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Properties of Metallic Hydrogen Under Pressure

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The properties of the metallic phase of hydrogen under pressure are investigated. (A detailed analysis of metallic hydrogen at zero pressure has been presented in a previous paper[1]). The static lattice energy and zero-point vibrations energy as functions of pressure are considered for a number of competing phases. The respective equations of state and thermodynamic potential of the metallic phase are found. This permits one to determine the pressure of transition from the molecular to the metallic phase. Various phase transitions which may occur in metallic hydrogen are studied and it is found that the structure of hydrogen under pressure in some respects resembles that of the liquid phase.

1. INTRODUCTION

IN an earlier paper[1] (henceforth cited as I) the authors carried out a detailed analysis of the structure of the metastable phase of metallic hydrogen at $P = 0$. It turned out that the lower energy state corresponds to a unique structure comprising a system of proton filaments forming a rigid triangular lattice in a plane perpendicular to the filaments, but which has no long-range order in the direction along the filaments. The structure of the next higher order in energy again constituted a family of filaments, but now having a quadratic lattice in the perpendicular plane.

The appearance of filamentary structures is connected to a considerable degree with the fact that the competition between the electronic contribution and the contribution of the ion lattice to the total energy causes the minimum of the energy to be realized in strongly anisotropic structures, in which the distances between ions along the chains are much smaller in this case than the distance between the chains ($c/a < 1$). This gives rise to a certain continuous family of three-dimensional structures having no energy barriers between them and going over one into the other upon parallel displacement of the chains of ions, the projection in the perpendicular plane being conserved.

With increasing pressure, however, the structure should change. Indeed, it is clear from general considerations that with increasing density an increase takes place in the relative contribution made to the energy by the ion lattice, and consequently, more symmetrical structures turn out to be favored energywise. By virtue of this, at a sufficiently high pressure, metallic hydrogen should have one of the most symmetrical structures (HPC, BCC, or HCP). Thus, a phase transition between the different metallic phases is inevitable. On the other hand, within the framework of the same structure, when the pressure increases the anisotropy decreases gradually. This should lead ultimately to violation of the conditions for the occurrence of a continuous family of structures, by virtue of which energy barriers are produced between different structures of the same family at $P = 0$, and the family will become split energywise. In this case different structures will already have the usual three-dimensional crystal symmetry.

As found in I, all the uniaxial structures have energy minima both at $c/a < 1$ and at $c/a > 1$, but the latter lie higher in energy at $P = 0$. With increasing pressure, both minima shift towards the ideal value of c/a. However, the relative positions of the minima shift towards the ideal value of c/a. However, the relative positions of the minima may vary in this case. Indeed, we shall show that this is precisely the situation, and under pressure the prolate (elongated) structures turn out to be more favored energywise.

Thus, on going from the filamentary metastable phase at $P = 0$ to the stable symmetrical phase at $P \to \infty$, we should observe a very unusual variation of the structure and of the phase transformations of metallic hydrogen under pressure. The analysis of this variation is the subject of the present paper. Just as in I, we consider only the case $T = 0$.

One of the most significant problems in the study of the properties of metallic hydrogen under pressure is, naturally, the determination of the pressure P^* at which the molecular phase becomes metallic. Numerous attempts were made earlier to determine even roughly the value of this pressure (see, e.g.,[2], where the corresponding references are cited). Unfortunately, it is impossible at present to determine the transition pressure with any degree of reliability. This is due to the unusual uncertainty in the theoretical determination of the thermodynamic potential of molecular hydrogen for high pressures. (The equation of state of molecular hydrogen was determined experimentally only up to $P = 20$ kbar[3].) To verify this, it suffices to compare the results of the most frequently cited paper by Trubitsyn[4] and the recently published paper by Neece et al.[5] We shall subsequently find the values of P^* corresponding to the results of both papers.

To find all the quantities of interest to us, we use the same method and the same approximation as in I. We discuss below only the final results.

2. PROPERTIES OF METALLIC PHASES OF HYDROGEN UNDER PRESSURE IN THE STATIC APPROXIMATION

In this section we carry out the analysis by considering only the static part of the total energy for different structures of metallic hydrogen. (The static part of the energy will obviously be identical for hydrogen and deuterium.) This makes it possible to reveal explicitly the entire qualitative picture. The complete quantitative picture, with allowance for the zero-point oscillations,

Ω_0/a_B^3	E, Ry/atom								
	PH_1	PH_2	RH_2	HCP_2	HCP	FCT_1	FCT_2	FCC	BCC
20	−1.06298	−1.05308	−1.05303	−1.05286	—	−1.05889	−1.05182	—	—
18	−1.06150	−1.05356	−1.05360	−1.05341	—	−1.05890	−1.05218	—	—
16	−1.05756	−1.05166	−1.05180	−1.05162	—	−1.05652	−1.05017	—	—
14	−1.04975	−1.04600	−1.04628	−1.04612	—	−1.05038	−1.04435	—	—
12	−1.03567	−1.03418	−1.03467	−1.03452	—	−1.03808	−1.03213	—	—
10	−1.01063	−1.01172	−1.01251	−1.01237	—	−1.01512	−1.0099	—	—
8	−0.96527	−0.96937	−0.97060	−0.97048	—	−0.97227	−0.96750	—	—
6	−0.87711	−0.88509	−0.88702	−0.88692	—	−0.88751	−0.88325	−0.88397	—
5	−0.80019	−0.81056	−0.81304	−0.81295	—	−0.81276	−0.80879	−0.81065	—
4	−0.67901	−0.69237	−0.69554	−0.69546	—	−0.69433	−0.69069	−0.69395	—
3	—	−0.48690	−0.49113	−0.49109	−0.47422	−0.48863	−0.48511	−0.49056	—
2	—	−0.06736	−0.07310	−0.07331	−0.05981	−0.06882	−0.06631	−0.07420	−0.07352
1	—	1.15867	1.14892	1.14900	1.14532	—	—	1.14552	1.14619

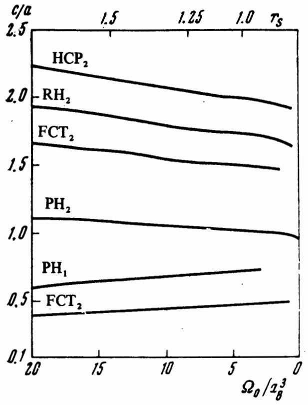

FIG. 1. Dependence of c/a on the volume for different structure.

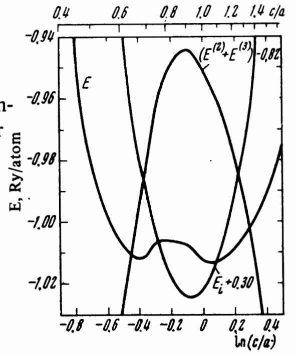

FIG. 2. Energy and individual contributions to it as functions of c/a for a primitive hexagonal structure at $\Omega_0/a_B^3 = 10.1$.

will be considered in the next section.

The table lists the values of the static energy E of different lattices in a wide interval of pressures. For a tentative comparison with the static pressure, we note that $P \approx 0$ at $\Omega_0/a_B^3 = 20$, $P \approx 2$ Mbar at $\Omega_0/a_B^2 = 10$, $P \approx 13$ Mbar at $\Omega_0/a_B^3 = 5$, $P \approx 90$ at $\Omega_0/a_B^3 = 2$, and $P = 350$ Mbar at $\Omega_0/a_B^3 = 1$. In the region up to $\Omega_0/a_B^3 \approx 8$ we can use the equation of state discussed below.

For each value of the density, we obtained the minimum of the energy as a function of c/a. The corresponding equilibrium values of c/a are shown in Fig. 1. (In lattices where the z axis coincides with the edge of the unit cell, the choice of the ratio c/a is obvious. For rhombohedral (RH) structures, the z axis, as in I, was chosen along the body diagonal. In this case the value of c for the primitive cube, for example, is equal to one-third of this diagonal, and the value corresponding to this structure is $c/a = 1/\sqrt{2}$, see Table I of I.)

The indices 1 and 2 alongside the designations of the structures correspond respectively to the left and right-hand minima on the $E = E(c/a)$ curve ("oblate" and "prolate" structures; in all monatomic uniaxial structures there are at least two minima—see Fig. 1 of I). The table lists the data for all the uniaxial structures of interest either at low or at high pressures. For simplicity, we have omitted only the data for primitive tetragonal (PT) structures in β-Sn, since they yield no new information in comparison with FCT lattices, and also the data for the RH_1 structure, which remain close to the PH_1 data. The absence of data for larger or smaller Ω_0 corresponds to the fact that the phase has no long-wave stability in the corresponding density region. An exception was made for the HCP lattice, where we retained the data, although in the wide density interval from $\Omega_0/a_B^3 = 25$ to $\Omega_0/a_B^3 = 8$ this structure turns out to be weakly unstable with respect to a shift of the sublattices relative to each other parallel to the basal plane. In a sufficiently broad density interval, the minimum value of E is possessed by the FCT_1 structure. However, as will be shown subsequently and as noted in I, allowance for the zero-point oscillations makes this structure highly unfavorable energywise compared with other structures. By virtue of this, we do not consider this structure in the discussion of the static results.

The foregoing data show, first, that up to very high pressures the anisotropic structures in metallic hydrogen remain stable and energywise favored, as before. Following the initial growth of the density, the absolute minimum, just as at $P = 0$, corresponds to "oblate" structures with $c/a < 1$, although the quantity c/a itself decreases (see Fig. 1). However, with further increase of the density, structures with $c/a > 1$ already become convenient. This can be easily traced using as an example the $E = E(c/a)$ dependence for a primitive hexagonal lattice at $\Omega_0/a_B^3 = 10$ (Fig. 2), especially if we compare it with the analogous curve given in Fig. 7 of I and pertaining to $\Omega_0/a_B^3 = 20.8$. We see that both minima have shifted with respect to c/a towards the ideal value, and the first minimum has now become deeper.

Figure 2 shows also the ionic and electronic contributions to the energy, which explain the character of the formation of these minima. We note that in the considered density interval the equilibrium values of c/a are still far from the ideal value, and the resultant phase transition is of first order.

The main structures with "prolate" unit cells (PH_2, RH_2, and HCP_2) have close values of the energy, and in a wide density interval the most convenient is the RH_2 structure, which is completely stable against arbitrary deformations. At $\Omega_0/a_B^3 \sim 8$, the FCC lattice becomes dynamically stable. It is instructive to trace the origin of the dynamic stability for the FCC phase. To this end, Fig. 3 shows the dependence of the modulus $B_{44} = C_{44}$ on r_s (curve E). At low densities it is precisely this modulus which is responsible for the instability of this structure (r_s is the average interelectron distance expressed in Bohr radii; see, e.g., I). The same figure shows the contributions from the ionic lattice (E_i) and the electronic contributions from the terms of second and third order, $E^{(2)}$ and $E^{(3)}$ (see I). We see that stability sets in only after the contribution of the ionic lattice begins to prevail over the electronic one. (We recall that in ordinary monovalent metals this is always satisfied[6].) For the modulus $B_{33} \equiv (C_{11} - C_{12})/2$, shown in the same figure, this occurs

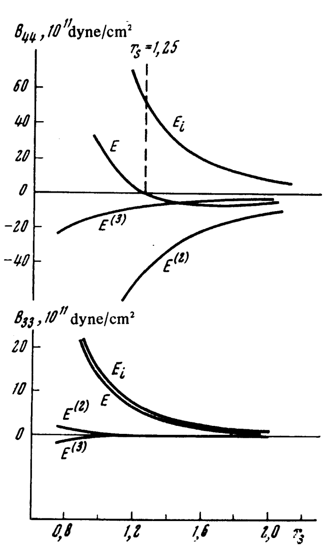

FIG. 3. Dependence of the elastic moduli B_{44} and B_{33} on the density (r_s) for an FCC lattice.

at larger r_s (and furthermore the contribution from $E^{(2)}$ is positive), and this modulus corresponds to stability in the entire density interval. In the case of the BCC structure (see Fig. 4), the modulus B_{44} becomes positive at smaller values of the density, but on the other hand the modulus B_{33}, owing to the predominance of the negative contribution from $E^{(2)}$, leads to instability up to tremendous densities corresponding to $r_s = 0.85$ ($\Omega_0/a_B^3 \sim 3$).

The stability of the FCC lattice means that one more minimum appears on the $E = E(c/a)$ curve for rhombohedral lattices at $c/a = \sqrt{2}$. However, the density must still be strongly decreased before the FCC lattice becomes energywise favored. It is of interest to trace how this minimum, which initially lies much higher in energy than the minimum of the RH_2 structure, becomes deeper at $\Omega_0/a_B^3 \sim 2.5$. For this purpose, Fig. 5 shows several $E = E(c/a)$ curves for the RH structure at different densities. (The energy origin is chosen arbitrarily, and the numbers are given in the table.) We see how the initially deep minimum for RH_2 ($c/a \sim 1.7$) becomes very shallow at densities $\Omega_0/a_B^3 \sim 1$, and vanishes completely at $\Omega_0/a_B^3 \sim 0.5$. As a result we are left only with a minimum at $c/a = \sqrt{2}$, corresponding to the FCC structure. The left-hand minimum vanishes similarly for the PH (PH_1) structure at $\Omega_0/a_B^3 \sim 3$, and the right-hand one (PH_2) goes over continuously into a structure with an ideal c/a ratio. The same is observed for HCP_2 at $\Omega_0/a_B^3 \approx 0.5$, after which there is only a minimum with the ideal ratio $c/a \approx \sqrt{8/3}$. At extremely high pressures, a BCC lattice is realized, corresponding to the predominant role of the ionic contribution (see I) and to the fact that the largest value of the Madelung constant α_M is obtained precisely in the BCC lattice. ($\alpha_M = -1.79186$ for BCC, $\alpha_M = -1.79172$ for FCC, and $\alpha_M = -1.79168$ for HCP.) We note that the final conclusion concerning the structure having the minimum energy makes it necessary to consider the zero-point oscillations every time.

3. EQUATION OF STATE. THERMODYNAMIC POTENTIAL

Before we proceed to determine the thermodynamic potential, we must find the contribution made to it by the zero-point oscillations. It should be noted immediately that in the case of metallic hydrogen, owing to the small mass of the proton and the associated high oscillation frequencies, the contribution of the zero-point oscillations turns out to be quite appreciable quantitatively, and in certain aspects also qualitatively.

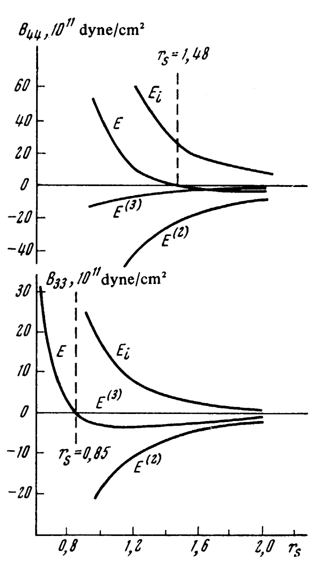

FIG. 4

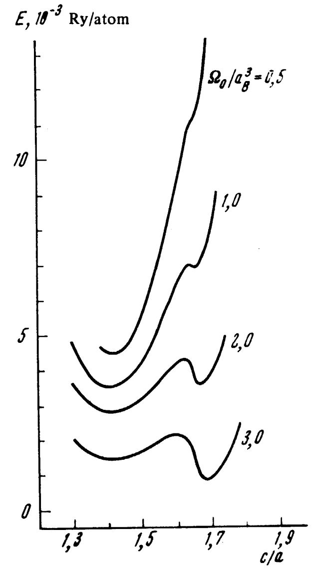

FIG. 5

FIG. 4. Dependence of the elastic moduli B_{44} and B_{33} on the density for a BCC lattice.

FIG. 5. Dependence of the energy on c/a for a rhombohedral structure at different volumes.

So far, in the estimate of the energy of the zero-point oscillations, a certain structureless approximation was used, based on the Debye approximation and its modifications (see[4,5]). In the case of anisotropic structures, however, which are typical of the pressure interval of interest to us, E_{vib} turns out to be quite sensitive to the type of lattice. Therefore, for a rigorous determination of E_{vib} we need, in principle, a direct calculation based on knowledge of the phonon spectrum in all of phase space for each value of the density. Since such a problem is exceedingly laborious, we use a certain approximate procedure, the gist of which consists in the following. For each lattice, we obtained all the elastic moduli for a given value of Ω_0. From these, by diagonalizing the corresponding matrix, we determined the sound velocities as functions of the direction of the wave vector $c_\alpha(q/|q|)$ for all three phonon branches. We then introduced an approximation wherein a simple sinusoidal form was assumed for the dispersion law of the phonon at a fixed direction q, under the condition that the frequency reaches a maximum on the boundary of the Brillouin zone. We then integrated over the entire phase space. Such an approximation was apparently adequate for the description of the integral characteristics, at least for the density interval of interest to us. This was demonstrated also by a direct comparison of E_{vib}, obtained from such an approximate scheme and with the aid of a consistently determined phonon spectrum carried out for a number of cases. The difference did not exceed several per cent. The results of the calculation for the four most interesting lattices are given in Fig. 6. In the case of deuterium,

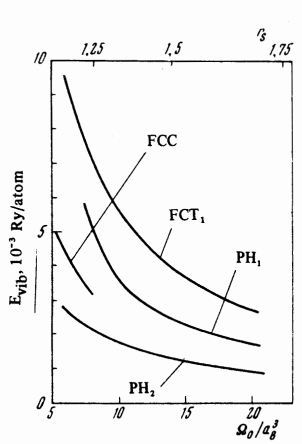

FIG. 6

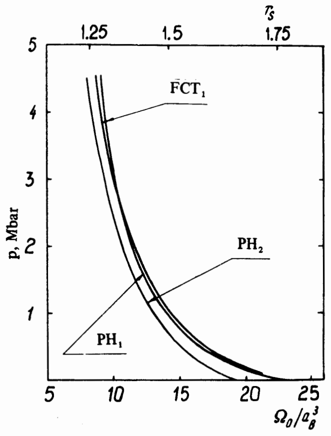

FIG. 7

FIG. 6. Energy of the zero-point oscillations for different structures as a function of the volume.

FIG. 7. Equations of state for different structures.

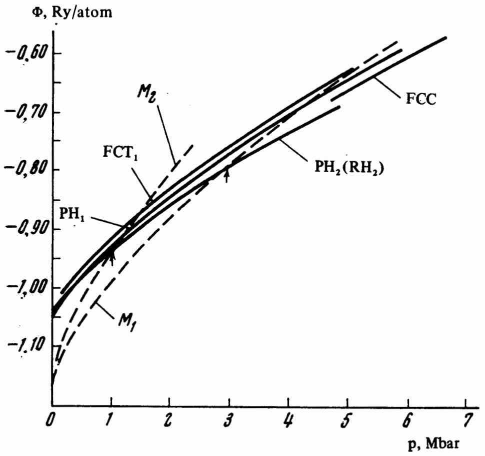

FIG. 8. The thermodynamic potential as a function of the total pressure for different structures.

all the results should be increased by a factor $\sqrt{2}$.

On the basis of the obtained data we can draw the following important conclusions, which apparently remain unchanged also when the zero-point oscillations are calculated more rigorously.

First, the energy of the zero-point oscillations depends indeed not only on the density but to a considerable degree also on the type of the lattice. The "planar" structures with prolate unit cells ($c/a > 1$) give smaller values than the filamentary ones ($c/a < 1$). The reason for this was noted already in I for $P = 0$. It is connected with the relative weakening of the shear moduli B_{66} and B_{33}. The situation remains the same also when the density is increased. This causes the energy gap between the planar and filamentary families to decrease, and the phase transition between them should occur at lower pressures than would follow from estimates of the static energy (see the table), the corresponding shift being more strongly pronounced in hydrogen than in deuterium. The conclusion derived at $P = 0$ remains valid also for the lattices of the "quadratic" family, (see I), and their vibrational energy is always much lower than for the "triangular" family. Therefore the triangular family turns out to be more favored energywise.

In addition, we call attention to the fact that in a relatively broad interval of variation of the densities, the vibration energy depends strongly on Ω_0, approximately like $1/\Omega_0$. It should be noted in this connection that the dependence of the vibrational energy on Ω_0, used in[2,4] ($E_{vib} = \text{const}/\sqrt{\Omega_0}$), which is valid in the region of extremely high pressures[7], turns out to be incorrect in the considered density interval. This is due to the fact that, as shown by direct analysis, the phonon spectrum in the main part of the phase space is determined at the given densities not by the oscillations of the ion lattice themselves, but is formed as a result of significant competition between the electronic and ionic contributions.

The results obtained above make it possible to find directly the equations of state for different phases of metallic hydrogen at $T = 0$ (the zero isotherm). These data are shown in Fig. 7 for the structures PH$_1$, PH$_2$, and FCT. The ordinates represent the total pressure, including the pressure from the zero-point oscillations. This contribution plays here a considerable role, increasing, in particular, the difference between the data pertaining to different phases. In addition, the zero-point oscillations also shift noticeably the equilibrium value of the volume ($P = 0$) for each phase, for example, for the "triangular" family we have now a value $\Omega_0/a_B^3 = 23.3$ instead of $\Omega_0/a_B^3 = 20.8$ for the static lattice.

Figure 8 shows the thermodynamic potential Φ as a function of the total pressure P for the same structures. Actually we show only the phases that have some qualitative singularities. For example, from among the members of the planar family, we give the curve only for the PH$_2$ structure, since RH$_2$ and HCP$_2$ give practically the same results, etc.

The data obtained enable us to draw a complete picture of the character of the phase transformations in metallic hydrogen in the initial pressure interval. The most convenient phase at $P = 0$, which was obtained in I and corresponds to a triangular filamentary structure, remains thermodynamically favored also up to an approximate pressure of 0.25 Mbar. In this interval (which is relatively narrow for the considered pressure scale), the energy barriers between the phases still do not manage to arise, and the triangular structures form a family with properties close to those described in I. This is followed by a transition into one of the structures with "prolate" unit cell. In this pressure region, the structures PH$_2$, RH$_2$, PT$_2$, FCT$_2$ are very close to each other in energy (see the table), although they are separated by a certain barrier (see, however, the next section). The structures of this "planar" family remain favored in a wide pressure interval, approximately up to $P = 90$ Mbar, when a phase transition into a symmetrical structure takes place (first into FCC, although BCC and HCP with ideal c/a ratio have close values of the chemical potential). At ultrahigh pressures, when the structure part of the energy is determined almost completely by the ionic lattice, the lattice with the minimal energy is BCC (see the preceding section).

We can conclude from the presented phase diagram that on going from the molecular phase to the metallic phase the latter, in all probability, has the structure of a planar ("prolate") family. Unfortunately, as already noted in the introduction, it is very difficult to say at which value of P* this will take place, owing to the great uncertainty of the results for the molecular phase. Figure 8 shows curves for the molecular phase in accordance with the results of Trubitsyn[4] and the recent paper of Neece et al.[5]. In the former case, the transition pressure is approximately 2.9 Mbar, and in the latter 1 Mbar. The difference between these values of the transition pressure is, of course, very large. It seems to us that at present, unfortunately, it is difficult to estimate the reliability of various results obtained for the molecular phase, and in any case the uncertainty here is incomparably larger than for the metallic phase of hydrogen.

4. LIQUID TENDENCIES IN METALLIC HYDROGEN

From the results of the preceding section it is clear that anisotropic structures correspond to the energywise most favored metallic phase. However, as already analyzed in I, in the case of noticeable anisotropy there occurs in metallic hydrogen a unique tendency towards formation of a family of structures with very close energies. At $c/a < 1$ these are structures that differ from one another by a shift of chains of protons in a direction parallel to the chains, and at $c/a > 1$ these are structures with fixed distances between the crystal planes, but with different arrangements of the ions in these planes. In the latter case, the energy changes little when the planes are displaced relative to one another and the distances between them are kept constant, by virtue of which there appear a "soft" modulus B_{44} (see I) and "soft" phonons characterized by a wave vector q parallel to the z axis, and with polarization vectors in the (x, y) plane. In a certain sense the picture recalls the situation in graphite, but is apparently even more strongly pronounced.

Direct calculations show that this result, which was obtained in I for $P = 0$, remains in force also when the pressure is increased, until the parameter c/a becomes noticeably smaller and energy splitting occurs for the different structures. This is connected with the fact that the tendency towards formation of a planar family, as incidentally also a filamentary family, is determined decisively by the geometry of the arrangement of the ions, and in this case it is determined by the large distance between the planes compared with the distances between the ions in each plane. It is precisely for this reason, for example, that the modulus B_{44} turns out to be small not because of random cancellation of individual contributions, but because of the smallness of all the individual contributions to it (see Fig. 10 of I).

The formation of a planar family is evidence of the unique liquid-like tendencies that take place in metallic hydrogen under pressure. Indeed, let us consider the limiting case when the modulus B_{44} and the frequencies of the transverse phonons with wave vector strictly parallel to z are equal to zero. Then the oscillations in the (x, y) plane are two-dimensional, and at finite temperatures the long-range order in this plane is lost. The result is three-dimensional matter with one-dimensional order. But such a structure, as shown by Landau[8], disintegrates at finite temperatures because of the same long-wave fluctuations, and we arrive at the liquid state.

To be sure, the character of the divergence is weak in both cases (logarithmic), and, for example at $T = 0$ the crystal structure does not disintegrate at all. Therefore, apparently, arbitrary small deviations from the considered idealized picture will stabilize the lattice. However, the noted tendency to form a liquid, in connection with the problem of the dynamic stability and in conjunction with the noticeable decrease of the energy of the zero-point oscillations on going from the filamentary to the planar family, raises the natural question whether the liquid phase of the metallic hydrogen can in general lie lower on the energy scale than its crystal phase in some pressure interval. Such a possibility cannot be excluded beforehand. Just as in the case of helium, for example, this is purely an energy question, and can be solved only by determining the thermodynamic potential of the liquid phase, and furthermore with high accuracy, because the energy differences may turn out to be very small. As a result it is impossible to exclude beforehand, in principle, the possibility that the transition from the molecular phase to the metallic phase is a transition into the state of a liquid metal. (It may turn out that the situation will be different in hydrogen than in deuterium.) The phase diagram could have in this case a very peculiar character. For example, with increasing pressure, the liquid phase could go over into the crystalline phase, but at extremely high densities a liquid would again be produced, but now as a result of the predominant role of the energy of the zero-point oscillations (see the paper by Abrikosov[7]). The metastable phase at $P = 0$ could remain crystalline in this case. However, the gain in the kinetic energy on going over from the planar family to the liquid may turn out to be so small, that it makes dynamically stable the crystalline phases which are energywise more favored in the entire pressure interval of interest to us. Thus, the question of the possible existence of liquid metallic hydrogen at limited densities—a new quantum liquid at $T = 0$—remains open. It is not clear whether an unequivocal answer to this question will be given first by theory or by experiment.

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