- 22. Brazhkin V V et al. Phys. Rev. B 56 11465 (1997)
- 23. Brazhkin V V et al. J. Appl. Phys. 84 219 (1998)
- Demishev S V et al. Pis'ma Zh. Eksp. Teor. Fiz. 78 984 (2003) [JETP Lett. 78 511 (2003)]
- Dyuzheva T I, Litaygina L M, Bendeliani N A J. Alloys Comp. 377 17 (2004)
- Dyuzheva T I et al. Kristallografiya 51 370 (2006) [Crystallogr. Rep. 51 342 (2006)]
- 27. Bolotina N B et al. J. Alloys Comp. 278 29 (1998)
- 28. Brazhkin V V, Popova S V, Voloshin R N Physica B 265 64 (1999)
- 29. Brazhkin V V et al. Phys. Rev. Lett. 100 145701 (2008)
- Popova S V, Brazhkin V V, Voloshin R N, Grimsditch M Usp. Fiz. Nauk 172 486 (2002) [Phys. Usp. 45 445 (2002)]
- Stal'gorova O V, Gromnitskaya E L, Brazhkin V V Pis'ma Zh. Eksp. Teor. Fiz. 62 334 (1995) [JETP Lett. 64 356 (1995)]
- Brazhkin V V, Lyapin A G, Popova S V, Voloshin R N *Phys. Rev. B* 51 7549 (1995)
- 33. Brazhkin V V, Lyapin A G J. Phys: Condens. Matter 15 6059 (2003)
- Tsiok O B, Brazhkin V V, Lyapin A G, Khvostantsev L G Phys. Rev. Lett. 80 999 (1998)
- Brazhkin V V et al. (Eds) New Kinds of Phase Transitions: Transformations in Disordered Substances (NATO Science Ser. II, Vol. 81) (Dordrecht: Kluwer Acad. Publ., 2002)

PACS numbers: 61.50.Ks, **62.50.**–**p**, **74.70.**–**b** DOI: 10.1070/PU2008v051n10ABEH006617

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

L N Dzhavadov, E L Gromnitskaya, G N Stepanov, Yu A Timofeev

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 = 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 lowinertial 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:

$$V(T, P) = V(T_{\rm r}, P) + \int_{T_{\rm r}}^{T} \frac{J_{S}(T, P) C_{P}(T, P)}{T} \, \mathrm{d}T$$

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 dT/dP. The relationship between the values of $(\partial T/\partial P)_S$ and the slope of the melting curve dT/dP 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 YBa₂Cu₃O_{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 $\sim 10 \ \mu m$ 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 31. 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.

References

- 1. Joule J P Philos. Mag. 17 364 (1859)
- 2. Boehler R, Getting C, Kennedy G C J. Phys. Chem. Solids 38 233 (1977)
- Dzhavadov L N, Krotov Yu I Fiz. Tverd. Tela 22 1245 (1980) [Sov. Phys. Solid State 22 728 (1980)]
- 4. Boehler R, Ramakrishnan H Geophys. Res. 85 (B12) 6996 (1980)
- 5. Dzhavadov L N, Krotov Yu I Prib. Tekh. Eksp. (3) 168 (1985)
- Dzhavadov L N Fiz. Tverd. Tela 27 3310 (1985) [Sov. Phys. Solid State 27 1993 (1985)]
- 7. Dzhavadov L N Zh. Fiz. Khim. 61 1106 (1987)
- 8. Dzhavadov L N High Temp. High Press. 21 401 (1989)
- 9. Dzhavadov L N Fiz. Tverd. Tela **47** 2223 (2005) [Phys. Solid State **47** 2315 (2005)]
- 10. Voronov F F, Grigor'ev S B Byull. Izobret. SSSR (2) 142 (1972)
- Khvostantsev L G, Vereshchagin L F, Novikov A R High Temp. High Phys. 9 637 (1977)
- Voronov F F, Goncharova V A, Stal'gorova O V Zh. Eksp. Teor. Fiz. 76 1351 (1979) [Sov. Phys. JETP 49 687 (1979)]
- 13. Voronov F F Adv. Space Res. 1 147 (1981)

- Goncharova V A, Chernysheva E V, Voronov F F Fiz. Tverd. Tela 25 3680 (1983) [Sov. Phys. Solid State 25 2118 (1983)]
- Goncharova V F, Chernysheva E V Semicond. Sci. Technol. 4 114 (1989)
- Voronov F F, Stal'gorova O V, Gromnitskaya E L Zh. Eksp. Teor. Fiz. 122 90 (2002) [JETP 95 77 (2002)]
- 17. Gromnitskaya E L, Stal'gorova O V Zh. Eksp. Teor. Fiz. **106** 1453 (1994) [JETP **79** 785 (1994)]
- Stal'gorova O V et al. Prib. Tekh. Eksp. 39 (6) 115 (1996) [Instrum. Exp. Tech. 39 880 (1996)]
- 19. Gromnitskaya E L et al. Phys. Rev. B 64 094205 (2001)
- Lyapin A G et al. Zh. Eksp. Teor. Fiz. 121 335 (2002) [JETP 94 283 (2002)]
- 21. Gromnitskaya E L et al. Phys. Rev. Lett. 98 165503 (2007)
- 22. Wijngaarden R J High Press. Res. 3 105 (1990)
- 23. Mao H K et al J. Appl. Phys. 49 3276 (1978)
- 24. Kankeleit E Rev. Sci. Instrum. 35 194 (1964)

PACS numbers: 01.65. + g, 71.18. + y, 73.20. - r DOI: 10.1070/PU2008v051n10ABEH006618

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 latticerelated 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