Building zero isotherm of hydrogen isotopes taking into account experimental results of isentropic compression up to pressures of several megabar

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Abstract. An isentropic compression of substances using ultra–high magnetic field makes it possible to effectively reach “cold” pressures of several megabar in a studied substance. The process is realized in a device based on magneto–cumulative generator MC–1. Arrangement of the experiments, where the isotherm of “cold” compression of hydrogen isotopes is studied, is described in the paper. Results of preliminary data analysis obtained at solid protium and deuterium compression are also presented. Achieved densities correspond to the pressures higher than 5 Mbar. A method of zero isotherm building, taking into account gradient and thermal corrections, is described. Errors, with which positions of experimental points in $P–\rho$ plane are determined, are associated mostly with a precision of sizes calculation of a reference and studied samples using x–ray image, obtained in the experiment. Deviations of the built points from the curve, extrapolating the experimental data on the diamond anvils to the multi–megabar range, lie within experimental errors. The zero isotherm, approximating the obtained nowadays-experimental data, is compared with several first-principles calculation results.

An interest to thermodynamic and kinetic properties of hydrogen within a wide range of pressures and temperatures is caused on one hand by their wide spread in the world, the role that they play in structure of stars and giant planets, and on the other hand by their practical importance as future basic energy sources (hydrogen fuel elements, possibility of superconducting state at room temperatures, etc.).

To get the equations of state of hydrogen both static [1] and dynamic [2] methods are used, both having advantages and disadvantages. In the former case a regime of an isotherm compression is usually realized at comparatively low temperatures ($T < 1000\text{K}$) up to the pressures not exceeding 1.5 megabars [3]. On the other hand, in the dynamic (shock-wave in the majority cases) regime the temperature could reach tens thousands degrees. But in this case a “cold” pressure does not exceed half of megabar (see, for example, [4, 5]).

The goal of this work is experimental plotting of the “cold” part of the equation of state of a solid protium and solid deuterium within the pressure range from 1 Mbar to $4 \div 5$ Mbar. (Initial temperature of the studied substance should be less than its melting point at atmospheric pressure: $< 14 \text{K}$ for $\text{H}_2$ and $< 18 \text{K}$ for $\text{D}_2$.) Experimental building of “zero” isotherms of hydrogen isotopes in the area of ultra-high pressures is one of the important and interesting tasks of a solid state physics with high energy density. To solve the task we used the dynamic technique of isentropic compression with the help of the ultra-high magnetic field pressure. Presently this research technique is, probably, the only one that allows obtaining the parameters of the “cold”...
curve of easily compressed substances in the megabar pressure range. Solid isotopes of hydrogen belong to these substances. This technique could be realized in a device, where a protium or deuterium, being in condensed initial state \((T_0 \approx 5 \text{ K}, P_0 \approx 1 \text{ bar})\), is isentropically compressed up to pressures of several megabar with an ultra-high magnetic field created by the magneto-cumulative generator [6].

The basic device components are the following (see Fig. 1): 1) magneto-cumulative two-stage generator MC–1 [7] as a pressure source; 2) a compression chamber, located in the generator cavity; 3) a cryogenic device that provides the required hydrogen isotope in a condensed phase and retains it in this state all the time of the test performing. The MC-1 generator includes a solenoid of the initial magnetic flux, a source of solenoid feed (capacitor battery), a ring high-explosive (HE) charge as a main energy source.

The compression chamber is formed by a copper tube and massive end plugs. Layers of the studied and reference materials, separated from each other and from the tube by contrasting shells, have to be located coaxially in the compression chamber [8]. The cryogenic device [9] consists of a vessel for coolant (liquid helium) storage and evacuated cryogenic piping.

The operation of the device takes place the following way. Before a test the compression chamber is evacuated, connected to a gas holder with gaseous hydrogen isotope, and inserted into a cryogenic piping, located along the MC–1 generator axis. Under effect of the small excess pressure, created in the cryogenic vessel, the helium goes upwards on the cryogenic line, and its low-temperature vapors (and then the helium itself) gradually cool the compression chamber. In this case the hydrogen isotope that fills the chamber passes first into liquid, and then into solid state. The investigated substance temperature is measured by calibrated semiconductive probes. (In every experiment the initial condensed gas temperature was \(T_0 = 5 \div 7 \text{ K}\), and in accordance with the performed calculations did not exceed the room temperature during a compression process.) A sinusoidal (period quarter \(\approx 70 \mu\text{s}\)) magnetic field, directed along the generator axis, is created in a solenoid cavity (in a gap between the solenoid and compression chamber) at discharge of the high-power capacitor battery on the solenoid. A ring HE-charge is detonated in such a way that the cylindrical converging shock-wave front, formed after detonation, reached the inner surface of the solenoid (the 1st cascade of the generator) at the time, when the magnetic field has maximum value \(B_0\). The letter is taken as an initial field of the generator. A shock wave causes implosion of the current-carrying liner-solenoid. (The second cascade of the generator is necessary to keep symmetry of the current carrying shell [10]). Since the implosion is rather fast (\(< 20 \mu\text{s}\)), the main part of the magnetic

![Figure 1. Compression device sketch: 1 — cryogenic container with the compression chamber, 2 — cryopiping, 3 — the second cascade of the generator, 4 — solenoid of the generator seed field, 5 — ring HE – charge, 6 — cryogenic vessel.](image-url)
flux, captured by the shell, is preserved. In the result the magnetic field in the generator cavity amplifies up to the megagauss values. During the operation time of the device this pulsed ultra-high magnetic field, created by MC generator, cannot penetrate inside a copper shell of the compression chamber (thickness of a skin-layer is less than the shell thickness at any time moment of the process) and makes on its outer surface the magnetic pressure $H^2/8\pi$. Under its effect the copper tube implodes and smoothly, without formation of the shock waves, compresses the substances, located in it, and thus creates the pressures of megabar range in them.

When performing the test pulsed x-ray imaging of the central part of the device is carried out at setup time moment of the compression process. Figure 2 presents the scheme of the x-ray imaging. An x-ray source – betatron [11] – rays the MC–1 generator and the compression chamber inside it by collimated horizontal beam of high and uniform intensity. The image is recorded by a set of x-ray films, having the amplifying screens. Compressions and densities of the substances inside the chamber are determined based on the results of the obtained images analysis. It was shown [12] that errors of all necessary sizes determination are small and do not exceed several percents. Based on the x-ray images of the chamber and the samples inside it we determine compression of the investigated sample and the reference sample. Having the reference sample density and using its known isentropic curve, one can determine pressure in the chamber. Initial densities are calculated accurately based on the sample initial temperature measured before the test. Aluminum is the best reference material, for which in accordance with static and shock-wave experimental results the most representative statistical data, corresponding to the range of the required pressures [13, 14, 15], has been stored and analyzed. Used “cold” Al isentropic curve corresponds to the paper [14], based both on obtained by the authors [14] data on Al static compression on diamond anvils up to a pressure of 2.2 Mbar, and on obtained earlier shock-wave compression up to 10 Mbar [16, 17]. In order to determine the sizes of the compressed samples with the x-ray image with acceptable precision, there is a thin layer of high-density material, located on the boundary, separating the samples from each other and from the compressing tube. The material consists of substances with large serial number in the periodic table. In our case this is a tungsten based alloy (WNiCu or WNiFe), containing 95% of tungsten.

The described method of ”cold” isentrope plotting provides satisfactory results, when pressure gradients in the operating zone of the compression chamber are small, and the x-ray images obtained in the experiments make it possible to determine the necessary sizes with relatively high precision. One can fulfill these two conditions by optimizing the geometry and operating regime of the experimental device. For this purpose we performed a series of preliminary

![Figure 2. Radiography scheme (top view)](image-url)
calculations of the compression process [18, 19], varying longitudinal and transversal sizes of the chamber and compressed samples, manner of their mutual location, and also the value of the initial magnetic field of the generator ($B_0 = 130 \div 190$ kG). The calculations were carried out with a one-dimensional magneto-hydrodynamic (MHD) and quasi-two-dimensional hydrodynamic codes (see [18]). These codes were used earlier for simulation of the magneto-cumulative generator operation and devices, based on the MC generator [20, 21]. Extrapolation of the “cold” isentropic curves, built on the data of the paper [3], was used for description of the $\text{H}_2$ and $\text{D}_2$ compression in the multi-megabar range. We also carried out calculations using more “rigid” curves, proposed in [22, 23]. This “rigidity” did not effect selection of the optimum values of the compression device parameters. Besides, several additional calculations were carried out for both isotopes. Now the Al equation of state (EOS) was selected not in the form, corresponding to the paper [14], but in two other forms: in the form proposed in the known paper [13], and in the form of so-called “equation of state with limiting density” [14]. These changes did not affect the optimization. However, after performance of the experiments we found out that their results matches the calculations better at description of the Al compressibility in accordance with [14].

The compression chamber geometry, presented in Figure 3 appeared to be optimum in both cases with $\text{H}_2$ and $\text{D}_2$. In this geometry the hydrogen isotope is located in the center, and the aluminum reference, separated from the studied sample and from the copper tube by the contrasting layers, is located between the hydrogen isotope and the compressing tube. The optimum value of the $B_0$ lies near 155 kG.

Based on the calculation results we selected the following values of the initial transversal sizes of the compression chamber and its elements: the compression chamber diameter is equal to 21.8 mm, thickness of both contrasting layers is 0.15 mm, thickness of Al layer is 2 mm, diameter of the studied sample of the hydrogen isotope is 13.7 mm. Speaking about the longitudinal sizes, we found out that for the performed experiments the most suitable is the compression chamber that has the distance between its ends, matching the length of the uniform magnetic field region and equal to 100 mm. (Deviation of the chamber length to the lesser side from the optimum leads to shortening of the uniform compression region. Deviation to the greater lengths leads to appearance of high-speed axial flows of the studied substance from the working region). Calculations showed that in the center section of such chamber the linear masses of the compressed substances are preserved (at the distance of $\approx 70$ mm). That is why to find out the reference and studied substance compression it is enough to know the transversal sizes of the aluminum and contrasting cylinder at room conditions and in the compression state, and also the coefficients of thermal expansion of their materials (high-precision data up to helium temperatures are available for these materials).

Figure 3. Scheme of the layers location in the compression chamber.

Figure 4, that is built based on the calculation results for the optimized compression device,
shows possibilities of the pressure measurement. Fig. 4a presents time dependence of pressures $P(H_2)(\langle \rho(H_2) \rangle)$, $P(W)(\langle \rho(W) \rangle)$, $P(Al)(\langle \rho(Al) \rangle)$ in $H_2$, contrasting layer and $Al$, correspondingly. 

Here $\langle \rho \rangle$ – sample density, averaged on the volume, in the central region of the compression chamber, where the sample is compressed uniformly along the axis. Similar dependencies are presented in Fig. 4b for $D_2$. (Time in Fig. 4 is counted from the beginning of the magnetic flux compression of the MC–1 generator). One can see that there is a rather large time interval on a fore and back front of the compression pulse – so called “working section”, when the pressures in the studied isotope and $Al$ have small difference. During analysis of the experimental data this difference could be considered by application of calculation based correction. It is also important that the pressure changes from $\sim 1$ Mbar to $\sim 4$ Mbar on the working sections, thus covering the whole pressure range that is interesting for us.

Two experimental series - one with $H_2$, another with the $D_2$ were carried out using this device. In each experiment we x-rayed the central section of the device at a moment, when the ultra-high pressure was achieved in the compression chamber. (We tried to hit the working section of the compression pulse). The image was made with several films. Based on the results of their analysis we found out the value of the outer radius of the aluminum cylinder $R(Al)$ and the inner radius of the contrasting cylinder $R$ (see Fig. 3). The used method [12] allows us to measure these values with the precision up to hundredth of millimeters. In this case the characteristic values of the measured radii themselves lie in the range of $1.5 \div 6$ mm. Using $R$ value we can find the cross-section of the studied sample, and, consequently, its compression. The density of the isotope is equal to $\rho = \rho_0 \delta$, where $\delta$ – compression, $\rho_0$ – a crystalline isotope density at normal pressure and helium temperature. ($\rho_0(H_2) = 0.088$ g/cm$^3$, $\rho_0(D_2) = 0.202$ g/cm$^3$ [25, 26]). The pressure in the studied sample is determined with the formula: $P = P(Al)(\delta(Al))(1 + \varepsilon)$. Here $P(Al)(\delta(Al))$ – expression for the “cold” isentropic curve of Al that corresponds to the paper [14], $\delta(Al)$ - aluminum compression relatively to its normal density, $\varepsilon$ – relative gradient correction.

The value of the external radius of the contrasting shell $R(W)$ that is necessary for Al compression calculation could be found from the condition of the pressures equality in the reference and in the contrasting shell: $P(Al)(\delta(Al)) = P(W)(\delta(W))$. (In Fig. 4 one can see that this condition is fulfilled with good precision on the whole working section of the compression pulse.) In this case the expression for the isentropic curve of the tungsten alloy is selected in the form, recommended in [13]. The values of the parameters – coefficients of the corresponding $D(U)$ ratio – are taken from the book [27], where they are presented for pressure interval that is interesting for us. It

![Figure 4. Pressures vs. time for optimized compression device: a) – $H_2$, b) – $D_2$.](image-url)
is necessary to note that variation of these parameters within the errors limits, with which they were measured (see [27]), do not affect significantly the measurement results. Using the $R^{(Al)}$ and $R^{(W)}$ we find compression $\delta^{(Al)}$, and further the pressure $P = P^{(Al)}(\delta^{(Al)})$. Taking into account $\varepsilon$ we find pressure $P$ in the studied substance.

The gradient correction could be found with calculations with the following way. Using the MHD code [18] we calculate the process, taking part in the central section of the compression device. In this case the measurements of the seed field in the considered experiment are taking into account. Then, based on calculation dependencies of the radii of the studied and reference samples on time – $R_{calc.}(t)$ and $R^{(Al)}_{calc.}(t)$ – we built in the plane $(R^{(Al)} - R)$ the corresponding “trajectory” $(R^{(Al)} - R$ diagram). Here we plot an experimental point $(R^{(Al)}; R)$ showing its measurement error. Figure 5 shows this by the example of one of the experiments with $H_2$. (For comparison the dotted line shows similar diagram that corresponds to the calculations, where the Al is described with isentropic curve [13] that is more rigid in comparison with [14].)

Then we find such “trajectory” point $(R^{(Al)}_{calc.}; R_{calc.})$ which is the most close to the experimental point. For the values of $R^{(Al)}_{calc.}$ and $R_{calc.}$, using the procedure presented above, we calculate $\delta^{(Al)}_{calc.}$ and $P^{(Al)}(\delta^{(Al)}_{calc.})$. We find the pressure in the studied substance $P(\delta_{calc.})$ using the expression for the “cold” isentropic curve of the hydrogen isotope, built in accordance with [3]. Relative gradient correction is equal to: $\varepsilon = \left( P(\delta_{calc.}) - P^{(Al)}(\delta^{(Al)}_{calc.}) \right) / P^{(Al)}(\delta^{(Al)}_{calc.})$. After building the sought curve of the “cold” compression in the first approximation, the gradient correction should be recalculated using the built curve in order to make the procedure of the correction search self-consistent.

In the used method the calculation precision of the density and pressure is determined, first of all, by the measurement precision of the transversal sizes of the aluminum and contrasting shells in initial and compressed states. The radii measurement errors $\Delta R$ and $\Delta R^{(Al)}$ of the compressed shells usually exceed on one order the measurement error of the initial sizes. That is why the latter is neglected on this stage of investigations. To find out the pressure measurement error $\Delta P$ we changed the point coordinates $(R^{(Al)}; R)$ on the value $\pm \Delta R^{(Al)}$ and $\pm \Delta R$, correspondingly. In the result there are four points in the $R^{(Al)} - R$ plane, that are slightly shifted relatively to the initial one. For each point we found the pressure $P$ in the studied sample using the above

![Figure 5. Experimental point and calculated curves in the plane $R^{(H_2)} - R^{(Al)}$.](image-url)
The difference between maximum and minimum of the obtained values was accepted as $2\Delta P$. The compression measurement error $\Delta \delta$ could be found with the same way, based on the error $\Delta R$, with which the inner radius of the contrasting cylinder was measured.

The gradient correction for most points appeared to be relatively small – not more than the error interval $2\Delta P$. But both in case H$_2$ and in case D$_2$ the correction slightly exceeded error interval for the points corresponding to the maximum and minimum of measured pressures. (It is not surprising since the pressures in these points lie outside the interval 1–4 Mbar, that correspond to the working section of the compression pulse.) In order to find out the effect of the hydrogen isotope EOS, used in the calculations, on the gradient correction, we calculated it one more time. But now we were based not on the zero isotherm [3], but using data from the paper [23], which correspond to more rigid “cold” curves of the hydrogen isotopes at the pressures > 1 Mbar. It was found out that in the cases when the initially calculated correction was small, it remained the same; for the mentioned extreme points the absolute value of the correction exceeded $2\Delta P$ again, but the relative correction $\varepsilon$ in this case did not change significantly. (Thus, for example, for the point, having the largest gradient correction from all multi-megabar points, the change of $\varepsilon$ was $\sim 9\%$). Thus, varying the “cold” compression curve in relatively wide range does not effect significantly on consideration of the gradient correction.

In the result of a series of full-scale experiments on determination of the “cold” curve of hydrogen isotopes there were built five experimental points for protium and the same number - for deuterium. They are presented in Fig. 6 in the coordinates $P – \delta$. Solid line in this figure shows the curve that approximates the obtained data. It represents a sum of the static-lattice pressure and contribution of zero-point oscillations. The theory of Mie-Gruneisen-Debye (see [28, 3]) was used at construction of this curve. At first, the pressure of the zero oscillations and the thermal component (which appeared to be negligibly small due to extremely low initial temperature of the studied sample) were subtracted from the total pressure for each point. After that the contribution of the static lattice was written in the form of the Vinet function [29]: $P_{SL} = 3K_0(V/V_0)^{-2/3} \left[ 1 - (V/V_0)^{1/3} \right] \times \exp \left( 3(K_1 - 1) \left[ 1 - (V/V_0)^{1/3} \right] /2 \right)$, ($V$ — molar volume). Fitting parameters have the following values: $K_0 = 0.744 \times 10^{-2}$ Mbar, $K_1 = 5.868$, $V_0 = 17.825$ cm$^3$/mol for H$_2$; $K_0 = 0.817 \times 10^{-2}$ Mbar, $K_1 = 5.959$, $V_0 = 16.875$ cm$^3$/mol for D$_2$. Dashed line in Fig. 6 shows extrapolation of the zero isotherm from [3] to the multimegarange. Here we also dotted a similar curve suggested in [23] (for molecular phase). On the initial section – at the pressures up to 1 Mbar – all three curves almost coincide with each other.
**Figure 7.** Comparison between experimental zero isotherm $H_2$ and theoretical equations of state: LDA molecular solid [30], PIMC molecular $H_2$ [31], QMC atomic and molecular solid [32, 33], CEIMC atomic $H_2$ [34].

If we consider the whole range of the studied pressures, one can see that the obtained data within the error limits agree with the zero isotherm [3]. Nevertheless, the experimental points lie slightly higher the specified isotherm at pressures of several megabars. Also one can see that the approximating curve appeared to be less “rigid” in comparison with [23].

In Figure 7 we compare our built isotherm for $H_2$ with the results of several first-principle calculations [30, 31, 32, 33, 34]. We think that the best matching is observed for the points obtained with the quantum Monte-Carlo [32, 33] and coupled electronic-ionic Monte-Carlo method [34].

On this stage of the investigations we did not discuss the issue of peculiarities existence on the compression curves, stipulated by possible lattice rearrangement. This is because the experimental data are not complete enough for this purpose. Thus, in Fig. 6a one can see that in order to make more definite and reliable conclusions about the course of the studied zero isotherm it is desirable to have additional protium points near 3.5 Mbar. For $D_2$ not excessive will be one more point near 5 Mbar, where the gradient correction and measuring errors are maximum.

In conclusion it is necessary to note that using the described method of the isentropic compression one can study the curve of the “cold” pressure of the number of other substances, consisting of the elements with small atomic number, such as helium, lithium etc.

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