THE PHYSICS AND CHEMISTRY OF IMPULSIVE PRESSURES (REVIEW)*

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Technical progress is largely determined by the creation of new materials with special physical properties suitable for service under extreme conditions. Such requirements have led to the accelerated development of high-pressure technology, the use of which in physical research has, in turn, had an important effect on theoretical questions of the structure of matter.

Table 1

Phase Transitions

Substance	Pressure, kb
$BaTiO_3$	~8
Bi	17—30
Fe	19.130
KCl	20
KBr	20
P	25.80
S	67—106
H_2O	115
NaCl	120
$CaCO_3$	150
SiO_2–molten	250
SiO_2–cryst.	400
C–graphite	400,600
I	700

The two- or threefold compression of a solid leads to fundamental changes in the electronic structure of the atoms, in particular, to the possibility of overlapping of the valence band and the conduction band and displacement of the electrons into deeper layers. Whereas chemistry is concerned with the outer electrons, and nuclear physics with the components of the nucleus, the physics of superhigh pressures opens up to the investigator the region of the inner electron shells of atoms, a region still unexplored.

Table 2

Conductivity

Substance	Pressure, kb
H_2O	30—125
$LiAlH_4$	50
S	70—200
I	80—130
P-red	<100
KI	170
RbI	200
CsI	200
NaCl	>210
Teflon	>210
CsCl	270
CsBr	270
Paraffin	700
Plexiglas	820

The study of the behavior of matter under pressure is useful not only for laboratory practice but in understanding a number of geological and cosmic phenomena.

Table 3

Refraction of Water

Pressure, kb	n	d	R
—	1.333	1.00	3.70
39	1.48	1.42	3.60
110	1.52	1.64	3.34
144	1.55	1.79	3.20

This aspect of high-pressure research has recently been attracting increasing attention.

There are two basic independent methods of creating high pressures: static and dynamic. Whereas, since Bridgman's work, the former has become an established branch of knowledge with an extensive literature, represented in the Soviet Union by the school of L. F. Vereshchagin, the application of impulsive pressures to physicochemical problems really began only 10–15 years ago and is still in its infancy.

Table 4

Alkali Halides

Substance	R_{in}	R_{comp}	Compression
LiF	2.69	2.10	1.39
NaCl	8.52	6.52	1.56
KCl	10.82	8.23	1.68
KBr	13.97	10.92	1.70
CsBr	18.48	15.07	1.63

The general theory of the physics of explosions and shock waves has been developed by Academicians L. D. Landau, M. A. Lavrent'ev, Ya. B. Zel'dovich, and N. N. Semenov , and their followers. The gasdynamic basis of shock wave theory has been quite fully examined in monographs by Zel'dovich [1], Courant and Friedrichs [2], Baum, Stanyukovich, and Shekhter [3], and Zel'dovich and Raizer [4], and accordingly there is no need to re-examine it here. The state of the theory is such that the qualitative nature of the phenomena can be predicted in almost all cases; however, it is still virtually impossible to make quantitative predictions about the behavior of matter under impulsive pressures. The basic reason for this is the dependence of such mechanical parameters as mass velocity, Grüneisen constant, compressibility, etc., on the atomic-electronic structure of matter. Attempts at a theoretical analysis of this dependence have only just begun, and the only real way of establishing it is still experimentation.

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There are two approaches to the experimental investigation of the behavior of matter under conditions of shock compression. One is to determine the compressibility curves by measuring the wave and mass velocities; the other is to make a direct physicochemical study of substances subjected to the action of an explosion. The first approach began to be developed 20 years ago in the United States and the Soviet Union; the second approach was proposed in the Soviet Union 10 years ago and rapidly began to be developed abroad.

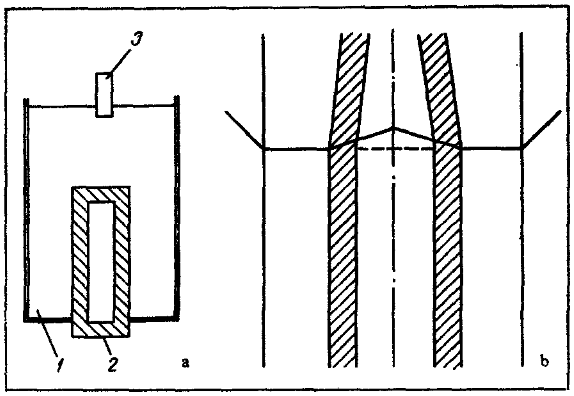

Fig. 1. Shock compression of a cylinder: a) diagram of experiment, b) diagram showing propagation of shock wave; 1) explosive, 2) bomb, 3) detonator.

Without dwelling on the principles and practical aspects of methods of registering velocities under conditions of dynamic compression, which are described in Al'tshuler's review [5], I shall briefly discuss the basic results obtained in such experiments.

Historically the situation was such that dynamic methods were applied first and most extensively to metals. In the first foreign publications [6–9] shock adiabats were obtained up to pressures of 500 kb,* Al'tshuler and coworkers [10,11] raised the upper limit first to 5 mb**, and then to 9–10 mb [12,13].

As a result of these studies it was shown that the density of monolithic samples exposed to superhigh pressures increases by a factor of two or more (in the case of alkali metals by a factor of 2.7–3.4). This compression corresponds to an important reduction in interatomic distances: for example, for alkali metals the atomic radii decrease by a factor of 1.4–1.5 and approach the values of the radii of the corresponding cations.

At the same time the application of impulsive pressures of even a few megabars to loose tungsten powders failed to compress them even to the normal density of the metal [14] owing to the developing thermal pressure.

Particularly interesting are the phase transitions observed in a number of metals exposed to dynamic loading. These transitions are revealed by a discontinuity in the shock adiabat due to a change in wave velocity in the modified medium. This discontinuity was first observed in iron at a pressure of 130 kb [15]. In this connection it is important that to detect new phases in dynamic experiments the transition time must be much less than the duration of action of the superhigh pressures on the material, i.e., less than 1 μsec. This indicates that changes in atomic structure can take place during shock compression and thus suggests the possibility of a new discipline, namely, the chemistry of impulsive pressures.

Studies of the shock adiabats of nonmetallic elements and ionic crystals have also revealed phase transitions. Al'tshuler [5] presents data on alkali halides obtained by Soviet and American scientists. An increase in density by a factor of 2–3.3 and a discontinuity of the adabatic curve indicating a transition from a NaCl to CsCl type lattice were regularly observed.

As Alder points out, phase transitions take place at any crystal orientation, but when the (III) axis is oriented at right angles to the shock front the transition takes place at lower pressures. This is because the structural transition NaCl → CsCl is equivalent to compression of the unit cell, i.e., to displacement of the atoms along the (III) axis.

After the removal of pressure the alkali halides return to the initial state. However, this mechanism is not general, and in the case of carbon De Carli and Jamieson [17] found small crystals of diamond in the shock compression products of graphite, i.e., the transition was irreversible. This fact was also used as a basis for further attempts to preserve the products of dynamic compression, i.e., the preservation studies discussed in the next section of this review.

To conclude our discussion of phase transitions we present a summary of the results achieved so far (Table 1).

As already mentioned, the sharp increase in crystal density during dynamic experiments is accompanied by an appreciable change in atomic dimensions and hence in the nature of the chemical bonds.

Table 5

Shock Compression Parameters of NaCl

d, g/cm^3	Explosive, g	σ	σ_0	p, kb	t, °C
1.14	50	2.28	1.20	240	1330
	100	2.50	1.30	500	1650
	150	2.50	1.30	500	1650
1.68	50	1.67	1.29	170	570
	100	1.83	1.42	330	730
	150	1.87	1.45	370	800
1.92	50	1.60	1.41	250	400
	100	1.69	1.50	360	610
	150	1.74	1.55	420	660

Since, as a rule, the anion radii are much greater than the cation dimensions in many coordination crystals, we may assume that the crystalline region is composed of anions, while cations occupy the interatomic space. Hence it is clear that it is mainly the

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*kb, kilobar, equivalent to one thousand atmospheres.

**mb, megabar, equivalent to one million atmospheres.

Table 6

Decomposition Topography of Shock-Compressed $CdCO_3$

Explosive, g	Weight of sample, g	% Cd in starting $CdCO_3$ = 63.5				Mean
		1	2	3	4	
30	1	64.3	65.2	65.4	67.4	65.6
	1.5	64.3	64.7	65.4	65.8	65.0
150	1	64.3	65.8	67.6	68.8	66.6
	1.5	64.6	65.0	66.3	67.7	65.9

anions that are compressed during the compression of crystals. Physically this is understandable, since the electron shells of the anions are looser than those of the cations, so that their compression is more favorable from the energy standpoint.

As compression increases and the dimensions of the anions decrease, the ratio $k = r_c/r_a$, which controls the geometric structure of the crystal, will increase. Thus, at values of k from 0.41 to 0.73 the octahedral configuration is stable, while at k = 0.73–1.37 the cubic configuration is stable.

Actually, sodium salts have the following values of k: NaI 0.45, NaBr 0.50, NaCl 0.54; the values for potassium salts are KI 0.60, KBr 0.68, KCl 0.73. Consequently, in order to attain the critical value k = = 0.73, above which a structure of the CsCl type is stable, it is necessary to obtain the following compression factors: NaI–4.2, NaBr–3.1, NaCl–2.5, KI–1.8, KBr–1.2, KCl–1.0. The experimental data are in qualitative agreement with this conclusion.

In the case of substances whose coordination number is 8, condensation may take place as a result of a further increase in coordination and a reduction in free free space; similar processes also result from further compression of the alkali halides enumerated above.

Shortening of the dimensions of the anions may result not only from squeezing of the outer electron shells but may also result from transition of some of the valence electrons into the conduction band. On the other hand a decrease in ionic radii may lead to an appreciable increase in ion mobility with respect to diffusion. Therefore it is natural to expect that under conditions of shock compression the electrical conductivity of the sample may increase.

The conductivity of dynamically compressed substances was first measured by Alder and Christian [18], and then by Brish, Tsukerman and Tarasov [19] on several organic and inorganic samples. A summary of the results based on the data of Duval and Fowles [20] is presented in Table 2.

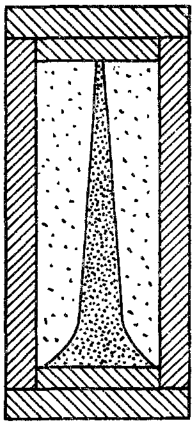

Fig. 2. Topography of red phase in sodium nitrate.

The nature of this effect is still not completely understood. Alder and Christian see the cause in a transition from the dielectric to the metallic state. Kormer et al. [21], improving on this idea, suggest a transition from the dielectric to the semiconducting state followed by the formation of free electrons as a result of thermal excitation.

On the other hand, David and Hamann [22] consider it possible for the conductivity of, for example, water to increase as a result of an increase in the ionization constant of H_2O under pressure. Al'tshuler et al. [23] also consider an ionic conduction mechanism most probable in the case of shock-compressed NaCl.

Refractometric data obtained in dynamic experiments [24, 25] apparently indicate that conduction in the shock compression of dielectrics is ionic in nature. Table 3 presents values of the refractive index,

Table 7

Iron Content of Compressed $NaNO_3$

Weight, g	Part of bomb	Standard, %	Al insert, %	Cu insert, %
1	1	0.23	0.14	0.055
	2	0.05	0.11	0.034
	3	0.27	0.13	0.071
	4	1.45	0.37	0.078
1.3	1	0.05	0.008	0.001
	2	0.03	0.014	0.006
	3	0.05	0.027	0.006
	4	0.62	0.030	0.008

Table 8

Variation of Number of Defects in Shock Compression

Substance	d_{in}	d_{comp}	$d_{x\text{-ray}}$	I_{in}/I_{comp}
$CaSO_4$	2.930	2.959	2.963	1.25
$BaSO_4$	4.362	4.476	4.480	1.69
$PbSO_4$	6.240	6.317	6.323	1.82
$Sr(NO_3)_2$	2.943	2.970	2.974	1.62
$Ba(NO_3)_2$	3.219	3.240	3.244	2.10
$MgSO_4$	3.421	3.356	3.450	0.33
$CuSO_4$	3.603	3.546	—	0.50
$CoSO_4$	3.720	3.659	3.747	0.90
$NaNO_3$	2.257	2.190	2.260	0.46
Na_2SO_4	2.650	2.590	2.663	0.60
Na_2CO_3	2.493	2.487	2.509	0.83

Table 9

Alkalinity of Compressed Nitrates

Substance	Part of bomb, from top to bottom	Loading density, g		
		0.7	1.0	1.3
$NaNO_3$	1	0.8	1.7	3.3
	2	0.9	1.7	3.3
	3	1.3	1.7	3.2
	4	1.6	1.7	3.3
KNO_3	1	0.2	0.8	0.1
	2	0.5	0.8	0.1
	3	0.7	0.8	0.1
	4	0.9	0.8	0.1
$RbNO_3$	1	0.9	1.0	0.9
	2	1.0	1.0	0.9
	3	1.4	0.9	0.9
	4	1.6	0.9	0.9
$CsNO_3$	1	1.2	1.2	1.1
	2	1.4	1.2	1.1
	3	1.8	1.2	1.1
	4	2.4	1.2	1.1

Table 10
Dielectric Constants of Compressed Nitrates

Substance	Part of bomb, from top to bottom	Loose packing		Dense packing	
		after explosion	after remelting	after explosion	after remelting
$NaNO_3$ (7.1)	1	7.7	7.3	7.0	7.0
	2	7.2	7.1	7.2	7.1
	3	7.3	7.1	7.2	7.1
	4	8.3	7.4	7.4	7.1
KNO_3 (4.5)	1	5.3	4.7	5.0	4.6
	2	5.2	4.7		
	3	5.7	5.0		
	4	6.2	5.6		

density [24], and mole refraction (electronic polarizability) of water under normal conditions and in shock compression. It is clear from the table that the electronic polarizability of water decreases monotonically with increase in pressure and is comparable in value with the refraction of water of crystallization (3.40 ± ± 0.2) [26], i.e., water molecules without hydrogen bonds. Thus, the compression of water takes place at the expense of breakage of the hydrogen bonds and closer packing of the H_2O molecules. However, the appearance of a metallic component in H_2O should also lead to an appreciable increase in the electronic polarizability of water.

A similar situation is also observed in the case of compressed crystals of alkali halides: corresponding data [25] are presented in Table 4.

The data presented also contradict the hypothesis concerning the presence of free electrons in shock-compressed crystals (up to pressures of about 700 kb).

The first studies of substances preserved after shock compression were reported by Ryabinin in 1956 [27, 28]. In these studies samples were placed in ampuls which in turn were inserted in metal cylinders surrounded with explosives. As a result of the explosion a convergent cylindrical wave was formed inside the ampul and, according to Ryabinin's estimate, this compressed the material to pressures of 500 kb.

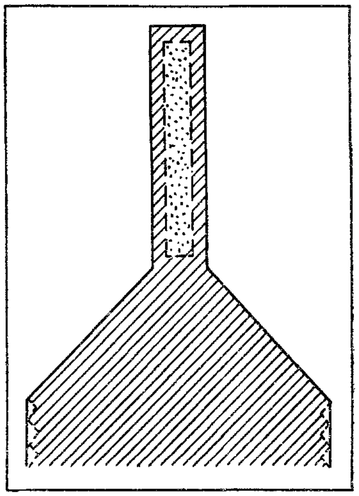

Fig. 3. Diagram of "cold" bomb.

The chemical substances thus compressed partly decomposed (NaCl, $CuSO_4$, $MgCO_3$, $Pb(NO_3)_2$, paraffin), underwent phase transition (sulfur), or remained unchanged (graphite). The absence of changes in the latter case was attributed by the author to lack of time: shock compression takes microseconds, although it is now known that phase transitions take much less time, 10^{-11} sec [25]. The reason for the lack of success in synthesizing diamond will be considered below.

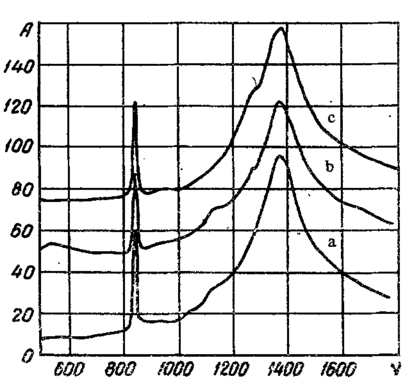

Fig. 4. IR spectra of sodium nitrate (absorption A in %; ν in cm^{-1}): a) after exposure to X-radiation, b) after shock compression, c) after addition of sodium nitrate.

In 1958 Nicholls et al. [29] reported that shock compression is accompanied by a process of decomposition with a reduction in metal valence: $Fe_2O_3 \rightarrow Fe_3O_4$.

Two years later publications appeared giving examples of substances and materials of practical value obtained under conditions of shock compression. Thus, Dharmateja [30] reported that as a result of the decomposition of organosilicon compounds α and β forms of SiC were obtained. Montgomery and Thomas [31] describe the possibility of an explosive technique for pressing metallic and nonmetallic powders. Finally, in 1961 De Carli and Jamieson [17] obtained small crystals of diamond from the dynamic compression of natural graphite (about 300 kb). It is interesting to note that they were unable to obtain diamond by compressing pure hexagonal graphite. In 1964 Coleburn [32] compressed synthetic (pyrolytic) graphite to 500 kb and did not observe a phase transition to diamond, the shock adiabat of this material differing substantially from the data of Alder and Christian [33] for Ceylon graphite in the pressure range above 100 kb.

Table 11

New Modification of UF_4

Property	Starting substance	After explosion	After annealing
Refractive indices	1.550, 1.584, 1.596	1.62–1.68	1.550, 1.584, 1.596
Dielectric constant	13.3	18.5	13.2
Density	6.7	7.7	6.7
Thermogram	Nothing up to 500°	Exo at 320°	Nothing up to 500°
IR spectrum	J=58%	J=21%	J=54%
Crystal system	Monoclinic	Cubic	Monoclinic

Hence it follows that the structure of the starting substance is of fundamental importance in relation to phase transitions during dynamic compression (and not only time as suggested by Ryabinin).

An important step forward was the investigation of the defects formed in a solid after the passage of shock waves. Thus, an electron-microscope study of compressed α-Fe showed that the dislocation density increased by two orders: before compression it was about $10^8/cm^2$, after compression (70 kb) about $10^{10}/$ $/cm^2$ [34]. An increase in the defects in a single crystal after shock compression has been observed by the EPR method in MgO [35] and from the magnetic susceptibility in ZnS [36]. In the latter case it was shown that the number of unpaired electrons in the material progressively increases with increase in the number of explosive compressions, the defects being completely annealed at temperatures of 570°–750° C. An interesting technical feature was the dynamic compression of samples of ZnS in evacuated quartz vessels which withstood up to 15 successive explosions.

In 1963 the first attempt was made to synthesize the chemical compound ZnO + Fe_2O_3 by dynamic compression in a cylindrical bomb [36]. The author noted that the chemical processes at the bottom of the bomb are much more intense than at the top. Finally, in 1965, Soviet physicists [37] demonstrated the possibility of polymerization under conditions of shock compression.

Thus the initial possibilities of dynamic high-pressure technology include the pressing of powders, the synthesis and decomposition of chemical compounds, the formation of defects and the realization of phase transitions. The uniqueness of the conditions, enormous temperatures and pressures and the instantaneous action of these factors leading to nonequilibrium states, suggests the possibility of obtaining important results.

Following the publication of the data of Ryabinin, De Carli, and Jamieson, in 1963 in their laboratories at the Novoskbirsk Scientific Center the author of this article and A. A. Deribas began work on testing explosive compression systems that allowed the compressed samples to be preserved for investigation. The first stage of this research, completed in 1963, produced a rather simple and reliable system (Fig. 1) and in 1964 systematic physicochemical studies of materials subjected to the action of an explosion were begun. Finally, in 1965 on the initiative of Academician M. A. Lavrent'ev and Professor S. S. Kutateladze a department of super-high pressures with the necessary complement of specialists in modern physicochemical methods of studying the structure of matter was set up at the Institute of Thermophysics Siberian Division AS USSR. During this period the dynamic experiments themselves were conducted in the laboratory of A. A. Deribas at the Institute of Hydrodynamics, and therefore the scientific results obtained in this direction are the joint achievements of the groups in question.

1. It is still not possible to make a direct determination of the thermodynamic parameters of shock compression in a cylindrical bomb. Therefore, in order to estimate pressure and temperature various indirect methods are employed. At the Institute of Thermophysics we have developed a method of plasticity indicators, which can be used to determine the pressure and temperature inside the bomb in the case of compression of a substance with a known equation of state.

Copper disks with an area equal to the bomb section are placed inside the bomb at equal intervals at right angles to the axis of the cylinder. After the explosion as a result of the action of the shock waves the walls of the cylinder move and compress the copper disks. The unloading wave and elastic deformation of the compressed materials expand the walls of the bomb, but as a result of its high plasticity the copper disk remains in the state of minimum compression. The ratio of the areas of the copper disk before and after compression indicates the degree of compression of the material, and from the shock adiabat it is easy to find the pressure corresponding to this compression.

The results of our experiments are presented in Table 5, which also contains values of the shock compression temperature calculated from the formula $T \approx$ $\approx T_0\sigma^2$ [4].

It is clear from Table 5 that in complete conformity with the theory the pressure and temperature inside the bomb increase with decrease in the packing density of the sample. Thus, to prevent thermal decomposition it is necessary to pack very tightly, using precompression or even fusion. Table 6 presents the results of complexometric analyses for cadmium of samples of $CdCO_3$ subjected to the action of an explosion, the contents of the bombs being divided into four equal parts at right angles to the axis of the cylinder (1, 2, 3, and 4 from the top).

The tabulated data show that decomposition increases from top to bottom, but is somewhat reduced with decrease in the weight of the charge and with increase in the packing of the bomb. The latter is perfectly natural,

Table 12
New Modifications of Neodymium Oxide and Boron Nitride

Substance	Property	Starting phase	New phase
Nd_2O_3	Refractive index	2.10	1.49
	IR spectrum	Max at 400 cm^{-1}	No absorption at 400 cm^{-1}
	X-ray spectrum	$\Delta L_{III} \approx 1$ eV	
BN	Refractive index	1.78	1.48
	Density	1.975	2.60
	Refraction	5.27 cm^3	2.76 cm^3

since an increase in the amount of material reduces the temperature as a result of the decrease in friction and because of the increase in the heat capacity of the compressed sample. In this connection it proved very convenient to add a small amount of water which has a high heat capacity and a low density in a mixture with $CdCO_3$. Experiments showed that in mixtures of 1 g $CdCO_3$ + 0.27 g H_2O and 1.5 g $CdCO_3$ + 0.17 g H_2O (occupying equal volumes) the content of Cd is 63.7 ± ± 0.1%, i.e., there is practically no decomposition. Other liquids have a similar effect.

Analogous results were also obtained in experiments with mercuric oxide. Dynamic compression of pure HgO leads to its decomposition, but when water, fluorinated oils, and certain liquids are added decomposition ceases.

Since these liquids are easily removed from the products of shock compression, the indicated method may be recommended for increasing the purity of compressed samples.

However, the compressed samples may be contaminated not only by the products of their own decomposition but also by the material of the bomb, i.e., in the standard system, iron. An examination of the bombs after dynamic compression showed that in the bottom plug there is a small crater, a depression apparently formed by the reflected wave. Spectral analysis of the bomb contents for iron revealed that it is present in an amount approximately corresponding to the iron split off the bottom plug. It was therefore natural to try and protect the compressed material by placing a disk of more plastic metal in the bottom of the bomb. Table 7 presents the results of a spectral analysis of $NaNO_3$ for iron after dynamic compression in a steel bomb; the accuracy of the analyses was 5–10 rel. % [38]. The analytical data show that dense packing of the material in the bomb in the presence of a copper insert at the bottom protects the compressed material from contamination with iron to within thousandths of a percent.

The above results are not final; we require both additional statistical data and an extension of the range of test materials. However, it is already possible to get an idea of the thermodynamic parameters by this method and to discover ways of preserving the purity of the compressed materials.

2. The physicochemical possibilities of dynamic compression are best examined from the standpoint of the mode of action of a shock wave on matter.

If the bomb is filled with a loose powder, the principal effect of the shock wave will be to compress it to the density of the material itself. This is the basis for the use of dynamic compression in powder metallurgy, but now there is a technically important trend in the direction of obtaining pressed crystals of a nonmetallic nature.

After the shock wave has compressed the sample to the crystalline state, it begins to propagate through a dense medium. In Alder's graphic expression, the shock front acts like a mill refining the material and creating a dense packing which is stable only under given conditions. In this case there is no need to destroy all the interatomic bonds, it being sufficient merely to raise the atoms to a higher vibration level, so that they can overcome the potential barrier of the previous structure. As dynamic experiments have shown, the density of matter in a shock front may exceed the normal density by a factor of 1.5–3.5.

Upon unloading the material may either return to the initial state or go over into another crystalline form. The latter possibility is discussed below, but for the time being we will consider a substance that returns to the initial state. Since at the instant of compression the material is a superdense continuum, it is natural that after sufficiently smooth unloading it should return to the monocrystalline state and therefore should not contain defects, microcracks, pores, and similar imperfections. This process of crystallization is also assisted by the heat released as a result of compression of the solid. However, in the case of chemically unstable substances, which also have a low heat capacity, the heat of shock compression may play a leading part and decompose the material. In the intermediate case decomposition may be so slight that it is more correct to speak of the formation of defects in the material without an appreciable change in composition.

Thus, depending on the stability of the chemical bonds the compressed material either approaches a defectless crystal or the number of defects and dislocations increases. For compounds of the type $MeEO_n$, which can decompose into MeO_x and EO_{n-x}, this boundary has been found; it is equal to $\Delta H = 50$ kcal/mole. Table 8 presents a list of such substances, the change in the number of defects being characterized by the values of the X-ray and initial densities of the compressed material, together with the ratio of the intensitites of the IR spectra [39].

We have observed the refinement of polycrystalline materials in relation to BN, Nd_2O_3, SiO_2 and BeO. After explosive compression beryllium oxide, which X-ray analysis showed to be amorphous, is converted to a crystalline powder with grain size of hundredths of a millimeter, a sharp roentgenogram, and optical anisotropy. Thus, in a time of the order of 10^{-6} sec the individual grain grew from a size of about 10^{-7} cm to 10^{-3} cm, i. e., crystallization proceeds at a velocity of about 10 m/sec. In the case of boron nitride and neodymium oxide the crystal grains reached dimensions of about 10^{-2} cm, i. e., the crystals grew at a rate of about 100 m/sec.

According to Alder [16], the intensified motion of the atoms in the shock front sharply reduces the nucleation time, which is frequently the limiting stage of crystallization at static pressures.

The problem of obtaining defectless crystals is a central problem of solid-state physics and related branches such as semiconductor and laser physics, and much remains to be done before it is solved, it is necessary to be able to control unloading (for example, it has been noted that the best results are obtained at maximum loading densities and maximum charges) and to orient the crystal grains and blocks during shock compression or unloading (or before the experiment). However, the results so far obtained may find application in chemical engineering for converting amorphous, finely dispersed substances that penetrate filters into granular materials more convenient for handling, packing, and transporting.

As far as defects are concerned, a detailed study has only just begun, and much remains unclear. In our laboratories attention has been concentrated on the formation of defects in nitrates of the alkali metals, which are oxidizers in many important processes. Shock compression of the nitrates causes a change in external appearance; a new reddish phase is formed along the axis and near the bottom of the bomb (Fig. 2). This region in the cylinder represents the zone of maximum pressures, this is where the cylindrical wave and the wave reflected from the bottom plug converge.

After being dissolved in water samples of shock-compressed nitrates display an alkaline reaction, not observed in the starting materials, although the chemical composition of the compressed nitrates is unchanged. Table 9 shows the topography of alkalinity (%) as a function of the bomb loading density for a constant charge of 130 g [40, 39]. It follows from the table that a topography develops only at low loading densities, the value of the alkalinity increasing from top to bottom. Shock compression of the same nitrates in bombs made of copper led to the same values of the alkalinity, i. e., the latter is a result of chemical conversion of the compressed material and not of impurities from the bomb walls.

In the case of $NaNO_3$ the alkalinity decreases with annealing of the sample, the more strongly the higher the annealing temperature. A study of the kinetics of this process has made it possible to determine its activation energy, 3.6 kcal/mole.

The compressed $NaNO_3$ has a density less than that of the starting sample, 2.19 as against 2.27 g/cm^3, but after annealing the density returns to the initial value. This is characteristic of the behavior of defects in solids.

As for the nature of the defects formed in nitrates of the alkali metals, in our opinion they are F centers resulting from charge transfer from anion to cation:

$$Na^+NO_3^- \rightleftarrows Na^0 + NO_3^0$$

with subsequent decomposition of NO_3 to NO_2, O, and their combination products. In water NaOH is formed as a result of the reaction

$$Na + H_2O \rightarrow NaOH + 1/2H_2.$$

The appearance of metallic sodium should increase the electrical conductivity of the sample and similarly its dielectric constant. This was confirmed by measurements of ε, as may be seen from Table 10 [39].

In order to detect the NO_2 group the samples were tested with Griess reagents, which revealed the presence of a small amount of nitrite, and, in addition, were investigated spectroscopically.

The UV spectra distinctly display two maxima: at 270–300 and at 355 nm for $NaNO_3$, 297 and 360 nm for KNO_3, etc. The longwave maxima are characteristic of NO_2 groups, according to published data which we have checked, but the reason for the shortwave maximum still remains unclear.

Registration of IR absorption spectra also revealed the presence of a spike corresponding to the NO_2 group, together with another maximum of unknown origin.

Since the defects in nitrates are annealed at temperatures of 150°–200° C, while 1.5–2 min after the explosion the standard bomb has a temperature of the same order [41], we made an attempt to accelerate cooling of the bomb after the explosion. To this end, we designed a "cold" bomb (Fig. 3), which was screwed to a heavy steel plate. After the explosion the residual heat is transferred to the whole plate, and therefore the bomb remains practically cold [42].

Registration of the UV spectra of nitrate compressed in a cold bomb revealed attenuation of the maximum corresponding to the NO_2 group and the appearance of two other spikes, for example, at 280 and 335 nm in the case of $NaNO_3$. It was found that these maxima also appear in sodium nitrate after it is exposed to X-rays (10 000 roentgens at room temperature). Registration of the IR spectra of irradiated $NaNO_3$ showed that radiation caused the same maximum as appeared in $NaNO_3$ subjected to the action of an explosion (Fig. 4).

Thus, in the compressed nitrates of alkali metals radiation defects as well as defects of thermal origin have been observed. It is possible to explain this on the basis of ideas concerning the metallization of a material under impulsive pressure. If we assume that free electrons appear during compression and disappear during unloading, we can appreciate the possibility of bremsstrahlung inside the compressed material, which is capable of producing radiation defects. Of course, this hypothesis requires experimental verification.

Defect-enriched substances may have practical applications in heterogeneous catalysis, where solids with an active surface are required. However, the impulsive techniques of shock compression previously developed proved incapable of ensuring the uniform saturation of substances with defects in sufficiently large quantities. We therefore developed a new plane system of explosive compression, in which high pressure alternated with rapid expansion, which favors the formation of defects. This system was used to study TiO_2, one of the most promising electronic catalysts. The investigations were made in collaboration with the Institute of Catalysis.

As a result of plane compression white TiO_2 powder acquired a grayish blue color owing to the partial reduction of titanium, as a result of which the actual composition came to correspond to the formula $TiO_{1.999}$. A study of the catalytic properties of this "defective" material showed that its activity had increased by a factor of 100–1000. The investigation of this material continues.

Another interesting topic is the question of the effect of defects induced in a substance by shock compression on its luminescent properties. According to A. M. Prokhorov, when this effect is positive, it may be useful for increasing the efficiency of laser instruments; however, the technical solution of the problem will become possible only after the introduction of means of dynamically compressing single crystals that do not entail their mechanical destruction.

3. As already mentioned, as a result of unloading the system may return not to the initial state, but to some other, generally speaking, metastable state. The latter may persist at low, and sometimes even at room temperatures.

It follows from the data presented above that up to the commencement of our research 13 substances had been obtained and preserved in new modifications as a result of dynamic compression, and of these only four were obtained for the first time.

In the course of our experiments on compressed nitrates of alkali metals we have observed and to some extent studied new modifications of $NaNO_3$ and KNO_3 [40, 42]. In the first case this was an isotropic phase with a refractive index of 1.52, in the second case a rhombic phase with indices $n_g = 1.513$, $n_m = 1.485$, and $n_p = 1.333$. Thermographic study reveals that the new phase of $NaNO_3$ anneals with an endo-effect at 170–210° C, and the new modification of KNO_3 at 55° C. Therefore this modification was obtained in a cold bomb. At room temperature the new form of KNO_3 "lives" for several days, and that of $NaNO_3$ for months. The splitting of the refractive indices in the case of KNO_3 and the isotropy of $NaNO_3$ indicate the escape of NO_3^- ions from parallel planes and their more random distribution in space. This approach is consistent with the reduction in density for the two modifications: 2.190 for $NaNO_3$ (as against 2.257 g/cm^3 for the starting material) and 2.098 for KNO_3 (as against 2.106 g//cm^3). An X-ray study of these two modifications gave a positive result only in the case of KNO_3, two new lines, whereas in the case of $NaNO_3$ nothing new was detected. The reason for this is a fundamental one; the formation of defects impairs the quality of the roentgenograms and, moreover, the new phases are quite probably formed precisely as a result of the appearance of defects or even at these defects.

More successful from the X-ray standpoint was a study of a new modification of UF_4 obtained as a result of shock compression. Table 11 presents comparative data on the initial and new modifications, together with the properties of the compressed material after annealing.

The appearance of new phase was also observed following shock compression of CeF_3. The starting substance had refractive indices $n_m = 1.607$ and $n_g = 1.612$ and $\varepsilon = 15.2$, while for the new form $n = 1.57$ and $\varepsilon = 18.0$. However, the new phase is the same with respect to density and roentgenogram. Investigation of the new form of CeF_3 is continuing.

Phase transitions have also been detected in oxides of the rare earth metals (REM) after shock compression. Oxides of the REM crystallize in three forms: A, B, C, where A is hexagonal, B monoclinic, and C cubic, the A and B modifications being distinguished by their higher density as compared with the C form. The latter form is known for all 14 REM, the A form for La, Nd, Pr, and Ce, and the B form for Sm, Eu, Gd, Gd, Tb, and Dy.

The phase diagram for the oxides of Ho, Er, Tu, Yb, and Lu shows that the transition C→B must be realized above the melting point and therefore cannot take place at normal pressures [43]. However, at high pressures the melting point increases and there is reason to hope that the C → B transition can be realized. Experiments have justified this expectation—as a result of triple explosive compression it proved regularly possible to detect the appearance of the B phase, the degree of conversion decreasing with increase in the atomic number of the REM. The refractive indices, density, IR spectra, and roentgenograms were taken as the experimental criteria of formation of the B phase.

This was not the first time that these transitions had been obtained; in 1964 American scientists were able to obtain the same modifications on static presses [44], although they did not make a detailed study of the physical properties.

Interesting phases were obtained in syntheses of Cr + S, Cr + Se, and Cr + Te. The chromium chalcides obtained had much lower densities than the ordinary modifications, but the same roentgenograms, while on heating endo-effects were observed in the region 300°–500° C, after which all the substances returned to normal density. Thus, as a result of dynamic synthesis "incomplete" crystalline forms of CrX were formed. The investigation of these modifications is continuing.

Fundamental changes in optical properties associated with polymorphic transformations have been observed in new modifications of Nd_2O_3 [45] and BN [46]. Table 12 summarizes the characteristics of the starting and newly obtained modifications, which we have called E forms from the Latin word for explosion.

A study of the structure and other physicochemical properties of E forms may throw light on the details of their electronic structure. However, such investigations have been complicated by the extremely low yield of new phase. It has barely been possible to obtain 0.6–1.0 mg of modified substance from as many as 10–20 experiments.

These results of the activity of the Department of Superhigh Pressures are, of course, preliminary, but, in our opinion, they confirm the need for a continued effort in this field.

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