

of the acoustic turbulence excited by an external source. If the sound intensity satisfies the criterion (3.2), then no energy redistribution over the spectrum takes place, since the sound attenuation due to turbulence exceeds the inelastic scattering of sound (3.1). In this case, the acoustic spectrum outside the pumping region will be "equilibrium"³: $E(\omega_s) \sim \omega_s^{-7/2}$. If the sound intensity exceeds the threshold (3.2), but all the criteria (3.5) are satisfied, then the interaction of the sound with sound can be studied in the approximation of the kinetic equation, and the sound interaction with the turbulence leads to isotropization of the acoustic spectrum with a time $\tau^{-1} \approx k_s \nu M (k_s L)^{-2/3}$ [see (2.19)]. In this case, the isotropic spectrum of Zakharov-Sagdeev is established⁷

$$E_s \sim k^{-2/3}$$

as the exact solution of the kinetic equation.

At higher intensities, the criterion (3.5) is violated and we fall into the region of strong acoustic turbulence where the Kadomtsev-Petviashvili spectrum exists.¹⁰

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Equation of state of molecular hydrogen. Phase transition into the metallic state

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The parameters of semi-empirical model equations of state of the solid and liquid phases of molecular hydrogen are obtained on the basis of experimental data on the isentropic compression and thermodynamic properties at atmospheric pressure. It follows from the equation of state of the molecular phases, which is derived in the present paper, and from the equation of state of the metallic phase as given by Kagan, Pushkarev, and Kholas [*Sov. Phys. JETP* 46, 511, (1977)] that the phase transition into the metallic state at $T = 0$ K can take place at a pressure from 2 to 4 Mbar. Two variants of the phase diagram of the solid and liquid molecular and metallic hydrogen are calculated.

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1. INTRODUCTION

One of the essential problems in the study of metallic hydrogen, is the determination of the state parameters at which the molecular hydrogen becomes metallic. The rather wide range of theoretical estimates obtained until recently for the possible transition pressures was due mainly to the uncertainty of the thermodynamic potential of molecular hydrogen, which could not be calculated reliably enough theoretically. Therefore in this paper, just as before,^{1,2} the equation of state of the

molecular phase at high pressures, and its zeroth isotherm, are determined from the aggregate of a variable and experimental data, while the theoretical concepts are used to construct a physically substantiated model-deduced semi-empirical equation of state.

In contrast to the preceding papers,^{1,2} we take the rotation into account in the equation of state of molecular phase. The zeroth isotherm and the zero-point oscillation energy in the equation of state of the metallic hydrogen are taken in accord with the data of Kagan,

Pushkarev, and Kholas.³ From the obtained equations of state of the three phases (solid and liquid molecular hydrogen and metallic hydrogen) we determine the phase diagram. Three phase diagrams of hydrogen are presented, corresponding to somewhat differing equations of state of the molecular and metallic hydrogen. In addition, we obtain a more accurate experimental value of the density of isentropically compressed hydrogen at a pressure $P \sim 7.4$ Mbar.

2. EQUATION OF STATE OF MOLECULAR HYDROGEN IN SOLID AND LIQUID PHASES, AND COMPARISON OF THE CALCULATIONS WITH THE AVAILABLE EXPERIMENTAL DATA

In the preceding papers^{1,2} we obtained the equation of state of solid and liquid phases of molecular hydrogen. In the present paper this equation is supplemented with a term that takes into account the rotation of the molecules. According to Ref. 4, at a temperature $T > \Theta_{\text{rot}}$ the contributions of the rotation to the free energy, to the internal energy, and to the entropy are respectively

$$F_{\text{rot}} = -RT \ln \frac{T}{2\Theta_{\text{rot}}}, \quad E_{\text{rot}} = RT, \quad (1)$$

$$\frac{S_{\text{rot}}}{R} = 1 + \ln \frac{T}{2\Theta_{\text{rot}}},$$

where Θ_{rot} is the characteristic temperature of rotation of the molecule. In the calculation we assumed the following dependence of Θ_{rot} on the density ρ :

$$\Theta_{\text{rot}} = \Theta_n (\rho/\rho_n)^{1/2},$$

where $\Theta_n = 85.4$ K and $\rho_n = 0.089$ g/cm³ is the density at $P=0$ and $T=0$. Allowance for the dependence of the rotation temperature on the density gives the contribution of the rotation to the pressure.

The equations for the free energy of the solid and liquid phases of molecular hydrogen, with account of a rotation of the molecule, will be expressed in the form¹

$$F_{\text{sol}} = E_x + \frac{1}{2} R\Theta + RT \left[3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right] + F_{\text{rot}}, \quad (2)$$

$$F_{\text{liq}} = E_x + \frac{1}{2} R\Theta + 3RT \left\{ \ln \left[\frac{\Theta}{T} (1+z)^{-n} \right] - b \right\} + 3RT \delta + F_{\text{rot}}. \quad (3)$$

In (2) and (3),

$$E_x = \frac{3}{\rho_c} \sum_{i=1}^3 \frac{a_i}{i} (\delta^{1/3} - 1), \quad \delta = \frac{\rho}{\rho_c}$$

$$\Theta = \Theta_0 \left[\frac{d^2 E_x}{d\delta^2} \Big|_{\delta=1} \right]^{-1/2} \left[2 \left(1 - \frac{n}{3} \right) \delta \frac{dE_x}{d\delta} + \delta^2 \frac{d^2 E_x}{d\delta^2} \right]^{1/2} \delta^{1/2},$$

$D(\Theta/T)$ is the Debye function,

$$z = lRT \left\{ 2 \left(1 - \frac{n}{3} \right) \delta \frac{dE_x}{d\delta} + \delta^2 \frac{d^2 E_x}{d\delta^2} \right\}^{-1},$$

$$f = c + \frac{a}{r} \left[\left(\frac{\delta}{\delta_0} \right)^r - 1 \right],$$

R is the gas constant, δ_0 and T_0 are the relative density and temperature at the melting point at atmospheric pressure, and a_i , a , b , c , l , n , and r are empirical constants. The numerical values of the constants used in the calculations are given in the first line of Table I.

Figure 1 shows a comparison of the calculated isotherm $T=0^\circ$ K with the experimental data of Stewart⁸ and Anderson.⁹ The figure shows also the calculated shock adiabat, corresponding to compression of hydro-

TABLE I.

Variant	a_1	a_2	a_3	a_4	a_5	n	l	r	a	b	c
	kbar										
I	-4.8905	61.8404	-149.602	102.8812	-10	2	4	-4	-4.888	1.2244	-0.4929
II	-15.012	85.362	-155.988	85.336	0	2	4	-4	-3.3552	1.28236	-0.51277

Note. Here $\rho_0 = 0.1335$ g/cm³, $T_0 = 14$ K, $\Theta_0 = 278$ K, $\delta_0 = \rho_0/\rho_c = 0.579$.

gen from the solid state¹⁰ at $\rho_n = 0.089$ g/cm³. As seen from the figure, the agreement is good. The filled circles in the figure are the results of the experiment of Kechin *et al.*¹¹ along the solid phase on the melting curve.

Figure 2 shows a comparison of the calculated shock adiabats for single and double compression with the experimental data taken from Refs. 12 and 13.² The agreement is satisfactory. The temperature is calculated by us ($T=1500$ K at $P=200$ kbar and $T=8200$ K at $P=900$ kbar) are close to those calculated in Ref. 12 (see Fig. 6 below).

In Fig. 3, the melting curve of molecular hydrogen, obtained from the equations of state of the solid and

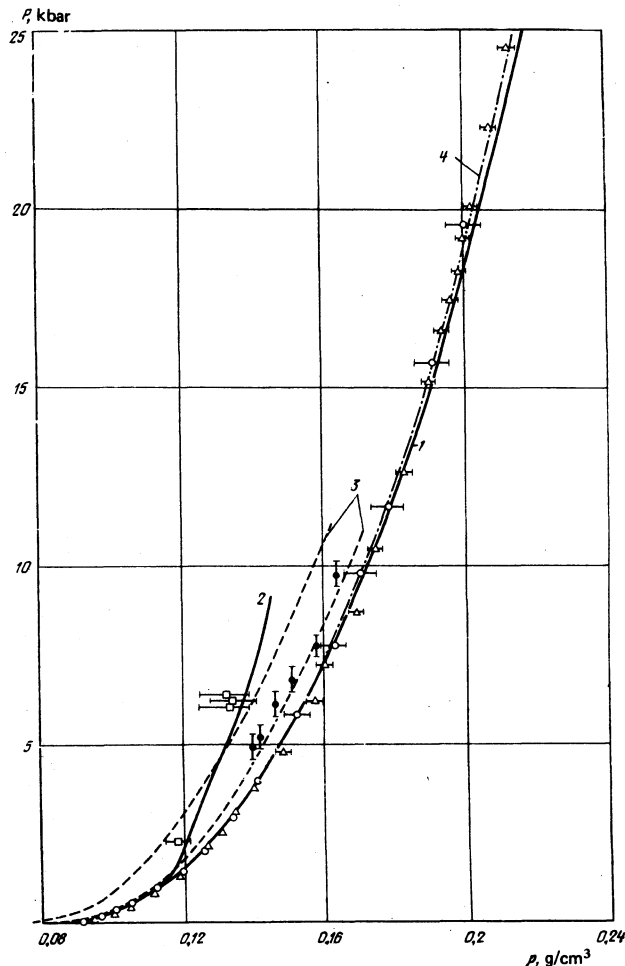


FIG. 1. Comparison of calculated zeroth isotherm (curve 1) and shock adiabat (curve 2) with the experimental data: O, Δ, □, and ●—Refs. 8, 9, 10, and 11, respectively. Curves 3—region of existence of solid and liquid phases, 4—calculated zeroth isotherm with the parameters II of Table I.

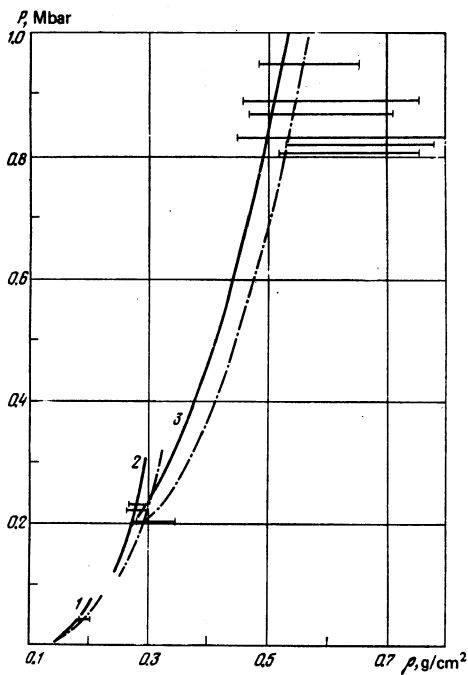


FIG. 2. Comparison of the calculated shock adiabats in single and double compression (solid curves) with the experiments of Van Thiel *et al.*^{12,13} (horizontal segments). Curve 1—single compression ($\rho_0 = 0.079$), 2—single compression ($\rho_0 = 0.085$), 3—double compression ($\rho_0 = 0.085$). Dash-dot curves—calculated shock adiabats with parameters II of Table I.

liquid phases [Eqs. (2)–(3)] is compared with the experimental data of Refs. 11 and 14. As seen from the figure, up to $T \sim 60$ K the calculated melting curve coincides with the experimental one,¹⁴ and above 60 K it agrees fairly well with the experiment.¹¹ Only at $T > 100$ K is a certain discrepancy observed.

Figure 4 shows a comparison of the isentrope calculated from equations of state calculated in the present paper for molecular hydrogen with the experimental data on isentropic compression of hydrogen as obtained in Refs. 1 and 2.

The position of the point at the highest density was determined by us more accurately. The average density of isentropically compressed hydrogen under these conditions ($P \approx 7.4$ Mbar) was 1.72 g/cm^3 with an uncertainty $\pm 10\%$ (see the last line of Table II).

The results of the gasdynamic computer calculations of the density and of pressure are given in Table II and Fig. 4 (triangles). As seen from Fig. 4 and Table II, up to $P \approx 3$ Mbar the densities of the isentropically compressed hydrogen, calculated from the equations of state of the molecular phase, agree well with the experimental values.

Thus, all the presently available experimental data on static,^{8,9,14,11} shock^{12,13} and isentropic^{1,2,13} compression of hydrogen and deuterium are satisfactorily described by the equations of states given above for the solid and liquid phases of molecular hydrogen.³⁾

The difference between the zeroth isotherm obtained in the present paper for molecular hydrogen and the zeroth isotherm for preceding papers^{1,2} (see Fig. 4) is due to allowance for the rotational degree of freedom, which led to an increase of the effective heat capacity, to a decrease of the temperatures in the isentrope, and to a decrease of the fraction of the thermal component in the isentropic compression of the hydrogen.

We note that if the characteristic temperature of the rotation of the molecules remains constant with increasing density, this will lead to an even greater lowering of the temperature on the isentrope, and the position of the zeroth isotherm of the nuclear hydrogen will be more rigid (lower density at a given pressure). Eqs. (2) and (3) remain the same as before, except that Θ_{rot} becomes a constant quantity and does not contribute to the pressure. In this case the numerical parameters of the equation of state of the molecular hydrogen have different values (see Table I, lower line). The equations of state of the molecular hydrogen calculated with these parameters, the isotherm at $T = 0$, and the shock adiabats are all shown in Figs. 1 and 2 by dash-dot lines. They agree better with the experimental data. At $P = 200$ kbar the temperature on the shock adiabat is $T = 4900$ K, and at $P = 900$ kbar we have $T = 6200$ K.

We call attention to the fact that even the more rigid zeroth isotherm of molecular isotherm, calculated in Refs. 16 and 17, disagree substantially with the isentropic-compression experimental data obtained in Refs. 1, 2, and 15. If the compression of the hydrogen is calculated using the zeroth isotherms from Refs. 16 and 17, then the hydrogen density turns out to be much low-

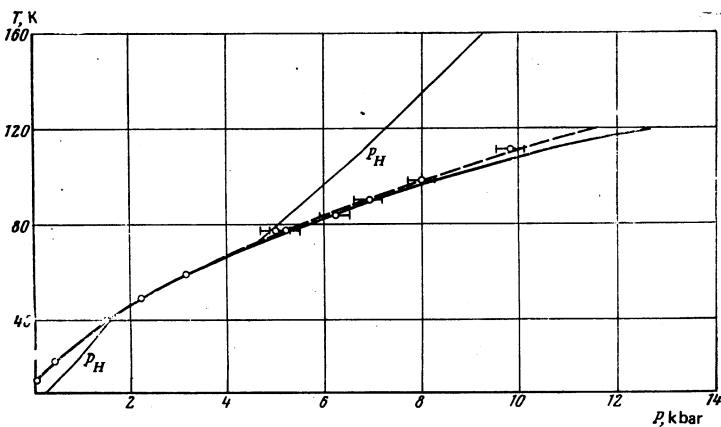


FIG. 3. Comparison of the calculated molecular-hydrogen melting curve—thick curve—with the experimental data: \circ — $T < 60^\circ \text{ K}$ from Ref. 14, \triangle —from Ref. 11, P_H —calculated shock adiabat corresponding to experiment¹⁰; the dashed curve was calculated from Simon's formula.

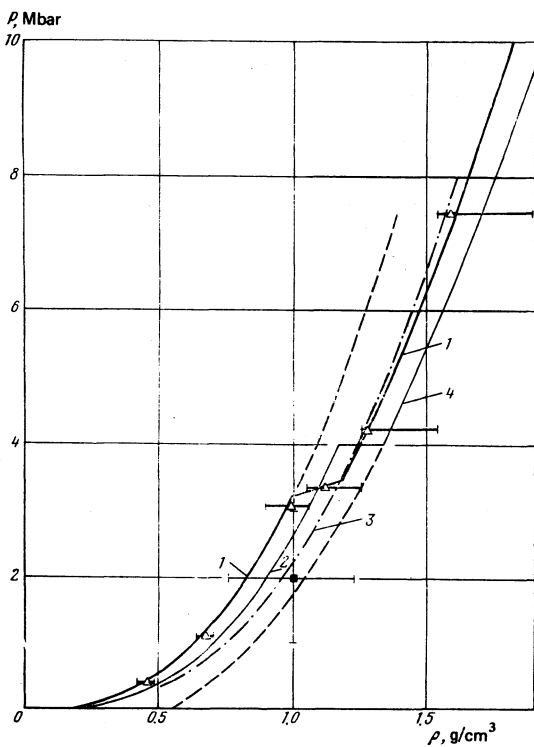


FIG. 4. Zeroth isotherms and isentropes of molecular and the product hydrogen: 1—isentropes calculated in the present paper, 2—zeroth isotherm of molecular hydrogen of the present paper, 3—zeroth isotherm of molecular hydrogen calculated in Ref. 2, 4—zeroth isotherm of molecular hydrogen calculated in Ref. 3. The six horizontal segments show the experimental data of the present paper of Refs. 1 and 2; ■—experiment,¹⁵ Δ gasdynamic calculation with a computer; dashed—extrapolation of the corresponding curves.

er than the value experimentally registered in Refs. 1 and 2.

3. PHASE TRANSITION INTO THE METALLIC STATE AT $T=0$

It is seen from Fig. 4 and Table II that, just as in Ref. 1, the experimental point on isentropic compression above three Mbar do not fit the equation of state of molecular hydrogen. Identifying, as before,¹ this anomaly with a transition of hydrogen into the metallic state, we obtain the pressure and density of this transition at $T=0$.

As the zeroth isotherm of the metallic hydrogen we use the data of Ref. 3 in the form

$$E_x = 13.00344 + 14.8647\rho^{1/2} - 25.35085\rho^{3/4} - 0.90763\rho^{-1/4} - 0.20196\rho^{-1/2} - 0.26932 \ln \rho - 0.1088\rho^{-1/4} \ln \rho. \quad (4)$$

The energy is reckoned from the energy of the isolated molecules plus the ionization and dissociation energy. The energy of the zero-point oscillations is written in

TABLE II.

ρ_{exp} , g/cm ³	ρ_{calc} , g/cm ³	P_{calc} , Mbar	T_{calc} , K	ρ_{exp} , g/cm ³	ρ_{calc} , g/cm ³	P_{calc} , Mbar	T_{calc} , K
0.45±0.03	0.46	0.4	2300	1.15±0.1	1.12	3.3	4000
0.67±0.03	0.68	1.1	3000	1.40±0.14	1.27	4.2	4000
0.98±0.08	1	3.0	4200	1.72±0.18	1.58	7.4	4700

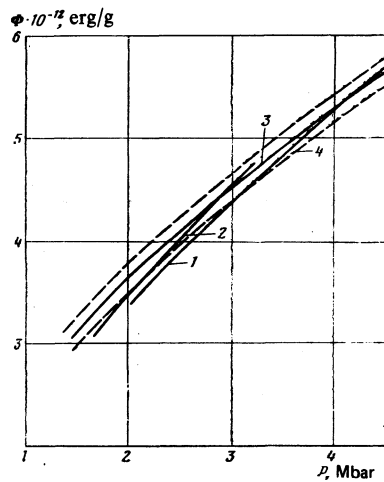


FIG. 5. Dependence of the thermodynamic potential on the pressure at $T=0$; 1—for molecular hydrogen with set I of the parameters in Table I; 2—for molecular hydrogen with set II of the parameters of Table I; 3—for metallic hydrogen according to Ref. 3; the dashed curve shows the region of uncertainty of curve 3 according to Ref. 5.

the form³

$$E_{zp} = 0.4761\rho^{1/2} - 0.01537\rho^{-1/4} - 0.23192\rho^{1/4}. \quad (5)$$

In (4) and (5), the numerical values are given in units of 10^{12} erg/g if ρ is in g/cm³.

The data of Ref. 3 for the metallic phase of hydrogen are represented by curve 4 on Fig. 4 in the form of a plot of $P_x + P_{zp}$ against the density, and by curve 3 in Fig. 5, which shows the thermodynamic potential $\Phi(P) = E + PV$ at $T=0$. The dashed curves in Fig. 5 characterize the degree of uncertainty of curve 3, estimated in Ref. 3. Curves 1 and 2 represent the thermodynamic potentials of the molecular hydrogen at $T=0$ as functions of the pressure, with the parameter sets I and II respectively of Table I. The intersection of curves 1 and 3 shows that the phase transition takes place at $P \approx 4$ Mbar with a density jump from 1.17 to 1.35 g/cm³. When curve 1 crosses the lower limit of the spread of the zeroth isotherm of the metallic phase, the transition drops to $P \approx 3$ Mbar. The more rigid zeroth isotherm of the molecular phase (see Fig. 1, dash-dot), whose thermodynamic potential is shown by curve 2 of Fig. 5, in conjunction with the same lower limit of the zeroth isotherm of the metallic phase, decreases the phase-transition pressure from ~ 3 to ~ 2 Mbar.

4. PHASE TRANSITION OF MOLECULAR HYDROGEN INTO A METAL AT $T \neq 0$

As already noted, the experimental data on isentropic compression at $P > 3$ Mbar do not fit the equation of state of the molecular phase of hydrogen, and the anomaly in the properties of the hydrogen in this pressure region, which was noted earlier,¹ still remains. Just as in Ref. 1, we identify this anomaly with a transition of hydrogen into the metallic state and describe all the experimental data with allowance for the fact that the phase transition takes place at $T \neq 0$ and $P \approx 3$ Mbar.

The equation of state of metallic hydrogen is assumed

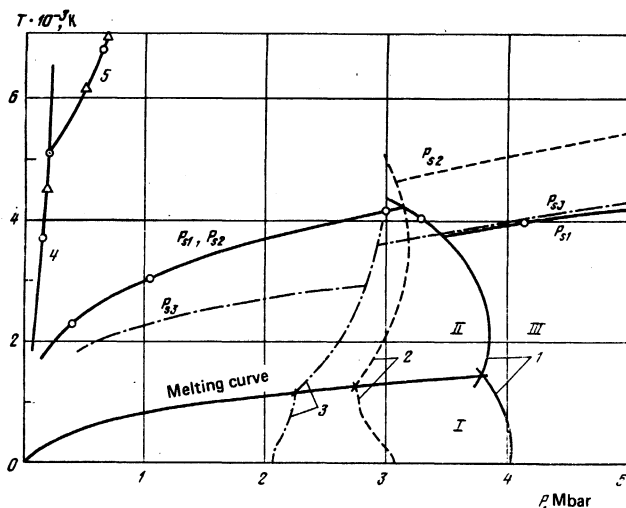


FIG. 6. Phase diagram of hydrogen: I—solid molecular phase, II—liquid molecular phase, III—metallic phase. The phase-equilibrium curves correspond to the following: 1—molecular phase with parameters I of Table I and metallic—the basic curve of Ref. 3; 2—molecular phase with parameters I of Table I and metallic phase according to the lower limit of the spread in Ref. 3 (Fig. 5, curve 4); 3—to a molecular phase with parameters II from Table I and a metallic phase from the lower limit of the spread.³ The curves P_{s1} , P_{s2} , and P_{s3} are the corresponding isentropes of the molecular and metallic hydrogen. The triangles and circles are the calculated values of Ref. 12 and of the present paper respectively. Curves 4 and 5 are the calculated shock adiabats of the present paper for single and double compression respectively.

to be⁴⁾

$$F_m = E_x + \frac{9}{8} R \Theta + RT [3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T)] - \frac{1}{2} \beta T^2. \quad (6)$$

The dependences of E_x and $E_{ep} = (9/8)R$ were taken in accordance with Eqs. (4) and (5); this determined also the $\Theta(\rho)$ dependence. The last term in (6) describes the thermal contribution of the electrons. In accord with the theory of free electrons, it is assumed here that

$$\beta = 45006^{-1/2} [\text{erg/g} \cdot \text{K}^2].$$

The phase diagram of hydrogen in T — P coordinates is shown in Fig. 6, where a transition between three phases is considered; solid and liquid molecular hydrogen and metallic hydrogen. Three variants of calculation are represented.

In the first (curves 1) the molecular phase was taken with parameters I of Table I, while for the metallic phase we took the basic curve from Ref. 3. As already indicated, in this case the transition from solid molecular hydrogen into metallic hydrogen occurs at $P \approx 4$ Mbar and $T = 0$, with a density jump from $\rho = 1.17$ to $\rho = 1.34$ g/cm³. At the point $T = 1440$ K and $P = 3.78$ Mbar (see Figs. 6 and 4) there exist three phases: solid molecular at $\rho = 1.16$ g/cm³, liquid molecular at $\rho = 1.11$ g/cm³, and metallic at $\rho = 1.29$ g/cm³. The isentrope of the molecular hydrogen at $\rho = 0.99$ g/cm³, $P = 3 \times 17$ Mbar, and $T = 4220$ K enters in the two-phase region, and at $\rho = 1.19$ g/cm³, $P = 3.44$ Mbar, and $T = 3740$ K it goes from this region into the metallic phase. The calculated isentrope agrees with the experimental data on the isentrope compression in the investi-

gated density region (see Fig. 4).

If we introduce into the equation of state of the metallic hydrogen a parameter z analogous to that used in Eq. (3) for the liquid molecular phase, and assume the zeroth isotherm to delay the limits of its value from Ref. 3 (see curve 4 of Fig. 5), then the phase diagram takes the form shown by curves 2 of Fig. 6. In this case $l = 3$. The triple point will be observed at $P = 2.74$ Mbar and $T = 750$ K, with a change of the density of the molecular hydrogen from 0.988 to 1 g/cm³, while the density of the metallic hydrogen is $\rho = 1.15$ g/cm³. The isentrope of the molecular hydrogen crosses the two-phase region at $P = 3.15$ Mbar, $T = 4200$ K, and $\rho = 0.988$ g/cm³, and goes from this region into the metallic phase at $P = 3.09$ Mbar, $T = 4630$ K, and 1.122 g/cm³.

Finally, the third variant of the T , P diagram, shown by the dash-dot curve in Fig. 6, was calculated on the basis of the molecular phase with parameters II of Table I, and of the metallic phase with curve 4 of Fig. 5. At $T = 0$ the phase transition occurs in this case at $P \approx 2.1$ Mbar, with a density jump from 0.868 to 1.06 g/cm³. The triple point is at $P = 2.25$ Mbar and $T = 1140$ K, with a density jump in the molecular phase from $\rho_{liq} = 0.874$ g/cm³ to $\rho_{sol} = 0.887$ g/cm³, and $\rho_m = 1.079$ g/cm³. The isentrope has a kink at $P = 2.85$ Mbar, $T = 2950$ K and $\rho = 0.922$ g/cm³, and goes into the metallic phase at $P = 2.92$ Mbar, $T = 3600$ K, and $\rho = 1.113$ g/cm³.

The intersection of curve 2 with the basic curve of Ref. 3 yields at $T = 0$ a phase-transition pressure $P \approx 2.8$ Mbar. In this case, however, the transition on the investigated isentrope should occur at $P \approx 3.7$ Mbar, which is higher than the observed anomaly.

The three variants of the calculated phase diagram shown in Fig. 6 cover all the possibilities of satisfactorily describing all the experimental data under different variations of the equation of state of the molecular and crystalline phases within the framework of the concepts assumed by us.

We note in conclusion that in the experiments performed to date^{1,2,13-15} only the energy, density, and pressure were assumed. To refine the phase diagram, and consequently also the equations of state of the hydrogen, in both the molecular and metallic phases, it would be most valuable to measure directly or indirectly the temperature in the already investigated compression processes.

- ¹⁾The form of the equations of state and the procedure of finding its parameters are derived in Refs. 5-7 and 2.
- ²⁾The data of Ref. 12, obtained with deuterium, have been converted here to protium by decreasing the intensity by one-half (see Ref. 2).
- ³⁾The earlier^{1,2} analysis of the experimental data on shock^{12,13} and isentropic^{1,2,15} compression of hydrogen and deuterium has shown that both hydrogen and deuterium are in the liquid phase in the entire investigated range of densities and pressures.
- ⁴⁾No distinction is made here between solid and liquid metallic hydrogen.

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The Callen-Welton and Kubo formulas for nonequilibrium states

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A self-consistent formulation of the fluctuation-dissipation theorem (FDT) is given for a macroscopic system in which the interaction of the particle can be separated into a strong and a weak part. The properties of the system considered determine not only the susceptibility tensor and the spectral densities of the internal parameters but also the spectral densities of the generalized forces conjugate to the internal parameters under consideration. As the weak interaction we consider the interaction of atoms via the fluctuating electromagnetic field in the dipole approximation. A theory of nonequilibrium fluctuations is developed. For nonequilibrium states the fluctuation-dissipation relation holds only for individual transitions and includes a dependence on the nonequilibrium distribution function. The corresponding kinetic equations, which describe, in particular, the process of relaxation to the Gibbs distribution, are found. In this case a spectral distribution in accordance with the equilibrium FDT is established. As an example, the kinetic equation for a gas whose atoms interact only via field fluctuations is obtained from the general kinetic equation. The first-moment approximation for the averaged density matrix and mean field is considered. The kinetic equation obtained can be used to describe the kinetics of equilibrium and nonequilibrium coherent states, e.g., in phase transitions and super-radiance in the atoms + field system.

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1. INTRODUCTION

We recall briefly the content of the well known Callen-Welton and Kubo formulas. This is necessary for the formulation of the problem of the present paper. We consider a macroscopic system with Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \quad \hat{H}_1 = - \sum_i X_i F_i(t), \quad (1.1)$$

where \hat{H}_0 is the Hamiltonian of a macroscopic system consisting of N particles interacting arbitrarily strongly, F_i are external forces, and X_i are the corresponding internal parameters.

The Callen-Welton formula establishes a connection between the dissipative (antihermitian) part of the sus-

ceptibility tensor $\alpha_{ij}(\omega)$ and the spectral density of the fluctuations of X_i in the absence of external forces, when $\langle X_i \rangle = 0$. The susceptibility tensor defines the relationship between the mean response $\langle X_i \rangle$ and the external force. In the notation of the book by Landau and Lifshitz [see Eq. (125.10) in Ref. 1], this formula has the form

$$\langle X_i X_j \rangle_\omega = \frac{i\hbar}{2} (\alpha_{ij} - \alpha_{ji}) \coth \frac{\hbar\omega}{2kT}. \quad (1.2)$$

The relationship expressed by this formula is called the fluctuation-dissipation theorem (FDT). The inverse relationship is called the Kubo formula.¹⁻⁴

The formula (1.2) is established by comparing the expressions for the susceptibility tensor and the spectral