurs in the front itself over a region corresponding to its actual width[70]. Physically the growth of entropy implies a transition from ordered translational motion of atoms or molecules of the substance in front of the wave into random motion in the front itself. This takes place in consequence of the non-head-on collisions between the moving atoms and the atoms already present in the front (in the system of coordinates associated with the shock-wave front). Thus in the shock-wave front there is always a sharp deviation from translational motion, i.e. components of atomic motion along the wave front appear.

From the macroscopic point of view, the shock wave effects monoaxial compression of the substance. When solids are compressed by shock waves with amplitudes less than the dynamic yield point, transverse displacements due to non-head-on collisions of atoms should also arise in the wave front. However, the energy of such displacements is less than the bonding energy in the crystal lattice. Therefore ultimately the atom remains at its original site but in an excited state. In this case compression leads to a change only in the interatomic distances along the wave, but the distances along the wave front remain the same. Such deformation of the crystal lattice is thermodynamically unfavourable, since a potential energy of displacement appears in addition to the potential energy of compression, so that the total potential energy is not a minimum[71].

Minimum potential energy is attained on compression from all sides when the crystal lattice undergoes a symmetrical deformation. Symmetrical compression of the crystal lattice by the shock wave occurs at compression pressures in excess of the dynamic yield point. Then tangential stresses in the solid exceed the critical value and the material begins to flow. In an examination of the process at an atomic level this implies that in a non-head-on collision the displacement of atoms along the shock-wave front becomes so great that the atoms acquire a certain freedom and no longer return to the previous site but remain in the coordination environment corresponding to the thermodynamic conditions ($P$, $T$) created on compression. If according to the phase diagram the substance should not undergo polymorphic transformations on shock-wave compression above the dynamic yield point, the state of the substance behind the shock-wave front corresponds to the initial crystal lattice but with lower parameters due to compression from all sides. On the other hand, if a new lattice is thermodynamically more favourable under the given conditions, a polymorphic transformation takes place.

Since a displacement of atoms from the equilibrium position, due to the passage of the shock wave, takes place in the matrix of the initial crystal lattice, it is possible that Libby's hypothesis[47], that the state of a substance subjected to shock-wave compression does not depend on the choice of the initial modification, is not always valid. This can be demonstrated by the fact that the Hugoniot curves for pyrolytic graphite and graphite containing domains of a rhombohedral structure are different. In the first case a transition to the diamond structure is not observed[72].

Two conclusions follow from the above discussion. Firstly the transition from elastic monoaxial compression to bulk-phase plastic compression is equivalent, as regards thermodynamics and gas dynamics, to a polymorphic transformation. Secondly the phenomenon of polymorphism under the action of a shock wave cannot occur at pressures below the dynamic yield point of the initial substance.

A change in volume along the shock compressibility curve during a polymorphic transformation is evidence that the transformation takes place to a very marked extent. In principle, one cannot exclude in this case the possibility that the rearrangement of the initial crystal lattice directly in the shock-wave front leads to the formation of large single crystals of a new phase, which then break down in the expansion wave after the removal of the pressure. However, it is probably more likely, and this follows from the considerations adduced above, that a large number of very small nuclei of a new phase, randomly distributed in relation to one another, are formed in the shock-wave front. Indeed it is difficult to suppose that the chaotic conditions arising in the shock-wave front simultaneously over the entire surface of the latter lead to a rigorously ordered arrangement of atoms corresponding to the crystal lattice of the new phase, i.e. it is essentially difficult to postulate an epitaxial growth of the crystals of the new phase in the shock-wave front. However, it is then necessary to explain how the substance consisting throughout of nuclei is converted into relatively large crystalline formations observed in the recovery tubes. Certain considerations concerning this problem will be put forward below in an examination of the possible mechanism of chemical reactions in a shock wave.

## 6. INCREASE IN THE PARTICLE SIZE OF NEW PHASES IN SHOCK WAVES

In crystalline lattices the position of atoms and the interatomic distances are determined by the equilibrium between forces of attraction and repulsion. The depth of the potential well in which each atom is located characterises the strength of the chemical bond. With increase of pressure, the atoms of the crystal lattice approach one another, the role of repulsion forces becomes more important, and the strength of chemical bonds falls. According to Kapustinskii[48], "the universal metallic state of matter", characterised by a complete disappearance of chemical differences between atoms and hence by the disappearance of all chemical bonds, arises when a substance is subjected to a sufficiently high pressure (about $10^8$ atm).

In shock-wave compression we usually deal with much lower pressures ($10^5$–$10^6$ atm) and therefore there can be only a weakening of chemical bonds. The situation is of course complicated by the fact that the temperature of certain substances subjected to shock-wave compression can reach tens of thousands of degrees when the intensity of shock waves is high. It is reasonable to suppose that the weakening of the strength of chemical bonds will be different in different cases. Let us consider a compound AB which decomposes on increase of pressure. One can imagine a case such that, under normal conditions ($P_0$, $T_0$), A–B bonds are energetically more favourable ($2E_{A-B}$ is greater than $E_{A-A} + E_{B-B}$), while at sufficiently high $P$ and $T$ the bonds A–A and B–B become energetically more favourable, i.e. at $P_0$ and $T_0$ the phase AB is stable, while

at $P$ and $T$ the stable phases are A and B. In this case, after attainment of the pressure $P$ and the temperature $T$, the thermodynamic conditions for the stability of the AB phase break down and decomposition of the compound becomes possible.

Examples of such reactions, found in the study of the effects of high static pressures on various substances, have been described in the literature. For example, according to Popova et al.[73], cuprous oxide disproportionates into metallic copper and cupric oxide at a pressure of 180 000 atm and 2000°C. According to Hoffman[74], $Pb_2O$ decomposes at 2000 atm with liberation of metallic lead, while $PbO_2$ decomposes at 12 000 atm into lead oxide (PbO) and oxygen. Arkharov and Bulychev[75] have stated that an increase of pressure favours the decomposition of the $Fe_{1-x}O$ phase into iron and $Fe_3O_4$ with a simultaneous decrease of the number of defects in the initial phase. DeVries[76] showed that at 25 000 atm and 1500°C $Al_2SiO_5$ decomposes into corundum and a silicate melt. On the other hand, it has been stated[35] that Coesu succeeded in obtaining at a pressure of 40 000 atm a substance with the composition $Al_2O_3 \cdot 3SiO_2$, which cannot be synthesised at the normal pressure. All these processes take place relatively slowly. Thus high pressures and temperatures in the shock wave create a thermodynamic background which determines the *possibility* or *impossibility* of the occurrence of both polymorphic transformations and chemical reactions.

The momentum imparted to atoms by the shock wave is insufficient for virtually instantaneous interpenetration of the reacting species of the initial reaction mixture. It is sufficient to recall that $\alpha$-particles moving at velocities higher by 3–4 powers of 10 than the velocity of matter in shock waves are stopped by layers a few tens of atoms thick. It would appear that even less comprehensible is the occurrence of decomposition processes in which separation of different types of atom from one another and not mixing at a molecular level is required, or the occurrence of synthetic processes where both requirements must be met. However, we believe that the occurrence of plastic flow makes it possible to overcome this difficulty. Here we have in mind the occurrence of extensive plastic flow of the substance in the recovery tubes. This is indicated by the significant residual deformation of the tubes themselves.

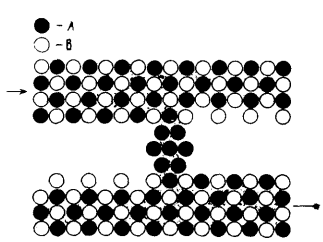



Figure 2. Scheme describing the decomposition of a compound AB during plastic flow in the rarefaction wave.

Fig. 2 presents a highly qualitative scheme representing chemical processes in the presence of plastic flow. When two layers of the substance are displaced relative to one another, the nuclei of phase A, located between them, can be regarded as a kind of roller about which oscillations are executed. With some approximation, phase A under these conditions can be regarded as a solid and phase AB as a liquid, since the strength of A–A bonds under these conditions is greater than that of A–B bonds. When the two layers of phase AB are displaced relative to one another, they transport past the nucleus, in its immediate vicinity, a multiplicity of atoms of both kinds. Since the time required for the rearrangement of electron shells ($10^{-13}$–$10^{-14}$ s) is much shorter than the time required for contact between atoms (it is easy to calculate that for a plastic displacement over a distance of the order of 1 mm†, dimensions of a single atom of 2 Å, and duration if shock-wave compression of $10^{-5}$ s, the time required for contact between two atoms is $2 \times 10^{-12}$ s) it follows that all the atoms A passing in the immediate vicinity of the nucleus have sufficient time to combine with the latter and this in fact may be the mechanism of the growth of the nuclei of the new phase. Of course, the same mechanism can operate also in the growth of phase B.

Thus, in contrast to the usual diffusional growth of crystallisation centres, in which each atom must find its way to the new phase, pushing apart its neighbours by virtue of the energy of thermal motion, in the growth of new-phase nuclei behind the shock-wave front the entire mass of the initial phase is transported by the plastic flow in the vicinity of the crystallisation centres and the required atoms combine selectively with the particles of the new phase undergoing continuous growth during this process.

An attempt may be made to estimate the dimensions of the new-phase particles, which can form by the mechanism proposed. For simplicity, it will be assumed that (a) the new phase forms in the plastic flow of an ideal crystal lattice of the initial phase, (b) the initial "nucleus" is a single atom X, (c) only atoms from a monatomic layer of the initial phase passing during the plastic flow above (below) the crystallisation centre can add to the latter, and (d) different crystallisation centres do not stick together.

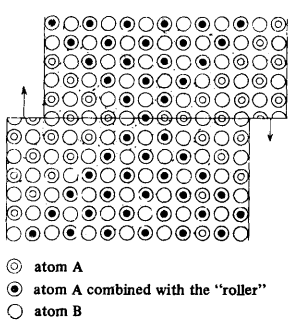



Figure 3. Representation of the phase AB in plan form along the slip plane during plastic flow; the atoms A which add to the initial atomic nucleus during plastic flow in the shock wave are indicated.

Fig. 3 shows in plan form the phase AB along the slip plane in plastic flow. The A atoms indicated add to the initial atomic nucleus when the AB phase moves in the vicinity of the roller being produced. The calculation of the number of atoms which can be combined into a new phase is simple. When two layers are displaced relative to one another over a distance $H$, the structure of each

† In practice up to 3–5 cm.[16]

layer is as shown in Fig. 3, and the distance A–B is $L$, then $N$, the number of atoms captured by the roller during the displacement of the layers, is defined by the expression,

$$N = 1 + 2\left[2 + 3 + \ldots + \left(\frac{H}{2L} - 1\right) + \frac{H}{2L}\right] = 1 + \frac{H}{2L}\left(\frac{H}{2L} + 1\right) \simeq \frac{H^2}{4L^2}.$$

For example, for $H = 1$ mm and $L = 1$ Å, we have

$$N = \frac{1}{(2 \times 10^{-7})^2} = 2.5 \times 10^{13} \text{ atoms.}$$

When the particles of the new phase are assumed to be cubic, their dimensions are $\sqrt[3]{2.5 \times 10^{13}} = 2.92 \times 10^4$ atoms $\simeq$ $2.92 \times 10^4 \times 1 \times 10^{-7} \simeq 0.003$ mm.

The same mechanism of the growth of new-phase particles can also operate in polymorphic transformations in the shock wave. In this case the relative motion and rotation of the nuclei insures their adhesion in a definite regular crystallographic arrangement. The return to the initial state on removal of pressure in those cases where polymorphism does not obtain is ensured by the usual processes, which also occur on removal of pressure in static experiments.

It is readily seen that in shock-wave compression of finely crystalline substances the random states of the single-phase particles in contact are identical and the particles are combined into a single mass during the plastic flow of which there is a possibility of the growth of larger particles. This can account for the increase in size and the improvement of the structure of a number of substances after shock-wave compression. Probably the maximum size of crystalline particles in the recovered specimen is restricted by the dynamic strength of the substance and the pressure gradient in the rarefaction wave. An approximate estimate of this size for real dimensions of explosive charges shows that it can reach several millimeters. However, it should be noted that plastic flow which, on the one hand, favours the growth of very small crystalline phase nuclei, can, on the other hand, break down fairly large particles.

The following considerations can be put forward concerning the polymerisation phenomenon in shock waves. Calculation of the temperature of acrylamide immediately behind the shock-wave front shows that, over the entire pressure range, between 20 000 and 80 000 atm, it is less than the melting point of the compound. This means that the polymerisation takes place in the solid phase. It may be suggested that the rearrangement of the crystal lattice, which leads to a decrease of the number of defects, plays an important role also in polymerisation process. At the very beginning of the crystal lattice rearrangement zone, active centres initiating polymerisation may arise. The polymerisation itself probably takes place during the formation of the new crystal lattice. The unusually high, explosive rates of polymerisation are probably due to the favourable relative orientation of the molecules in the monomer crystal[77], particularly when it is remembered that the monomer is compressed to the density of the polymer. The "roller" mechanism of the growth of polymer chains is of course also possible.

## 7. COMPARISON OF DYNAMIC AND STATIC STUDIES

The most interesting aspect of the investigation of the action of shock waves on matter is comparison of static and dynamic studies. However, methodologically it is a fairly difficult task. The point is that in static studies the aim is as a rule to investigate the $P$–$T$ diagrams, while in dynamic studies data on $P$–$V$ diagrams are most readily obtained. Experimental determination of temperatures in shock waves has been achieved for an extremely limited range of compounds[6]. In other cases one is restricted to calculated data and furthermore only the Hugoniot curves without breaks or, more precisely, only those sections of Hugoniot curves which correspond to pressures below the first break, are susceptible to exact calculations. At the present time such calculations have been made mainly for metals[3].

Another methodological difficulty encountered in the comparison of static and dynamic data consists in the fact that in most cases static experiments are performed at pressures up to 100 000 atm, while published dynamic data usually refer to pressures starting with 50–100 000 atm. A decrease of the initial density (increase of porosity) of the test specimen increases the temperature in the shock wave, which permits the use of dynamic methods in the region of the $P$–$T$ diagram above the Hugoniot curve. The same result can be obtained when preheated monolithic specimens are investigated. The region of the $P$–$T$ diagram below the Hugoniot curve of the monolithic specimen can be penetrated to some extent by carrying out preliminary cooling of the specimen or be applying special methods of shock-wave compression in which the final pressure in the specimen is attained in stages. This lowers the temperature developed in the specimen at the same final pressure. However, the region of the $P$–$T$ diagram immediately adjacent to the pressure coordinate is in principle inaccessible to dynamic investigations.

At the present time comparable experimental data derived from dynamic and static studies are available for only a small range of substances. These are mainly metals. For example, it is possible to compare the $P$–$T$ diagrams for iron[78] with data obtained in dynamic studies[79,80].

McQueen and Marsh[79] present data for the Hugoniot curve of the iron calculated from the results of an investigation of the shock compressibility of iron. The point of intersection of the $P$–$T$ Hugoniot curve with the curve for the $\alpha$-Fe $\rightleftharpoons$ $\epsilon$-Fe phase equilibrium agrees fairly well, as regards pressure, with the beginning of the break in the shock compressibility curve (131 000 atm). Jonson et al.[80] studied the temperature variation of the phase-transition pressure in iron by subjecting to the action of shock waves specimens which had been first heated or cooled. It was assumed that in the shock-wave compression the temperature virtually did not change and the transition pressure was estimated from the depth of the iron layer in which irreversible phase transitions were observed and from the rate of decay of the waves in iron, which the author determined. Despite these assumptions and other simplifications made in the interpretation of the results, the data obtained agree entirely with the phase diagram for iron. It is surprising that, at the time of the publication of their paper, Jonson et al. were apparently unaware of the existence of the $\epsilon$-modification of iron. The existence of this modification, which is stable at high pressures, was confirmed by Jamieson and Lowson[81] one month later in static experiments, but this result might have been suggested also by the work of Balchan and Drickamer[82].

It is also interesting to compare the data from static and dynamic studies on germanium. Two breaks were found in the Hugoniot curve for this element[83], corresponding to the onset of plastic flow (44 000 ± 4000 atm) and the phase transformation (114 000–122 000 atm at 160°C). The values obtained for the phase transition in germanium by the dynamic method differ to a smaller extent from the results

of static studies carried out by various investigators than they differ from one another [78,84].

Static [78,85] and dynamic [12] data for silicon are similar to those for germanium. The Hugoniot curve for this element also shows two breaks, the first corresponding, as in germanium, to the onset of plastic flow and the second to a polymorphic transformation.

Fig. 4 presents the phase diagram for metallic bismuth [86,87], the points corresponding to the breaks in the Hugoniot curve for bismuth specimens subjected to preliminary heating or cooling being indicated [88]. The breaks in the Hugoniot curve for bismuth evidently correspond to the bismuth I–bismuth III transition. The region of stability of the bismuth II phase, located between them, is so narrow that it is not reflected in the dynamic curve. The fact that the point $x$ is in the region of stability of the liquid phase appears so far incomprehensible. On the whole, the agreement between dynamic and static experiments on bismuth may be regarded as satisfactory.

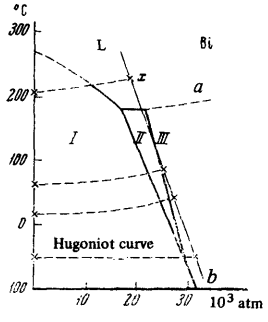



Figure 4. Phase diagram for metallic bismuth and data obtained in dynamic experiments; *a*) Refs.86 and 87; *b*) Ref.88.

However, the agreement between static and dynamic studies is not always as good as this. For example the Hugoniot curve for graphite, treated, following Alder and Christian [2], as corresponding to the transformation of graphite into diamond, occurs at a pressure of the order of 200 000 atm and a temperature of about 300°C, while the $P$–$T$ diagram for carbon [78] (Fig. 5) does not show any phase equilibrium lines in this region. If it is assumed that the agreement between static and dynamic studies must be always satisfactory, then the transition may be attributed only to metastable fusion of graphite. However, so far there are no data confirming such a view.

A similar situation is observed also in the analogue of crystalline carbon–boron nitride. According to Bundy [89], the dense modifications of boron nitride (borazon) become stable at comparatively low pressures (not greater than 40 000 atm). However, our data on the shock compressibility of the graphite-like boron nitride [21] show that under dynamic conditions the phase transition begins at only about 130 000 atm, although the temperature does not then exceed 200–300°C. On the other hand, according to the indirect data obtained by Bundy [89], unstable fusion occurs at very much higher pressures. However, it should be noted that, when boron nitride specimens subjected to shock-wave compression are preserved, the formation of the hexagonal wurtzite-like variety of borazon is observed and not the cubic sphalerite-like modification. The region of stability of the former modification in the phase diagram for boron nitride and the corresponding phase-equilibrium lines have not been elucidated hitherto. One cannot exclude the possibility that the break in the Hugoniot curve is associated with the phase-equilibrium line of precisely this modification.

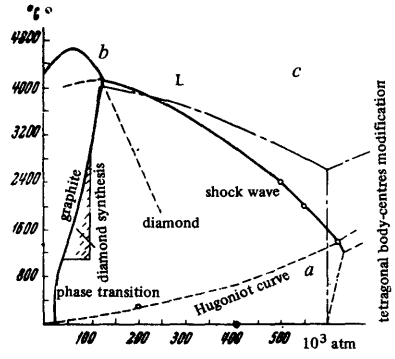



Figure 5. Phase diagram for carbon and data obtained in dynamic experiments: *a*) Ref.2; *b*) Ref.78.
* Tentative interpretation (Ed. of Translation).

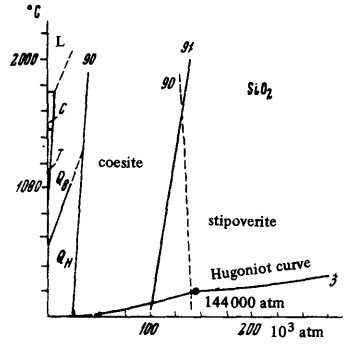



Figure 6. Phase diagram for silica and data obtained in dynamic experiments [3,90,91] (the numerals against the curves denote literature references).

The question of whether or not dynamic and static studies on crystalline quartz are comparable has not been inadequately elucidated. On the one hand, it follows from the work of Wackerle [3] that the latter observed a phase transition at 144 000 atm under dynamic conditions. The temperature (about 200°C) and pressure of this transition lie satisfactorily on the coesite–stishovite phase-equilibrium curve determined in Boyd's experiments [90], but differ markedly from the static experiment of Stishov [91] (Fig. 6). At the same time the point of intersection of Wackerle's Hugoniot curve [3] with the coesite–stishovite phase-equilibrium line obtained by Stishov [91] corresponds satisfactorily to the first break in the compressibility curve for vitreous silica obtained in Wackerle's dynamic experiments. On the other hand, Adadurov et al. [4], who used the method of dynamic volume compression ("method of mixtures") [92], showed that the phase transformation under these experimental conditions begins only at 200 000 atm,

but no phase-equilibrium lines are found in this region of the phase diagram for silica.

Although the possibility of achieving both chemical and phase transformations is determined by the thermodynamic background, it is probable that significant deviations from results expected on thermodynamic grounds may also occur due to the peculiarities of shock-wave compression. Here we have in view both the enormous rates of application of the load (small width of the shock-wave front) and the high rates of removal of the load (the duration of application of high pressures to the substance).

As already stated, plastic flow in shock-waves accelerates various transformations but does not make them infinitely fast. Under favourable conditions the transformation can occur immediately beyond the intersection of the Hugoniot curve and the corresponding phase-equilibrium line on the $P$–$T$ diagram. However, it should be noted that the transformation induced by the shock wave can begin also at much higher pressures than the pressure corresponding to the above point of intersection. This can be due to at least two factors. On the one hand, the dynamic yield point can exceed the pressure indicated by the phase diagram, and, until this yield point is passed, the compression remains monoaxial and the mobility of atoms is insufficient for a change in their coordination environment during short periods. Possibly the characteristic features of the shock-wave compression of crystalline quartz and the absence of breaks in the compressibility curves in the region of the quartz–coesite equilibrium are due precisely to the exceptionally high yield point of both crystalline and vitreous quartz (the dynamic yield point of crystalline quartz is 35 000–60 000 atm along the $x$ axis, 65 000–80 000 atm along the $z$ axis, and 98 000 atm for fused quartz [3]). On the other hand, one cannot exclude cases where, despite a vigorous plastic flow, the duration of the transformation is nevertheless fairly high and there is not sufficient time for the process to occur in the shock wave. Here there may be two cases. If the relaxation time falls with increasing pressure, then at a sufficiently high shock pressure there may come a moment when there is sufficient time for the transformation to occur in the shock wave and we obtain results differing significantly from static experiments, i.e. higher pressures. The characteristic features of the shock-wave compression of graphite and boron nitride can be fully accounted for by the effect of this factor. On the other hand if the relaxation time increases with impact pressure, then the transformation cannot be achieved at all.

Polycrystalline or powdered materials rather than single crystals are most frequently investigated by dynamic methods, particularly in experiments with recovery of the specimen. In such cases it should be borne in mind that pressures significantly exceeding the average pressure which obtains in the specimen after all the pores have been closed up inevitably arise in microregions. This local excess pressure may give rise to local thermodynamic conditions suitable for the transformations, although the average pressure in the specimen is still much lower than would be required in accordance with the phase diagram.

The irreversibility of the processes occurring in the shock wave is determined not only by the phase diagram but also by kinetic factors, in the first place the characteristic features of the removal of shock-wave load. The removal of load during the passage of the rarefaction wave occurs much more slowly than the generation of high pressures and temperatures in the application of the shock-wave load to the substance and there is then no random mobility of the atoms. However, the time of removal of pressure is still smaller by a factor of many powers of ten than can be achieved in static experiments. Since the removal of load is adiabatic, just as rapid a fall of temperature is observed simultaneously. As a result, it is possible to quench the high-pressure phases, provided of course that they are capable of metastable existence at the residual temperatures which obtain after the passage of the shock wave. If the residual temperatures are fairly high, the phases formed at high pressures (metastable under normal conditions) may be annealed. Thus, despite the fact that Hugoniot curves indicate virtually complete conversion of graphite into diamond on shock-wave compression, the temperatures in the recovered specimens are so high that the diamond formed is almost completely reconverted into graphite. On the other hand, we have already mentioned that in many cases there is so far no direct evidence of the occurrence of processes in the shock wave itself during the application of high pressures. One cannot exclude the possibility that many processes occur exclusively due to the residual temperatures. A good example of this may be the present authors' investigation of the behaviour of antimony oxides, which decompose until the liberation of metallic antimony when the specimens are kept in iron tubes but remain virtually unchanged when copper tubes are used. In the first case the appearance of metallic antimony is entirely due to the interaction of the oxides with the material of the tube walls.

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Shock-wave compression of condensed systems makes it possible to achieve a number of chemical and phase transformations in unusually short times. The pressures set up by shock waves are at present unattainable in static apparatus. Furthermore, shock waves can also affect the substances to which they are applied as a result of very high temperatures (up to tens of thousands of degrees in the shock wave and up to several thousand degrees after the passage of the expansion waves).

The possibility of applying such high pressures and temperatures to matter arose in chemical investigations only in recent years. As in any new field of study, so far the number of problems and puzzling phenomena is much greater than the available answers. Only the first steps have been taken to bring into closer correspondence and make more consistent the dynamic and static experiments and to elucidate the mechanism of the processes occurring in the shock wave.

However, it is quite clear that the elucidation of the laws governing the reactions in shock waves would not only provide experimenters with the means of obtaining thermodynamic parameters in those regions of temperature and pressure which will remain unattainable by other methods in the forseeable future, or a method whereby it will be possible to influence radically the kinetics of many processes, but also it will provide the means for a significant modification of the properties of many substances and their preparation in new, previously unknown forms. Further development of experimental methods for the recovery of substances on removal of the high pressures associated with shock-wave compression and the theoretical study of this aspect of the problem will play a special role in this.

Until recently the sole aim of deformation was destruction. The development of studies on the effect of shock waves on matter will make it possible to consider the application in synthetic chemistry of the energy of powerful explosions, including nuclear explosions.

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# Application of Electrical Spin Resonance in Chemical Kinetics

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The application of electron spin resonance (ESR) in the study of the kinetics of chemical reactions involving free radicals and paramagnetic ions is a very promising and rapidly developing field of study. In the first part of the review certain theoretical aspects and latest advances in studies on the kinetics of chemical reactions by the ESR method are discussed. Particular attention has been given to methods of analysis of the ESR spectra of free radicals, to methods for the calculation of concentrations, and also to a new method for the determination of local concentrations of paramagnetic centres from the dipole-dipole contribution to ESR line width.
In the second part of the review examples of the application of electron spin resonance in chemical kinetics are examined, and studies on radical reactions and the cage effect in solid matrices, and also measurements of steady-state concentrations of active radicals directly in the course of chemical reactions are discussed in detail.

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## I. INTRODUCTION

This review was written on the suggestion of the late V. V. Voevodskii, one of the first scientists to understand the exceptionally great promise of the application of electron spin resonance in chemical studies. Thanks to him, Soviet science now occupies a leading place in the field of chemical ESR spectroscopy.

The application of radiospectroscopic methods, nuclear magnetic resonance (NMR), and electron spin resonance (ESR) led to significant advances in studies on the fundamental problems of theoretical and applied chemistry. Radiofrequency techniques enable often hitherto unobtainable information about the structure of matter and the dynamics of the processes occurring in it to be obtained. In particular, electron spin resonance