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On the 50th anniversary of the L F Vereshchagin Institute for High Pressure Physics, RAS

(Scientific outreach session of the Physical Sciences Division of the Russian Academy of Sciences, 23 April 2008)

S M Stishov; L G Khvostantsev, V N Slesarev; S V Popova, V V Brazhkin, T I Dyuzheva; L N Dzhavadov, E L Gromnitskaya, G N Stepanov, Yu A Timofeev; E M Dizhur, V A Venttsel, A N Voronovskii; V N Ryzhov, A F Barabanov, M V Magnitskaya, E E Tareyeva

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A scientific outreach session of the Physical Sciences Division of the Russian Academy of Sciences (RAS) was held on 23 April 2008 at the Institute for High Pressure Physics, RAS, Troitsk, Moscow region. The session was devoted to the 50th anniversary of the Institute. The following reports were presented:

(1) **Stishov S M** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region) ''The Institute for High Pressure Physics is now 50 (opening address)'';

(2) **Khvostantsev L G, Slesarev V N** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region) ''Large-volume high-pressure devices for physical investigations'';

(3) **Popova S V, Brazhkin V V, Dyuzheva T I** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region) ''Structural phase transitions in highly compressed substances and the synthesis of high-pressure phases'';

(4) **Dzhavadov L N, Gromnitskaya E L, Stepanov G N, Timofeev Yu A** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region) ''Studies of the thermodynamic, elastic, superconducting, and magnetic properties of substances at high pressures'';

(5) **Dizhur E M, Venttsel V A, Voronovskii A N** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region), ''Quantum transport at high pressures'';

(6) **Ryzhov V N, Barabanov A F, Magnitskaya M V, Tareyeva E E** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region) ''Theoretical studies of condensed matter'';

(7) **Bugakov V I, Antanovich A A, Konyaev Yu S, Slesarev V N** (Institute for High Pressure Physics, RAS, Troitsk, Moscow region) ''Designing new construction and superhard materials and related tools.''

An abridged version of reports 1 – 6 is presented below.

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The Institute for High Pressure Physics is now 50 (opening address)

S M Stishov

Today, 23 April 2008, we celebrate the 50th anniversary of the founding of the Institute for High Pressure Physics (IHPP). In fact, the corresponding paper of the Presidium of the USSR Academy of Sciences, the USSR Council of Ministers, and the Central Committee of the Communist Party of the Soviet Union was formally signed on May 23, 1958. I believe that no one will blame us for this slight deviation from the formal date. The point is that at the end of May there will be a general meeting of the Russian Academy of Sciences with a more elaborate program. But let us turn to our jubilee.

Sometimes the question is asked as to what end these or those institutions are created at all. Someone can say that they are created for solving important scientific problems. In reality, this appears to be a delusion, since there cannot exist an organization, a council, or people who have decided to meet and have said that there is a problem, or a talented person that can solve this problem and that, therefore, an institution should be founded so this person could develop this scientific area. In reality, events occur in quite a different way; usually, a new institution is created due to the efforts of a single talented person or a small group of people. They are real initiators, going through various stages, applying to various authorities, organizing advertising campaigns, etc. We should also understand that in order to found an institution it is insufficient to possess only scientific talent. One should also have some quite special talents. Leonid Fedorovich Vereshchagin, the founder of our institute, possessed such talents to the full extent. I believe that the history of the creation or organization of our institute should be traced from the period when L F Vereshchagin was working at the Kharkov Physico-Technical Institute, which suffered heavily in 1939, when part of its workers were arrested and part were shot, so that many people left. While working in Kharkov, Vereshchagin designed an efficient apparatus for creating high pressures (hydrocompressor,

Figure 1. L F Vereshchagin with his hydrocompressor.

Figs 1, 2). He then moved to Moscow, bringing along his apparatus. The only place where his knowledge was needed and where he could work at that time was the Institute of Organic Chemistry, USSR Academy of Sciences, where Academician N D Zelinskii had then been working. Zelinskii had initiated the establishment of the Laboratory of Ultrahigh Pressures, which became headed by L F Vereshchagin. But soon World War II began and Vereshchagin's compressor proved to be quite useful for military needs. High pressures produced by the compressor made it possible to provide autofrettage for gun barrels, as well as to produce explosives of enhanced power. In general, L F Vereshchagin participated in a number of defense projects; during this work, he made many acquaintances among all sorts of people, which helped him in his subsequent activity. In 1948 a high-pressure technology for producing polytetrafluoroethylene (teflon) was developed at the laboratory, and was successfully introduced into industry; a number of workers who participated in this work obtained government awards and L F Vereshchagin received a Stalin Prize in 1951 for the development of the hydrocompressor. In 1954, the independent Laboratory of Physics of Ultrahigh Pressures was organized at the USSR Academy of Sciences. Figure 3 illustrates from what this laboratory was begun. The building shown in Fig. 3 is now located behind the Institute of Inorganic Chemistry, Russian Academy of Sciences. In 1954, this building was a storage room; traces of the initial building

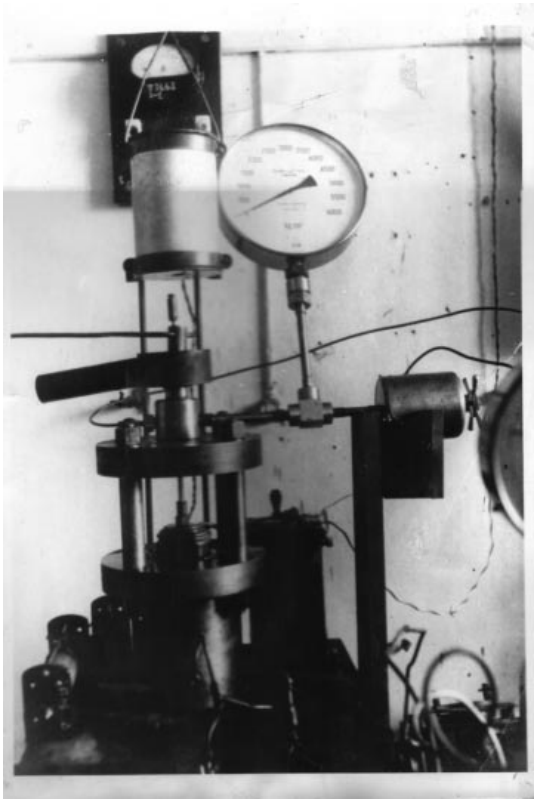

Figure 2. Hydrocompressor for generating high pressures.

work aimed at its accommodation for the laboratory are seen. At the front of the photo, L F Vereshchagin and his father-in-law, Academician N N Andreev, can be seen. Quite quickly, the laboratory received the status of an institute. Note that in 1958 the Institute had no towering scientific achievements. Correspondingly, L F Vereshchagin had to prove himself in many new fields. He tried to develop many disciplines, such as hydroextrusion and supersonic streams, and even attempted to take part in the issue of thermonuclear synthesis, but unfortunately without success. But it so happened that in 1955 the General Electric Company and, simultaneously, a Sweden research laboratory of the ASEA Company reported on a successful synthesis of artificial diamond. It is interesting

Figure 3. Laboratory of High-Pressure Physics, USSR Academy of Sciences. From left to right: N N Andreev, L F Vereshchagin, an unknown person, and G A Seviyants.

that, as it became known later, the small diamond crystal that was described in the first communication published by the General Electric Company as a result of the synthesis proved to be the crystal of natural diamond. Actually, it was used as a seed, then the same crystal was found by the experimenters and the result was published. Forty years later, the researchers, who had already retired by that time, discovered this crystal in the archives, analyzed it, and decided that they were wrong in the 1950s and that this was a natural diamond. Nevertheless, artificial diamonds were later prepared at General Electric.

In the Soviet Union, the problem of synthesis of artificial diamonds was addressed by the Institute of Crystallography, USSR Academy of Sciences, which could not solve it for a long time in view of many (mainly subjective) causes. To the best of my knowledge, the then Director of the Institute of Crystallography A V Shubnikov willingly and gladly handed over this subject matter to L F Vereshchagin, to the deep disappointment of the 'diamond' group of the institute, which was liquidated.

Thus, this research area went to L F Vereshchagin and, strangely enough, this problem was solved quite fast. Why is this strange? This is strange because at that time there was no single person in the institute who understood anything about materials science. I mean mainly the methods of characterization of a material (optical properties, density, X-ray diffraction, etc.). All this was a result of the specificity of the institute personnel at that time. At the same time, young researchers who possessed good educations and began to play a progressively more important role in 'diamond affairs' began to appear

In any event, the problem was solved and in the spring of 1960 L F Vereshchagin announced the successful synthesis of diamonds (Fig. 4) and, later, of cubic boron nitride (borazon). The synthesis of diamond and borazon proved to be possible due to the successful design of a new very efficient high-pressure cell of the 'chechevitsa' (lentil) type, which has been widely used even up to now. The synthesis of diamond and borazon at the IHPP triggered the development of an industry of superhard materials in the Soviet Union. Already in the autumn of 1960 the technology developed was introduced to various enterprises of the country. In particular, equipment developed at the institute was taken to the Kiev Central Design Technological Bureau for Superhard Alloys and Tools, which later was transformed into the Institute of Superhard Materials, Ukrainian Academy of Sciences. The equipment was mounted there and the personnel was taught by our workers.

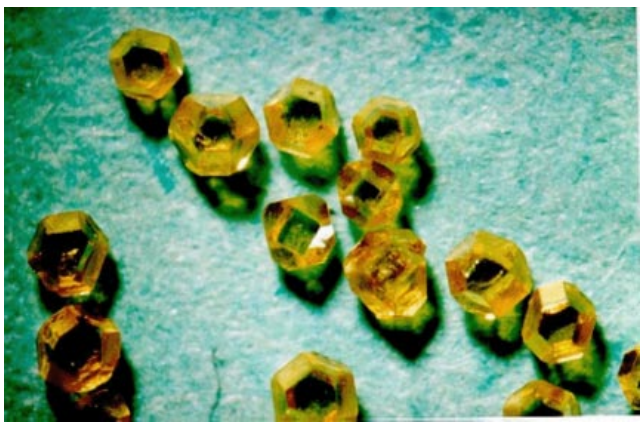

Figure 4. Crystals of diamond synthesized at high pressure.

In 1961 L F Vereshchagin, V A Galaktionov, and Yu N Ryabinin received the Lenin Prize for their work on the synthesis of diamond. In 1963, L F Vereshchagin became a Hero of Socialist Labor and the institute was awarded with an Order of Labor Red Banner. Many other specialists at the institute were awarded with orders and medals. Note that a prize is, naturally, an important thing, but obtaining it requires a thorough effort while it is also important because the people that award prizes later become spell bound by the 'magic' of the prizes, and it becomes easier for a person who has obtained a prize to live and guide an institute.

As was said above, the institute was first located in a small building on Leninskii Prospect in Moscow; later, it moved into the old building of the Institute of Crystallography on Pyzhevskii Pereulok. In 1962, a resolution was adopted on the construction of the modern complex of buildings in Pakhra (today Troitsk), a small town 40 km away from Moscow along Kaluga Shosse, where at that moment the Institute of Earth Magnetism and Propagation of Radio Waves, USSR Academy of Sciences, already existed. In 1966, the Institute moved to Pakhra (Fig. 5). At the same time, unsuccessful attempts were undertaken to sharply turn the direction of investigations toward the field of semiconductors and even lasers. In addition, research was carried out on the effect of high pressures on the properties of metals (an electron-topological transition in zinc was revealed); studies of phase transitions under pressure in elements and compounds were performed; and X-ray diffraction, ultrasonic, optical, and low-temperature investigations under pressure were developed.

After the sudden death of L F Vereshchagin in February 1977, the institute was sequentially headed by deputy directors, first E N Yakovlev and later Yu S Konyaev. From 1989 to 1991, the director of the institute was A A Abrikosov (2003 Nobel Prize in physics; has lived in the United States since 1991).

Below, I give a brief list of our achievements, which represent a real contribution to the science world. An exhaustive review of our activity will be given in the subsequent reports.

So, the most important achievements of our institute are as follows.

• Development of a high-pressure chamber of the lentil type and the subsequent synthesis of diamond and cubic boron nitride (Vereshchagin L F et al., 1960).

• Synthesis of dense silica — the substance in the Earth's mantle (Stishov S M, Popova S V, 1961).

Figure 5. Building of the Institute for High Pressure Physics, Russian Academy of Sciences, in Krasnaya Pakhra, Moscow region.

• Ultrasonic investigations of solids at pressures up to 100 kbar (Voronov F F et al.).

• Invention of a high-pressure cell of the 'toroid' type (Khvostantsev L G et al., 1977).

• Investigations of phase transitions in liquids (Brazhkin V V, Popova S V, Voloshin R N,1989).

• Synthesis of superconducting diamonds (Ekimov E A, Sidorov V A, 2004).

Most of our achievements are based on the invention of a high-pressure cell of the lentil type. It was used to synthesize diamond and cubic boron nitride (see Fig. 3). Later, this cell was employed to prepare dense silica (Fig. 6), which made our institute famous. Quite soon after the dense silica was obtained in the laboratory at our institute, it was discovered in the Arizona meteorite crater (Fig. 7) and was called stishovite in honor of the present writer. In view of the very important role of silica as the main component of the depths of the Earth and other planets and because of a quasi-detective situation related to the discovery of its dense modification, this story had huge resonance.

F F Voronov has done very much in the field of ultrasonic investigations. L G Khvostantsev and his colleagues invented a high-pressure cell of the toroid type (Fig. 8), which is now the main tool for high-pressure processing, both in this country and abroad. V V Brazhkin, S V Popova, and R N Voloshin published an important paper on phase transitions in liquids. Recently, a superconducting diamond was synthesized (Figs 9, 10). This activity is now being intensely developed; this is one of the most important achievements in the field of the solid state physics in recent years. Apart from the physics itself, there is a quite clear potential for industrial applications here.

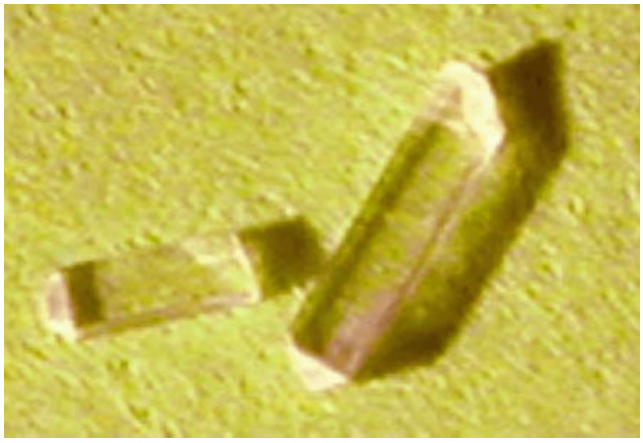

Figure 6. Crystals of dense silica (stishovite).

Figure 7. A meteorite crater in Arizona, USA.

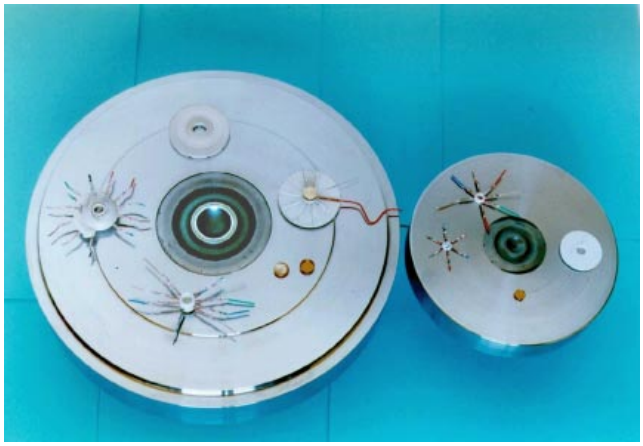

Figure 8. High-pressure cells of the toroid type.

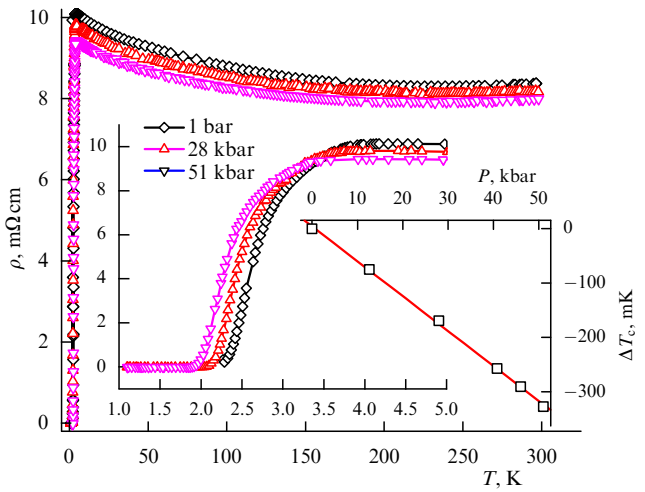

Figure 9. Superconducting transition in diamond doped with boron.

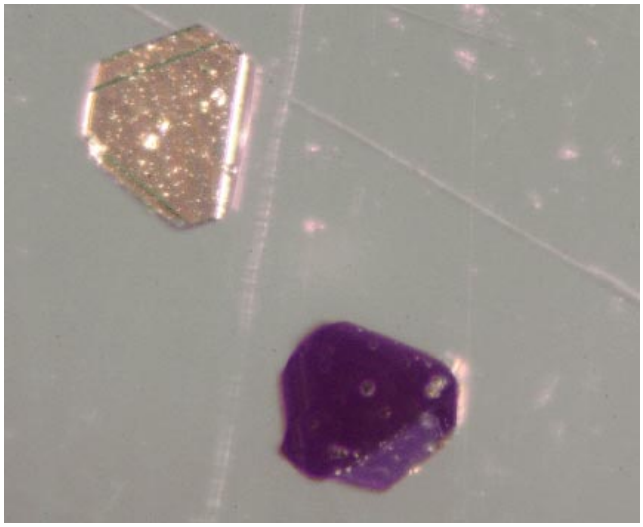

Figure 10. Diamonds doped with boron.

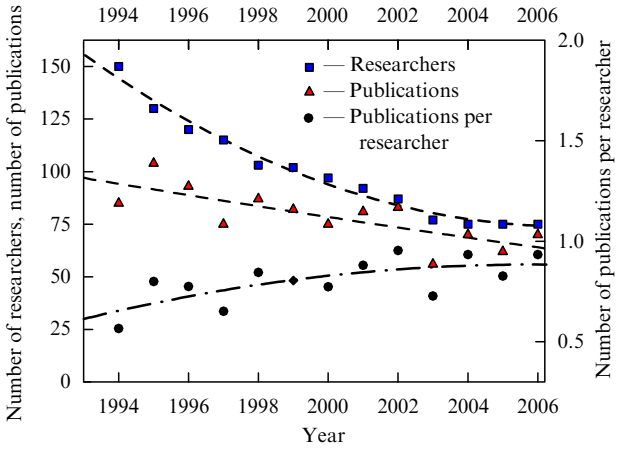

Figure 11. Variation of the number of researchers and number of scientific reports at the IHPP.

At present, the proportion of fundamental research is increasing noticeably at the institute. Although high-pressure materials science and the development of apparatuses remain among the main scientific focuses of the institute, the emphasis in investigations has shifted toward the fundamental problems of the physics of condensed matter, including phase transitions at high pressures, quantum critical phenomena and strongly correlated electron systems, the thermodynamics and kinetics of phase transitions in disordered systems, and the physics of nanosized forms of carbon.

Unfortunately, the institute is not free of the problems that are common to all academic institutions. In the last 15 years, the number of workers at the institute has decreased by a factor of more than three. Figure 11 displays the dynamics of the changes in the number of researchers at the institute, the total number of publications per year, and the number of publications per researcher per year. A certain optimism comes from the fact that, as is seen from the figure, the number of publications per researcher has increased quite noticeably. However, the fraction of young researchers remains insufficient, in spite of the existence of a base chair in the Moscow Physico-Technical Institute (The Physics of Condensed Matter under Extreme Conditions) and of academic postgraduate courses, as well as of intimate cooperation with the Moscow Institute of Steel and Alloys and the Departments of Physics and Chemistry at Moscow State University.

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Large-volume high-pressure devices for physical investigations

L G Khvostantsev, V N Slesarev

In this report, we briefly describe the development of domestic high-pressure engineering (above 5 GPa) in large volumes for physical investigations. We give the technical characteristics of the high-pressure cells of the 'toroid' and 'chechevitsa' (lentil) types invented at the institute and show their experimental potential in studying the structure and properties of condensed matter. We describe a number of examples of studying solids and liquids by various methods using these devices. The possibility of efficient application of the lentil and toroid cells in industry for the synthesis of superhard materials is noted.

High-pressure physics deals with studying a large totality of phenomena in condensed matter under high compression. As the density of solids and liquids increases, noticeable changes in their physical properties, their crystal and electronic structures, and the mutual arrangement of atoms in them are observed. Studying these phenomena, especially in combination with low and high temperatures and magnetic fields, yields valuable information necessary for the further development of concepts of the structure of condensed matter. On the other hand, this information is important for solving the main problem of materials science — preparation of new materials with unique properties — which is related to the synthesis of high-pressure phases that are formed as a result of irreversible polymorphic transformations.

The choice of phenomena to be studied is determined by the capabilities of the high-pressure equipment. High-pressure cells are characterized by the ranges of working pressures and temperatures and by the magnitude of the working volume. Large volumes are necessary for obtaining more complete and reliable information, since in cells with a large volume homogeneous pressure and temperature fields can be produced, samples of a desired size can be used, and various sensors, including pressure and temperature gages, as well as heaters, thermal isolation, and coils for generation of magnetic fields, can easily be mounted.

To produce high pressures reaching thousands and tens of thousands of atmospheres, two types of high-pressure devices have been used from the beginning of the 20th century, namely, the piston–cylinder apparatus and Bridgman anvils (Fig. 1) [1, 2]. In apparatuses of both types the pressure is created due to a decrease in the volume of the substance to be pressed. In the piston–cylinder cell the compression of the substance can be any size: the production of maximum pressures is limited by the strength of the construction materials. Devices of this type make it possible to perform investigations in large volumes ($1-100$ cm^{-3} and greater) at pressures that are, as a rule, no more than $3-5$ GPa. In the apparatus of the anvil type, Bridgman used the principle of a compressed seal, which consists in the fact that a thin gasket placed in the gap between approaching parts of the apparatus can keep the high pressure created in the working volume. Since the gasket (compressed seal) unavoidably has a small thickness, the volume of the compressed substance is also small. The anvils, made of a hard alloy, make it possible to easily reach pressures of more than 10 GPa, but only in very small volumes of $10^{-2}-10^{-3}$ cm^3 at a sample thickness of ~ 0.1 mm.

The problems of physics, geophysics, and materials science, the most important of which was the problem of synthesizing artificial diamonds, required the development of cells of a larger volume (0.1 cm^3 and greater) capable of sustaining high pressures (>5 GPa) and temperatures ($>1500\,^\circ$C) for long periods. These problems were solved in different ways, which finally led to the development of numerous devices of various constructions, combining (in various proportions) ideas that were laid in the initial variants, i.e., in the apparatuses of the anvil and piston–cylinder types.

In the West, apparatuses of two main types, namely, of the belt type and multianvil type, have been developed (see Fig. 1)

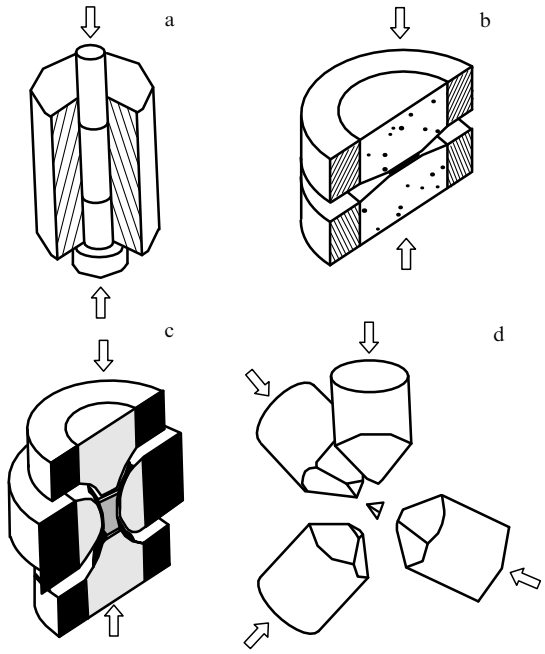

Figure 1. Main types of foreign high-pressure cells: (a) piston–cylinder; (b) Bridgman anvils; (c) belt: and (d) multianvil cell.

[1, 2]. It is using the belt-type cell that artificial diamonds were synthesized for the first time at the General Electric Company. Cells of both types made it possible to reach pressures above 6 GPa (8–10 GPa at present); in the United States, Europe, and Japan they are now the basic apparatuses for synthesizing superhard materials and are employed for physical and geophysical investigations. At present, multistage devices based on the belt-type apparatuses and multianvil cells with the use of elements made of diamond or cubic boron nitride at the final stage make it possible to reach pressures of 20–30 GPa in relatively large volumes (~ 10 mm^3). Apparatuses of the piston–cylinder and Bridgman-anvils types have also diligently been perfected. Thus, the piston–cylinder cell with an all-round support make it possible to achieve pressures to 5–7 GPa in a volume of ~ 10 cm^3 [3]. The creation of cells with anvils made of diamond and the employment of gaskets made of high-strength metals and alloys made it possible to reach pressures as high as 300 GPa; investigations at pressures around 100 GPa are at present routine problems. However, the volumes that can be processed in diamond anvil cells are very small (10^{-6} to 10^{-9} cm^3).

In Russia, cells of the toroid and lentil type have been successfully employed for scientific investigations for more than 40 years; because of their unusual construction, they have not been used for a long time in other countries [4]. The designing of chambers of a large volume for creating pressures exceeding 5 GPa in Russia was based on the idea used in Bridgman anvils.

Work on designing high-pressure apparatuses of large volume at the Institute for High Pressure Physics, Russian Academy of Sciences, (IHPP) were initiated in 1958 in connection with the objective of synthesizing diamond and cubic boron nitride taken on by the institute. When studying the method of Bridgman anvils, the idea arose that the compressed sealing gasket can efficiently work in the case of compression not only by parallel planes but also by diverging surfaces. This makes it possible to construct a high-pressure cell of large volume using the principle of the compressed seal. The approach of the cell elements necessary for compressing a large volume can be provided by creating negative pressure gradients in this volume from the center to the periphery. These ideas were used as the basis for constructing a cell of the lentil type, in which a ring seal with an approximately conical profile of a ring cross section reliably maintains pressure in a lentil-like cavity of the high-pressure cell. After a thorough study of the mechanism of the functioning of the chamber, a construction was designed that permitted one to reliably reach pressures of more than 8 GPa at temperatures of up to 2300 K, which can be maintained for a long time (Fig. 2). In this way, the parameters required for the synthesis of diamond and cubic boron nitride were reached [5, 6]. The creation of a lentil-type cell was in fact a breakthrough into a new range of pressures and temperatures in domestic science and engineering. In 1960 the lentil-type setup was used at the IHPP to synthesize diamond and cubic boron nitride for the first time in the Soviet Union. Cells of this type had working parameters (pressure and temperature) close to those characteristic of the belt-type cell; however, they were much cheaper and much simpler to handle than apparatuses from the West. A powerful diamond industry developed in the Soviet Union and Comecon (Council for Economic Assistance) countries, mainly based on the employment of just this type of high-pressure cell. The lentil-type cell is still used in industry for the synthesis of abrasive powders based on diamond, cubic boron nitride, and composite superhard materials.

Using the lentil-type cell, for the first time in the world combinations of pressures of more than 9 GPa and tempera-

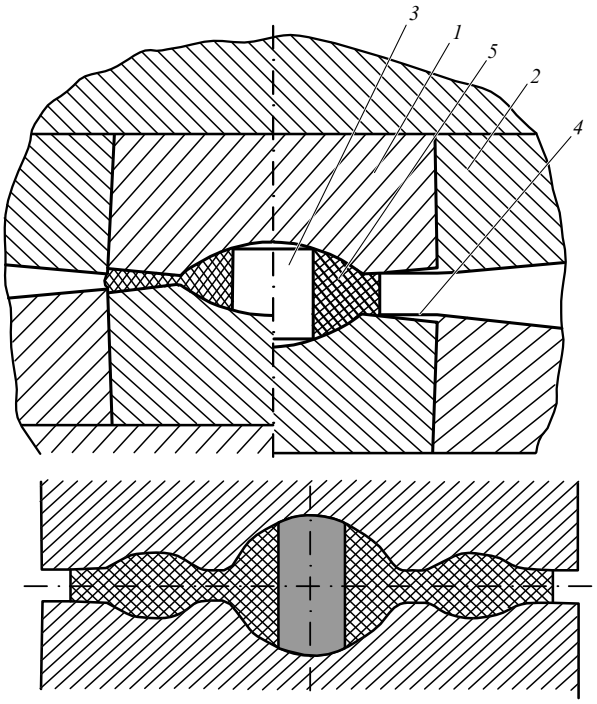

Figure 2. High-pressure cells developed in Russia. At the top, a lentil-type cell: (*1*) punches made of a hard alloy; (*2*) supporting steel rings; (*3*) working volume; (*4*) protruding part of the ring; and (*5*) compressible seal made of a lithographic stone (on the right, the initial position; on the left, the working position). At the bottom, a toroid-type chamber; the parts and the materials are analogous.

tures of 1500 °C necessary for the synthesis of the dense phase of silica (stishovite) in large volumes were obtained [7]. The discovery of stishovite made it possible to obtain a consistent model of the lower mantle of the Earth. The role of phase transitions in the formation of the structure of the Earth and other planets was thus experimentally shown. This discovery is one of the most important contributions to the development of the Earth sciences.

There are a number of designs of the lentil-type cell with different volumes (with the diameters of the hole from 15 to 50 mm). In 1963 the IHPP in cooperation with which industry designed a cell with a record large volume of ~ 200 cm^3 (diameter of the hole ~ 100 mm) and with a high-temperature zone of ~ 60 cm^3 operative at pressures of up to ~ 6 GPa and temperatures of ~ 1900 K (Fig. 3) [8]. The synthesis of abrasive diamonds carried out in this cell gave an output of ~ 24 g per cycle.

The following step in the development of high-pressure devices of large volume was the invention at the IHPP of a cell of the toroid type [9], whose construction is a logical continuation of the idea of the lentil-type cell (see Fig. 2). What distinguishes the toroid-type cell from the previous designs is the presence of a toroidal depression around the central part of the working surface of the punches. The pressure that is generated in the region of toroidal depression fulfills two functions. First, it sharply decreases the extrusion of the central part of the gasket. Even at maximum pressures, the clearance between the anvils remains sufficiently large, permitting the introduction of a large number of measuring wires. On the other hand, the pressure in the toroidal depression reduces the value of shear stress in the punch, which leads to an increase in the ultimate pressures and in the mechanical reserve of the cell. The ultimate pressure in the toroid-type cell (just as in the lentil-type cell) depends on the working volume. The values of the ultimate pressures in the toroid-type cells made from a high-quality hard alloy are given in the table, depending on the diameter of the central hole.

The values given in the table exceed the appropriate pressures accessible in apparatuses of the belt type and in the multianvil cells of comparable working volumes. Recently, a design was developed on the basis of the toroid-15 cell (diameter of the hole ~ 15 mm) with an ultimate pressure of 15–16 GPa in a volume of 0.3 cm^3, which is a record combination of these parameters for single-stage high-pressure cells made of hard alloys [10]. A number of designs employing not only hard alloys but also other high-strength materials have been created. A steel chamber of the top/bottom toroid type with toroidal depressions made in its working surfaces permits producing pressures of up to 7 GPa in volumes of ~ 10 cm^3 and greater [11]. The use of superhard materials makes it possible to reach pressures as high as dozens of GPa in small volumes. Toroid-type (just like lentil-type) cells with the central part made of a synthetic-diamond material of the carbonado type makes it possible to obtain pressures of up to 35 GPa in a volume of 0.1 mm^3 [12]. Pressures of ~ 25 GPa in volumes of 10 mm^3 can be reached with the use of a two-step device on the basis of a toroid-type cell with inserts made of diamond compacts [13]. Apart from the pressure and volume, an important characteristic of a high-pressure cell is the possibility of obtaining maximum information in the course of experiments. In toroid-type cells, the electric leads can easily be introduced into the high-pressure zone and are retained in the working state even after many cycles of pressure rise and relief. The introduction into the toroid-type cell of dozens of wires for measuring physical properties is a routine problem (Fig. 4). The geometry of lentil- and toroid-type cells makes it possible to conduct structural studies by using gaskets which weakly absorb and scatter the incident radiation (e.g., amorphous boron or beryllium for X-ray diffraction studies; Ti–Zr, Ti–Nb, and aluminum alloys or bronzes for neutron-diffraction investigations). The devices that were developed make it possible to study the behavior of solids both in the case of quasi-hydrostatic pressures and under conditions of purely hydrostatic compression (Fig. 5).

Active investigations of the various properties and structure of substances have been performed for more than

Table. Maximum pressure P (GPa) in the toroid-type cells with various diameters d of the central hole (mm).

d	10	15	25	35	50
P	14	12	10	9	7

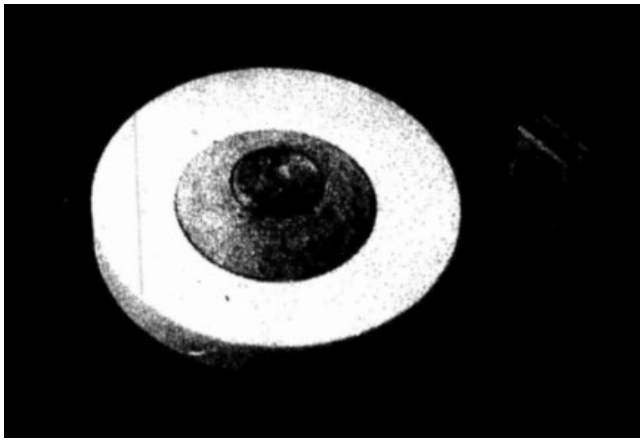

Figure 3. The high-pressure cell of the lentil type with a volume of ~ 200 cm^3.

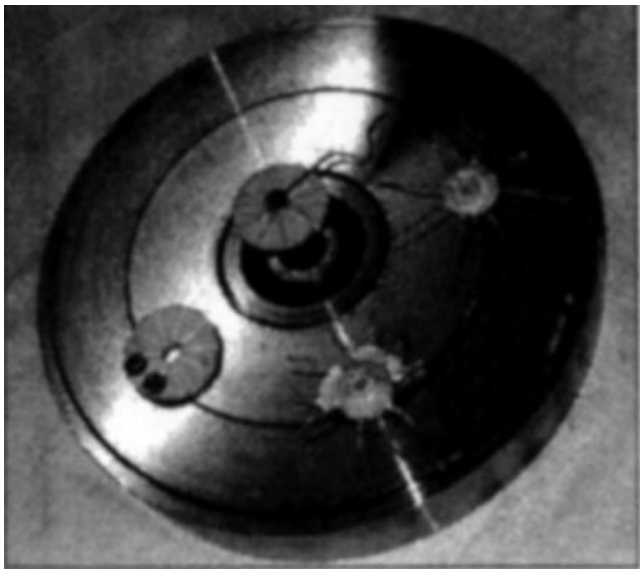

Figure 4. A toroid-type cell with electric leads. Diameter of the central part is 25 mm.

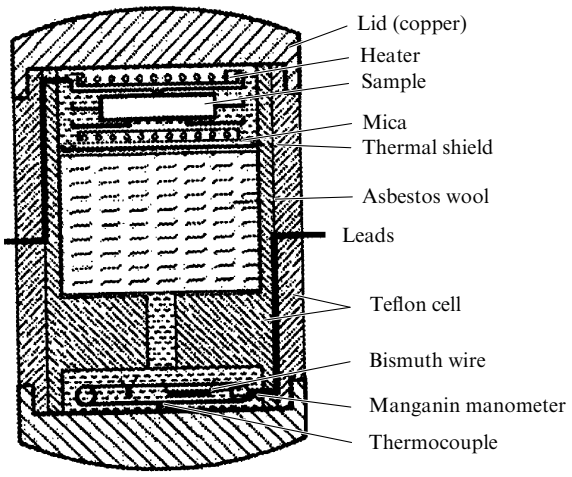

Figure 5. Hydrostatic cell of the toroid-type device.

40 years using these devices in the Soviet Union and Russia in many institutions, e.g., the Institute for High Pressure Physics, Institute of Solid State Physics, Institute of Experimental Mineralogy, Physics Institute of Dagestan Research Center (Russian Academy of Sciences, Russia); Institute of Superhard Materials (Kiev, Ukraine). Because of some specific construction features, the lentil-type cells are suitable predominantly for the synthesis of materials both in the laboratory and in industry, while the majority of electrical measurements and structural studies are performed using cells of the toroid type. Toroid-type cells are also used for high-pressure synthesis of new phases and superhard materials, such as diamonds of the carbonado type and PTNB-type (polycrystalline hard boron nitride) composites.

At the IHPP, various new high-pressure phases in different systems have been synthesized [14 – 16]. For example, new carbon phases based on fullerites and carbines with unique properties have been prepared [17, 18]; new magnetic and superconductive materials [19], as well as semiconducting and superconducting diamonds [20, 21, 37] have been synthesized; a number of large single crystals of high-pressure phases have been grown, such as diamond, Mg_2Sn, Mg_2Ge, and Mg_2Si phases with an incommensurate structure [22], dense phases of silica (coesite [23] and stishovite [24]), and TiO_2 phases [25] (Fig. 6).

In these four decades, numerous physical studies have been carried out using different methods. The elastic properties of hundreds of substances have been investigated by ultrasonic techniques in a wide range of temperatures and pressures [26, 27]. Systematic studies of the elastic properties of substances in the vicinity of phase transitions under pressure made it possible to explain the mechanisms of some polymorphic and isomorphic transformations. Measurements of the linear dimensions of samples using miniature strain gouges allowed conducting unique studies of relaxation phenomena and transformations in powder systems consisting of ultradisperse particles [28, 29] and in glasses and amorphous solids [30, 31] (see Fig. 4). In the last few years, the tensometric technique of measuring the compressibility of substances has been substantially improved and can now be used for measurements at high temperatures [32]. The use of thermal analysis and differential thermal analysis made it possible to carry out a cycle of studies of thermodynamic anomalies at high pressures, including phase transitions

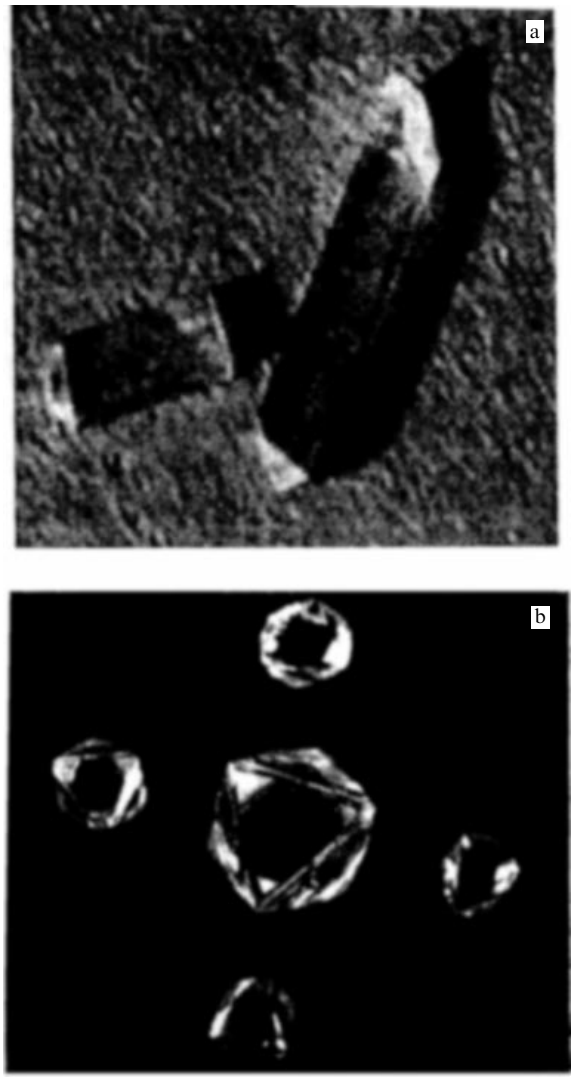

Figure 6. Single crystals of some high-pressure phases synthesized at the IHPP: (a) stishovite, a crystal 3 mm in size; and (b) superconducting diamonds, the central crystal 1.2 mm in size.

between crystalline phases in different classes of materials at high temperatures (to 2000 K) and the melting of substances [33, 34]. The use of thermobaric analysis (TBA) and differential thermal analysis (DTA) together with measurements of electrical resistance made it possible for the first time to study transformations in the melts of elements [35]. Cells with central punches made of Al_2O_3 ceramics supported by rings made of beryllium bronze were used for investigating EPR spectra and magnetic measurements [36]. A wide spectrum of electrophysical investigations under pressure has been performed. Measurements of electrical resistance [40 – 42] (e.g. by the Van der Pauw method [43]), thermal emf [44, 45], Hall resistance [46, 47], and thermal conductivity [48] have been carried out. Studies of transformations under pressure in semiconductors of different classes [49, 50], including compounds with a variable valence [51, 52], have been performed.

Special modifications of miniature cells of the lentil and toroid types were actively used for X-ray diffraction studies [38, 39]. The structures and phase transformations in dozens of substances at pressures of up to 20 GPa in a wide

temperature range have been studied. The miniature cells were widely employed for low-temperature studies, including studying superconductivity under pressure [53, 54]. Active studies of magnetic susceptibility and of magnetic transitions under pressure, as well as of heat capacity (also at low temperatures) were carried out with the use of various types of cells. The miniature cells of the toroid type made of nonmagnetic alloys are at present used for complex studies of quantum phase transitions at ultralow temperatures [55, 56]. Active use of toroid-type cells with anvils made of a hard alloy and diamond composites for neutron research with the use of a neutron source at the Joint Institute for Nuclear Research [57, 58] has begun.

Both at the IHPP and abroad, work on the employment of cells of the lentil and toroid types with the central anvils made of composites on the basis of diamond and cubic boron nitride continue actively, which makes it possible to study the structure and properties of substances in relatively large volumes (several cubic millimeters) in the megabar pressure range.

In the West, high-pressure devices developed in Russia have been in active use in the last 10 – 15 years. The numerous studies carried out in Russia using cells of the toroid and lentil types have demonstrated a number of their advantages over foreign-made devices. In Great Britain, France, the United States, and Japan devices of the toroid type are used to conduct neutron diffraction, X-ray diffraction, and ultrasonic studies. Devices of the toroid and konak (a modification of the lentil type) types are mainly used for the synthesis of new materials.

To conclude, it can be said that cells of the toroid and lentil types give the possibility of conducting structural studies and measurements of various physical properties of substances in the condensed state, and of synthesizing new high-pressure phases in a wide range of pressures and temperatures. They are also very efficient in the industrial production of superhard materials.

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Structural phase transitions in highly compressed substances and the synthesis of high-pressure phases

S V Popova, V V Brazhkin, T I Dyuzheva

This report is devoted to studies of structural phase transformations under pressure that have been performed at the Institute for High Pressure Physics, Russian Academy of Sciences (IHPP). Conditionally, this activity can be subdivided into the study of transformations under pressure in crystals *in situ* (mainly, by X-ray diffraction) and the synthesis of new phases that are metastable at normal pressure. The study of solid-state amorphization and transformations in disordered media (liquids, glasses) under pressure deserves independent examination. Each of these areas has been considered in more than a hundred articles; here, we briefly mention what are, in our opinion, only several of the most important results of such studies.

Pioneering work on the study of the high pressure influence on the crystal structure of substances by X-ray diffraction was performed at the IHPP in 1950–1960 in the group headed by S S Kabalkina with the use of a piston–cylinder apparatus with beryllium windows. The maximum pressures in this cell were 2 GPa, which is insufficient for studying phase transitions in the majority of simple inorganic substances. However, for organic molecular compounds, this pressure range is sufficiently high. At the IHPP, the compressibility and polymorphism of paraffins, urea, and isomorphic hydrocarbons of the group of linear polyphenyls were studied [1]. A noticeable breakthrough in the field of X-ray diffraction studies at high pressures was the creation (in the 1960s) of X-ray diffraction high-pressure devices of the 'chechevitsa' (lentil) type with hard-alloy anvils and the use of amorphous boron as the pressure-transmitting medium transparent to X-rays. These devices made it possible to conduct studies at pressures of 16–18 GPa. In this pressure range, structural phase transitions in many elemental substances and simple compounds have been discovered. Special attention should be given to the discovery and study of structural transformations in Ga, Si, Ge, Sb, Bi, $A^{III}B^{VI}$ compounds (CdS, CdSe, CdTe), MF_2 (M = Mn, Co, Ni, Zn), and Mg_2X (X = Si, Ge, Sn) [1]. The next step in the development of X-ray diffraction studies under pressure was the creation of a high-pressure cell with diamond anvils with the range of working pressures to 50 GPa. Such cells were used to study the polymorphism of transition metal hydrides (TiH_2, ScH_2, ZrH_2) [2–4], phase transitions in $A^{III}B^{VI}$ compounds (TlS, TlSe, InS, InTe) [5, 6], and transformations in metal trifluorides (LaF_3, CeF_3) [7]. As a separate reference, the detection and study of the 'collapse' of compressibility in compounds such as UO_3, ReO_3 [8, 9] deserve mention.

Another approach to the study of phase transitions and polymorphism under pressure *ex situ* consists in the method of quenching high-pressure phases, including new compounds that are metastable under normal conditions. One of the first metastable phases obtained at the IHPP was stishovite — an ultradense phase of silica with a rutile-type structure [10]. The possibility of the existence of structures with a sixfold coordination of silicon atoms relative to oxygen atoms has enormous importance for understanding the internal structure of the Earth and planets. In subsequent years, a large series of works on the study of polymorphism of AX_2 compounds such as fluorides, sulfides, selenides, and tellurides of simple and transition metals was performed at the IHPP [11]. The data obtained confirm conclusions (based on crystallochemical considerations) that during compression there must appear structures in which progressively more dense packings of atoms and molecules are realized with an appropriate increase in the coordination number. It is hardly expedient to analyze the pressure influence on the synthesis of new compounds in binary systems on the basis of the comparison of the coordination numbers of initial components and their compounds. In this case, it is better to use a 'volumetric' factor, since the application of pressure favors alloying reactions proceeding with a decrease in the specific volume. Note that the effects of the so-called 'chemical compression' in the compounds can be very significant. Thus, the extrapolated volume per atom of Si and Ge in binary compounds corresponds to the ultradense modifications of Si and Ge that are stable only at megabar pressures. As interesting examples of new compounds synthesized under pressure, we can mention tungsten germanides and rhenium carbides. In the W–Ge system, no intermediate phases exist at atmospheric pressure, while under a pressure of 8 GPa four metastable phases have been synthesized from a mixture of elements, namely, two phases of W_5Ge_3 composition and two phases of WGe_2 composition [12]. In the Re–C system at normal pressure, no intermediate phases are present either, while at 4 GPa an ReC phase with a hexagonal structure of the γ'-MoC type is formed from a mixture of elements upon heating, and at pressures of more than 10 GPa, a superhard ReC phase with a cubic structure of the NaCl type is crystallized [13, 14]. Some interesting results were obtained when studying polymorphism of hydroxyl-containing compounds using the example of systems such as $M_2O_3-H_2O$ (M = Fe, Al, Sc, La) [15]. Depending on the P, T conditions of synthesis, the compounds $MO(OH)$ and $M(OH)_3$ with different structures were obtained [15]. These results are extremely important for the solution to the problem of the existence of bound water in the Earth's mantle. For MF_3 compounds (M = Sc, La, Y), the following sequence of structural transformations has been established: ReO_3 type $\rightarrow$ YF_3 type $\rightarrow$ LaF_3 type [15]. In this case, the first type of transformation in the trifluorides (ReO_3 type $\rightarrow$ YF_3 type) is accompanied by a record change in the specific volume ($\sim$ 53%).

Some groups of substances synthesized at high pressures should be considered separately. This refers, for example, to new superconductors synthesized under pressure. Thus, in the 1970s at the IHPP the compound Nb_3Ge was for the first time synthesized under pressure in the bulk with a record temperature (for that time) of the superconducting transition $T_c = 22.3$ K [16]. Using high pressures, it was possible to synthesize a series of new superconductive sesquicarbides of rare-earth elements [17]. Many high-pressure modifications have not only sufficiently high T_c, but also high values of critical magnetic fields and currents [17, 18]. It is sufficient to mention the synthesis of a metastable superconductive ($T_c = 10$ K) high-pressure phase of TaN with a cubic structure of the NaCl type [18]. Note that the bulk single-phase samples of the high-temperature superconductor $HgBa_2Ca_2Cu_3O_{10}$ with a record high critical temperature ($T_c = 132$ K at normal pressure) also was synthesized under

pressure by researchers at Moscow State University and the Institute for High Pressure Physics, Russian Academy of Sciences [19]. A veritable development in the physics of superconductors and the physics of condensed matter as a whole was the high-pressure synthesis of superconductive diamond doped by boron [20]. The exceptional mechanical and thermal properties of diamond, together with sufficiently high values of $T_c \sim 7$ K and upper critical fields of ~ 5 T, make superconductive diamond one of the most promising materials for future electronics.

The study of carbon materials bears special mention. At the IHPP, during the entire 50-year period of its existence comprehensive studies of the graphite – diamond transition have been carried out. In recent years at the IHPP pressure-induced phase transitions have been actively investigated for new metastable carbon modifications — C_{60} fullerites and carbines [21]. During the transformation into the stable phases of carbon (graphite and diamond), these carbon states undergo a number of transformations into carbon forms that are intermediate in energy. Thus, C_{60} fullerite undergoes one-, two-, and three-dimensional polymerization of C_{60} molecules at high pressures and temperatures; with a further increase in pressure and (or) temperature, the fullerites are transformed into bulk amorphous states [22]. A number of carbon modifications obtained from fullerites possess unique mechanical properties [23]. A P, T treatment of carbines leads to the synthesis of metastable amorphous phases of carbon with interesting electron-transport properties [24].

In the case of polycrystalline samples of the new materials obtained using high pressures, it is frequently impossible to solve the crystal structure and perform a detailed study of physical properties. In this connection, an especially urgent problem is growing large single crystals of high-pressure phases that are metastable under normal conditions. In recent years, interesting results have been obtained at the IHPP in this field. In particular, large single crystals (several mm in size) of high-pressure phases of silica (coesite and stishovite), TiO_2, FeO(OH), etc. have been grown [25, 26]. In growing single crystals, the need to correctly determine crystal structure manifested itself vividly when studying high-pressure phases of Mg_2X (X = Sn, Ge, Si). It turned out that these modifications crystallize into structures with incommensurate crystal lattices, which, certainly, could not be established from the powder-diffraction data [27].

The term 'structural transformations' is traditionally related to crystalline substances. However, at a high pressure, as was shown in a whole series of experimental works performed at the IHPP, changes in the short-range-order structure in melts and glasses can occur not only gradually, in a wide P, T range, but also sufficiently sharply. In this case, a change in the short-range-order structure is accompanied by 'jumps' in the volume and physical properties, similar to the case of first-order transitions in crystals. Such transitions were found both in elemental melts (sulfur, selenium, iodine [28]) and in the melts of binary compounds (for example, As_4S_4 [29]).

The high pressure influence on the structure of a material has one additional aspect: compression can lead to a disordering of the crystal structure. This phenomenon, known as solid-state amorphization, has been investigated in a series of works performed at the IHPP, which made it possible to establish the main laws governing this process. The investigation of the solid-state amorphization of stishovite upon heating made it possible to study the kinetics of this process; in particular, it was found that the activation energy of the amorphization process is low in comparison with the activation energy of diffusion [30]. These results, together with the discovered softening of the shear modulus upon solid-state amorphization of the ices of H_2O and D_2O [31], made it possible to construct a model of solid-state amorphization. Note that the solid-state amorphization of high-pressure phases is the only process which enables producing bulk samples of amorphous tetrahedral semiconductors on the basis of Si and Ge, and $A^{III}B^{V}$ compounds [32].

The investigation of phase transformations in glasses (SiO_2, GeO_2, B_2O_3) [33] made it possible to establish that these transformations can occur in a wide range of pressures and temperatures and are characterized by an unusual logarithmic kinetics of transitions [34]. At present, at the institute work on the study of the structure of short-range order and the physical properties of melts under pressure actively continues [35]. The detection of specific transformations in glasses and melts once again demonstrated the generality of the phenomenon of structural phase transitions in condensed matter upon compression.

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Studies of the thermodynamic, elastic, superconducting, and magnetic properties of substances at high pressures

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In this work, we briefly describe experimental methods developed at the Institute for High Pressure Physics, Russian Academy of Sciences (IHPP), and some experimental results obtained.

1. Method of pulse-adiabatic modulation of pressure

The first measurements of the temperature response of a system upon an adiabatic change in pressure were performed, apparently, by Joule [1]. However, systematic studies using this method were renewed only more than 100 years later [2–9], which can be explained by the complexity of such experiments when using inertial measuring devices. An isentropic compression can be realized using modernized high-pressure equipment intended for the creation of static pressures. However, the realization of this process for the interval of pressures above 100 MPa is difficult, since it is connected with the application/relief of a relatively large force in a period of time which is subject to a number of restrictions, such as the shockless character of compression on the one hand, and the absence of heat transfer on the other hand (hydrostaticity and the constancy of entropy, $S = \text{const}$). In addition, it is also necessary to take into account stress relaxation in the elements of the high-pressure equipment. One alternative is the modulation method — measurement of the derivative $(\partial T/\partial P)_S$. In this case, the necessary conditions can be ensured comparatively easily, although, to the detriment of informativeness, in the presence of a first-order transition, the small amplitude of pressure modulation can prove to be insufficient to change the concentration of phases from 0 to 1. Among the diverse constructions of high-pressure apparatuses, it is apparently only the apparatus of the piston–cylinder type that makes it possible to control pressure, although even in this case there remain limitations caused by friction in the piston sealing. At the IHPP, a low-inertial version of controlling force was used. The front of the loading pulse at a low pressure does not exceed 10 ms. The static force is transferred to the piston through a spring, and the additional force for the modulation of pressure is applied directly to the piston [5]. The device makes it possible to record the temperature response of a sample upon a sharp change in pressure by about ± 50 MPa. The maximum pressure is 3 GPa; the permissible range of temperatures is 273–700 K. The pressure-transmitting medium is liquid. The criterion of adiabaticity is the presence of a cutoff in the $\Delta T(t)$ curve.

When calculating thermodynamic functions from the results of adiabatic experiments, it is assumed that the system is in an equilibrium state and that the characteristic times of the relaxation processes, such as the diffusion mechanism of the formation of point defects (vacancies, interstitial atoms) is less than the time of measurement. Obviously, in this case the following condition must be satisfied:

$$\left(\frac{\partial T}{\partial P}\right)_{S,\Delta P>0} = \left(\frac{\partial T}{\partial P}\right)_{S,\Delta P<0}.$$

Formally, the problem reduces to the solution of the differential equation

$$\left(\frac{\partial T}{\partial P}\right)_S = J_S(T,P)\,,$$

where $J_S(T,P)$ is an analytical function which describes the results of measurements. The sought adiabatic curve $T_S(T_0,P)$ for the initial (at $P=0$) temperature $T=T_0$ is found as a result of solving this equation, which can be performed numerically. Given a set of adiabatic curves and boundary conditions, for example, the temperature dependence of entropy at normal pressure $S(T,0)$, we can easily calculate the $T-P$ dependence of such quantities as the entropy S, heat capacity C_P, and thermal expansion $(\partial V/\partial T)_P$. If in addition to these data we know the pressure dependence of volume at a certain temperature T_r, we can calculate the equation of state:

$$V(T,P) = V(T_\mathrm{r},P) + \int_{T_\mathrm{r}}^{T} \frac{J_S(T,P)\,C_P(T,P)}{T}\,\mathrm{d}T.$$

If C_V is a function of (T/Θ) and if Θ depends only on volume, the ratio (T/Θ) and, consequently, C_V are also constant at the adiabatic curve. In this case, given $J_S(T_S,P)$, we can easily calculate the pressure dependence of the characteristic temperature Θ.

Figure 1 displays the results of measurements for Li, Na, and K. As is seen, the values of the derivative $(\partial T/\partial P)_S$ in the mixed state (i.e., in the mixture of solid and liquid phases) approach the appropriate derivative of the melting curve $\mathrm{d}T/\mathrm{d}P$. The relationship between the values of $(\partial T/\partial P)_S$ and the slope of the melting curve $\mathrm{d}T/\mathrm{d}P$ makes it possible to draw the conclusion that the adiabatic compression must lead to the crystallization of liquid sodium and to the melting of solid lithium.

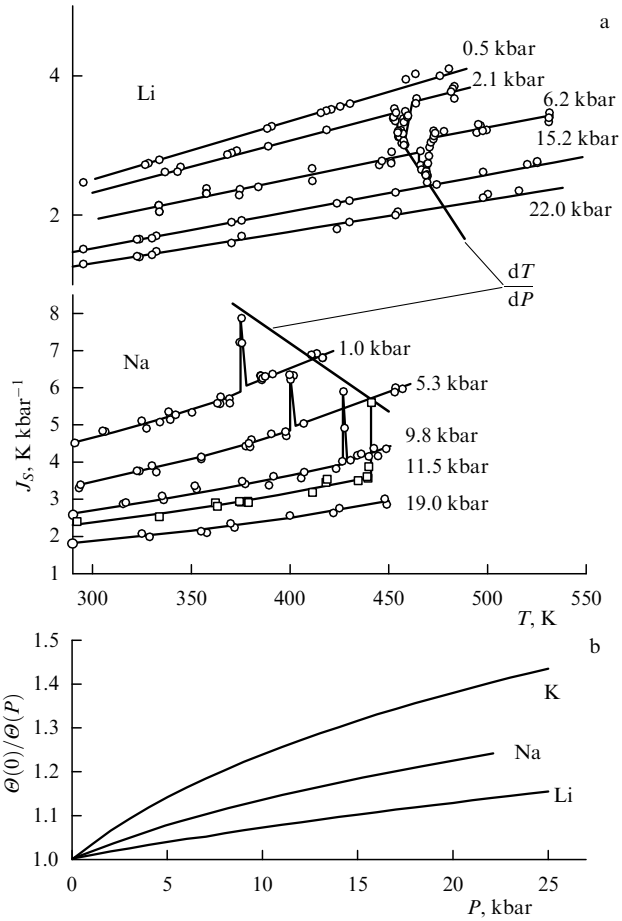

Figure 1. (a) Temperature dependence $J_S = (\partial T/\partial P)_S$ for lithium and sodium at various pressures. (b) Pressure dependence of the characteristic temperature Θ for Li, Na, and K.

2. Elastic properties of solids at high pressures

An ultrasonic method developed and used at the IHPP makes it possible to continuously observe changes in the state of a substance under different thermodynamic conditions and to obtain pressure and temperature dependences of elastic characteristics, which gives information for constructing phase diagrams. It should be noted that ultrasound is also successfully used for testing new substances synthesized at the IHPP, which makes it possible to improve the technological process of their preparation.

The development of a modification of the toroid-type cell with a catlinite container as the high-pressure device suitable for ultrasonic investigations (Fig. 2) (toroid with a flat bottom) made it possible to conduct studies at pressures of up to 9 GPa at room temperature using various samples, including single crystals [10, 11]. The pressure in each experiment was determined from the jumps in electrical resistance at phase transitions in reference metals Bi, Tl, and Ba. Quartz plates with a carrier frequency of 5 and 10 MHz were used as piezoelectric gages. With the use of this cell, a large class of substances, such as alkali metals, single crystals of semiconductors, alkaline halides, $A^{III}B^{V}$ compounds, etc. have been studied [12–17]. Let us note a number of the most interesting results.

For the first time, a softening of longitudinal acoustic modes of the phonon spectrum of cerium upon the electronic

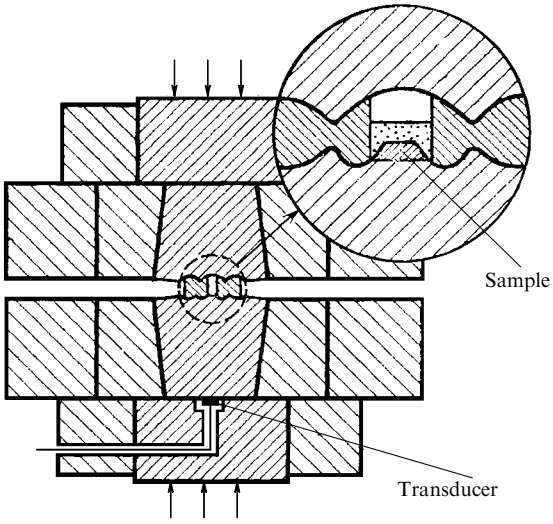

Figure 2. Modified toroid-type device for ultrasonic investigations.

isostructural $\gamma-\alpha$ transition (at 0.75 GPa) was discovered; at the same time, upon the structural $\alpha-\alpha'$ transition (at 5.1 GPa) a softening of the transverse acoustic modes of cerium was observed [12]. The softening of acoustic modes in the phonon spectrum of γ and α cerium explains, in accordance with the ideas of Lindemann, the specific features of the phase diagram of cerium, in particular, the negative slope of the melting curve.

For the first time, elastic characteristics of cesium at pressures of up to 5.0 GPa have been determined [16] and anomalies in the elastic properties upon CsI–CsII–CsIII–CsIV transitions have been revealed. The compression of cesium at high pressures leads to a considerable decrease in volume ($\sim 50\%$ at 5 GPa) and to a number of interesting phenomena connected with changes in its crystal and electronic structures. The appearance of a soft shear mode in the phonon spectrum of cesium in the pretransition region of the CsI (bcc)–CsII (fcc) transition has been observed. A number of anomalies in the pressure dependences of the bulk modulus, shear modulus, and their derivatives with respect to pressure and lattice parameter have been revealed at $P > 1.4$ GPa, which indicates a change in the nature of conduction electrons (s–d transition) and confirms the known theoretical calculations. It has been established that the CsII–CsIII electronic–structural transformation is preceded by the appearance of an anomalous compressibility of the fcc phase and by a softening of the longitudinal and transverse acoustic modes of the phonon spectrum of cesium.

The following step in the modernization of the ultrasonic technique was the extension of the temperature range of measurements. There was developed a low-temperature ultrasonic piezometer capable of operating in the range of pressures of 0–3 GPa and temperatures of 77–360 K, which, to the best of our knowledge, remains unique up to now [18]. The pressure and temperature dependences of the velocities of longitudinal and transverse ultrasonic waves are determined with the aid of an Akustomer-1 device, which was also developed at our institute. The accuracy of measurements of the time of propagation is 0.001 μs, and of the path of propagation, 0.005 mm. The cryogenic temperatures are obtained using liquid nitrogen or its vapors. The temperature is determined with the aid of copper–constantan thermocouples to an accuracy of ± 1 K.

Later, this setup was used to study the elastic properties of ices (H_2O and D_2O), metallic gallium, and polycrystalline fullerite at high pressures and various temperatures, as well as a number of other substances. To exemplify, we consider the investigations of ice and gallium.

The ice of conventional water H_2O is characterized by a very complex phase diagram; it contains no fewer than 12 crystalline and a number of amorphous modifications. On the basis of our experimental data, for the first time an experimental confirmation of the mechanical instability of the crystal lattice of ice upon solid-state amorphization under pressure was obtained, and the phase diagram of ice was substantially updated; isotopic effects in the temperature dependences of the elastic properties (bulk modulus) of H_2O and D_2O were revealed [19, 20].

The investigation of gallium, which is a rare example of a substance with the coexistence of the covalent and metallic types of bonding in one phase (GaI), revealed an unusually high value of the derivative of the bulk modulus with respect to pressure and an increase in the Poisson ratio with pressure, which we explain by a weakening of covalence of GaI upon compression. The ultrasonic studies also discovered an uncommon behavior of elastic moduli during the GaI – GaII phase transformation. The strong decrease in the bulk modulus (30%) and in the shear modulus (55%), as well as the increase in the Poisson ratio from the 'covalent' (≈ 0.22) to 'metallic' (≈ 0.32) value, indicate the disappearance of covalence and the transformation of Ga into a usual metal (Fig. 3) [21].

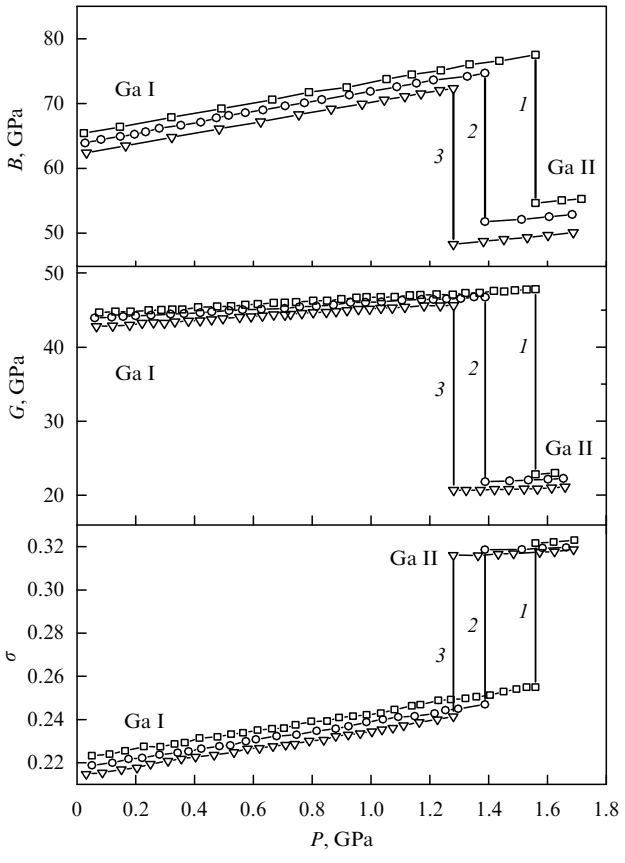

Figure 3. Pressure dependences of the bulk modulus B, shear modulus G, and Poisson coefficient σ for gallium at various temperatures: (*1*) $T = 247$ K, (*2*) $T = 259.5$ K, and (*3*) $T = 268$ K.

3. Registration of superconductivity in diamond anvil cells by the method of laser modulation of the sample temperature

To register superconductivity, a modulation method is used consisting in the separation of the background signal from the signal from the superconductive sample. This method is based on the periodic destruction of the superconducting state of the sample near the superconducting transition, which leads to an amplitude low-frequency modulation of the high-frequency signal (10 kHz) achieved by a weak periodic heating of the sample by laser radiation which is modulated in amplitude at a low frequency (25 Hz) and is focused on the sample.

The registration of the signal is carried out as follows. The high-frequency output signal from a system of induction coils located in the high-pressure cell is applied to a compensating block to decrease the background component, then to a high-frequency amplifier (10 kHz) and a synchronous detector, where the low-frequency component of the signal (25 Hz) is separated. The low-frequency signal is applied to an amplifier and then to a low-frequency synchronous detector for the separation of the constant component that arrives at the computer for the accumulation and processing of the data. When using this method, the superconducting transition is seen as a peak in the temperature dependence of the amplitude of the low-frequency signal.

The experimental results for the sample of $YBa_2Cu_3O_{7-x}$ are displayed in Fig. 4. The two peaks shown correspond to atmospheric pressure and a pressure of 4.3 GPa. The temperature of the superconducting transition was determined from the position of the maximum of the peak. The superconducting transition temperature T_c was 80.8 K at atmospheric pressure and 94.8 K at a pressure of 4.3 GPa. This change in the temperature of the superconducting transition with pressure corresponds to a pressure coefficient equal to 3.3 K GPa^{-1}, which agrees with the literature data [22].

4. Setup for the investigation of the Mössbauer effect under pressure at low temperatures

In certain cases, for example, when studying the pressure influence on a magnetic field in atomic nuclei, a decrease in the temperature of the substance investigated can be

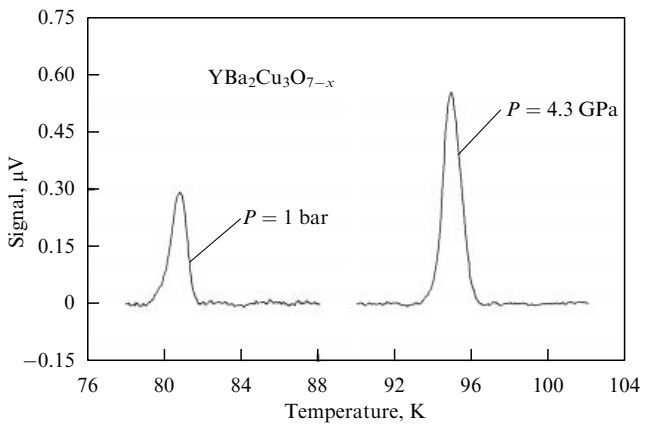

Figure 4. Superconducting transitions in the superconductor $YBa_2Cu_3O_{7-x}$ registered by the method of laser modulation of the temperature of the sample under investigation.

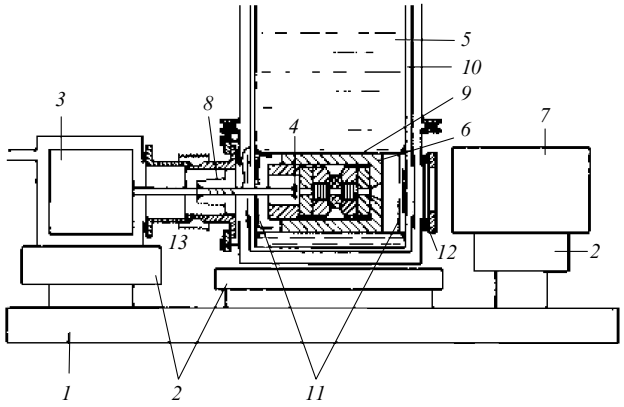

Figure 5. Low-temperature Mössbauer spectrometer for investigations in a diamond cell (schematic).

important. The main parts of the setup (Fig. 5) are the vibrator *3*, which ensures the Doppler scanning of the energy of the γ-rays source *4*, cryostat *5*, high-pressure cell *6*, and a detector of γ radiation *7*. Cell *6* ensures the adjustment of the mutual arrangement of the diamond anvils and the fixation of the force applied to them. The radiation from source *4* passes through the anvils along their axis. The diamond anvils (with their overall thickness of 4 mm) transmit $\sim 80\%$ of the incident γ radiation of the isotope ^{119m}Sn with a quantum energy of 23.8 keV. If the diameter of the working area of the diamond anvils is ~ 0.3 mm, then the metallic gasket between the anvils, which is made from W or Re and plays the role of a collimator, has a thickness of 0.03 mm. The diameter of the gasket hole is ~ 0.1 mm. The two diamond anvils and the gasket form the walls of the high-pressure cell, while the gasket hole represents the working volume. In the working volume, there is placed a layer of the substance to be investigated and a ruby grain ~ 10 μm in size for measuring pressure from the shift of the R_1 ruby luminescence line [23]. For transmitting pressure to the sample, the working volume can be filled with, for example, a polyethylsiloxane liquid PES-5. The ruby luminescence lines R_1 and R_2 remain resolved up to 80 GPa. A good resolution of the R_1 and R_2 lines does not mean, however, the ideal hydrostaticity of pressure, since the pressures in the center of the working volume and near its walls differ by $\sim 10\%$. For work at reasonable exposures (usually no less than 7 days), it is necessary to use sources *4* with a high intensity and absorbers enriched by Mössbauer isotopes. The oscillating source *4* must be located in the immediate proximity to the base of the diamond anvil for guaranteeing a large solid angle in which the γ radiation propagates. Cell *6* is cooled in a cryostat. Into the lower part of the vessel for liquid helium a copper tube *9* is soldered. Cell *6*, whose lateral surface is greased with a vacuum grease to improve heat exchange, is placed in the tube *9*. At the butt ends of the tube *9* copper shields *11* with openings are mounted. One of the shields is soldered to tube *9* by a low-melting solder; the second shield is detachable. The openings in shields *11* and in the 'nitrogen skirt' of the cryostat were sealed up with a piece of thin aluminum foil. The construction does not contain cooled vacuum-tight windows for the passage of γ radiation, which significantly increases the vacuum tightness of the cryostat. The oscillating source *4* is located in the vacuum space of the cryostat. The regions of high vacuum (location of the heat insulation of the cryostat) and rough vacuum (location of oscillator *3*) are connected by a soft sylphon bellows. Flange *13* is sealed after the adjustment of source *4* relative to the cell *6*. In this case the position of source *4* relative to cell *6* does not change. Source *4* during adjustment must be arranged so as to allow for the decrease in the length of the helium vessel while filling it with liquid helium or nitrogen; i.e., at room temperature source *4* is arranged higher than in the working state by ~ 2 mm. Thus, to perform the experiment it is necessary to create a desired pressure, place cell *6* into the cryostat, adjust source *4* and the sealing of flange *13*, and pump out the cryostat. The precooling of the cryostat and of cell *6* with liquid nitrogen continues no less than 24 h, since cell *6* is cooled through a vacuum gap. The volume of the vessel with liquid helium is 3 l. The evaporation of helium continues 3 days. At prolonged exposures, helium is added to the vessel. The temperature of cell *6* after pouring liquid helium and cooling is 4.5 K. Lower temperatures (to 2.5 K) can be obtained by pumping out helium vapors. The high-stable motion of the source and the data acquisition was ensured using special electronic devices operating according to the Kankeleit scheme [24].

5. Setup for measuring the density and kinetic properties of condensed gases

The setup makes it possible to mix gases and liquids in assigned proportions and to measure the temperature and pressure dependences of density, viscosity, thermal conductivity, and electrical conductivity. The permissible ranges of pressures and temperatures are 0 – 150 MPa and 0 – 150 °C.

The main problems that are encountered upon determining the equation of state of gases are their large compressibility and the possibility of an uncontrollable leakage through sliding seals. In our work, this problem is solved with the aid of a membrane separator and controlling volume in that part of the membrane separator (liquid) that is connected with the high-pressure pump (Fig. 6). In this case, upon release of the substance under investigation into the membrane separator the increase in the volume can be determined from the quantity of liquid extruded from the separator. The estima-

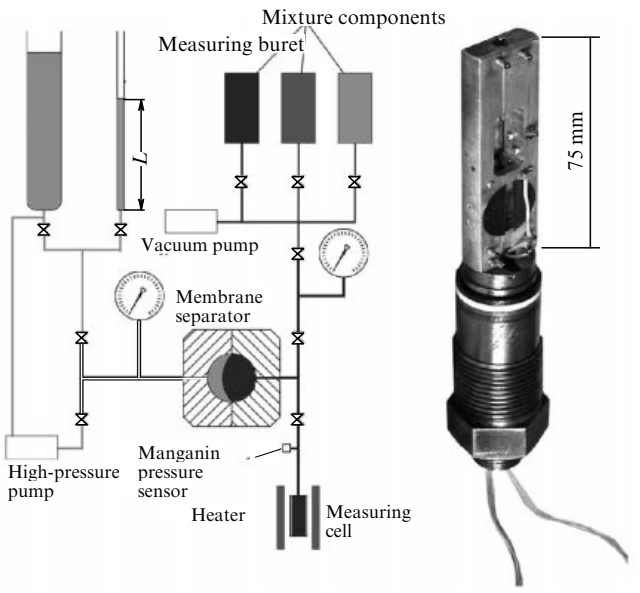

Figure 6. Setup for the determination of the equation of state and kinetic properties of condensed gases (schematic).

tion of the volume during pressure relief is preferable to that during pumping, since during pumping there is possible a leakage of the working fluid through the sealing of the stock of the pump.

For measuring pressure, a manganin sensor is used or, to be more precise, four pieces of a wire connected into a bridge circuit located in the same housing in the 'cold' zone, outside the heater. Two elements of the bridge (located along the diagonal) are placed in the high pressure; zone two others, in the normal pressure zone. This variant of the connection makes it possible to increase the sensitivity by a factor of two in comparison with a single manganin sensor in the high pressure zone and to considerably decrease the temperature dependence, since all the elements of the bridge are located at one and the same temperature.

The presence of a pump and a membrane separator makes it possible to prepare a mixture of a given concentration in the measuring cell. In the filling process, the pressure in the cell grows to the maximum value (at room temperature). Preliminarily, the pressure dependence of the volume of the displaced liquid during pressure relief with an unfilled measuring cell $L_0(P)$ is recorded for the selected working fluid. The registration of the same dependence with a filled measuring cell $L_1(P)$ makes it possible to determine the volume occupied by the substance under investigation, depending on pressure, i.e., to find the function $\rho(T_0, P)$. For determining the equation of state of a mixture $\rho(T, P)$, the data on the isothermal compressibility at room temperature are supplemented by the results of measurements of the temperature dependence of pressure during the warming-up of the measuring cell under isochoric conditions at different initial pressures.

In the measuring cell, there are sensors for measuring viscosity, thermal conductivity, and electrical conductivity. For measuring viscosity, the vibration viscosimeter method, i.e., the registration of frequency and damping of free vibrations of a rod after impact excitation, is used. The impact excitation is performed by applying a rectangular current pulse to one of two electromagnets. The recorded signal is proportional to the angle of deflection of the rod. For thermal-conductivity measurements, the method of a heated wire is used. The electrical conductivity is determined based on the current between two plates to which a voltage is applied.

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Quantum transport at high pressures

E M Dizhur, V A Venttsel, A N Voronovskii

Unlike other areas of condensed state physics — which can be classified according to the objects of their study (for example, the physics of semiconductors) or according to the nature of the phenomena studied (magnetism) — what unifies high pressure physics is the common investigation method, the use of high pressure to study the physical properties of various objects.

Measurements of the pressure dependence of electron transport as a means to probe physical models of condensed state were started at the Laboratory of Electric and Galvanomagnetic Phenomena headed by A I Likhter, which has been part of the Institute for High Pressure Physics, RAS (IHPP) since the very foundation of the institute in 1958.

Coincident with the foundation of the institute was a spurt in the study of electron energy spectra in metals. It was during that time that the school of I M Lifshitz came to prominence with its advances in solid state theory and it was then that Fermi surfaces (FSs) of normal metals started to be extensively studied. The application of high pressure to these studies was pioneered by IHPP scientists as early as 1963, in a work [1] that provided experimental data on the resistivity, the Hall constant, and the magnetoresistivity of graphite under a pressure of up to 1 GPa at temperatures from room temperature to 450 K. By comparing the experimental data with the analytical expressions for the galvanomagnetic properties of graphite, it proved possible to separate lattice-related effects (relaxation time) from those related to conduction electrons and to refine the energy spectrum parameters underlying the theoretical model used.

In the next major development, E S Itskevich and his Oscillation Phenomena Group (later to become the Laboratory of Quasiparticle Energy Spectra) succeeded in observing a change in the behavior of magnetoresistance in cadmium that confirmed the earlier prediction of a change in the FS topology [2]. Later, in Ref. [3], a direct measurement of the de Haas – van Alphen effect under a pressure of up to 2 GPa revealed the emergence of a new FS cross section in cadmium [3].

Zinc and cadmium have very similar electronic properties. In fact, from this viewpoint they are only different in the value

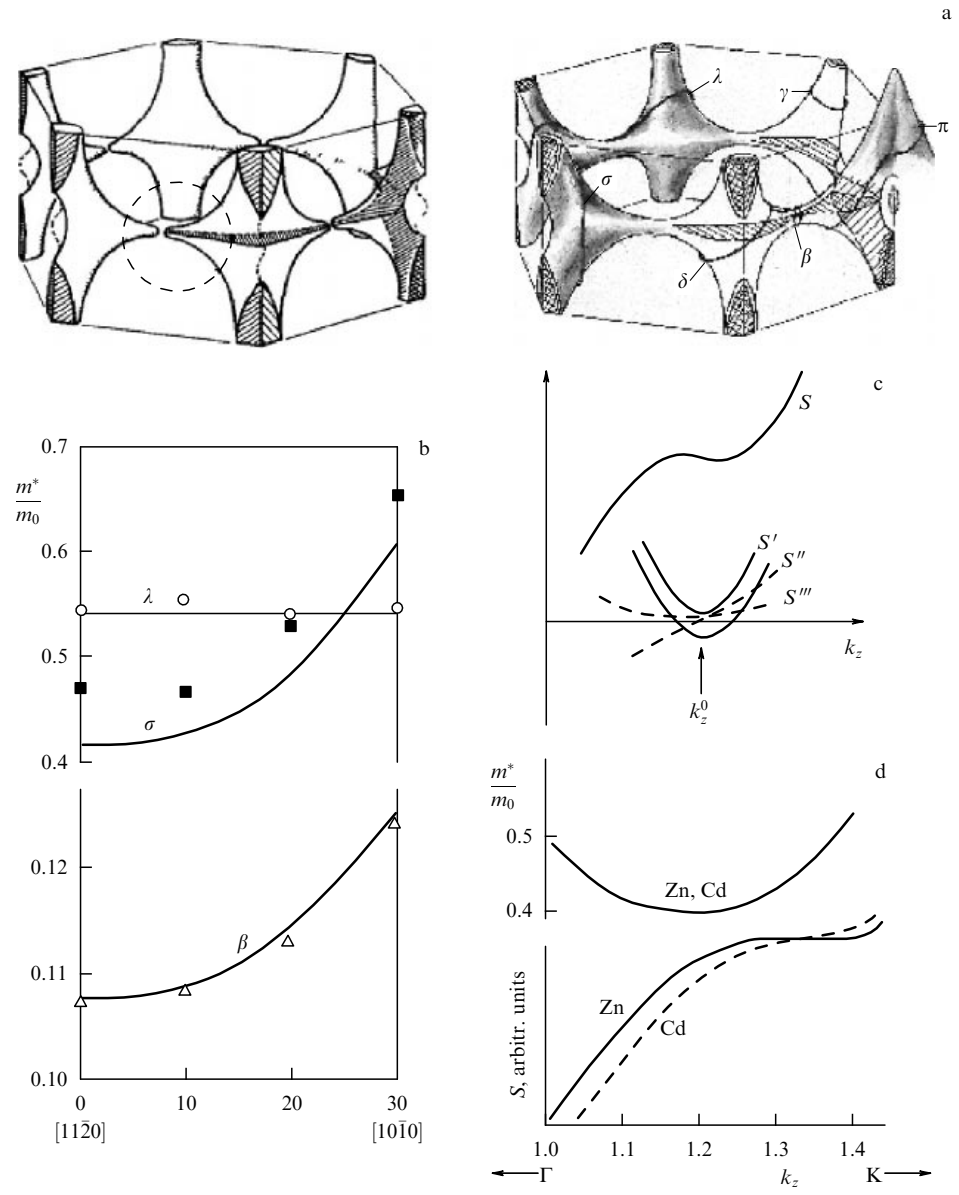

Figure 1. (a) Fermi surface of cadmium (left) and zinc (right) at normal pressure. When under pressure, the cadmium FS acquires a neck (in the circled region). (b) Comparison of de Haas – van Alphen (symbols) versus cyclotron resonance (solid lines) effective masses for various portions of FS. (c) Special section $S(k_z)$ and its derivatives. (d) Special sections and their effective masses.

of the axis ratio c/a. As cadmium is compressed, its c/a ratio approaches that of zinc, for which reason it was quite appropriate to study the properties of both. The nearly free electron models of zinc and cadmium Fermi surfaces are very realistic. Magnetic breakdown experienced by narrow energy gaps in the spectra of these metals lead to a very complex picture of FS cross sections as a function of the orientation and magnitude of an applied magnetic field. Band structure calculations show that using the nonlocal approximation and taking into account the influence of the d band results in the disappearance in the third and fourth zones of very large electron portions of the Fermi surface near the L-point of the Brillouin zone. To obtain a correct band structure, systematic studies were performed at normal and high pressures. The fundamental question of whether electron portions of the FS do or do not exist near the L-point was resolved in the negative (thus strengthening the nonlocal model) by simply analyzing the sign and magnitude of the baric coefficients of the FS that could be identified with the oscillation frequencies observed.

Direct information about the FS shape and how it deforms with pressure can be obtained from oscillation phenomena. The development of techniques for de Haas – van Alphen effect measurements in pulsed and stationary magnetic fields under hydrostatic pressure [4] has made it possible to measure, under true hydrostatic conditions, the shift in the oscillation phase, a quantity directly related to the baric coefficient of the FS cross section area $\mathrm{d}\ln S/\mathrm{d}P$. Precision measurements showed that the effective mass m^* corresponding to the new pressure-produced FS cross section in Cd differs markedly from the cyclotron resonance value of m^* [5]. It was assumed that this new cross section was analogous to the σ section of the zinc 'monster' (Fig. 1). A detailed analysis performed for zinc showed that the effective

mass for any other cross section does not depend on the measurement method used, whereas that for σ does.

Analysis of all the related phenomena led to the conclusion that the cross section σ of the monster is a *special section* of the Fermi surface. A theory of the de Haas – van Alphen effect developed for special cross sections [6] showed that for such a section the first derivative of the section area S at quasimomentum $p_z = p_z^0$ is nonzero (the section is not extremal), but the second derivative vanishes. For this special section, major changes occur in the Lifshitz – Kosevich expression for the oscillating magnetic moment — in particular in the form of an oscillating Airy function term,

$$\mathrm{Ai}\left[\left(\frac{nc}{e\hbar H}\right)^{2/3}\left(\frac{2}{S'''}\right)^{1/3}S'\right],$$

where n is the electron density, e is the electron charge, $\hbar$ is the Planck constant, c is the speed of light, H is the magnetic field, and S' (S''') is the first (third) derivative of the section area. If the argument is positive, the Airy function falls off exponentially, and if the argument is negative it oscillates, i.e., its behavior is determined by the sign of the product $S'''S'$. In zinc this sign is negative, and the σ section is well observed and demonstrates a nonmonotonic magnetic field dependence of the oscillation amplitude. In cadmium, where under normal conditions $S'''S' > 0$, the applied pressure deforms the monster and makes $S'''S'$ negative. Calculations show that the effective mass is extremal at quasimomenta other than those producing the special section. The reason for this is that, whereas the de Haas – van Alphen mass is associated with the special section, that observed in the cyclotron resonance is the extremal effective mass. That is why the two masses are markedly different (see Fig. 1).

A transition due to a change in the FS topology can be called an electron phase transition of order 2.5, and the appearance at this transition of a new branch in the electron density of states results in all kinetic phenomena starting to show some special features in their behavior. In investigating these phenomena, one of the most sensitive and relatively simple methods has proved to be thermal-EMF measurements under pressure, an approach in which various types of transitions can be distinguished. By measuring the temperature dependences of the longitudinal and transverse thermal EMF of cadmium in the 4 to 300 K temperature range under a pressure of up to 3 GPa [7], it was found that for $P < 1.2$ GPa

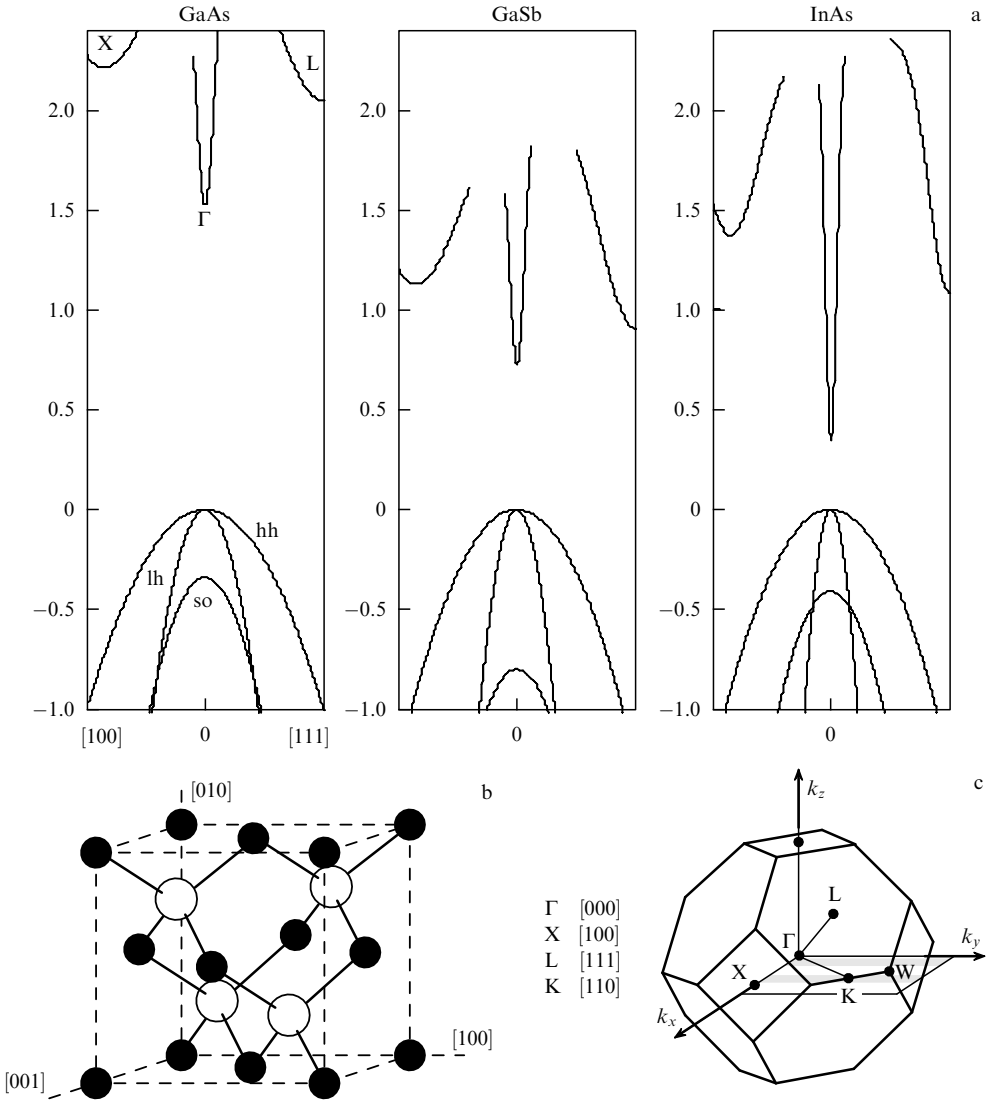

Figure 2. (a) Pressure effect on the band structure of some $A^{\mathrm{III}}B^{\mathrm{V}}$ compounds; lh (hh) is the light (heavy) hole band, so is the spin-orbit split band. (b) GaAs unit cell: ●, Ga; ○, As. (c) High-symmetry points in the first Brillouin zone.

the two curves are more or less similar, but for $P > 2$ GPa the transverse thermal EMF curve shows a positive sign anomaly. An important observation was a positive spike in the thermal EMF due to the order 2.5 transition — i.e., due to the appearance of a hole neck.

Studies of order 2.5 phase transitions have not only proved their existence but also have greatly expanded the arsenal of measurement tools suitable for high pressure conditions — expanding, in turn, the scope of studies and promoting high pressures as an instrumental means to address problems of topical interest in solid state physics. These methodological developments, along with the resistive, galvanomagnetic, and thermoelectric measurements already mentioned, include tunneling, electron-optical, and neutron diffraction measurements.

Low-temperature high-pressure studies of Pb/Al, Sn/Al, and In/Al tunnel junctions have identified those of then existed models that were the best for describing the relation between the critical temperature and the directly measured superconducting gap [8].

Methodologically, one distinguishes two subranges in the pressure range used in low-temperature electron transport studies: up to 3 GPa (hydrostatic pressure) and from 3 GPa to megabar pressures ('quasihydrostatics'). Accordingly, our studies use two types of high-pressure cells: a fixed-pressure cylinder – piston cell and a toroid cell which is loaded (at room temperature) using a minipress placed directly in the cryostat. While in cells of the first type advanced measurement techniques can be adapted relatively simply to high pressure conditions, in the range up to 3 GPa the scope of study is limited by the need to work with pressure-sensitive objects — primarily, semiconductor and semimetal systems, where pressure-induced changes in the energy bands are on the scale of the carriers' Fermi energy.

Characteristic from this point of view is the behavior of tetrahedrically bonded semiconductors, i.e., Ge and Si, as well as $A^{III}B^{V}$, almost all $A^{II}B^{VI}$, and some $A^{I}B^{VII}$ compounds. All these semiconductors have a multivalley conduction band consisting of a spheroid centered at the Γ-point of the Brillouin zone, six ellipsoids centered at the X-points, and eight semi-ellipsoids at the L-points. While for all these FS sheets the pressure-induced energy shifts of the corresponding valleys are almost the same, with respective pressure coefficients of 10, −1, and 5 meV kbar^{-1}, at normal pressure the relative energy positions of the sheets vary (Fig. 2). For example, in GaAs the energy gap is direct (a minimum at Γ), whereas Ge and Si are, respectively, L-valley and X-valley semiconductors with an indirect gap, implying that a pressure of 2 GPa can, for example, transform the band structure of Ge into that of Si. (This fact was used in high-pressure tunneling measurements on Ge to determine the macroscopic Grüneisen constants for the [111] and [100] phonon branches [9].)

New and broad prospects were opened up by the application of high pressures to the study of a two-dimensional electron gas in GaSb/InAs/GaSb quantum wells. In such a well, in the absence of pressure, the conduction band edge of InAs is below the valence band edge of GaSb, so that the system develops spatially separated electron-hole layers within itself, the ionization of surface states on the interface resulting in the electron concentration in the well exceeding the hole concentration in the barriers. When pressure is applied, the bottom of the well goes up, leading to the disappearance of holes, after which, as the bottom of the well approaches the surface state level, the electron concentration falls to zero (Fig. 3). Such a pressure-induced transition from a 'semimetal' two-carrier-type state to a 'semiconductor' one-carrier-type state, and further to the insulating state, has been observed in magnetoresistance

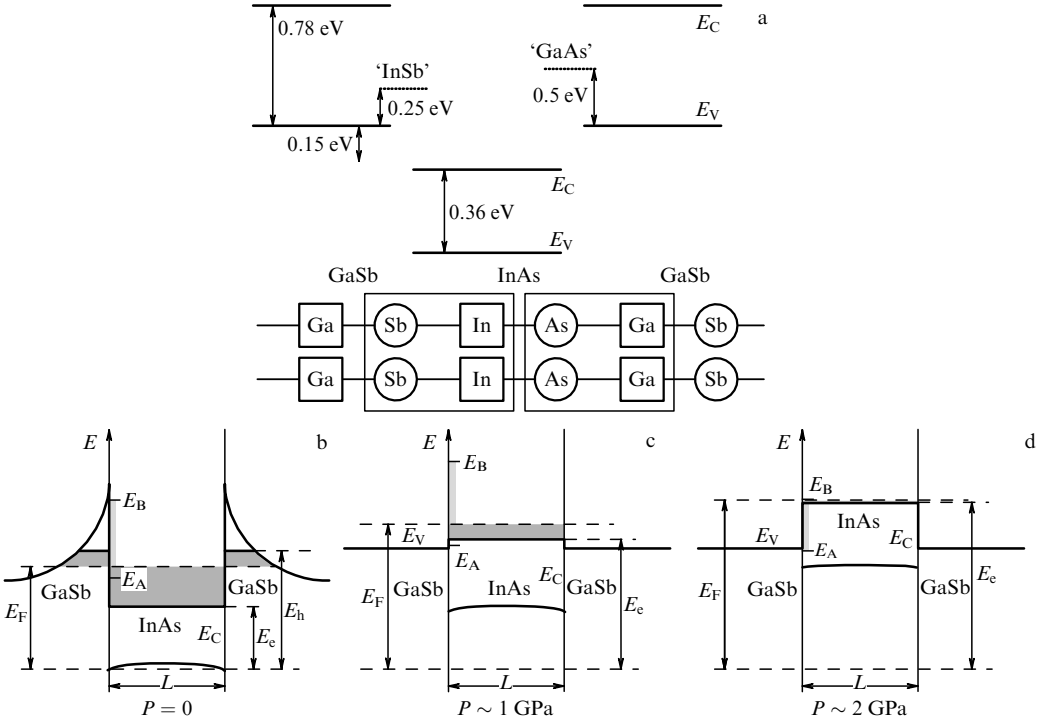

Figure 3. (a) Band edge diagram for a GaSb/InAs/GaSb quantum well and the formation of two types of interfaces. (b – d) Schematics for the effect of pressure and surface donor states on carrier concentration. E_V' (E_C) is the valence (conduction) band; E_B (E_A) is the band of bonding (antibonding) states; E_e (E_h) is the first band of quantum confinement of electrons (holes); E_F is the Fermi level.

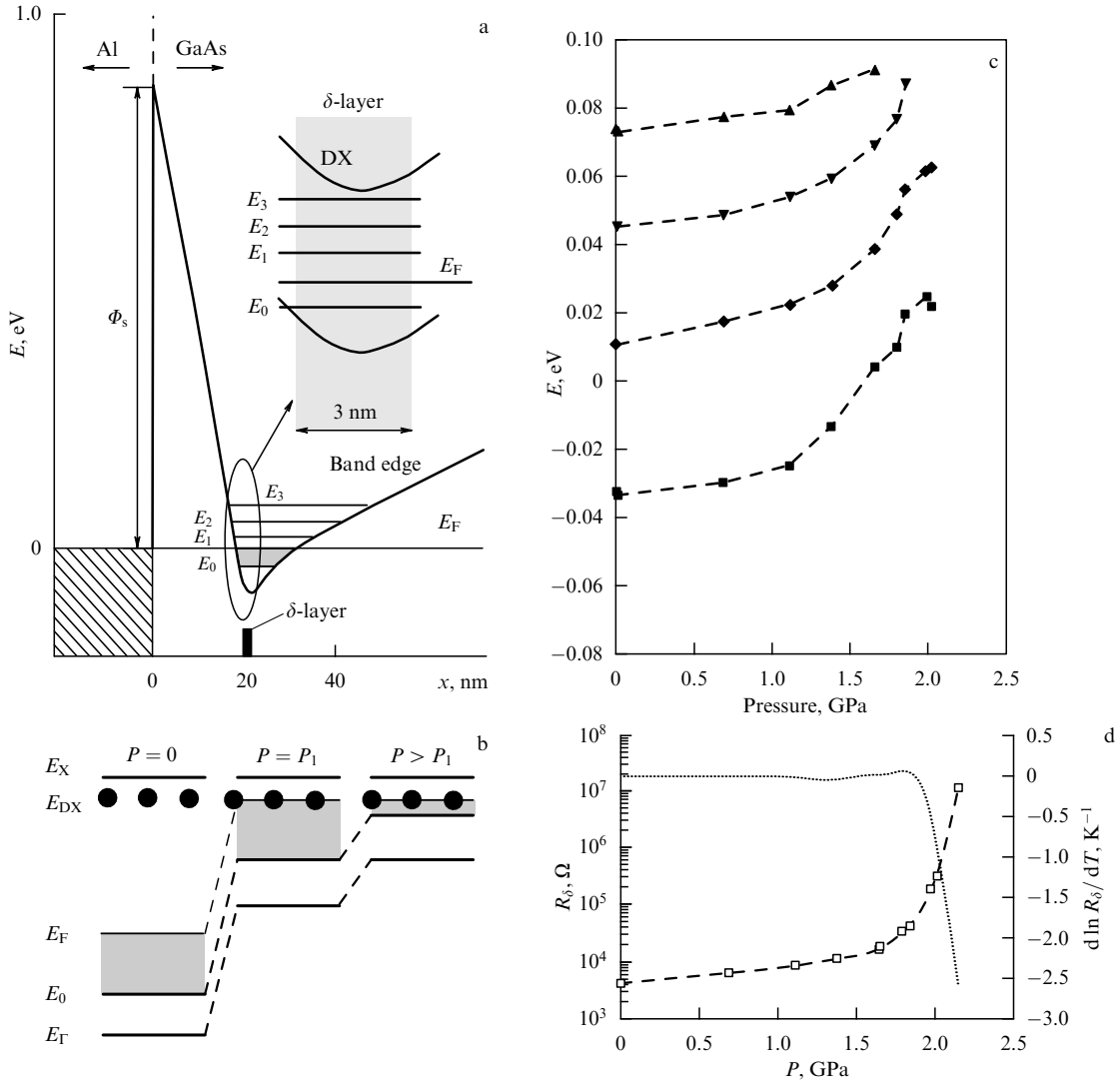

Figure 4. (a) Interface potential profile and the system of quantum confinement levels. (b) Pressure-induced change in the relative position of major energy levels; E_X, the edge of the X valley; E_{DX}, the level of DX centers; E_F, Fermi level; at a pressure P_1 the Fermi level becomes coincident with that of the DX centers, E_0 is the edge of the lower quantum confinement subband, $E_{1,2,3}$ are the successive quantum confinement bands, Φ_s is the potential barrier height, E_Γ is the conduction band edge (Γ valley). (c) Pressure dependence of the positions of quantum confinement subbands as obtained from tunneling spectra. (d) Pressure dependences of resistance R_δ (−□−) and the temperature resistance coefficient of the δ layer (dotted line).

oscillations under pressure. Furthermore, because varying the layer deposition sequence in the molecular-beam epitaxy allowed two types of interface — 'GaAs' and 'InSb' — to be formed, the spectra of surface states for both interface types were determined from high pressure measurements [10].

The above approach of varying carrier concentration by applying high pressure at a constant level of doping was used further in the study of the two-dimensional electron system in near-surface Si δ doped GaAs [11]. In this study, advantage was taken of the fact that substitutional impurities (Si, Sn, and Te) form so-called DX centers, whose position is tied to the conduction band X valley. Due to the Γ valley approaching the DX center level, quantum well electrons localize on the latter and so reduce in concentration, thus enhancing the role of interaction and reducing correlation (Fig. 4). By simultaneously measuring the resistance of the δ layer and the spectra of normal tunneling to the δ layer it was shown that this metallic-to-diffusion conduction crossover produces a density-of-states gap at the Fermi level. It should be noted that, unlike magnetotransport measurements, tunneling not only pinpoints the position of the filled levels of quantum confinement but also determines the way in which the unfilled upper-lying quantum confinement levels change their position with pressure.

A further possible application of high-pressure techniques is to vary the effective dimensionality when studying the one-dimensional systems of the family MX_3 (M = Ta, Nb; X = S, Se). The substances of this group are highly anisotropic three-dimensional (3D) conductors consisting of conducting chains weakly bonded by van der Waals forces. Unlike 3D metals, whose electron properties are well described by Landau Fermi liquid theory, a one-dimensional (1D) system has no electron excitations, and those elementary excitations present are collective charge and spin modes. This state is called a Luttinger liquid. On the other hand, in quasi-one-dimensional conductors the electron – phonon interaction usually leads to a Peierls phase transition, resulting in the appearance of a charge-density-wave (CDW) state. It had been known that MX_3 compounds vary considerably in their electron properties. For example, $TaSe_3$ is a metal; $NbSe_3$, while

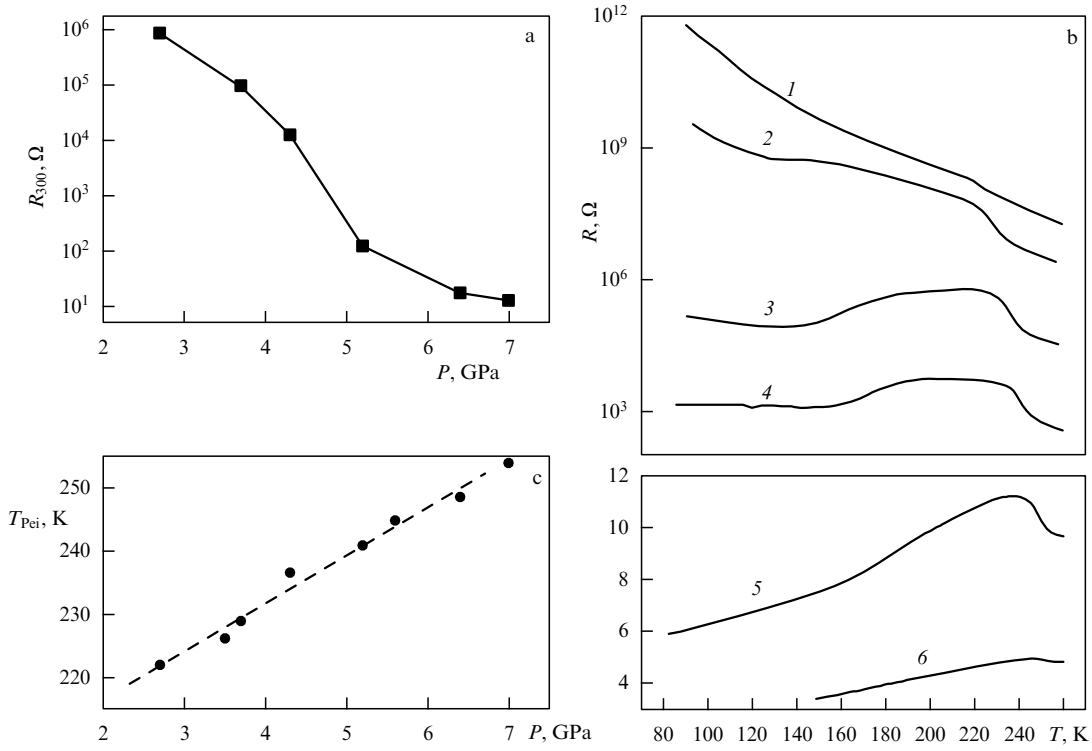

Figure 5. (a) Resistance versus pressure for NbS_3 at room temperature. (b) Resistance versus temperature for NbS_3 at pressures in GPa of 2.7 (*1*), 3.7 (*2*), 4.3 (*3*), 5.2 (*4*), 6.4 (*5*), and 7.0 (*6*). (c) Peierls transition temperature as a function of pressure. Dashed line is for $T^* \approx 7.5P + 202$.

undergoing CDW-forming transitions, remains metal-conducting at low temperatures; in TaS_3, the formation of CDW at 220 K makes the electron spectrum fully dielectricized; NbS_3 exhibits dielectric properties at both low and room temperatures. Thus, the metallic nature of conduction is enhanced in the order $NbS_3 \rightarrow TaS_3 \rightarrow NbSe_3 \rightarrow TaSe_3$.

At the Institute of Radioengineering and Electronics, RAS, the temperature and field dependences of conductivity were obtained for quasi-1D TaS_3 and $NbSe_3$ with cross sections of tens to hundreds of nm, which revealed a transition in these conductors from metallic (3D) behavior at room temperature to nonmetallic (1D) behavior below 50–100 K, with the CDW state either disappearing or surviving in the transition, and which also showed that the smaller the cross section of the thread-like crystals, the weaker the metallic nature of the conductivity. It was therefore of interest for us to see how pressure affects the conductivity of a quasi-1D 'insulator' NbS_3, with a view to reduce the chain-to-chain separation and to test the current understanding of the physical conduction mechanism. This understanding is that impurities in 1D chains form tunnel barriers that break the chains into segments and that a Luttinger-liquid state can exist if the electron hopping integral between the chains is smaller than the quantum confinement energy in the chain segments between the impurities. Because the hopping integral should increase with pressure, it was reasonable to expect that increasing pressure should cause the disappearance of CDWs and a transition to 3D behavior. Such behavior was indeed first observed in experiments on thread-like crystals of NbS_3 [12], in which applying a hydrostatic pressure of 6 GPa produces an increase in room temperature conductivity of more than five orders of magnitude and causes the temperature resistance coefficient to change sign. Another observed feature is a jump in the resistance versus temperature curve, which brings to mind the Peierls transition and whose position depends linearly on the temperature (Fig. 5).

In the quasihydrostatic pressure range, the occurrence of structural phase transitions allows the experimental study of even such objects that do not really exist under normal conditions. Work along these lines [13] was primarily concerned with the discovery and study of superconducting high-pressure phases in 'natural' superconductors — tallium, lead, and niobium diselenide — as well as in a number of substances that do not exhibit superconducting properties at normal pressure: bismuth, stibium, bismuth–stibium alloys, barium, and some semiconductors and semiconductor compounds (tellurium, bismuth telluride, silicon and germanium, and gallium and indium antimonides). Throughout this list, the superconducting transition temperature of a high pressure phase depends on the type and initial concentration of carriers. As studies under pressure [14] showed, magnetoresistance is a very sensitive means for detecting phase transitions even if electrical resistivity has a small or no jump. This in turn enables using galvanomagnetic measurements to determine the behavior of carrier concentration in each high pressure phase.

The study of the properties of high pressure metastable phases at normal pressure can also be considered part of this area of research. Using high-pressure synthesis, those portions of the phase diagram unachievable at normal pressures can be realized. Sometimes, it is only in this way that some compounds can be produced. In particular, due to the high partial pressure of oxygen or another metalloid it proves possible to get cations that are stabilized in a highly oxidized state. If there is a marked structural rearrangement (for

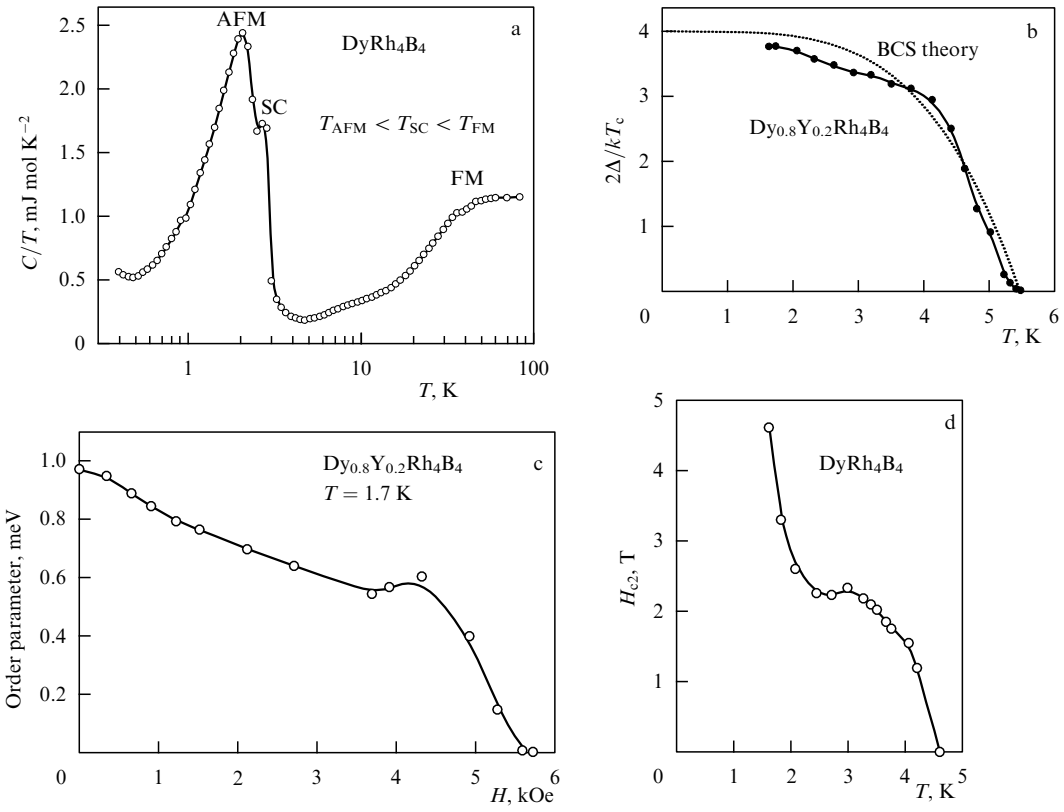

Figure 6. (a) Heat capacity versus temperature for $DyRh_4B_4$. FM, AFM, and SC denote the ferromagnetic, antiferromagnetic, and superconducting transition points, respectively. (b) Measured versus BCS temperature dependence of the energy gap. (c) Field dependence of the order parameter in $Dy_{0.8}Y_{0.2}Rh_4B_4$. (d) Temperature dependence of the second critical field for $DyRh_4B_4$.

example, bond forming or bond breaking) involved in a transition between high- and low-pressure phases, then a 'quenched' metastable state can be obtained by cooling the high pressure stable compound before removing pressure. Such substances include, in particular, perovskite compounds with highly coordinated cations, oxygen-bond-rich compounds, and compounds whose high-pressure phase has a higher symmetry. Examples are the superconductor Nb_3Ge, the T_c-record holder of the 1970s, and mercury-based superconductors, the highest-T_c materials of today. Another important gain from using high pressure in composite material synthesis is the possibility to markedly increase the critical current density, a key characteristic of a superconducting material.

One of the most interesting and important problems in condensed matter physics is to understand how superconductivity and magnetism, two collective macroscopic quantum phenomena, can coexist. Heat capacity versus temperature plots for IHPP-produced metastable high-pressure phases of magnetic superconductors $(Dy,Y)Rh_4B_4$ reveal the existence of three phase transitions: antiferromagnetic, superconducting, and ferromagnetic, with $T_{AFM} < T_{SC} < T_{FM}$ [15].

The temperature dependence of the energy gap differs in both shape and size from what is predicted by the BCS theory. In another finding, the field dependence of the energy gap and the behavior of the second critical field are also far from typical in that in a certain range of magnetic fields the number of superconducting carriers increases, rather than decreases, with field. All this suggests a different superconducting mechanism, possibly one involving triplet pairing (Fig. 6).

This talk covers only part of what high pressure measurements have contributed to the synthesis of appropriate materials and to the understanding of electron transport in systems that involve interactions between the quasiparticles which exist in the electron, phonon, and spin subsystems and whose properties, in turn, can be strongly dependent of the presence of crystal lattice defects. The arsenal of measurement tools includes resistive, tunneling, galvanomagnetic, thermoelectric, electron-optic, and neutron diffraction measurements under pressure. This research is the main focus of activities of the Laboratory of Low Temperatures, which is genetically related to the IHPP divisions mentioned above and which works along these lines in close cooperation with the Institute of Radioengineering and Electronics, RAS, and the Laboratory of Strong Magnetic Fields, Polish Academy of Sciences, under support from RFBR and the RAS Presidium Program.

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Theoretical studies of condensed matter

V N Ryzhov, A F Barabanov, M V Magnitskaya, E E Tareyeva

This talk briefly reviews the basic directions the Theoretical Department of the Institute for High Pressure Physics, RAS, (IHPP) has been pursuing in condensed matter research during the 50-year existence of the institute.

In the 1960s, the IHPP Theoretical Department became one of the first research centers in our country to employ first principle computational methods — i.e., ones that involve no fitting parameters and thus are experiment-independent — to study the physical properties of and phase transformations in solids, in particular under high pressure conditions. This research is usually carried out in close cooperation with experimenters using experiment/theory comparisons to clarify the underlying physics of the phenomena being observed. Along with known materials, new high-pressure phases first obtained at the IHPP are being investigated. Starting in the 1960s and 1970s, appropriate computational techniques using electron density functional theory, such as the Augmented Plane Wave and Korringa–Kohn–Rostoker methods and their modifications and extensions, have been further developed and revised by IHPP theorists.

The early work by R G Arkhipov, E S Alekseev, and A P Kochkin [1] used the approximate Wigner–Seitz spherical cell method, with a unit cell replaced by an equal-sized sphere, to study the relation between the electronic structure and phase transformations in simple metals under high pressure at $T = 0$. A major finding of this study, a phase transition with a volume change in K, Rb, and Cs, was explained in terms of an electron s–d transition, i.e., as resulting from a pressure-induced change in the mutual arrangement the of s and d bands. The discovery, made due to advances in experimental techniques, and subsequent studies of new low-symmetry high-pressure phases in simple metals brought fresh relevance to this line of research. At present, IHPP researchers use modern theoretical methods (in particular, based on the first-principle pseudopotentials) not only to exactly determine structural sequences in simple metals under pressure at $T = 0$, but also to study $P - T$ phase diagrams at finite temperatures $T \neq 0$, on the basis of the phonon spectra calculations by the density-functional linear-response method [2].

The IHPP's M V Magnitskaya and colleagues from outside Russia [3] have calculated the electron and phonon spectra and the electron-phonon coupling (EPC) for a recently discovered high-pressure metallic phase of sulphur S-IV, which exhibits the incommensurate modulation of atomic positions in the direction [010] (charge density wave, CDW). The first-principle calculation produced a correct crystal structure for the modulated phase of S-IV. The transition to the CDW state can be interpreted as a distortion of the higher-density S-V phase (which has the β-Po type crystal structure). The results of calculations show that in the β-Po structure one of the transverse phonon modes on the vector $\mathbf{q}_{\mathrm{CDW}}$ becomes softer with decreasing pressure. Upon further decrease in pressure to $P \approx 135$ GPa, the frequency of this mode becomes zero, $\omega(\mathbf{q}_{\mathrm{CDW}}) = 0$, corresponding to the S-V phase being unstable relative to the transition to the S-IV phase in which this unstable phonon is 'frozen' into a CDW. The location of the minimum of the phonon mode is in excellent agreement with the experimental modulation vector $\mathbf{q}_{\mathrm{CDW}}$. To analyze the role of the electron–soft mode coupling, the contributions from various phonon modes to the matrix elements of the EPC were calculated. It has been established that the soft-mode contribution is maximum on the vector $\mathbf{q}_{\mathrm{CDW}}$, suggesting that the experimental jump at $p \approx 150$ GPa from 14 to 17 K in the superconducting transition temperature T_c can be due to the fact that at $p > p_{\mathrm{CDW}}$ the electron density of states at the Fermi level increases and the electron–soft mode coupling contributes significantly to T_c. This jump, as well as the subsequent increase in T_c in the interval to $P \approx 200$ GPa, is explained by the competition between the soft mode frequency $\omega(\mathbf{q}_{\mathrm{CDW}})$ and the electron–phonon coupling constant [3].

In the 1970s, due to improvements in computational techniques, institute theorists started broad-scope studies of transition and rare-earth metals, intermetallic compounds, and alloys, covering in detail pressure-induced magnetic phase transitions, as well as alloying and phase stability, galvanomagnetic effects, optical and photoemission spectra, etc. Of particular note are the studies of the magnetic properties in double and triple Laves phase materials, including new compounds, first synthesized at the IHPP [4], of the magnetic 3d metals Fe, Co, and Ni with calcium. Considerable interest was generated by studies by N I Kulikov and colleagues of the effect of pressure on the properties of magnetically ordered metals and alloys, including complex — incommensurate and noncollinear — antiferromagnetic (AFM) structures, for example, chromium and yttrium and their respective alloys, the systems Pt_3Fe, FeRh, etc. [5]. In this context, the excitonic dielectric model combined with band calculations proved a very fruitful approach, offering a single framework for explaining how congruent Fermi surface regions give rise to various AFM orderings. For chromium, in which AFM ordering can be thought of as an incommensurate spin density wave the AFM-destroying effect of the EPC was investigated [6]. A series of publications by N I Kulikov and coworkers on the development of the coherent potential method and its application to disordered systems examined in detail the relation between structural disordering and the magnetic properties for various binary alloys of transition metals and for the disordered alloys of 3d metals with Si, Al, etc. [7].

Finally, one more area of research that emerged in the 1970s was the study of the compounds — carbides, nitrides, hydrides, etc. — which transition and rare earth metals form

with light elements. E S Alekseev and coworkers, who carried out the first principle calculations, and IHPP experimenters, who synthesized these compounds and explored them under high pressure, studied these compounds in close cooperation as promising construction materials (for example, the refractory and hard WC, ReC) and as possible high-temperature superconductors (NbN, TaN, etc.). The theoretical aspects considered were structural transitions, chemical bonding, superconductivity, electrical resistance, and other properties [8]. In a series of papers on hydrides, N I Kulikov and coworkers investigated phase transitions in the metal–hydrogen systems and provided simple approximation estimates for the EPC constant and the superconducting transition temperature T_c [9].

As is known, recently new, intermediate-T_c superconductors have been discovered, including Y_2C_3 ($T_c = 18$ K), MgB_2 ($T_c = 40$ K), and complex borocarbides ($T_c = 15$–23 K)—a discovery which rekindled interest in the compounds of metals with light elements (H, B, C, N, O) that exhibit phonon-mediated superconductivity. Calculations by M V Magnitskaya and A E Karakozov in cooperation with a research group from the P N Lebedev Physics Institute yielded the phonon spectra, EPC, and superconducting properties for a number of cubic carbides and nitrides of transition metals with a general chemical formula of AB over a wide range of pressures [10]. For NbC, the experimentally best studied carbide, the calculated optical and kinetic characteristics involving and related to the EPC are in excellent agreement with experiment, implying that the results of these first-principle calculations are sufficiently accurate to be used in the analysis of what affects the value of T_c in this class of compounds. Other than NbC, the effect of high pressure on phonon-related and superconducting properties was studied in much detail for the cubic nitrides ZrN and HfN, for which high-pressure experimental data are available. The theoretical phonon densities of states for ZrN and HfN are in reasonable qualitative agreement with the Raman spectra measured at various pressures in the range of up to 32 GPa. The spectral density of the EPC and the baric derivative of the critical temperature dT_c/dp for ZrN are in good agreement with measurements obtained at $p \approx 0$ and low pressures, respectively. At high pressures, T_c goes down (measurements at higher pressures were not carried out). Calculations performed suggest that upon further increase in pressure, T_c undergoes a linear decrease, and for $p > 10$ GPa the dependence $T_c(p)$ becomes nonlinear in a way that slows down the decrease in T_c. It is shown that the pressure-induced decrease in T_c results from a decrease in the EPC constant λ, which is due primarily to an increase in phonon frequencies rather than to electron-spectrum-related factors.

An analysis was made of the reasons why cubic carbides have a relatively low T_c compared, for example, with MgB_2. In most of the compounds studied, electrons in light atoms are coupled rather weakly to high-energy optical phonons because in a light atom B the partial electron density of states at the Fermi level, $N_B(E_F)$, is low. A typical example here is NbC. However, compounds with high $N_B(E_F)$—for example, the hypothetical cubic yttrium carbide YC not as yet synthesized stoichiometrically—have also been found to have a low T_c. It is established that in YC carbon's electrons and optical phonons are also weakly coupled, but the reason for this is not the low $N_B(E_F)$, as in NbC—it is the fact that the electron states at E_F are not hybridized and are almost pure p states of carbon. This leads to small matrix elements of EPC and thus to a low T_c. It seems it is only in carbides and nitrides with more complex crystal structures that the hybridization of C or N p states with s or d states can coexist with a high $N_B(E_F)$ (and hence with a high T_c) [10].

Since 1964, studies have been carried out on the use of classical statistical mechanics in the microscopic description of phase transitions, including the superconducting phase transition, orientational transitions in molecular crystals, the theory of melting in two and three dimensions, the Kosterlitz–Thouless transition, transitions in spin-glass systems, and liquid–glass and liquid–liquid transitions in real systems.

One example is an approach, developed by E E Tareyeva, in which superconductivity is treated in tight-binding approximation successfully adapted to describe the effect of pressure. The pressure dependence of the isotope effect in superconductors calculated in this way [11] later gained partial experimental support. The problem of symmetry-changing phase transitions gave rise to a research field using the mathematical theory of the branching solutions of nonlinear integral equations (Lyapunov–Schmidt theory). One of the major results in this area of work was the first microscopic explanation of the Landau symmetry change rules for the second-order phase transition [12].

The description of orientational disorder in molecular crystals was another successful application of this branching theory approach. One result was a detailed microscopic picture of the transition to the four-sublattice ferroquadrupole phase in solid molecular hydrogen [13]. Later applications to more complex problems—in particular, to the orientational transitions in fullerites—led to results in excellent agreement with experiment in terms of the transition temperature, the type of ordering, the order of transition, and the relative proportions of the preferred mutual orientations (the so-called P and H states) [14].

V N Ryzhov and E E Tareyeva [23, 28, 29] proposed using the equations for the conditional multiparticle distribution functions of classical statistical mechanics

$$F_{s+1}\left(\mathbf{r}_1|\mathbf{r}_1^0\ldots\mathbf{r}_s^0\right)=\frac{F_{s+1}(\mathbf{r}_1,\mathbf{r}_1^0,\ldots,\mathbf{r}_s^0)}{F_s(\mathbf{r}_1^0,\ldots,\mathbf{r}_s^0)}$$

to describe various space-symmetry-breaking situations, where $F_s(\mathbf{r}_1,\ldots,\mathbf{r}_s)$ is the usual s-particle distribution function. The conditional functions satisfy the equations

$$\frac{\rho F_{s+1}(\mathbf{r}_1|\mathbf{r}_1^0\ldots\mathbf{r}_s^0)}{z}=\exp\left\{-\beta\sum_{k=1}^{s}\Phi(\mathbf{r}_1-\mathbf{r}_k^0)\right.$$
$$+\sum_{k\geqslant 1}\frac{\rho^k}{k!}\int S_{k+1}(\mathbf{r}_1,\ldots,\mathbf{r}_{k+1})$$
$$\left.\times F_{s+1}(\mathbf{r}|\mathbf{r}_1^0\ldots\mathbf{r}_s^0)\ldots F_{s+1}\left(\mathbf{r}_{k+1}|\mathbf{r}_1^0\ldots\mathbf{r}_s^0\right)\mathrm{d}\mathbf{r}_2\ldots\mathrm{d}\mathbf{r}_{k+1}\right\},$$

where z is the activity, ρ is the density, $S_{k+1}(\mathbf{r}_1,\ldots,\mathbf{r}_{k+1})$ are irreducible Mayer diagrams, and $\beta = 1/k_B T$.

Using the fact that the symmetry-breaking analysis of a single-particle function yields the liquid–crystal transition, a fundamentally new approach to the theory of crystallization was proposed and developed [15–17], which later came to be known as the density functional method in crystallization theory. The essential point is that with this method, knowing the liquid direct correlation function alone, it is possible to

obtain the crystallization temperature and the volume change due to the transition and also to predict which type of lattice will result. It is mostly this method which is currently used in melting curve calculations and which has enabled, in particular, concrete calculations for a number of model systems, as well as melting curve calculations for molecular hydrogen [18] and, later, for fullerite [19].

In the 1990s, the melting theory of three-dimensional systems was extended to the case of two dimensions [20, 21]. The microscopic theory of two-dimensional melting depends to a large extent on the description of the orientational ordering of bonds in simple liquids (in terms of the violation of isotropy of the two-particle distribution function) and on the correct account of fluctuations. An important development here was the derivation of microscopic formulas for elastic and Frank moduli of two-dimensional systems and their application to constructing a theory of two-stage melting. Using this theory, it proved possible to determine potentials for which two-dimensional melting proceeds via two continuous transitions and those for which it occurs via a single first-order transition [22–27].

Closely related to the studies of two-dimensional melting was the 1990s research on the statistical mechanics of a system of vertices in a thin superconducting film. A microscopic approach developed within this research has, among other things, provided the description of the Kosterlitz–Thouless transition and also allowed the analysis of vortex–vortex interactions in a finite thickness thin film [30–36], whose results compared well with experiments on a niobium film in which a system of vortices passes through a hexatic phase occupying a large region of the H–T phase diagram (where H is an external magnetic field).

Soon after the first classical publications on the theory of spin glasses, its extension to a number of more complex systems was proposed by E E Tareyeva and her colleagues. In this way, a description of quadrupole glass in a mixture of para- and ortho-hydrogen was developed, in which — and this is a fundamental point — the order parameter increases smoothly and without a phase transition with decreasing temperature, as is indeed the case experimentally [37]. Another important, but later, development was a theory describing the transition to the orientational glass state in molecular para-hydrogen under pressure, when the system can be thought of as a mixture of $J = 0$ and $J = 2$ molecules [38]. The calculated results are in quantitative agreement with experiment. Interesting results, also in quantitative agreement with experiment, were obtained for orientational glass in fullerite. An example is the first theoretical calculations of the relative proportions of the P and H states for a wide range of temperatures and pressures [39].

The cluster-model description of the liquid–glass transition is yet another interesting application of spin-glass-theoretical methods. This description was made possible by showing, using the distribution function method, that the orientational interaction of cluster changes sign as a function of cluster size [40, 41].

Based on the above research into complex spin glass systems, and considering the results of a number of model studies (in particular, a detailed study of the Potts model [42–45]), it has proved possible, first, to establish a number of regularities (universality) in the behavior of glasses depending on the presence (or absence) of reflection symmetry and, second, to develop a consistent theory of non-Ising spin glasses.

Whereas first-order phase transitions in crystals as a function of external parameters is quite a mature field both experimentally and theoretically, the study of pressure- and temperature-induced phase transitions in disordered condensed matter, including liquids and amorphous solids, is still in its infancy. In the work by V N Ryzhov and S M Stishov [46, 47], a system with a purely repulsive potential of 'collapsing' hard spheres, i.e., a hard sphere potential with an added repulsive step, was used to model the liquid–liquid transition. The thermodynamic functions were calculated by the thermodynamic second-order perturbation theory in the step-height-to-temperature ratio; the zeroth order approximation was taken to be a system of solid spheres, whose properties were calculated in the Perkus–Yevick approximation. Note that this theory is analogous to the van der Waals theory for the liquid–gas transition. Using this theory, the thermodynamic functions of the system were calculated, including the free energy and isotherms. A major result was the discovery on low-temperature high-density isotherms of van der Waals loops corresponding to the liquid–liquid transition. Using the Maxwell rule, the liquid–liquid transition line was calculated, as was the friction coefficient between different liquid phases along it. The transition line was shown to terminate at a critical point. The isotherms obtained for the potential of 'collapsing' hard spheres characteristically intersect in the region of low densities — implying that the temperature extension coefficient becomes negative in a certain temperature–density range. Note that this anomalous behavior is characteristic of a number of liquids, including water. The transition line lies below the melting curve and can be observed only in the metastable region, as appears to be the case for a supercooled water. However, by varying the potential parameters, it is in principle possible to move the transition line to the stability region of the system. Melting curve calculations for the potential of 'collapsing' hard spheres using the Hansen–Verlet criterion show that in the neighborhood of the liquid–liquid transition line the melting curve in the pressure–temperature plane goes successively through a maximum and a minimum before becoming a straight line characteristic of the hard sphere potential. Note that adding an attractive term to the potential of 'collapsing' hard spheres leads, in a certain range of parameters, to the appearance of a second critical point, that of the liquid–gas transition [48].

Over more than 30 years, A F Barabanov's team at the IHHP's theoretical department has been investigating the highly topical subject of strongly correlated systems, including in particular systems with heavy fermions, mixed valency systems, manganites, magnetic semiconductors, and compounds that exhibit high-temperature superconductivity (HTSC) when doped. Because such compounds contain rather strongly localized f or d electrons, they fail to be described by conventional band theory, which is a one-particle approach, and their microscopic theory is as yet far from complete. The fundamental questions which still remain open concern current carriers and the magnetic subsystem (namely, their spectra and their mutual influence as a function of temperature); the number of carriers, and the dimensionality of the system; the nature of the normal state and the possible existence of the superconducting state; and the anomalous behavior of kinetic coefficients.

In the field discussed, new results have been obtained and new approaches developed. In particular, a diagrammatic technique was developed for the regular Anderson model

[49 – 51]. Calculations to high order in the hybridization interaction exactly revealed the presence of large logarithms $\ln(D/T)$ and $\ln(D/\varepsilon_f)$ in this model, where D is the conduction band width and ε_f is the position of a localized level with respect to the chemical potential. The developed technique allowed these logarithms to be taken into account in the analysis of phase transitions in mixed valency systems (in particular, in cerium under pressure) [51, 52]. Two further developments were the construction of RVB-type no-sublattice states for low-dimensional systems [53 – 55] and the study of the motion of carriers on an RVB sublattice (RVB standing for resonant valence bond).

The discovery of HTSC triggered the study of the spectrum of carriers in a two-dimensional $S = 1/2$ doped antiferromagnet, which provided the basis for the small-radius spin-polaron approach and for investigating the kinematic mechanism of superconducting pairing by taking into account strong correlation effects [55 – 57]. To correctly describe the spin subsystem, a self-consistent, spherically symmetric theory of a two-dimensional (2D) antiferromagnet was developed [58 – 60]. In particular, the damping of spin excitations was taken into account [61], enabling the analytical derivation of the scaling behavior of spin susceptibility for weakly doped cuprates [62],

$$\frac{\chi_{2D}(\omega, T)}{\chi_{2D}(\omega, T \to 0)} = f\left(\frac{\omega}{T}\right),$$

$$\chi_{2D}(\omega, T) = \int \mathrm{d}\mathbf{q}\ \mathrm{Im}\ \chi(\mathbf{q}, \omega, T)$$

$$f\left(\frac{\omega}{T}\right) = \pi\Theta\left[\left(\frac{\omega}{T}\right)^2 - \beta^2\right] + \arctan\left\{\frac{\alpha\omega/T}{\left[\beta^2 - (\omega/T)^2\right]}\right\},$$

and verifying the linear temperature behavior of the gap, $\Delta = \beta T$, and of the damping, $\gamma = \alpha T$.

The experimental data for the non-spin-wave (nonSW) behavior of magnetic susceptibility of cuprates in the superconducting state are reproduced using a spherically symmetric self-consistent approach within the framework of the frustrated Heisenberg model and introducing a polarization operator resonant with the superconducting state (scs) [63]:

$$\chi''_{\mathrm{scs}}(\mathbf{q}, \omega) = \frac{\Gamma F_{\mathbf{q}}}{Z^2 + \Gamma^2},$$

$$\Gamma = \gamma\omega + M''_{\mathrm{scs}}(\mathbf{q}, \omega) = \gamma\omega + \frac{\lambda\omega\Phi_{\mathbf{q}}}{(\omega^2 - \varepsilon^2)^2 + \lambda^2\omega^2},$$

$$Z = \omega^2 - \omega_{\mathbf{q}}^2 - M'_{\mathrm{scs}}(\mathbf{q}, \omega);$$

$$M'_{\mathrm{scs}}(\mathbf{q}, \omega) = \frac{\Phi_{\mathbf{q}}(\omega^2 - \varepsilon^2)}{(\omega^2 - \varepsilon^2)^2 + \lambda^2\omega^2}.$$

With this approach it proved possible to explain

(a) the appearance of a lower spin excitation branch (incommensurate peaks), which splits off from the resonance **Q** peak (the calculated resonance energy of 40 meV is close to the observed value);

(b) a marked decrease in the spectral weight in the neighborhood of the point ($\widetilde{q}_{x,\,\mathrm{nonSW}} \approx 0.065$ r.l.u., $\omega_0 \approx \varepsilon \approx 60 - 80$ meV), a neighborhood which corresponds to the experimentally observed 'dark region' located near point ($\widetilde{q}_x = \widetilde{q}_y \approx 0.1$ r.l.u., $\omega_0 \approx 50$ meV) (the abbreviation r.l.u. stands for reduced lattice unit, meaning that the vectors **q** are defined relative to the reduced lattice); and

(c) traces of the so-called 'silent band' lying in a narrow (in $\widetilde{q}_x$) region near $\widetilde{q}_{x,\,\mathrm{nonSW}}$: if, based on the positions of the maxima of $\chi''_{\mathrm{scs}}(\mathbf{q}, \omega)$ with respect to ω (at fixed **q**), we introduce an 'effective' spectrum $\widetilde{\omega}^+_{\mathrm{scs}}(\mathbf{q})$ for the upper branch, then, as q increases, the spectrum $\widetilde{\omega}^+_{\mathrm{scs}}(\mathbf{q})$ passes through an inflection point, and the intensity of the maxima of $\chi''_{\mathrm{scs}}[\mathbf{q}, \widetilde{\omega}^+_{\mathrm{scs}}(\mathbf{q})]$ will have a minimum.

Further, in the framework of various strongly correlated models (Emery, regular s-d, Hubbard), a theory of charge excitations was developed for a doped antiferromagnet taking into account the scattering of a spin polaron by spin fluctuations [64, 65]. The obtained results are simplest to understand for the regular s – d model with a Hamiltonian of the form

$$\widehat{H} = \widehat{h} + \widehat{J} + \widehat{I}, \quad \widehat{h} = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} a^+_{\mathbf{k}\gamma} a_{\mathbf{k}\gamma},$$

$$\widehat{I} = \frac{1}{2} I(1-p) \sum_{\mathbf{R},\,\mathbf{g}} S^{\alpha}_{\mathbf{R}+\mathbf{g}} S^{\alpha}_{\mathbf{R}} + \frac{1}{2} Ip \sum_{\mathbf{R},\,\mathbf{d}} S^{\alpha}_{\mathbf{R}+\mathbf{d}} S^{\alpha}_{\mathbf{R}},$$

$$\widehat{J} = \frac{J}{\sqrt{N}} \sum_{\mathbf{k},\,\mathbf{q}} a^+_{\mathbf{k}+\mathbf{q},\,\gamma_1} S^{\alpha}_{\mathbf{q}} \hat{\sigma}^{\alpha}_{\gamma_1\gamma_2} a_{\mathbf{k}\gamma_2},$$

where $\widehat{h}$ describes bare Fermi carriers and contains the spectrum $\varepsilon_{\mathbf{k}}$ of bare holes; $\widehat{I}$ refers to the frustrated antiferromagnetic (AFM) interaction between spins $S = 1/2$; vectors **g** and **d** are for the first and second neighbors; $I_1 = (1-p)I$ and $I_2 = pI$ are the corresponding AFM interaction constants; and p $(0 \leqslant p \leqslant 1)$ is the frustration parameter.

The term $\widehat{J}$ in this expression describes the interaction of carriers with the subsystem of localized spins $\mathbf{S}_{\mathbf{R}}$, $\widehat{\sigma}^{\alpha}$ are the Pauli matrices, and repeated indices — both Cartesian α and spin-related γ_1, γ_2 — are summed over. For characteristic values of $J \simeq 0.1$ eV, the Hamiltonian $\widehat{J}$ is that of a bare hole strongly interacting with the spin subsystem.

A 'good' minimum to take as a site set is the following set of basic operators:

$$\varphi^{(1)}_{\mathbf{r}\sigma} = a_{\mathbf{r}\sigma}, \quad \varphi^{(2)}_{\mathbf{r}\sigma} = \left(\frac{3}{4}\right)^{-1/2} S^{\alpha}_{\mathbf{r}} \hat{\sigma}^{\alpha}_{\sigma\sigma_1} a_{\mathbf{r}\sigma_1},$$

$$\left\langle [\varphi^{(i)}_{\mathbf{r}\sigma}; \varphi^{(j)+}_{\mathbf{r}\sigma}]_+ \right\rangle = \delta_{i,j},$$

$$\langle \widehat{A} \rangle = \mathrm{Tr}\{\hat{\rho}^0 \widehat{A}\}, \quad \hat{\rho}^0 = Z_0^{-1} \exp\left(-\frac{\widehat{H}_0}{T}\right).$$

Here, $\varphi^{(1)}_{\mathbf{r}\sigma}$, $\varphi^{(2)}_{\mathbf{r}\sigma}$ provide a full set of local, single-hole spin-polaron operators, $\varphi^{(2)}_{\mathbf{r}\sigma}$ and $\varphi^{(1)}_{\mathbf{r}\sigma}$ being analogues of singlet and triplet one-site states, respectively. Even in the local operator basis, the bare band $\varepsilon_{\mathbf{k}}$ splits into two bands, the spectral weight of a bare hole in the lower band being strikingly different from unity. A further inclusion of spin polaron damping in the lower band permits the description of how a pseudogap develops close to the boundary of the magnetic Brillouin zone. The well-known kink structure of the spectral density and the closure of the pseudogap with increasing doping are also accounted for using this theory.

A kinetic equation derived by using the polaron approach and a many-moment solution method developed by accounting for the extremely anisotropic scattering of holes by spin fluctuations [66] have allowed the description of the anomalous kinetics (electrical resistance $\rho(T)$ and the Hall coefficient $R(T)$), providing a single framework for ade-

quately treating the dielectric regime, the low-doping regime, and the regime close to optimum doping. It has been shown [67] that the energies $E_{\mathbf{k}}^{(s)}$ and residues $Z_{\mathbf{k}}^{(s)}$ in the collision term

$$P_{ll_1}^{s,s_1} = J^2 \frac{1}{N^2} \sum_{\mathbf{k},\mathbf{q}} \left[F_l^s(\mathbf{k}) - F_l^s(\mathbf{k}+\mathbf{q})\right] \times \left[F_{l_1}^{s_1}(\mathbf{k}) - F_{l_1}^{s_1}(\mathbf{k}+\mathbf{q})\right] Z_{\mathbf{k}}^{(s)} Z_{\mathbf{k}+\mathbf{q}}^{(s_1)} \times n_{\mathrm{F}}(E_{\mathbf{k}}^{(s)}) \left[1 - n_{\mathrm{F}}\left(E_{\mathbf{k}+\mathbf{q}}^{(s_1)}\right) n_{\mathrm{B}}(E_{\mathbf{k}+\mathbf{q}}^{(s)} - E_{\mathbf{k}}^{(s_1)})\right] \times \chi''\left(\mathbf{q}, E_{\mathbf{k}+\mathbf{q}}^{(s_1)} - E_{\mathbf{k}}^{(s)}\right)$$

should be those of polaron bands. This provides an adequate description of the anomalous temperature dependence exhibited by the resistance and Hall effect in cuprates.

The observation over ten years ago of Bose–Einstein condensation in diluted metal vapor opened up new possibilities for the study of macroscopic quantum phenomena in degenerate systems. These systems, typically diluted and spatially inhomogeneous, usually consist of several tens of thousands of atoms gathered into a limited size cloud near a minimum of the external potential. The atoms involved are cooled by laser cooling followed by a partial evaporation from a trap. Because higher energy atoms evaporate at a higher rate, the evaporation causes the gas to cool, leading to temperatures of hundreds of nK and allowing the observation of Bose condensation.

The modern theoretical description of a dilute Bose gas in a trap has as its basis the famous 1947 work by N N Bogolyubov, in which it was shown that weak repulsion leads to a qualitative change in the excitation spectrum. The key point of Bogolyubov's approximation was the separation from the second-quantized boson annihilation operator ψ of its classical part, which describes the condensate. The Gross–Pitaevskii equation for a trapped Bose condensate is obtained by extending Bogolyubov's theory to the spatially nonuniform case. This equation looks like a nonlinear Schrödinger equation and is essentially classical even though it contains a quantum constant.

Many interesting new effects in the behavior of trapped Bose condensates show up in experiments on mixtures of supercooled gases. Some important aspects of such mixtures — namely, phase separation and vortical states in binary mixtures of condensates in the case of coincident and shifted trap centers; and the stability of the Bose system in a Bose–Fermi mixture with attraction between bosons and fermions — were studied by V N Ryzhov and E E Tareyeva and their coworkers [68–77]. The obtained results fit well the experimental data on condensate mixtures consisting of rubidium atoms in two spin states and on a mixture of boson atoms of rubidium and Fermi atoms of potassium.

For a Bose condensate with coincident traps and with two components corresponding to two spin states of the rubidium atom, the following results have been obtained [69, 70]. It has been shown that interaction between the condensates leads to phase separation and the formation of shells. Critical angular rotation velocities of the condensate have been obtained, the term critical meaning critical for the formation of stable vortical states. How this picture depends on particle concentration in the condensates has been examined. Further, for the same problem but with initially displaced trap centers [71, 72], (1) it was shown, in agreement with experiment, that the resulting center-of-mass displacement of the condensates is considerably larger due to the interaction between the condensates; and (2) vortex stability in the external and internal condensates was investigated as a function of trap potential minimum displacements along the rotation axis.

Although primarily of interest for creating degenerate (and possibly superconducting) Fermi systems, the behavior of the boson–fermion mixture is also of interest in itself. For example, because spin-polarized fermions do not interact in the s-wave approximation due to the Pauli principle, the evaporative cooling of a Fermi system can be effective due to indirect interaction (if any) with a fermion subsystem in a different spin state or, alternatively, due to interaction with the boson subsystem of the Fermi–Bose mixture.

V N Ryzhov and E E Tareyeva [73–77] derived an effective Hamiltonian for the Bose component in a fermion–boson system and analyzed the stability of this system for the case of attraction between bosons and fermions. Because the absence of the fermion–fermion interaction in the s-wave approximation makes the action quadratic in fermion operators, the exact integration over the Fermi fields can be performed formally, leading to an effective action which depends on the temperature and the number of fermions and which contains only boson fields. Using the quasiclassical Thomas–Fermi approximation, the effective action was obtained in an explicit form, which can be expanded in a series in the boson field. It is shown that interaction with fermions decreases the effective boson–boson interaction corresponding to the fourth-order expansion. If there is attraction between bosons and fermions, then the behavior of the system is determined by the negative sixth-order term in the boson field. In this case, by analogy with a system of attracting bosons, a variational principle with a Gaussian bosonic wave function can be used to estimate the energy of the system. The behavior of the system is determined by the competition between the positive kinetic energy of zero-point oscillations (which is due to the existence of the trap), the positive energy of the interboson repulsion, and the negative energy due to the sixth-order term in the boson field. As the number of fermions increases, the last term increases in magnitude, resulting in an increased density of bosons at the center of the trap. At a certain critical value of the number of bosons, the sum of the positive kinetic energy and the interboson repulsion energy is insufficient to stabilize the system, leading ultimately to the collapse of the boson component. The critical number of bosons depends on the number of fermions and the temperature. The results of the calculations were applied to a system consisting of fermionic ^{40}K atoms and bosonic ^{87}Rb atoms and gave good agreement with experiment. For the same system, the structure and stability of vortex states was investigated using the variational approach and the Thomas–Fermi approximation. It was shown that in the presence of a vortex more bosons are needed for the system to collapse. The dependence of the critical velocities for the formation of vortices on the number of bosons and fermions was examined. Using the numerical solution of the generalized Gross–Pitaevskii equation corresponding to the effective Hamiltonian, it was shown that the Thomas–Fermi approximation is highly accurate in describing the behavior and collapse of the system.

Further, based on the effective Hamiltonian for the boson subsystem in the mixture of harmonically trapped degenerate Bose and Fermi gases, the critical temperature displacement

of a Bose gas was calculated as a function of the number of bosons and fermions. It was shown that the presence of the Fermi component results in the displacement behaving differently from the case of a single interacting Bose gas in a trap: the dependence of the critical Bose condensation temperature T_C on the number of bosons N_B has a different curvature in the presence of the Fermi component [78].

To summarize, the fifty years of the Theoretical Department of the IHPP, RAS, were those of wide-ranging research in the most topical areas of condensed matter physics, whose results not only matched but indeed established the world level. On the other hand, the department staff is actively involved in teaching activities — one aspect of which is that a number of able young scientists have joined the staff after obtaining candidate or doctoral degrees. So, all in all, the department has every reason to be optimistic about its future.

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