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Development of dynamic high-pressure techniques in Russia

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Abstract. In the mid-1950s, experimental studies of condensed matter at extremely high pressures (i.e. high energy densities) started to appear in the scientific literature, made possible by using strong shock waves to influence intensively the state of the substance being studied. Russian Federal Nuclear Centres in Sarov and Snezhinsk and their Academy of Sciences counterparts in Moscow, Chernogolovka, and Novosibirsk were instrumental in developing dynamic measurement techniques and forming this new line of investigation of extreme states of matter, based on application of shock waves in high-pressure physics.

1. Introduction

The progress of natural sciences today is characterized by dramatic advances in our understanding of the extreme states of matter. This is due in large part to the development of dynamic methods [1, 2], which involve the generation and measurement of very short-lived, high-density and high-temperature states occurring at megabar pressures behind strong shock waves.

Apart from providing equation-of-state data for many chemical elements and compounds over very wide pressure – temperature ranges, the use of the shock wave as a tool for physical research also allowed scientists to obtain high-temperature melting-point and boiling-point curves; to produce strongly nonideal plasmas; to discover previously unknown electronic reconstructions in metals; to investigate shock-induced phase transformations accompanying fast intense deformations, and to study a series of other phenomena that occur at extremely high values of physical parameters unattainable by other methods. Not only is such information necessary for perspective atomic power projects, both military and peaceful, but it also is useful for the analysis of many problems pertaining to geophysics, astrophysics and planetology, high-speed impacts, dynamic material synthesis, etc. Today, it is mainly dynamic studies which provide reference data for the static megabar pressure range [3, 4].

The development of dynamic methods is inseparable from the history of atomic weapons. Military-oriented shock wave research was initiated in the USA in the framework of the Manhattan project in 1945 [5, 6]. In the Soviet Union this program was launched independently in 1947 at the Russian Federal Nuclear Centre in Arzamas-16 (now the town of Sarov), also known as the All-Russian Scientific Research Institute of Experimental Physics (Russ. abbr. VNIIÈF). Headed by Academician Yu B Khariton from its very start to 1996, this was in a sense a 'hidden world' where a multidisciplinary team of physicists, mathematicians, designers and experimenters was given most favourable working conditions and where fundamental science and defence mutually benefited each other.

Experimental work at VNIIÈF was carried out in close cooperation with Ya B Zel'dovich, A D Sakharov, D A Frank-Kamenetskiĭ, and E I Zababakhin, all prominent Soviet scientists and trailblazers, in fact, in an entirely new scientific discipline of the physics of high energy densities. The authors of the present article had the good fortune to test the inimitable creative atmosphere of a unique scientific school promoted by these scientists. It is safe to say that it was Ya B Zel'dovich who contributed most significantly to this field of knowledge. It seems Ya B Zel'dovich lived through a whole number of careers, each devoted to explosions of one kind or another, whose power progressively increased as his

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interest shifted from the detonations and explosions of chemical substances, through increasingly powerful chain reactions and nuclear explosions, and finally to the Big Bang, from which Universe emerged 15 billion years ago. Combustion and detonation were Zel'dovich's first and lifelong love, a passion to which he remained faithful until his last days. Ya B Zel'dovich's school for the study of the extreme states of substances was recognized internationally. When speaking at the 1969 International School of Physics of High Energy Density, E Teller, the creator of the American hydrogen bomb, along with Los Alamos physicists, also distinguished Ya B Zel'dovich and L V Al'tshuler who, in his words, 'seem to have contributed most in the discovery of this new research area' [8]. In 1991, one of the present authors (L V A) received the American Physical Society's award for 'a valuable contribution to the development of research on matter at shock-wave compression' [9].

2. Detonation of condensed explosives

The role of the explosion products of condensed explosive in atomic weapon prototypes is one of a 'working fluid', the same water vapor plays in a heat engine. It so happened that the top agenda problem Ya B Zel'dovich and VNIIÈF group heads V A Tsukerman, E K Zavoĭskiĭ, and L V Al'tshuler had to face in 1947 was to determine the detonation pressure of condensed explosives. The reason was that whereas the power of the atomic charges then under development was dependent on the pressure of explosion products in convergent detonation waves, the theoretical pressure values as predicted by different models were more than a factor one and a half apart. In the shortest time, reliable experimental data were collected, which enabled the results of the first Soviet atomic test of 1949 to be predicted.

The works which form milestones in the theory of detonation processes are those of Mikhel'son [10], Chapman [11], Jouguet [12], and Zel'dovich [13]. The main difference between the shock wave and the self-forming detonation wave is that the latter propagates at constant velocity. The first to analyze this effect was Professor V A Mikhel'son at the Moscow Agricultural Institute (the now K A Timiryazev Agricultural Academy). In a publication of 1893 [10] he wrote: 'As regards detonation, here we encounter an extraordinarily interesting case in which, owing to the specific chemical and thermal processes involved, the conditions for constant velocity propagation are indeed satisfied.' In the pressure – volume diagram of Fig. 1, the steady propagation velocity corresponds to a straight line which Zel'dovich [14] quite justifiably dubbed the Mikhel'son line. According to Chapman (1899), the velocities of the explosion waves are the smallest possible, and states behind their fronts are remarkable in that, due to the condition Jouguet established in 1904, the sound speed in detonation products exactly equals the velocity of steady detonation with respect to those products.

Zel'dovich [13], von Neumann [15], and Döring [16] independently carried out analyses of and provided justification for Jouguet's state selection mechanism in 1940, 1942, and 1943, respectively. According to their collective ZND concept, the key structural elements of the detonation transformation front are the shock compression front of the original explosive; the stationary region of chemical decomposition, and self-similarly expanding explosion products adjacent to the chemical zone. The calculated detonation wave amplitudes at the boundaries of the chemical zones (i.e.

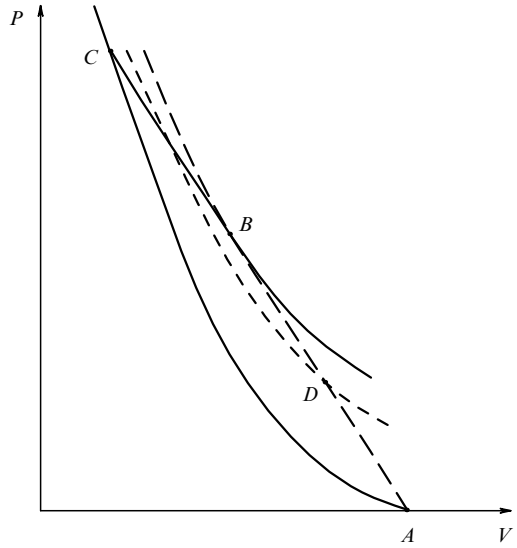

Figure 1. $P-V$ diagram of steady detonation: $A-C$, shock adiabat; B, Jouguet point; $B-C$, reaction zone, D — undercompressed detonation state.

predicted detonation pressures) depend on the assumed form of the equations of state (EOS) for compressed and heated explosion products.

In the van der Waals covolume EOSs most commonly used in the mid-1940s, the 'occupied volume' of the detonation products played the role of the covolume (generally pressure-dependent). According to another concept (1945) of Landau and Stanyukovich [17], rather than using a gas EOS, a more valid approach is to compare the decomposition products with a liquid which expands adiabatically from the Jouguet state and in which the pressure P and volume V are related by an expression of the type $PV^n = \text{const}$. According to the covolume approach of German authors [18], the detonation pressure of trinitrotoluene was estimated to be 12 GPa as compared with 19 GPa given by Landau and Stanyukovich. Zel'dovich and Kompaneets, who basically followed the approach of Ref. [17], wrote back in 1955: 'The results obtained with the Landau – Stanyukovich equations of state appear as predictions yet to be verified' [19].

In the United States, experimental work on this subject was initiated in 1945, although it was only in the mid-1950s that results were published [20, 21]. As mentioned earlier, in 1948 VNIIÈF experimenters independently developed a number of techniques for measuring detonation pressures. Those included [2]:

— pulsed X-ray photography of X-ray-opaque markers behind the detonation wave front (Tsukerman);

— the spall technique, which measures the initial velocities of plates of various thicknesses attached to the charge (Al'tshuler, Krupnikov);

— the magnetoelectric measurement of the velocity of explosion products behind the detonation wave front, based on the velocity with which a conductor inserted into the charge moves in a uniform magnetic field (Zavoĭskiĭ).

All three methods went through many ups and downs in their early development [22] and showed the Landau – Stanyukovich approach to be correct. Extensive efforts at improving, developing, and extending these techniques have subsequently been made at VNIIÈF and Russia's other research centres. For example, Zubarev's pulsed X-ray

technique for measuring the velocity of explosion products [23] enabled the asymptotic detonation parameters of heterogeneous explosives to be estimated. Special mention should be made of the Institute of Chemical Physics of the Russian Academy of Science (Russ. abbr. IKhF), where Nobel laureate Academician N N Semenov, friend and colleague of Academician Yu B Khariton, initiated the study of combustion and detonation processes and where Ya B Zel'dovich began his illustrious career.

As a natural extension of the spall method, a variety of techniques for the precision measurement of shock wave attenuation in anvils adjacent to the explosive were developed. Of these, the most sensitive technique is that due to Voskoboĭnikov and his colleagues at IKhF [24], in which the brightness of radiation from the shock front is measured in a liquid tracer adjacent to the charge and previously graduated for shock compression. Liquid tracers have been used in studying a number of explosives [25–27], and through their use as 'window materials', data on the detonation temperature of condensed explosives have been collected [28, 29].

A very effective time-tested technique for the study of the detonation regimes of condensed explosives is that of A Levin, which involves the laser measurement of wave velocities (the 'LMWV method') in layered transparent anvils adjacent to the charge [30, 31]. In Fig. 2a, results on detonation wave profiles in trinitrotoluene are represented by curves for wave velocity attenuation in plexiglass anvils for various charge lengths. Consistent with classical ZND theory, experiments indicated a steady zone of explosive chemical decomposition and self-similar rarefaction waves adjacent to it. For desensitized explosives, the existence of detonation wave profiles was first demonstrated in the steady undercompressed detonation regime predicted by Zel'dovich (point D in Fig. 1) [32]. Measurements on a desensitized PETN (Fig. 2b) show a steady zone of successive decomposition of an explosive and a desensitizer and self-similarly extending plateaus. An LMWV study also revealed an unusual detonation regime in high-density (so-called agatized) hexogen and octogen charges [33] (Fig. 2b). In this regime, explosive in the shock front decomposes completely or partially with no pressure increase occurring in the chemical zone.

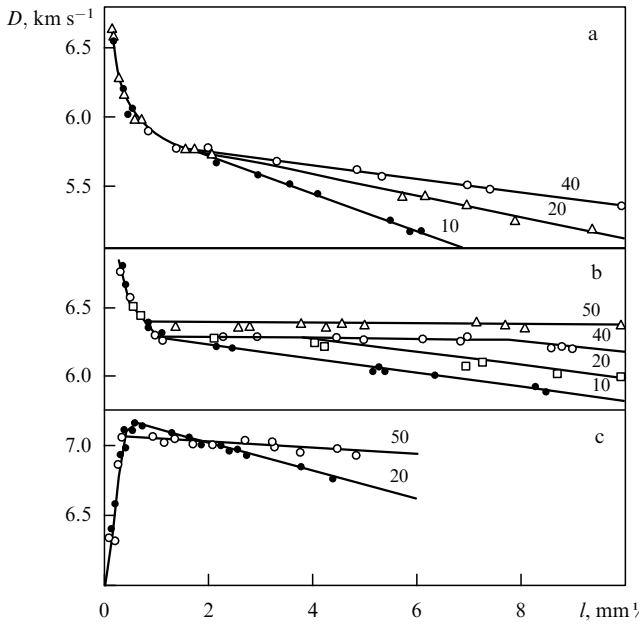

Figure 2. Variation of shock wave velocity in plexiglass with the distance from the (a) trinitrotoluene, (b) desensitized PETN, and (c) agatized hexogen charge. Numbers alongside the curves show the charge length in mm.

In an innovative method proposed in Ref. [34], changes in the contact resistance in highly pressurized metallic foils are used to determine shock wave attenuation curves for metals.

A magnetoelectric method capable of directly measuring the velocities and pressures of explosion products was used by Zubarev in the mid-1950s [35] and re-introduced at IKhF in the mid-1960s [36–38]. While inferior to LMWV in terms of resolving power, the method permitted an extended measurement time and made it possible to extrapolate data to effective pressure values. The technique was widely used to determine the parameters of many explosives and compositions with desensitizing and inert additions. Since 1970, the technique has also been used by American workers [39].

The use of manganin sensors offers yet another possibility for measuring pressure profiles in explosion products. Kanel' [40, 41], the first to apply the technique to detonation studies in the USSR, investigated, in particular, shock wave propagation and detonation wave formation in trinitrotoluene and other explosives. These results, combined with the laser interferometry data on detonation wave reaction zone [42], provided insight into the kinetics of energy release in shock and detonation waves [42, 43].

Analysis of extensive work performed in this country and the USA shows that explosive detonation parameters are now known to within 2–3% [31]. Table 1 summarizes the initial densities ρ_0, shock velocities D, experimental pressures P [31] and temperatures T [29] for the steady detonation of the most widely used explosives. For most blasting explosives, the index of isentrope accounting for the thermodynamics of explosion products in the Landau–Stanyukovich equation is 3, to a good accuracy.

Table 1. Explosive parameters

Explosive	ρ_0, g cm^{-3}	D, m s^{-1}	P, GPa	T, K
Trinitrotoluene	1.6	6895	18.4	3140
Hexogen	1.71	8400	30.9	3740
PETN	1.66	7950	27.0	—
Octogen	1.80	8735	36.1	3700
Trinitrotoluene-hexogen 50/50 alloy	1.67	7650	25.0	3460

In the early 1960s, on Zel'dovich's initiative, experimental work was launched at VNIIÈF to elucidate the nature of the high pressure observed in explosion products: to what extent it is determined by the thermal motion of molecules and to what, by their elastic deformation. For this, the additive EOSs of explosion products were constructed from EOSs of basic decomposition components of explosives [44, 45]. Specifically, the shock adiabats of carbonic acid and nitrogen were measured and used together with already known Hugoniots for water and graphite. The result was that 30–55% of the pressure is of a thermal nature. It was a real revelation for theoretical physicists when Brish, Tarasov and Tsukerman [46] observed the large electrical conductivity of explosion products in the layer adjacent to the detonation wave front.

3. Shock adiabats of metals

In 1947, VNIIÈF experimenters were confronted with the massive challenge of investigating the EOSs of fissionable materials and determining their shock compressibility at megabar pressures. At that time, uncertainties in EOSs of fissionable materials and in detonation pressure values prevented power characterization of the first nuclear weapon test scheduled for 1949, neither did they allow the effectiveness of other atomic projects to be gauged. In the shortest possible time, methods for determining the shock-wave characteristics of compressed materials and the necessary facilities involving the use of explosive power were developed.

The first to develop dynamic methods for studying compressibility were Goranson et al. [5], Los Alamos researchers Walsh and Christian [47] and Mallory [48] in the USA and independently VNIIÈF researchers in the USSR [49, 50]. All of the American and some of the early Soviet studies employed spall techniques (see Ref. [49]), which measure the velocity of the specimen free surface (a broken off piece) W_{sp} after it reflects the shock wave. This velocity is the sum of the particle velocity behind the shock front U and the velocity due to expansion. For shock waves of relatively low intensity, the former is, to a good approximation, $U \approx W_{sp}/2$. In the megabar pressure range the spall method is invalid.

Instead, in 1948 Al'tshuler proposed the 'arrest method', later to be described in Ref. [49], in which the measured parameters are the shock velocity in the specimen D and the velocity W of the shock-producing impactor. In contrast to the approximate spall technique, Al'tshuler's method has no pressure restrictions [49]. For a specimen and impactor made of the same material, $U = W/2$. Otherwise this relation does not hold. To overcome this, an impactor of a reference material with known dynamic adiabats is used. Iron and aluminium generally fulfilled the role of a reference material at VNIIÈF.The knowledge of the shock adiabats of reference materials made it possible to determine the dynamic compressibility by means of the reflection method developed by the authors of Ref. [50] in cooperation with G M Gandel'man.

The spall technique was used in Russia only for pressures of up to 50 GPa. Experimental data were obtained by using tailormade explosive charges which had a flat detonation front; the plate with specimens arranged on it was in contact with the charge (Fig. 3a). To extend the shock pressure range to 200 GPa for medium-atomic-number metals and to perform arrest measurements, the so-called flat speed-up impact systems were employed, which use explosion products to propel the plate-impactor [51, 52]. Figure 3b illustrates the flat-shock measuring device now in use.

In Russia, laboratory pressures of up to 1 TPa — much higher than in the USA — were achieved for many metals in the early history of the work but, until recently, no information has been available on the specific shock wave generators used. As recently as 1988, Livermore researchers wrote [55]: 'The absolute Cu and Pb data near 1 TPa of Al'tshuler, Bakanova, and Trunin [53] and Kormer et al. [54] were obtained by an undescribed shock generation system and until now never reproduced.'

Since its introduction in 1948 by Al'tshuler, Zababakhin, Zel'dovich, and Krupnikov [56], a hemispherical charge initiated simultaneously over its outer surface (Fig. 4a) has been an ideal tool for shock compressibility work at VNIIÈF. In this scheme, a thin-walled metallic shell inserted into the

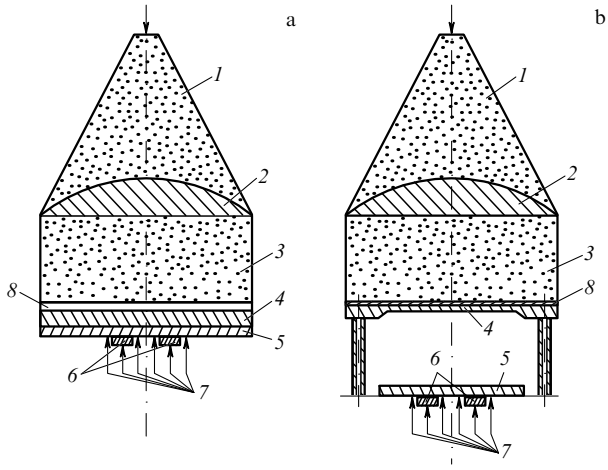

Figure 3. (a) Contact explosion measuring device, and (b) explosion measuring device with a steel impactor: *1* — lens explosive charge; *2* — plane wave lens; *3* — master charge; *4* — gasket (a) and impactor (b); *5* — shield of reference metal; *6* — specimen under study; *7* — electric contact sensors; *8* — air gap (a) and plexiglass gasket (b).

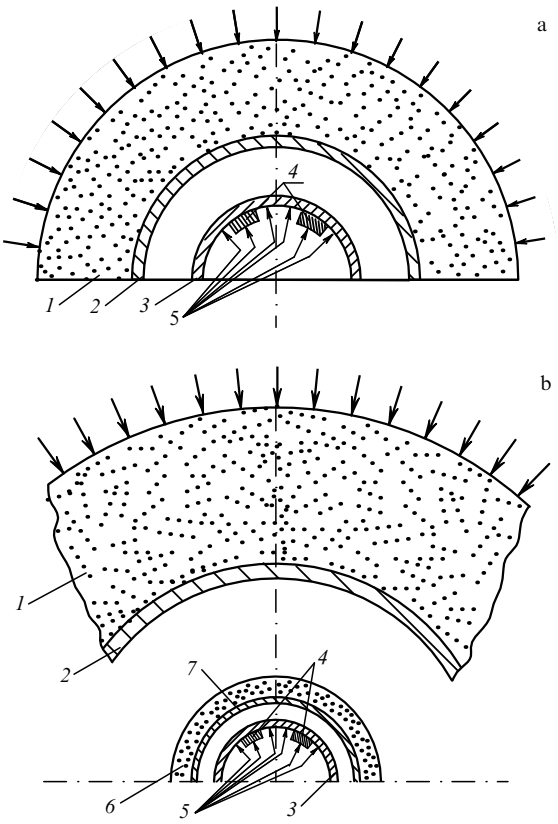

Figure 4. (a) Hemispherical explosion device, and (b) two-cascade hemispherical explosion device: *1* — explosive charge; *2* — shell; *3* — shield; *4* — specimens under study; *5* — electric contact sensors; *6* — second-cascade explosive charge; *7* — second-cascade shell.

explosive charge is propelled to the centre of the charge by the explosion products of a convergent detonation wave, thus making the shell strike the hemispherical specimen.

The earliest results, on Fe and eight other metals, were published in 1958 and covered pressures up to 500 GPa [49, 50], which is an order of magnitude higher than that reached

in American work at the time [5, 45, 47, 57]. In the United States, the 200 GPa level was reached in 1960 [52], and a pressure of 430 GPa, in the early 1980s, when two-cascade light-gas guns were introduced [55].

Subsequently, the data of Refs [49, 50] were corrected and the pressure range was extended by a factor of 2 to reach 1 TPa. These achievements were made with hemispherical measuring devices by using more powerful explosives, substantially reducing the shell heating by the overcompressed detonation wave, reducing the shell thickness, and taking smaller specimen location radii [51, 53, 58, 59]. In interpreting the results, corrections for shock attenuation in the specimens, which are quite significant for Pb, were improved.

On such devices, apart from Fe, Hugoniot adiabats for Ni, Cu, Zn, Cd, Sn, and Pb at pressures of up to 900 GPa were measured [53]. Figure 5 shows the shock adiabats of these seven metals [52, 53], and Fig. 6 compares Russian and American data on Al and Cu obtained with explosive measuring devices and two-stage light-gas guns [51, 52, 60, 61]. The close similarity of the results is indicative of the high precision of the dynamic methods involving pneumatic and explosive measuring devices. In the work abroad, the application of the hemispherical measuring devices is mainly limited to compressibility studies of U and Fe [62].

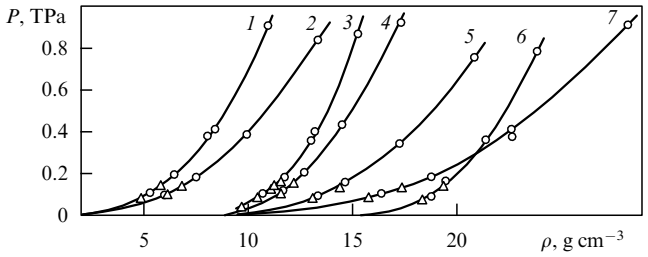

Figure 5. Shock adiabats for seven metals: *1* — Cu ($\rho - 7$ g cm^{-3}); *2* — Cd ($\rho - 7$ g cm^{-3}); *3* — Fe; *4* — Ni; *5* — Sn ($\rho + 2$ g cm^{-3}); *6* — Zn ($\rho + 8$ g cm^{-3}); *7* — Pb ($\rho - 2$ g cm^{-3}); △ — [52]; ○ — [53].

In terapascal studies at VNIIÈF, so-called 'cascade' measuring systems have become widely used. In 1948, Academician Zababakhin [63] advanced a scheme of one-dimensional cascade plate acceleration, in which a plate driven to a high velocity by the explosion products of the first charge impacts the second charge creating in this latter an overcompressed detonation wave which, in turn, drives another, thinner plate.

Pressures close to 1 TPa were first reached by Krupnikov et al. [64] using the hemispherical two-stage scheme of Al'tshuler, Kormer, Krupnikov, and Ledenev [65]. As the first stage, the hemispherical one-stage charge described above (Fig. 4a) was used. Within this, a second cascade (Fig. 4b), a hemispherical explosive layer with a 2-mm steel shell adjacent to its inner side, was mounted. With this measuring device, in the late 1950s pressures of up to 1.3 TPa in Fe [66] and 1.8 TPa in U [67] were achieved (Fig. 7), corresponding to a Fe-shell impactor velocity of 15.5 km s^{-1}.

In later work, Ternov and Fortov [68 – 73] used a 'gradient acceleration' cascade technique to propel thin Mo impactors to velocities of 12 – 14 km s^{-1}. The maximum pressures ($\sim$ 1.8 TPa in Cu) were generated by combining the geometrical and gradient cumulation effects, with a Mach shock wave produced by convergent conical detonation waves [73].

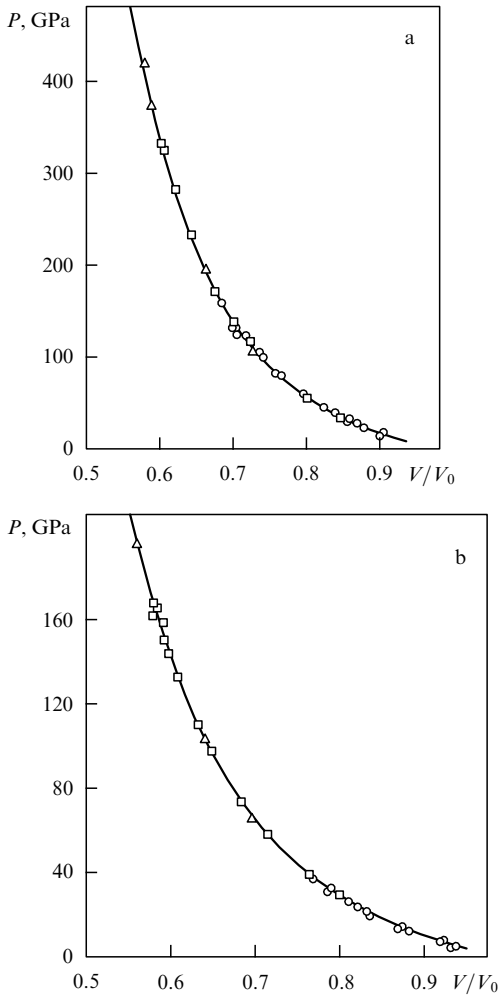

Figure 6. Shock adiabats for (a) Cu and (b) Al. Explosion device data from: △ — [51]; ○ — [52, 60]. Light-gas-gun data: □ — [61]. V_0 is the initial volume.

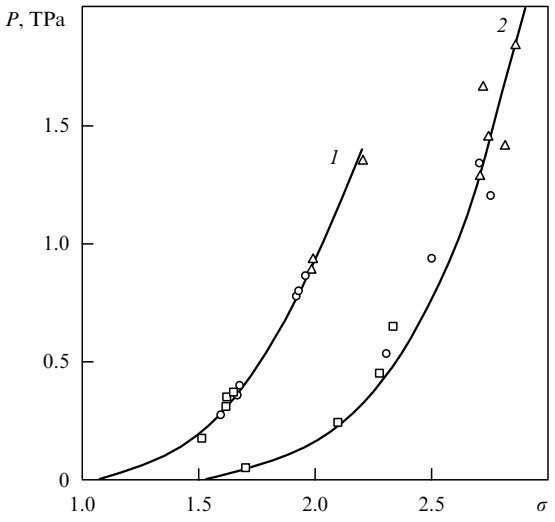

Figure 7. Shock adiabats: *1* — Fe; *2* — U ($\sigma + 0.5$). ○ — data from one-cascade measurements; △ — data from two-cascade measurements; □ — after Ref. [62]. Relative density $\sigma = \rho/\rho_0$.

Originally intended for the study of nuclear explosive materials, shock-wave methods have been widely used in investigating a large number of elements, chemical compounds, and minerals. Shock compressibility values have now been obtained in various pressure ranges for more than 60, i.e. the majority of, naturally occurring metals. Particular attention has been given to the revision of the shock adiabats of the reference metals Al and Fe.

Russian and foreign dynamic data on metals up to 1977 are surveyed in Ref. [66]. The results are classified according to the form of $D(U)$ dependences, which involve five types of adiabats. The first three are smooth linear and parabolic adiabats. The fourth and fifth types will be discussed in the next section.

Figure 8 illustrates the change in atomic volume as dynamic pressure levels become progressively higher. As pressure increases, it is seen that periodic volume changes decrease in amplitude, and at 1 TPa the periodicity reflecting the atomic shell structure is only weakly seen. The slopes of the shock adiabat curves $D(U)$ (see above) show a similar level-off behaviour.

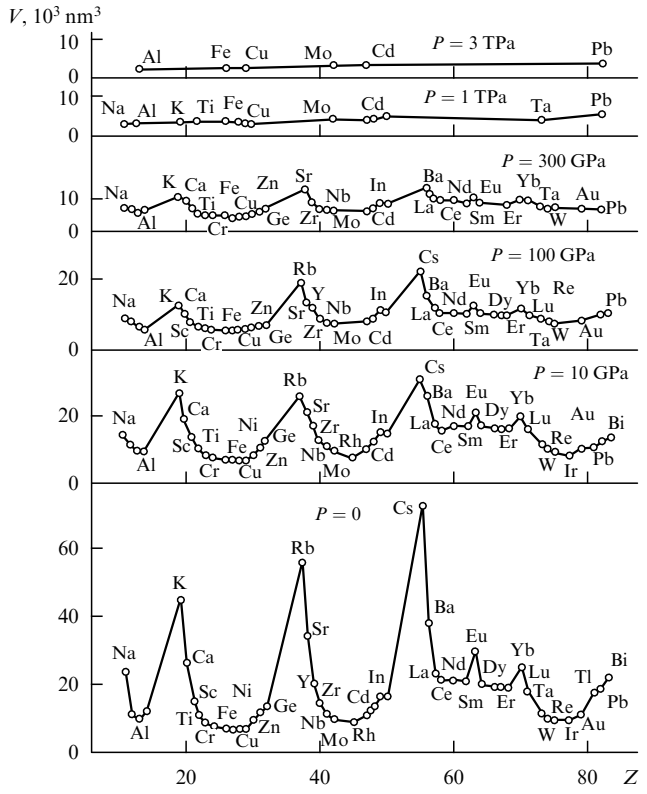

Figure 8. Atomic volume curves $V(Z)$ at normal conditions ($P = 0$) and various shock pressure levels.

4. Electron transitions and shock polymorphism

In the 1960s, the properties of shocked rare-earth and alkaline-earth metals came under the scrutiny of the shock wave community. When in a normal state, a rare-earth metal has a close-packed crystal structure and is trivalent due to its $4f^h5d^16s^2$ electron configuration with fully (in La) or partially unfilled f-shells containing a different number of f-electrons. A common belief was that megabar pressure would force s-electrons into the unfilled f-shell, giving rise to a superhigh-density metal as a result of a structural transformation. These, however, were overly naive expectations, as even early studies [74] showed. The $P-\sigma$ data in Fig. 9a [75] indicate adiabat kinks occurring at certain critical compression parameters, implying that compressibility of metals decreases nonmonotonically and corresponds to second-order phase transitions involving the reconstruction of electronic spectra. The pioneering data of Refs [74–77] were corrected and revised in the works of foreign researchers [78, 79] in 1973–1975. The $D-U$ diagram in Fig. 10 compares data for Nd and Dy.

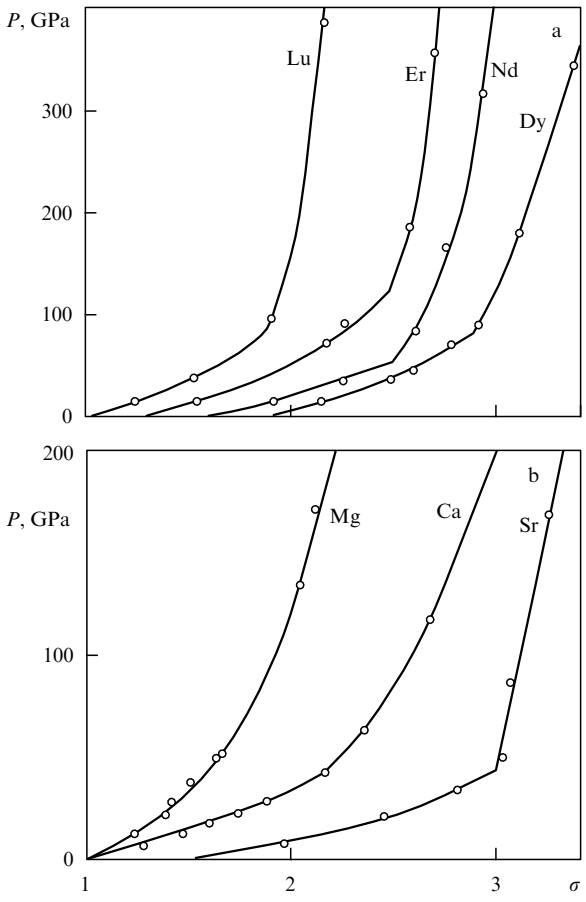

Figure 9. Shock adiabats of (a) rare-earth metals La, Er ($\sigma + 0.3$), Nd ($\sigma + 0.6$), Dy ($\sigma + 0.9$), and (b) alkaline-earth metals Mg, Ca, Sr ($\sigma + 0.5$).

The origin of adiabat kinks is currently controversial [80]. While the first publication on this matter [74] does not elaborate on the nature of this phenomenon, the explanation it suggests is generally correct: 'The factors determining the slanting portion of the adiabat are apparently the compression of the outer 6s-shells and the attendant processes of interband electron redistribution going on at one time. The kinks shown by adiabats then imply the completion of these processes and the formation of hardly compressible electron configurations.' Qualitatively, this is the same view taken in Ref. [81] for Cs and Rb. Refs [82, 83] present a quantum mechanical treatment of the effect of compression on the reconstruction of rare-earth electronic spectra. As a rare-earth metal is compressed, it is shown that its 6s-band moves above the Fermi level. For La, and also for Nd and rare-earth metals of close atomic number, all with less than half-filled f-

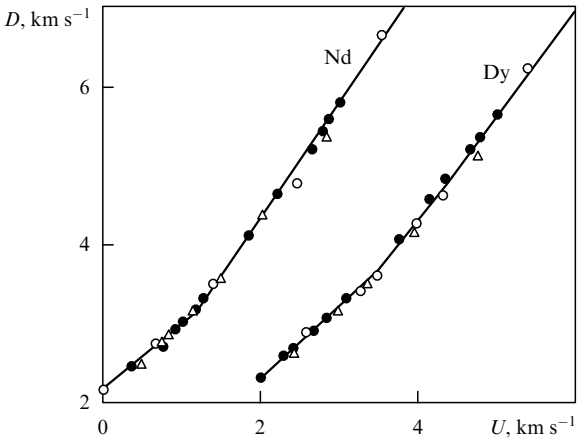

Figure 10. $D(U)$ diagrams for Nd and Dy ($U + 2$ km s^{-1}). Data from: ○ — [75]; △ — [78]; • — [79].

shells, the rearrangement of electrons has the effect that more of them occupy f-states. In the 'heavy' lanthanides with their f-shells nearly filled, increasing the pressure induces s–d transitions, which is also characteristic of the alkaline-earth metals. This process gives rise to adiabat kinks in alkaline-earth metals, first observed by Bakanova and Dudoladov [76] in 1967 (see Fig. 9b).

When subjected to a shock, there are a variety of phase transitions a solid may undergo; this is the so-called shock polymorphism phenomenon. Shock-induced polymorphic transitions have been found in many metals, semiconductors, ionic compounds, and in virtually all minerals and rocks known. A characteristic feature of polymorphic transitions is that they usually occur at the same pressure, whether observed under static or dynamic conditions. This is true of Fe, KCl, Si, Ge, and some other substances. One exception is quartz, in which the shock transition pressure corresponds to the elastic limit of shock compression and exceeds the static value. The reader is referred to review papers [2, 84, 85] for a discussion of original works.

The high rate of phase transitions in shock waves is indicative of their martensite nature due to the shear strain of a material. The formation of a high-pressure phase is preceded by the motion of an elastic precursor, and at the front of the wave that corresponds to a phase transformation the defects are produced which become the nuclei of crystallization under overcritical conditions. In Alder's [86] figurative manner of speaking, 'the shock front could be likened to a mill, which atomizes the low-density material ahead of it and then transfers the atoms to the high-density domain where atomic states are stable under these conditions'.

Martensite type structural changes were first discovered in data on the microstructure of shocked steel specimens. This work, whose description can be found in Ref. [87], was carried out in the 40s in the X-ray Laboratory at the USSR Academy of Sciences Engineering Science Institute and was headed by V A Tsukerman, the founder of pulsed X-ray technology. A correct interpretation of the results, in which dark zones correspond to the phase transition, and zone boundaries to a pressure of 13 GPa, became possible [2] after the discovery of $\alpha \rightarrow \varepsilon$ phase transition in Fe by Bancroft, Peterson, and Minshall [88].

Phase changes in shock waves received considerable attention at VNIIÈF, the list of approaches spanning shock compressibility techniques; electromagnetic- and manganin-based methods for measuring behind-the-shock parameters; determination of optical and electrical parameters; pulsed X-ray structural analysis, and the study of structural changes in load-surviving specimens. The materials covered, apart from a large number of elements, also include the halides of alkali metals, carbides and nitrides, oxides, rocks, and organic substances.

Ivanov, Novikov, and colleagues [89–91], in their study of phase transformations in Fe, measured shock wave profiles and found the phase transition front width to be 2×10^{-7} s. For the first time, 'smooth' spalls formed by colliding rarefaction shock waves were observed. An analysis of the experimental data obtained in Refs [90, 91] was given by Zel'dovich [1]. A rarefaction shock wave was detected directly using a manganin pressure sensors [92].

As an illustration, the results, due mainly to Pavlovskiĭ and coworkers, on phase transformations in the group IV elements C, Si, Ge and in KCl are presented below.

Figure 11a shows shock adiabats for Si and Ge [93]. These elements, when shocked, form high-pressure phases corresponding to a closer than original atomic packing presumably of metal type. The three-wave shock profile observed in Si [93] (see inset to Fig. 11a) involves an elastic precursor with a pressure amplitude of 4 GPa (which is much higher than in metals), a phase transformation at 13 GPa, and an applied shock pressure of 20 GPa.

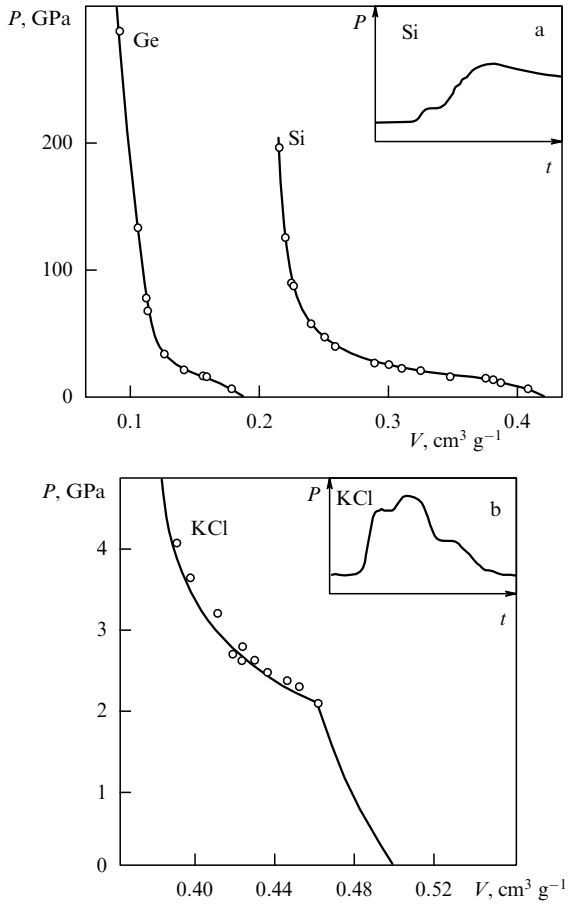

Figure 11. Shock adiabats for (a) Ge and Si [93], and (b) KCl [99]. Insets: shock wave profiles $P(t)$ in (a) Si [93], and (b) KCl [142].

In KCl, which has been the subject of extensive research over decades both in Russia and elsewhere [94 – 100], the transformation from the NaCl- to CsCl-type phase occurs at a relatively low pressure of only 2 GPa. Data on the shock-induced transition, obtained in particular with a manganin sensor [97], show that the pressure for the direct phase transition coincides with the equilibrium value [94], while that for the inverse is well below [97]. The experimental data are shown in Fig. 11b. The X-ray diffraction analysis shows the existence of intermediate transition stages in shock compressed KCl [100].

Shock wave experiments on group IV transition metals Ti and Zr showed a similar hysteresis loop, thus providing further evidence for the martensite nature of the phase transformations. In these metals, high-pressure phases were detected in shock pulse profiles [101, 102] and in load-surviving specimens [103, 104]. The shock structure in the region of $\alpha \rightarrow \omega$ transformations in Ti is also analyzed in Ref. [105].

Although a phase transformation with a change in crystal structure was observed in NaCl under static loading conditions at 29 GPa [106, 107], no definitive dynamic laboratory data exist on the phase transition in this material. At the same time, underground explosion measurements on rock salt [108] do confirm the occurrence of the transformation. In these, states corresponding to the virgin phase, phase mixture, dense phase, and a liquid state were consecutively observed, the transition pressure being approximately equal to its static value.

The shock compressibility of graphite up to 90 GPa was examined by Alder and Christian [109]. The assumption used in this work was that at 40 GPa graphite transforms to the diamond structure and at higher pressures, to a close packing of the metal type. A shock wave study on graphite and single-crystal diamond [110 – 112] confirmed the formation of a diamond-like phase stable throughout the pressure range spanned to 600 GPa and invalidated the assumption of denser metallic states.

Studies in Russia and the USA have provided a great deal of information on the shock compressibility of minerals and rocks. The early work of Hughes and McQueen [113] yielded the shock compressibility of gabbro and dunite up to 70 GPa [113]. The adiabats of minerals and rocks up to 100 – 400 GPa were studied systematically by Al'tshuler, Trunin, and co-workers [114 – 125]. At present, shock compression data for more than 120 rocks and minerals are available.

For quartz, the first shock wave measurements were made in 1962 by Wacerly [126] and independently by Dremin and coworkers [127]. Podurets, Trunin and their colleagues in Sarov and Krupnikov, Zhugin and others in Snezhinsk continued this work in their detailed studies of different quartz varieties for various initial states over a wide range of thermodynamic parameters [128 – 136]. However, the diverse and at times controversial results of these studies are beyond the scope of this work and indeed warrant a special analysis.

Shock experiments have shown that at certain critical pressures in the range below 10 – 50 GPa, almost all minerals and rocks undergo phase transformations yielding high-density forms of relatively low compressibility. While below these pressures shock adiabats show great diversity, post-transition curves become very much similar. Direct experiments on quartzite, dolomite, and other minerals reveal that new phases mainly form at the front of the shock wave [123].

In accord with Birch's [137] and Ringwood's [138] hypotheses, high-pressure phase transitions in minerals lead ultimately to their breaking into close-packed oxides of metals and silicon. This fact has been used to calculate the dynamic adiabats of minerals and rocks based on their composition. Al'tshuler and Sharipdzhanov [139] justified the use of the principle of additivity for obtaining adiabats based on their oxide isochemical composition above 50 GPa. An alternative approach of Trunin and Telegin [140] used the correlation-regression analysis of experimental $D - U$ data for rocks and minerals when obtaining the high-pressure phases of such adiabats on the basis of the oxide composition.

5. Sound speeds and the strength of shocked metals

The speed of sound behind the shock in the megabar pressure range was first measured in Ref. [141]. In this work two techniques were developed, in which the propagation of sound perturbations was examined by detecting the arrival of sound at the shock front. In one technique, known as the lateral surface unloading method, sound speed measurement involved shock wave propagation along a cylindrical specimen with a step-wise lateral surface profile. Expansion waves starting from the origin on the ledge overtake the front thus causing a pressure drop in the peripheral zone. The arrival velocity of the leading rarefaction wave is determined from the difference in shock wave arrival times at the specimen end surface.

The second approach, the so-called overtaking unloading technique proposed by the authors of Ref. [141] together with Academician E I Zababakhin, is to measure shock wave attenuation in the target as this latter is impacted by a thin plate. The sound speed was calculated from the shock pressure change at the unloaded portion of the wave path. The method provided bulk sound speeds in shocked Al, Fe, Cu, and Pb in the pressure range from 40 to 350 GPa.

Using the lateral surface unloading method, two sound wave propagation velocities, C_B and C_L, were discovered for the first time [141]. While the lower velocity C_B was that of the 'plastic' wave characterizing the bulk compressibility property, the higher, C_L, was the velocity of the elastic longitudinal wave inherent in one-dimensional compression. Measurements were made at ~ 40 GPa for Cu and Fe. Further studies of the propagation of elastic and plastic rarefaction waves relied on the more informative overtaking unloading method [142, 143] and provided more details on the flow behind the shock during the incipient interaction of the wave under study with the overtaking elastic rarefaction waves in the 30 – 80 GPa [142] and 110 – 180 GPa [143] pressure ranges.

In the 1980s, Brown, McQueen, Shaner and other American researchers [144 – 148] made a significant contribution to the method of overtaking unloading by using optical attenuation detection techniques in their shock wave studies on transparent liquid tracers. The variation of the elastic sound speed C_L with the shock pressure was examined for Al, Fe, Ta, and Mo. Using the calculated $C_B(P)$ dependences consistent with the Al and Fe data [141, 143], the melting point of a shocked material was estimated from a decrease in the $C_L - C_B$ difference (the decrease reflects the variation of the Poisson ratio and its approach to the liquid state value of 0.5).

Of particular interest are the data on Fe [144, 148], interpreted as indicating the $\varepsilon \rightarrow \gamma$ phase transition at

200 GPa and the melting of the γ-phase at 240 GPa. Referring to Fig. 12, the $C_L(P)$ and $C_B(P)$ dependences for Fe [141, 143, 144] and Cu [141, 143] demonstrate the above methods to be fully consistent. The decrease in the $C_L - C_B$ difference for Cu agrees well with the theoretical estimate for the melting point of a shocked material [149].

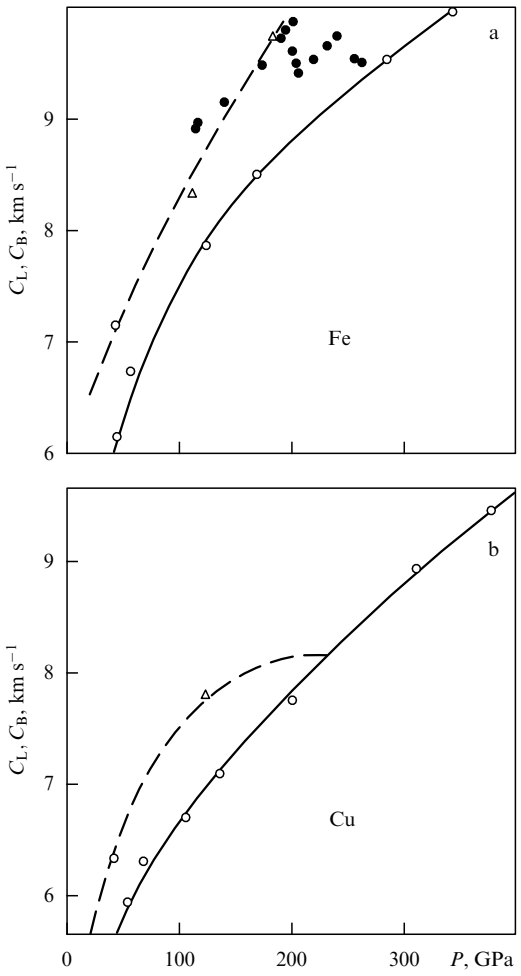

Figure 12. Pressure dependence of the longitudinal (dashed line) and bulk (solid line) velocities in (a) Fe and (b) Cu. The data are from: ○ — [141]; △ — [143]; • — [144].

Flows encountered in plane shock wave experiments are one-dimensional ones. The front of a relatively weak shock wave has a two-wave configuration consisting of an elastic precursor propagating with a longitudinal sound velocity C_{L0} plus a plastic wave whose velocity D depends on the applied pressure. The precursor amplitude is determined by the dynamic yield point of shock compression, whose measured value is currently known very accurately for many materials [43].

The amplitude of the elastic rarefaction wave, like the elastic precursor, determines the value of the dynamic strength under shock compression. By estimating this amplitude from the particle velocity of the shock wave at its trajectory it proved possible to evaluate metal strength characteristics such as the compressibility modulus, the coefficient of elasticity, the shear modulus, the dynamic strength, and the Poisson ratio behind the shock [142, 143].

Data on material deformation behind the shock wave were obtained by G Kanel' from pressure profile measurements using the manganin sensor technique [40]. In Ref. [150], measurements on rarefaction and reshocking waves were made for Al and Cu at 18 and 25 GPa, respectively. It was shown that the relaxation of shock-front shear stresses, which causes the material behind the shock to be isotropic, occurs at pressures far below the shock melting point. Taking into account the stress relaxation, the shear strength Y determined by the overtaking unloading method is [143]: for Fe, 5.4 GPa at $P = 185$ GPa, and for Cu, 3.2 GPa at $P = 122$ GPa — several times the initial shear strength in either case.

An alternative technique for determining shear stresses in a shocked material involves the manganin sensor measurement of the main stresses in two mutually perpendicular directions [150–155]. This, however, is hardly a practical method to implement because advanced perturbations travelling in longitudinal slots complicate the detection of lateral stresses in high-density materials like Cu or Pb [150, 154]. The method under discussion fails to relate the measured shear stresses to their critical values [155]. Critical shear stresses (with the separation into critical and relaxation components behind the shock) are determined by the Asay–Lipkin 'self-consistent' method [156]. Shear strengths have been obtained for Al, Be, and other metals [157, 158]. In Ref. [154], a dynamic strength comparison of self-consistent and main stresses measurements is made for the case of Al. There is evidence [150, 154, 157] to confirm the existence of the relaxation of shear stresses in the pressure range above 10 GPa.

Shear strength evaluation is one of the most topical and controversial problems in the calculation and theoretical analysis of elastoplastic deformation in shock waves [122]. The dissipative processes associated with the propagation of a shock wave under hydrostatic pressure is a manifestation of the viscosity property involved in Maxwell's relaxation theory of deformation.

For viscosity studies, Academician A D Sakharov, in 1957, suggested that the determination of the time evolution of plane shock front perturbations be followed by a comparison with theoretical predictions. The experimental work in this program was carried out by Oleĭnik, Mineev and coworkers at VNIIÈF [160–162], and the necessary data processing was performed by Zaĭdel' [163].

In this work, an explosive charge in contact with the specimen of material under study was used to generate a plane shock wave in the specimen. To produce a perturbation in the shock, parallel sine-profiled cavities were introduced into the bulk of the specimen, the distance between them determining the length of the wave. As the wave travelled across the specimen, changes in its shape were monitored. Perturbations of various wavelengths were created on geometrically similar specimens. The attenuation of the perturbation amplitude with distance was conditioned by viscosity manifestation, as also was the detected phase shift [163]. The most comprehensive measurements were made on Al at 31 GPa; the viscosity coefficient was found to be 2×10^4 P (2×10^3 Pa s). Close values were observed in Cu, Pb, and plexiglass [161]. For water, attenuation experiments [162] also showed a phase shift corresponding to a viscosity coefficient of $\sim 10^3$ Pa s.

In the studies of Refs [164, 165], the viscosity of shocked water and glycerine was estimated from the entrainment of a cylindrical body (wire) placed into the specimen. To measure the wire displacement velocity, a magnetoelectric method was

employed [2]. The viscosity was also determined by comparing the velocity with its theoretical value. Inexplicably, however, the viscosity values for water at 8 GPa proved to be substantially lower than in Ref. [162].

In Ref. [166] the viscosities of liquid inert materials and liquid explosives were determined by measuring impurity conductivity and dipole polarization relaxation. The materials studied were nitroglycerine, nitrobenzene, glycerine, and butyl alcohol, and the pressure range extended to 10 GPa.

With modern experimental techniques, the subnanosecond resolution of shock structure is possible. In the studies of Refs [43, 167], a strong-current pulsed proton accelerator KALIF provided with two differential laser interferometers was used to generate 'short' shock waves, which enabled the viscosity and spall strength of metals at deformation velocities up to 10^{-8} s to be measured. Interestingly, as the deformation velocity increased, the spall strength increased by about an order of magnitude, thus approaching the theoretical metal strength.

6. Multimegabar pressure range

P W Bridgman, the classic of a physics experiment, in his last review article wrote: "The very highest pressures will doubtless continue to be reached by some sort of shock wave technique. Perhaps some fortunate experimenters may ultimately be able to command the use of nuclear explosives in studying this field" [168]. It so happened that researchers at VNIIÈF were that fortunate late in the 60s. By working in the near zone of the underground nuclear explosion, it proved possible to increase dramatically the amplitude of shock waves and to resolve a number of fundamental problems in dynamic high-pressure physics. The significance of the results so achieved can hardly be exaggerated. In the very first experiments, the relative compressibilities of Fe, Pb, Cu, Cd [169 – 171], and U [67] were determined in the pressure range 4 – 5 TPa. Mo, Cu, Cd, and Pb were also studied at 1.5 TPa [170, 172]. Light substances such as Al, quartz, water, and some others, were investigated up to 2 TPa [171, 173]. Comparative compressibility data were obtained using various modifications of the reflection method with the shock adiabats of Pb and Al as standards [114, 169 – 171].

These measurements were disadvantageous, however, in that the desired material parameters were directly dependent on the position of the reference adiabat and that a change in the adiabat caused all the rest of the parameters to vary. Nevertheless, the 'relative approach' remained the only one to resort to whenever parameters were studied in pressure ranges unattainable in the laboratory or data relating reference wave parameters to those of the material under study were accumulated. It was assumed that a subsequent determination of the wave and particle velocities in the shield material would allow the results to be recalculated to the absolute pressure scale. Difficulties involved in such experiments prevented data collection for a long time, and it was not until the mid-70s that Trunin, Podurets and coworkers performed absolute measurements of the kinematic parameters of Fe using the arrest method in the near zone of an underground explosion [174, 175]. The experimental scheme chosen and optimized by the researchers satisfied the impactor acceleration requirements of the method. The heating of the impactor during its acceleration was substantially reduced, the integrity of the impactor was retained, and a good level of its in-flight symmetry maintained. The impactor approached the target at a constant velocity and it was twice the particle velocity in the target material at the moment of collision. The absolute compressibility of iron was measured at 4.1, 5.5, and 10.5 TPa. The results of these

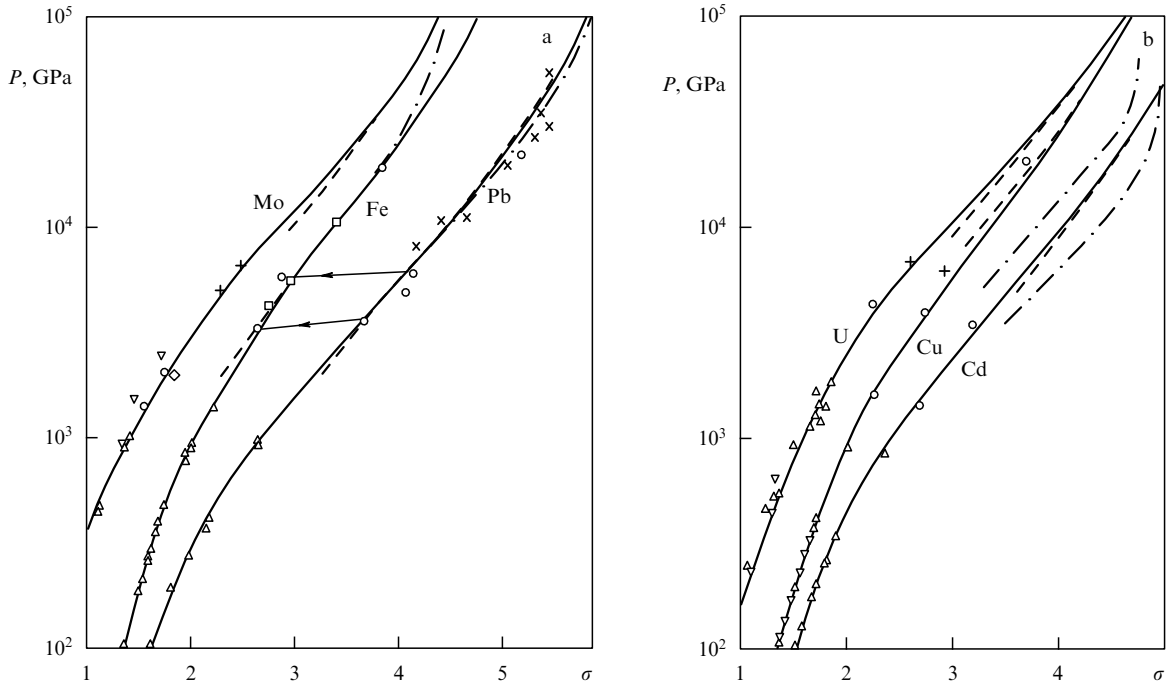

Figure 13. Laboratory and underground shock compressibility data on (a) Mo ($\sigma - 0.6$), Fe, and Pb, and (b) U ($\sigma - 0.5$), Cu, and Cd. △ represents laboratory data from [66]; ▽ — the same from [55]. Underground measurements: □ — absolute data from [88]; ◇ — the same from [95]; ○ – relative data from [66, 169, 174]; + — relative data from [182 – 185]; × — the same from [180]. Dashed lines are calculations for the TFPK model [182, 185], dash-and-dot lines are calculations for the SCF model [264].

measurements, published in 1992–1993 [174, 175], were analyzed together with the laboratory data and actually granted Fe the status of a reference metal [65]. A comparison of underground explosion data with the predictions of the quantum-statistical 'TFPK model' (Russ. abbr. for the Thomas–Fermi model corrected for quantum and exchange effects by Kirzhnits [176] and Kalitkin [177] and for internuclear interaction by Kopyshev [178]) yielded the lower applicability limit of this quasi-classical model.

Knowing the shock adiabat of Fe up to 10 TPa allowed, with necessary recalculations, to consider as absolute the measured results obtained for other metals with Fe as a shield. The main results of shock compressibility measurements in underground explosions are reviewed in Ref. [179]. Figure 13 presents the shock adiabats of Mo, Fe, Pb, U, Cu, and Cd after all necessary processing is done; the arrows mark the results for Fe (after Ref. [169]) obtained with the Pb adiabat as the standard.

In 1986, Avrorin, Simonenko et al. [180] used Fe as a standard in comparative measurements on Pb and Al. For Pb, a pressure range from 8 TPa to the record value of 50 TPa was examined. Trunin et al. [181] carried out comparative measurements for Pb and Cu at 20 TPa, and for Ti at 14 TPa. The results obtained were used to calculate shock compression parameters for these metals and to compare the experimental data with calculated TFPK adiabats in the pressure range close to 20 TPa. Once more, a comparison of theoretical predictions with experimental data was made. Using the Fe standard made it possible, with the aid of already available loading devices [58, 59], to extend the laboratory pressure range to 2.4 TPa in Mo and Ta, and to 1 TPa in Al and Ti.

The underground explosion experiments by Ragan and colleagues at Los Alamos [182, 183] detected terapascal states in many elements and in some chemical compounds by taking Mo as a standard. These data and those of Refs [184, 185] generally show a fairly satisfactory US–Russia agreement (see Fig. 13). However, Ragan's 2-TPa point for Mo disagreed with the parameters of the adiabat then in use in Russia. Accordingly, additional laboratory and underground experiments were made to revise the Mo adiabat [58, 172], which showed the Russian results to be correct after all. The discrepancy between our Cu and Pb data and those of the Livermore researchers [186] was due to the Al standard used by the latter: a large compressibility difference between Al and materials under study necessitated corrections of a rather unclear nature to be introduced.

There is a significant scatter in the shock compression data for Al above 200 GPa, partly obtained by Scidmore and Morris [62] and partly on laboratory loading devices in Russia (where they were published after 1960 [66, 73, 187, 188]). An analysis of these data is given in Ref. [173], where underground explosion results may also be found and the data of Ref. [180] are reprocessed. Data obtained with larger measurement bases in the near zone of underground explosions are more trustworthy. Examples of such work are measurements by the reflection technique [173, 180] and, most important, by the γ-benchmark method developed by Simonenko, Volkov and others at the All-Russian Research Institute of Engineering Physics (Russ. abbr. VNIITF) in Snezhinsk [189, 190]. The latter method involves the detection of γ-emission from special markers — tablets of a radioactive material, which are placed within the Al block under study and whose displacement determines the wave and particle velocities of the shock wave. The velocity of the benchmark motion was considered to be the same as the particle velocity in Al. The method was verified in laboratory work with the hemispheric measuring device at the highest shock pressures achievable [59], and the results proved to be identical to those from the γ-benchmark method. The sum total of Al data yielded a Hugoniot which interpolates satisfactorily to the applicability region of the TFPK model.

Throughout the pressure range studied, the laboratory and testing ground results on six metals are amenable to a description by $D-U$ relations with parameters whose values are listed in Table 2. The lowest-pressure portions of the curves represent the laboratory work, the upper, the asymptotic quantum-statistical results from the TFPK model [177, 178]. At the matching points, equating the functions and their derivatives up to the second order secures the monotonicity of the curves. The monotone behaviour of the shock adiabats is explained by band broadening due to the shock-induced overlap of wave functions. Of the elements listed in the table, each can serve equally well as a standard for dynamic measurements. The reader is referred to review papers [179, 191] for a detailed discussion of some aspects of multimegabar physics.

Table 2. Shock adiabat parameters of metals for the relationship $D = a_0 + a_1 U + a_2 U^2$

Metal	a_0, km s^{-1}	a_1	a_2, s km^{-1}	Range of applicability
Fe	3.664	1.79	-0.0342	$1.4 < U < 8$
	5.869	1.239	0.00017	$8 < U < 22$
	6.982	1.190	0.00011	$U > 22$
Cu	3.899	1.534	-0.0129	$U < 12.5$
	5.905	1.212	3.76×10^{-5}	$U > 12.5$
Cd	2.456	1.734	-0.0424	$U < 6.5$
	4.251	1.182	7×10^{-5}	$U > 6.5$
Mo	5.08	1.294	-0.00288	$U < 22.5$
	6.711	1.149	34.1×10^{-5}	$U > 22.5$
Pb	1.972	1.571	-0.0335	$U < 6$
	3.18	1.169	5.52×10^{-5}	$U > 6$
Al	5.331	1.417	-0.015	$U < 8.2$
	6.371	1.164	10^{-5}	$U > 8.2$

In Figure 14, the dynamic compressibility ranges achieved in laboratory and underground work at VNIIÈF, VNIITF and in the USA are presented on a logarithmic scale for the elements studied. In 1957, Al'tshuler, Zel'dovich and Styazhkin at VNIIÈF proposed a fundamentally innovative and particularly sensitive method for evaluating the isentropic compressibility and EOS of the fissionable materials U and Pu [192]. The method was put to practice in the late 50s and came to be known as the method of nonexplosive chain reactions. Simultaneously, the same method was developed in the USA, where it was called the method of 'hydraulic nuclear processes' [7, 193].

The idea of the method was to experiment with spherical explosive charges containing not enough fissionable material to cause a macroscopic energy release. The maximum allowable energy release was taken to be 1 kg of the trinitrotoluene equivalent, implying a huge ($\sim 10^{17}$) number of fission events and the corresponding number of neutrons escaping the charge. For such charges, the hydrodynamic stage in the framework of this method is calculated for core masses for which the released nuclear energy has virtually no effect on the compression and divergence of the core.

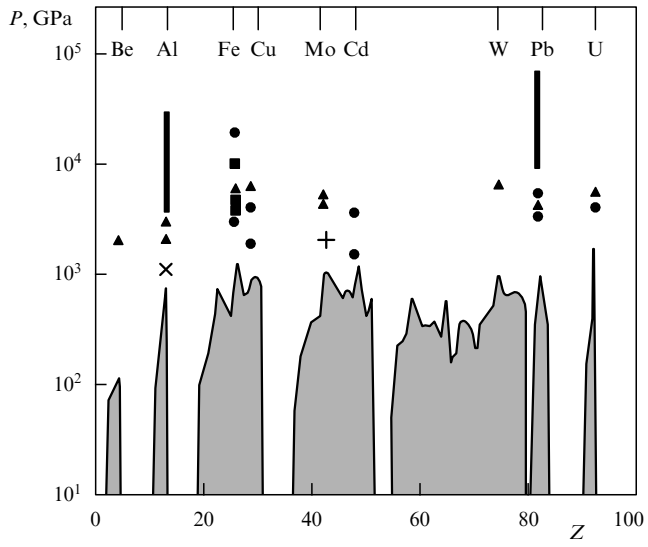

Figure 14. Ranges of absolute and relative measurements, achieved in laboratory and underground tests: shaded region — absolute laboratory measurements; ■, • — absolute and relative measurements at VNIIÈF; ×, |, the same at VNIITF; +, ▲, the same from American work.

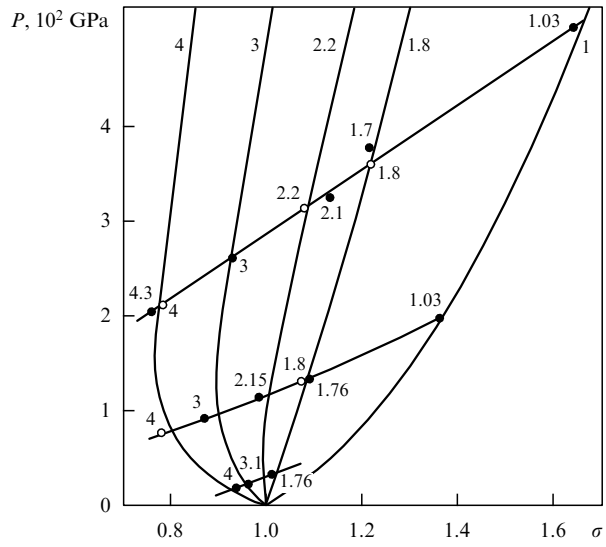

Figure 15. Shock adiabats for W of various initial density [195]. The numbers indicate the porosity; • — experimental data; ○ — interpolation of experimental data using relations for one device data.

The intensity of neutron multiplication and hence the total number of fission events in an explosion experiment depend to a great extent on the maximum core pressure. The quantitative relation between the number of fission neutrons detected and the densities achieved is obtained from hydrodynamic and neutron calculations. An 1% variation in compressibility changes the neutron flux by two orders of magnitude. Work along these lines has provided very accurate data not only on the isentropic compressibility and EOSs of fissionable materials at pressures of 10 – 15 TPa, but also on the physical processes in the core.

7. Wide-range phase diagrams of metals

The dynamic high-pressure studies of the compressibility of metals [1, 2] provide information about energy, pressure, and density on a shock adiabat. Ya B Zel'dovich in his 1957 seminal paper 'On the study of the equation of state using mechanical measurements' [194] advanced two methods capable of extending the range of the phase diagram, one involving the adiabats of 'porous' materials (i.e. of those with a reduced initial density) and the other measuring the expansion isentropes of the shocked material. The former idea was realized in the early stages of dynamic work, in 1949, when the Hugoniots of both solid and porous Fe and U were found. Results on shocked Fe were presented in the first Soviet publication on the high-pressure shock compressibility of solids [49]. Although the 20% initial porosity of the material did not allow the range of investigation of the state to be extended very much, the results thus obtained yielded the Grüneisen coefficients and made it possible to revise the EOSs of these metals over comparatively narrow phase diagram ranges.

The first comprehensive shock compressibility study for different initial porosities (up to $m = 4$, m being the normal to initial density ratio) was made on W by Krupnikov et al. [195]. Experimental results (Fig. 15) confirmed the paradoxical theoretical predictions of states with lower-than-normal density, developing in a shocked porous material under high-pressure conditions.

Kormer, Funtikov, Sinitsyn, and Urlin with coworkers provided further insight into the problem by working at pressures of up to 800 GPa on Al, Cu, Ni, and Pb [54] and four ionic crystals [196]. To evaluate the dynamic compressibility of porous materials, special laboratory explosive devices were designed [197]. Shock adiabats of porous materials were found to have portions with positive and negative slopes due to the thermal excitation of electrons [54].

The next step in extending the range of achievable states was taken by Trunin and colleagues [198 – 200] who studied the shock compression of Cu, Mo, Ta, and Ni specimens with about twice the porosity used in previous works. The preparation of specimens for these experiments definitely marked a technological breakthrough in this area. A subsequent series of studies yielded shock data for 14 metals with a maximum porosity of 20. Also explored were the gently sloping portions of adiabats corresponding to compact states of near normal density that form in the relatively low pressure range [198, 199].

Underground explosion technology made feasible much higher pressures accessible for work with porous materials. Terapascal data were obtained for porous Cu, W, and Fe [200, 201], whose $D - U$-type shock adiabats are presented in Fig. 16. The change in the slope of adiabats with increasing pressure indicates the approach to the theoretical values [177, 178]. Laboratory results for porous Cu and Ni are plotted as $P - \sigma$ diagrams in Fig. 17.

In developing this method, the study on shocked aerogels, finely dispersed media with record high porosity of $m \sim 400$ [202, 203], was a logical step to take. The interpretation of shock wave data for porous media in high-density, multiply ionized nonideal plasma revealed such effects as Coulomb nonideal behaviour, the discrete electron degeneracy spectrum, and thermal and pressure-induced ionization [204].

According to Zel'dovich [194], the region of accessible $P - V$ space can also be extended by using release isentropes for unloading from the shocked states of solid or porous specimens. In this context, experiments with rarefaction

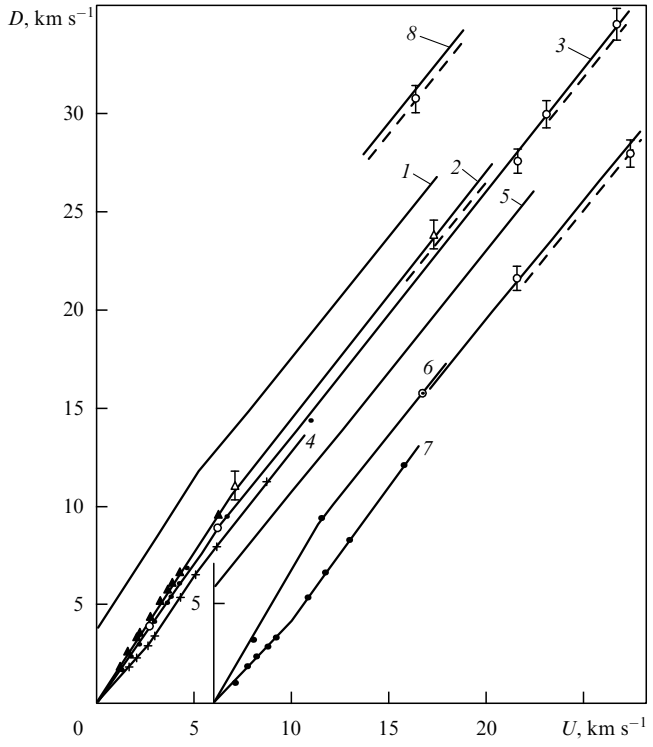

Figure 16. $D(U)$ diagrams for porous Fe, Cu, and W. Shock adiabats: *1–4*, for Cu, porosity $m = 1, 3, 4, 10$; *5–7*, for Fe ($u + 6$ km s^{-1}), $m = 1, 3.5, 20$; *8*, for W, $m = 3.1$. The symbols ▲, •, + indicate laboratory measurements; △, ○ are underground measurements; the dashed lines are TFPK calculations [177, 178].

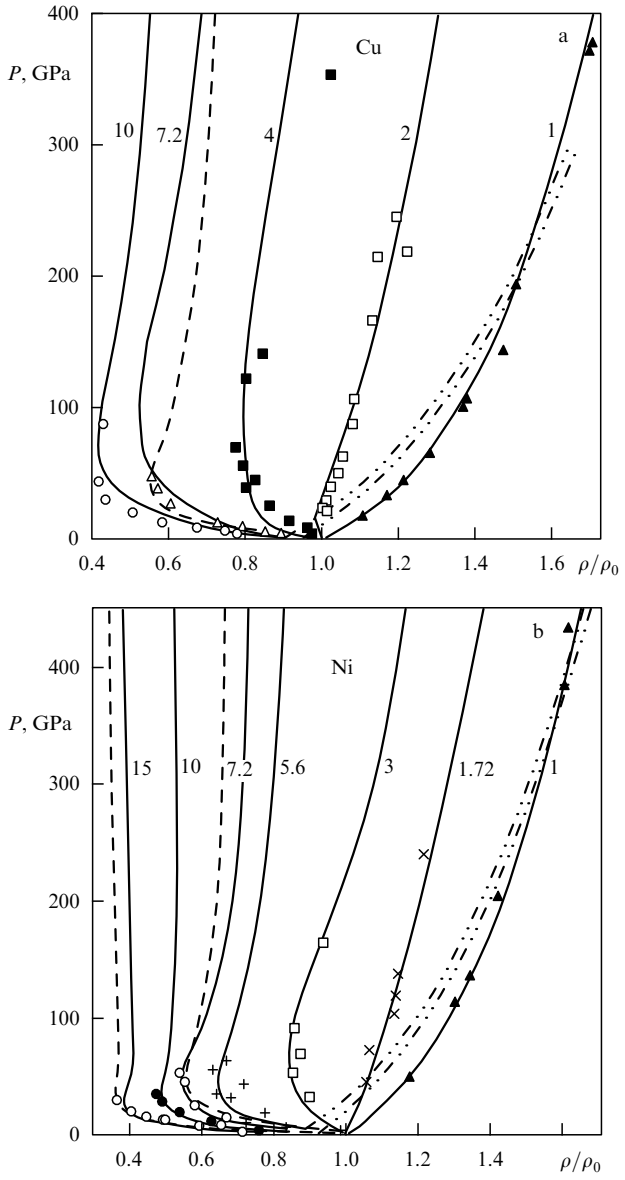

Figure 17. Shock adiabats for (a) Cu, and (b) Ni. Symbols — experimental data after [54, 198–200]; solid lines — calculations from [149]; dashed lines — calculations from [266]; dash-and-dot lines — melting boundaries after [149]. Numbers indicate porosity m.

waves involving nearly critical states are especially noteworthy [205]. Extensive expansion isentrope measurements using the so-called 'soft anvils' scheme were made at the Institute of Chemical Physics in Chernogolovka (IKhFCh) and at VNIIÈF [73, 206–212]. As anvils, materials with known Hugoniots, such as Al, Mg, plastic materials, Ar, Xe, and air at various pressures, were used.

Results on release isentropes for shocked solid and porous specimens of Cu and Pb unloaded to near-criticality were published by Al'tshuler [210] and Bakanova et al. [211]. In their survey paper Glushak et al. [73] presented new data on Al and Bi and also additional Cu data for an initial shock pressure of 1.4 TPa achieved with laboratory explosive devices [68–72]. The $P-U$ and phase diagrams of Cu are shown in Figs 18a and 18b, respectively [173].

Expansion isentropes link the isentropic states of degenerate superhigh-density plasma with near-critical states of weakly ionized vapor. On entering the two-phase liquid–vapor region, the energy and volume values on the isentropes are consistent with equilibrium curve parameters and, as shown in Ref. [194], the temperatures and entropies known for the low-pressure low-density region on the lower sections of an isentrope allow one to calculate these parameters all along the isentrope, thus yielding the complete $P-V-T$ diagram of the substance. Zel'dovich's idea [1, 194] of determining the temperature from shock experiments and by measuring adiabatically unloaded final states was first realized by Fortov and Krasnikov [213] and then by Fortov and Dremin [214] to obtain EOS data for Cs and Cu, respectively.

With current advances in quick-response solid-state photoreceivers and fiber-optic lines, it is now possible, along with gas-dynamic measurements, also to detect optical emission from an expanding hot plasma [215–217]. From the sum total of gas-dynamic and optical data, the high-temperature portion of metal boiling curves up to the critical point has been determined [73, 215, 218, 219] and nonequilibrium condensation and evaporation effects in rarefaction waves have been analyzed [220, 221]. It is also pointed out that the material can achieve intra-spinodal states and that the nonequilibrium time scale is greatly reduced due to the marked ionization on binodals [222]. Curiously, the time shape of the optical signal gives valuable information about the absorption coefficients of nonideal plasma [215, 218, 223], which, along with direct spectroscopic data [224, 225], indicates the upper excited states of atoms and ions to be suppressed in high-density plasmas.

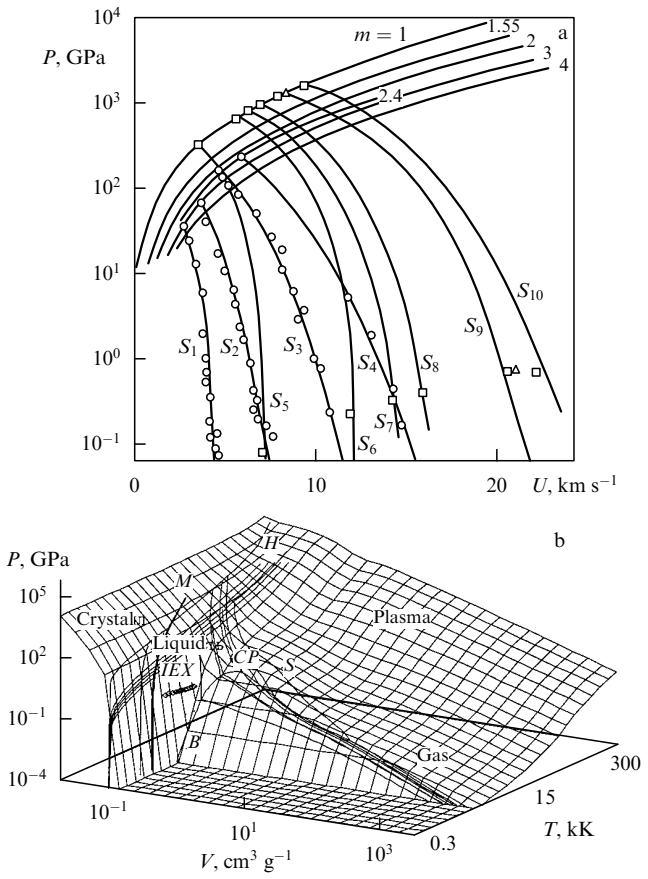

Figure 18. (a) Shock adiabats and expansion isentropes for Cu: m — shock adiabats for various porosities; $S_1 - S_{10}$ — expansion isentropes. (b) The state surface of Cu in the pressure – volume – temperature coordinate system: M — melting curve; B — the boundary of the two-phase liquid – gas region; CP — critical point; H — shock adiabats of continuous and porous specimens; IEX — the region of experiments using pulsed isobaric heating by current; S — expansion isentropes.

8. Optical studies of shocked dielectrics

A strong shock wave heats the compressed material to several tens of thousands of kelvins, and if the material is transparent, radiation can pass through the noncompressed layer thus providing information about the state of the material behind the shock. The first measurement of brightness temperature in the front of a strong shock wave in a gas was performed by Model' [226], who observed a dramatic drop in the measured brightness temperature compared to that calculated behind the shock. Zel'dovich and Raĭzer [1] presented a theoretical analysis of the optical effects occurring in powerful shock waves in gases and, among other things, interpreted Model's observation as resulting from radiation screening by the heated plasma layer before the shock front.

In the mid-50s, the optical properties of transparent, shocked, condensed materials were most comprehensively studied by S B Kormer and his colleagues M V Sinitsyn, G A Kirillov, V D Urlin, K B Yushko, and others, much of their success being due to Academician Zel'dovich's participating directly in the analysis of the results. These studies, in turn, triggered the research work of Kormer et al. [227], which appears unique in many respects even today. Temperature measurements on transparent, shock compressed ionic crystals and dielectrics [228] considerably improved the EOS data for this class of materials and extended their melting curves previously limited to the range of only few GPa to as high as 50 – 250 GPa. For high pressures, a melting heat increasing almost linearly with temperature and a significantly reduced volume jump were observed on melting. It was shown for the first time that when shocked to half their volume, the crystals of LiF, NaCl, KCl, and CsBr remain solid up to ~ 4000 K [228]. Also, assuming a Debye heat capacity function, it was found that the Mie-Grüneisen EOS for the solid phase of the investigated crystals quite satisfactorily describes not only the pressure – density relation along a Hugoniot but also the temperature of the shocked solid body up to the melting curve. This implies that anharmonism of lattice thermal vibrations has little effect on the heat capacity of the solid phase of these crystals. Ref. [149] summarizes the equations of states and melting curves obtained for the materials studied. A comparison of computed curves with experiment is presented in Fig. 19 for the NaCl phase diagram calculated with account for the NaCl- to CsCl-type structural transformation.

Brightness temperature measurements of shocked ionic crystals at low pressures of a few GPa showed the detected light fluxes to be well in excess of what might be expected from the calculated temperatures [227]. For NaCl, this corresponds to pressures of 27 and 40 GPa (see Fig. 19). This nonequilibrium glow is found to be of a luminescent nature. As the shock pressure increases, the brightness of luminescence fades to a subthermal level thus ceasing to affect the temperature values measured.

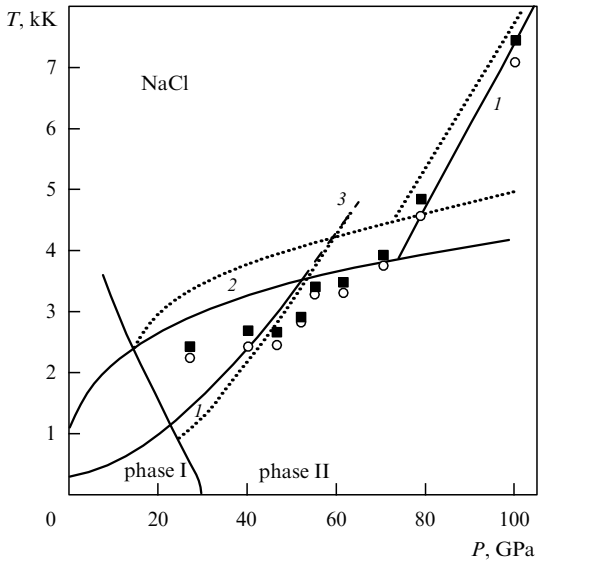

Figure 19. Phase diagram of NaCl: ■, ○ — measured temperatures in the spectral regions $\lambda = 0.478$ and 0.625 μm, respectively; *1*, shock adiabat; *2*, melting curve; *3*, shock adiabat of the 'overheated' solid phase; solid lines — calculation for phase I; dotted lines — calculation for phase II.

Another kind of nonequilibrium emission was observed in shock wave experiments on five ionic crystals in the pressure range 200 – 500 GPa [229]. In these crystals, a brightness of radiation far below the equilibrium-temperature value was found, an effect which Zel'dovich, Kormer, and Urlin [230] explained by invoking the kinetics of transition to the thermodynamic equilibrium between electrons and lattice in the shock wave front.

Optical shock wave studies were also carried out for liquid Ar [231] and liquid Xe [232]. In these works yet another class of materials lends support to the ideas involved in the construction of the multiphase EOS and in the theory of heating kinetics of shock front electrons [230]. Figure 20 illustrates the calculated pressure dependences of the equilibrium temperature and the brightness temperatures for Xe in the red and ultraviolet ranges of the spectrum. Also shown in the figure are the experimental values of the brightness temperature obtained in Russia [232] and the USA [233] in the red and ultraviolet light, respectively.

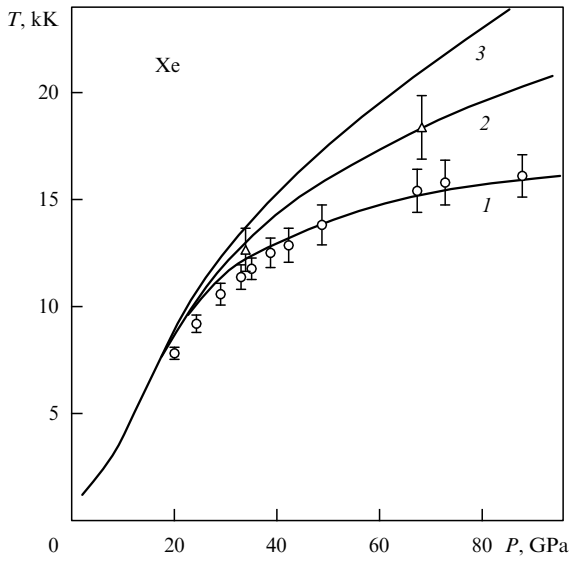

Figure 20. Variation of shock front brightness temperature with pressure in Xe. Experimental data: ○ — $\lambda = 0.67$ μm [232]; △ — $\lambda = 0.32$ μm [233]. Calculated results: *1* and *2*, brightness temperatures for $\lambda = 0.67$ and 0.32 μm, respectively [232]; *3*, equilibrium temperature.

The optical properties of the shock wave front in a transparent dielectric also depend on the reflecting power and transparency of the material behind the shock, reflecting power depending, in particular, on the smoothness and thickness of the front. A technique for measuring the reflecting power of transparent, shock compressed, condensed materials was developed by Kormer, Yushko, and Krishkevich [234]. It was found that the density jump in a shock in condensed materials occurs in a layer less than 10^{-6} cm thick and takes less than 10^{-12} s to form. The shock front is to a large extent smooth and its roughness is less than 10^{-6} cm. An order of magnitude higher wave front roughness was observed in a detonating liquid explosive in Ref. [235]. The same study also showed that the refraction index of both liquid and solid materials increases linearly over a wide range of compressions and can reach twice its original value. Up to pressures of order 100 GPa, it was found that for most materials the reflecting power of the shock front is 2%. Owing to the high sensitivity of the method to the density gradient it proved possible to see shock front structure in materials undergoing polymorphic transformations [236]. The reader is referred to [227] for a survey of optical shock wave works performed on dielectrics in the 1960s.

Interest in the EOS and shock compression data for water stems primarily from its great abundance in nature, either free or bound in compounds. In US laboratory studies, the water shock adiabat was recorded up to 42 GPa in 1957 [237], and to 85 GPa in 1982 [238]. In the Soviet Union, the same range was achieved as early as 1958 [239] and later studied in detail in Refs [240 – 242]. The shock compressibility of water was also measured in the near zone of underground nuclear explosions [243, 244] at ultrahigh pressures of 100 and 1400 GPa. All the experiments report quite reliably a kink in the water adiabat at 11 GPa, an anomaly which indicates that the compressibility of water decreases in a discrete fashion. In elucidating the physics of the kink, transparency measurements on shocked water were particularly important. The first, not entirely perfect measurements [239] indicated the disappearance of transparency at kink pressures, giving rise to the hypothesis that at these pressures water freezes to form ice VII crystals. However, detailed measurements in the 4 – 30 GPa pressure range [240, 241] showed no transparency changes to confirm the data of Ref. [239]. At the same time, double shocking experiments show that if the first wave corresponds to pressures from 2 to 4 GPa, then, given a sufficiently wide pressure range, the second shock wave displays diffusion scattering of light and no transparency behind its front — possibly due to the formation of small ice crystals. It is possible, though, that the cessation of transparency may be attributed to a leading role of surface phenomena and chemical reactions [245].

Ref. [246] presents a systematization of shock wave data on water, including shock temperatures [227] and the shock compression of ice and snow, i.e. of water of different initial densities. In Figure 21, data for water are presented in the form of a $D - U$ diagram. High-pressure EOS data for water [242, 247, 248] agree with these data.

Note that, as shown in Ref. [249], the shock adiabats of saturated halide and sulfate water solutions are similar to those of water and likewise possess two intersecting branches, whose slopes and intersection point parameters are close to those for water.

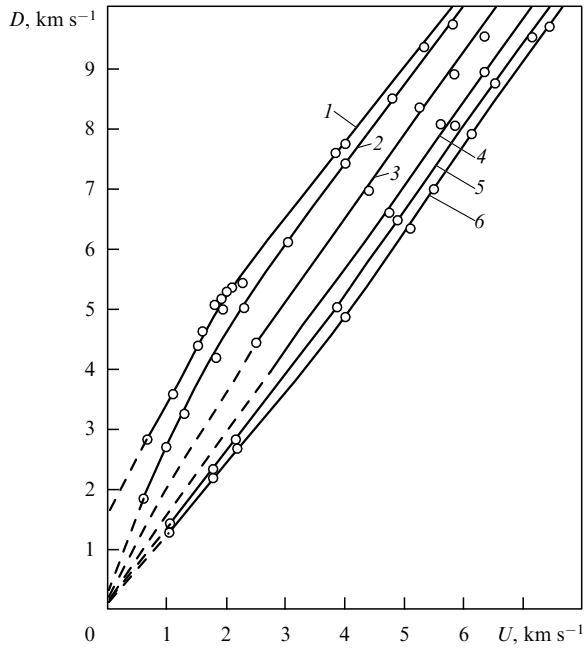

Figure 21. $D - U$ diagram of water and ice of various initial densities: *1* — 1.0; *2* — 0.915; *3* — 0.6; *4* — 0.35; *5* — 0.25; *6* — 0.15 g cm^{-3}.

9. Description of compressed and plasma states

At present, the highly developed methods of quantum mechanics and statistical physics provide an adequate picture of a substance at either high or low densities, when interparticle interactions are described by the classical (Debye – Hückel) or quasi-classical (Thomas – Fermi) approximation, respectively. In the intermediate highly nonideal region, theoretical analysis faces a strong-interaction disorder situation which prevents applying perturbation theory to a quantum mechanical many-body system. The conventional approach is therefore to employ simplified physical models using functional relations whose form is dictated by theory and coefficients, by experiment [250, 251].

Equations of state commonly used in the range of moderate temperatures [1] contain three components accounting for the elastic interatomic interaction (which depends only on the density), thermal atomic motion, and the thermal excitation of conduction electrons. For a solid phase, the free energy is described by the Debye model of a crystal body. Numerous applications of such equations to the isotherms and shock adiabats of simple materials show that this model reflects the nature of the solid state reasonably well. A good agreement between the computed and experimental temperatures of shocked ionic crystals [196, 227] further supports this conclusion.

One of the major high-pressure research directions is the compressibility of materials at zero and normal temperatures. In [252], zero isotherms for the EOS of ionic crystal are represented by the Born – Meyer potential, an approach which was fist applied to metals in Ref. [53] and was further developed in Ref. [253]. As discussed in [254], the parameters of the Born – Meyer potential can be directly determined from the shock adiabat $D - U$ relations in terms of the initial bulk modulus and its pressure derivative. In the same paper, potential parameters obtained in this way are given for 25 metals. Compared to the American reference isotherms [255], the normal-temperature isotherms calculated for pressures up to 400 GPa are essentially the same for Cu, agree fairly well for Pb, and agree not so well for Al. A good agreement is also observed for Au, which has been suggested as a standard material in the metrology of static measurements [4].

In Refs [256, 257] the elastic compression curve in the EOS of a condensed material was represented as an expansion in powers of the cubic root of the density. The interpolation coefficients were obtained from the static, bulk compressibility curve at low pressures and by matching this curve to the TFPK behaviour at high pressures [177, 178]. The correction of the interpolated dependence of elastic compression using a single data point on a shock adiabat in the megabar range [257] enabled shock adiabats and isotherms to be described satisfactorily over a wide pressure range for a whole series of metals. The interpolation-based description of elastic compression curves from initial to ultrahigh pressures with the use of statistical Thomas – Fermi models is employed in semiempirical wide-range EOSs [54, 212, 250, 251].

The shock adiabats of continuous and porous materials at sufficiently high pressures and temperatures lie in the region of liquid and plasma phases. The thermal components of the EOSs of a crystal or a liquid near the melting curve are similar and depend on the generalized Mie-Grüneisen EOS, in which, assuming atomic and ionic vibrations to be small, the lattice Grüneisen coefficient depends on the density alone and is related to the first and second derivatives of the elasticity curve [2, 258]. To describe the adiabat of a porous material at high temperatures it is necessary to include the anharmonism of atomic vibrations and to change over to a perfect gas equation [54]. A convenient way to interpolate the thermal contribution to atomic free energy was suggested in Ref. [54]. A theoretical analysis of the influence of melting [149, 259] shows that although kinematic shock parameters (and hence the adiabat $P(\rho)$) are affected little, on the $P - T$ diagram the expenditure of energy on melting leads to sharp kinks in the adiabat (see Fig. 19). This can be accounted for by empirically correcting the free energy of the liquid phase [149].

In transition metals, with high values of electron heat capacities and associated Grüneisen coefficients, the electron components of the EOS become important at relatively low temperatures. In Ref. [54], temperatures of the order of several electronvolts were achieved in continuous and porous shocked metals. The values of an electron Grüneisen coefficient corresponding to experimental data for porous metals were used [54] to present EOS electron components as approximations to the asymptotic forms for degenerate and nondegenerate (in the Thomas – Fermi temperature model sense [260]) states. For dielectric materials, the effect of electron components becomes appreciable at temperatures above 1 eV. As shown in Ref. [196], these components are well described by band theory.

Figure 17 illustrates the shock adiabats for Cu and Ni of various porosities, which were calculated with EOS parameters from Ref. [149] and agree satisfactorily with the experimental data [54, 198 – 200]. A certain amount of discrepancy which exists is probably due to the averaging of parameters obtained from the measured data and may also be ascribed to experimental errors. For densities much below normal, metals could turn into energy-gap dielectrics as a result of electron level rearrangement. It is seen from Fig. 16 that if one takes into account the ionization of the material at the corresponding temperatures, then shock adiabats obtained with the resulting EOS for Cu with normal initial density and porosity $m = 4$ are also quite accurate up to 20 TPa and agree well with underground explosion data [179].

The principle underlying the semiempirical EOS of Ref. [54], namely, the representation of the thermodynamic potential as a sum of lattice and electron contributions, was later developed for and used in the so-called multiparametric wide-range EOSs [212, 250]. Using the resulting EOS models, thermodynamic metal characteristics, including liquid – vapor phase boundaries and melting behaviour, can be described over a wide pressure – temperature range from normal to extremely high values. Importantly, a correct description of theoretical asymptotic behaviour is secured. Ref. [212] presents EOSs for Cu and Pb, and Ref. [250], for 25 more metals. The energy surface of Cu constructed from the wide-range EOS of Ref. [250] is shown in Fig. 18b, where experimentally achievable states and the phase boundaries of melting and evaporation are clearly seen.

An alternative approach to the construction of an EOS of the liquid phase [261, 262] is a generalized van der Waals model using the elastic compression isotherm as a covolume for material compressibility. At high temperatures, the thermal ionization of atoms is included and a Saha type equations are employed for describing ionization equilibrium. This EOS also adequately describes the existing data on porous and highly porous metals and on expansion isentropes. The calculated Cu and Ni Hugoniots are essentially identical to those in Fig. 17.

For a material initially of normal density, a theoretical picture of shock compressibility at superhigh pressures is obtained by invoking the solid-state concept of the Wigner–Seitz cell, on which a number of boundary conditions are imposed. For the purpose of comparison with experiment, the statistical Thomas–Fermi model was initially adopted [171] for electrons and a perfect monatomic gas of nuclei, which was later improved by introducing quantum and exchange corrections [176, 177] and interactions between nuclei as, for example, in Ref. [178] (TFPK model). This model is statistical and while predicting the thermodynamic characteristics to depend monotonically on the atomic number of the element, it fails to account for the shell structure of atomic electrons. To remedy this at high pressures, high temperatures, and successive shell ionization, the Hartree–Fock model [83] with Slater's exchange interaction [263] or the pseudo-band self-consistent field (SCF) model [264] can be employed. The shell models differ considerably from one another and typically yield thermodynamic parameters that vary highly nonmonotone — in some cases unrealistically so — in the range of high compressions. In this range one therefore prefers quantum statistical models, which agree better with experimental data on shock compressed metals. The lower limit of applicability of TFPK shock adiabats lies at 15–20 TPa [171]. Figure 13 illustrates the applicability of TFPK results by $P-\sigma$ diagrams for the metal shock adiabats in a hundred megabar range.

A theoretical picture of states in a wide pressure–temperature range corresponding to the shock compression of highly porous metals and to expansion isentropes has been developed by Gryaznov, Iosilevskiĭ, and Fortov [204, 265–267] based on a highly nonideal plasma model. At the heart of this 'quasi-chemical' approach is the calculation of the equilibrium ionization composition, which is performed by minimizing the free energy corrected for the interparticle interaction of atoms and ions. Notice that the megabar-pressure normal-density region corresponds to states of a highly nonideal, partly degenerate plasma with an ionization degree of up to 4–5. Apart from the introduction of partially degenerate free electrons, Coulomb nonideality, and multiple ionization, the success in describing shock compression data on highly porous metals [198– 200] crucially depends on adding a strong short-range repulsion between ions due to their own volume ('limited atomic volume model') [265]. As discussed in Ref. [265], the validity of the chemical model in the range of states of interest is to a large extent related to such additional features as the proper volumes of atoms and ions of various ionization degree; interparticle attraction, and the correction of these parameters based on the characteristics of the material under normal conditions (density, energy, sublimation). The calculated adiabats of Cu and Ni are shown in Fig. 17.

The body of data currently available on the shock compressibility and adiabatic expansion of condensed materials at high energy densities is summarized in Ref. [268], which presents about 2,500 experimental points for 200 individual substances, chemical compounds, construction materials, alloys, and solutions and in which generalizing relations describing experimental dependences may also be found.

10. Conclusions

The total amount of data collected in Russia on all the subjects discussed above is too large to cover in a single — even a review — paper. Some comprehensive studies on shock strength and the deformation of metals and on shock compression of quartz, rocks, and dense plasma were only briefly mentioned, and because of the lack of space neither the methods used nor results obtained were discussed. The list of omissions also includes: the shock compression of metallic alloys, hydrides, carbides, and nitrides of metals, and of fusible metals initially in the liquid state; double compressibility data; pulsed X-ray diffraction analysis in shock waves, including shock polymorphism; pulsed X-ray compressibility studies; a huge amount of work on organic materials, both liquid and solid; chemical reactions in shock waves, and many other aspects of the field, among them the generation of powerful shock waves using intensive beam technologies (lasers, soft X-rays, relativistic electrons, light or heavy ions) and the electro-explosion of metals, having their origins in the above-discussed dynamic high-pressure techniques. All these topics deserve special discussion and have been addressed in detail in a number of monographs and review papers in recent years.

The comprehensive dynamic shock wave data presented in this survey resulted from the pioneering efforts of Russian researchers and are of fundamental importance for an understanding of the physics of extreme states of matter.

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