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Effect of electron-lattice interaction on the formation of the equilibrium structure of a metal

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The calculation of the derivatives of the total energy of a metal with respect to the lattice parameters is investigated. Since direct differentiation of the perturbation-theory series leads to infinite corrections when the Fermi surface is tangent to the Bragg plane, a program for the direct calculation of the derivatives is sought. Particular attention is paid to the tangency of the Fermi surface to an edge of the Brillouin zone. It is found that differentiation with respect to the parameter $\gamma = c/a$ that describes the oblateness of the lattice is finite, and that the correction for the intersection of the edge is of the order of $W^{5/2}$ (W is the electron-lattice interaction constant). The derived equations are used in the analysis of the stability of the strongly anisotropic structure of metallic hydrogen. It is shown that upon closer analysis the simple hexagonal structure predicted within the framework of ordinary perturbation theory to be metastable at zero pressure can be metastable only under pressure.

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The pseudopotential method is now used successfully to calculate the cohesion energy of metals; many papers are devoted to the principles of the method, to the selection of the pseudopotential, and to the calculation of the properties of various metals.[1,2] A number of questions, however, call for additional study, particularly the question of the correct assessment of the role of the electron-lattice interaction in the formation of the anisotropic metallic structure. The point is that the electron-lattice interaction constant of a number of metals cannot be regarded as small and it becomes necessary to take into account higher orders of perturbation theory, the third[3] and even the fourth.[4-6] The situation is made more complicated by the fact that when this constant increases energy considerations favor the formation of highly anisotropic structures[7] for which it is important to take correct account of the intersection of the Fermi surface with the faces and edges of the Brillouin zone. It is known that perturbation theory leads to infinite corrections for the band energy $\varepsilon(\mathbf{k})$ if the wave vector $\mathbf{k}$ is close to a Bragg plane. If, however, this energy is integrated over the states within the Fermi sphere, the result is finite and, as shown by a detailed analysis, this method can be used to calculate the correction to the total energy in the second[1,2] and third[4] orders of perturbation theory.

The search for the energywise most favored structure at a given volume includes also the variation of the anisotropy parameter $\gamma = c/a$, but the equations of the simple perturbation theory no longer permit calculation of the derivatives of the total energy with respect to γ. The derivative calculated in this manner becomes infinite when the Fermi sphere is tangent to a Brillouin-zone face or edge. Calculation of the energy for one Bragg plane without the use of perturbation theory[2] leads, of course, to a finite derivative.

The purpose of the present paper is the calculation of the total energy and its derivative with respect to the parameter γ in the case when the Fermi surface is tangent to an edge of the Brillouin zone. To this end we consider in detail the singularity of the produced in the state-density curve by the presence of the edge, and determine the parameters of the Van Hove singular point. It is shown that the derivative with respect to the parameter γ has a finite correction of the order of $W^{5/2}$ (W is the electron-lattice interaction constant), and the question of the stability of the spectrum in the case of a tangent edge is determined by the competition between the various contributions to the total energy.

The obtained procedure is used to analyze the stability of a simple hexagonal (SH) structure of metallic hydrogen, in view of the mentioned difficulties encountered in the perturbation-theory calculations. The electron-lattice interaction parameter of metallic hydrogen is large because there are no ionic cores, and at low pressures the strongly oblate anisotropic SH structure is favored.[7,8] It is shown that tangency of the

Fermi surface to the edge of the zone does not make the lattice stable, that the total energy decreases monotonically with decreasing density, and the structure becomes more anisotropic. The pressure needed to preserve the structure is also estimated.

The atomic unit system $e - m = \hbar = 1$ is used.

1. CALCULATION OF THE DERIVATIVES OF THE TOTAL ENERGY

We consider a metal for which the local potential (or pseudopotential) of the electron-lattice interaction and its Fourier components V_K have somehow been calculated. Using perturbation theory to calculate the energy, we exclude from consideration the contribution of the potential components with the highest values of **K**. The contribution of these components to the total energy will be calculated separately. For the oblate SH structure which we consider, all six such vectors lie in the plane $k_z = 0$, so that the calculations reduce to a solution of the Schrödinger equation for the two-dimensional band energy $\varepsilon(\mathbf{k})$. The integration for the calculation of the total energy is over the total three-dimensional zone for the band energy $\varepsilon_i(\mathbf{k}, k_z) = \varepsilon(\mathbf{k}) + k_z^2/2$.

Consider the Brillouin zone of a two-dimensional hexagonal (triangular) lattice, or more accurately one-sixth of it (Fig. 1a). Assuming the states with three-dimensional energy lower than the chemical potential μ to be occupied, we obtain the density $n(\mu)$ and the total energy per unit volume $E(\mu)$:

$$n(\mu) = \frac{1}{4\pi^3} \int_{\varepsilon_i(\mathbf{k}) < \mu} d^3 k, \quad E(\mu) = \frac{1}{4\pi^3} \int_{\varepsilon_i(\mathbf{k}) < \mu} \varepsilon_i(\mathbf{k}) d^3 k; \quad (1)$$

the integration with respect to k_z can be carried out analytically, so that Eq. (1) reduces readily to two double integrals over the two-dimensional Brillouin zone. If the parameter of the problem is the density, then the first equation in (1) determines the chemical potential as a function of density.

The zone energy is a function of the wave vector **k**, of the Fourier component $V_K = -V$ of the potential, and of the vector a^* of the planar reciprocal lattice. The number of parameters can be decreased by expressing all the vectors in fractions of the distance $q = a^*/2$ to the nearest Bragg plane, and all the energies in fractions of q^2, i.e., by changing to a zone with $q = 1$ and Fourier component $W = V/q^2$ of the potential. All the quantities pertaining to the dimensionless zone are primed; in particular,

$$\varepsilon(\mathbf{k}) = q^2 \varepsilon'(\mathbf{k}/q). \quad (2)$$
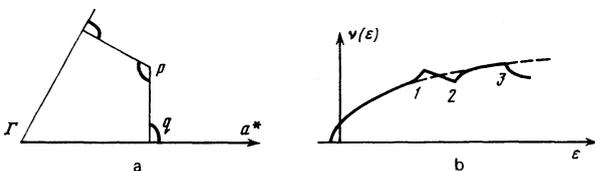
FIG. 1. Two-dimensional Brillouin zone of plane hexagonal lattice, showing pieces of the Fermi surface (a) and the corresponding state-density curve (b).

We can calculate integrals $n'(\mu')$ and $E'(\mu')$ similar to (1) by using a chemical potential $\mu' = \mu/q^2$ and an external potential W. The new quantities are connected with (1) by the scale transformation

$$E(q, \mu) = q^5 E'(\mu'), \quad n(\mu) = q^3 n'(\mu'). \quad (3)$$

We note that in the "reduced" zone $q = 1$ the energy depends only on W and μ', and we shall henceforth regard the function E as a function of q, n, and W.

In addition to the energy itself, to determine the optimal structure we must calculate the derivatives of the energy with respect to the parameters q and W. Whereas the derivative $(\partial E/\partial W)_{q,n}$ can be calculated by differentiating the perturbation-theory series, the derivative $(\partial E/\partial q)_{W,n}$, as already noted, is not always obtainable by this method. However, the fact that in the calculation of $E(q,n,W)$ all the Fourier components of the potential lie in the same plane allows us to find a simple formula for the derivative of the energy with respect to q at constant n and W. To this end we write $E(q,n,W)$, which is the energy per unit volume, as a function of q, n, and W, and then use (3) to calculate to derivative at constant density:

$$\left(\frac{\partial E}{\partial q}\right)_{n,W} = \frac{\partial}{\partial q}\left[q^5 E'\left(\frac{n}{q^3}, W\right)\right]_{n,W} = q^4\left[5E' - 3n\left(\frac{\partial E'}{\partial n'}\right)\right]. \quad (4)$$

The derivative of the Energy E' with respect to the "density" n' is the chemical potential μ', so that

$$(\partial E/\partial q)_{W,n} = (5E - 3\mu n)/q. \quad (5)$$

The density n' in the reduced zone is directly connected with $\gamma = c/a$, namely, for univalent hydrogen the volume of the occupied states in momentum space $4\pi^3 n$ is equal to half the volume of the Brillouin zone. For the SH structure, simple operations lead to the following equations:

$$\gamma = \frac{c}{a} = \frac{3^{1/2}}{2}\left(\frac{a^*}{c^*}\right) = \frac{3}{4\pi^3 n'}. \quad (6)$$

Defining in the usual manner the Fermi momentum k_F as the radius of a sphere with volume $4\pi^3 n$, we introduce the parameter $\eta = q/k_F = a^*/2k_F$. The parameter r_S is connected with the density $4\pi r_S^3/3 = n^{-1}$. These parameters are also interrelated:

$$\gamma = 9\eta^3/4\pi, \quad r_S k_F = (9\pi/4)^{1/3}. \quad (7)$$

We use these equations to connect the derivatives of the total energy with respect to q, η, and γ at constant density n (or k_F) and W:

$$q(\partial E/\partial q) = \eta(\partial E/\partial \eta) = 3\gamma(\partial E/\partial \gamma). \quad (8)$$

The intersection of the Fermi surface with the faces and edges of the Brillouin zone correspond to the Van Hove singularity on the state-density curve. Figure 1b shows schematically the state density plot $\nu(\varepsilon)$ as a function of energy, and the numbers designate the Van Hove singularities corresponding to the first two energy bands $\varepsilon_1(\mathbf{k})$ and $\varepsilon_2(\mathbf{k})$. The point 2 with energy $\varepsilon_2(\mathbf{q})$ corresponds to the bottom of the second band, i.e., to a singularity of the M_0 type. Point 1 with energy $\varepsilon_1(\mathbf{q})$ corresponds to the appearance of a neck or to tangency of the Fermi surface to an edge of the zone; this is usually a singularity of type M_1. We are interested at

present in the behavior of the $\nu(\varepsilon)$ plot near the point 3 (singularity of type M_2, corresponding to tangency of an edge of the zone–the point p, to the Fermi surface). Singularities of this type correspond to a square-root increment to the state density at an energy higher than $\varepsilon_c = \varepsilon_1(p)$. To take this increment into account, we calculate the energy ε_c itself and the effective mass near the point p. The point p corresponds to threefold degeneracy of the unperturbed energy $\varepsilon_0(k)$. The splitting of the degenerate states under the influence of the perturbation can be determined by finding the eigenvalues $\varepsilon(k)$ of the 3×3 matrix

$$\left\| \begin{array}{ccc} \varepsilon_0(k) & -W & -W \\ -W & \varepsilon_0(k-a^*) & -W \\ -W & -W & \varepsilon_0(k-b^*) \end{array} \right\|. \tag{9}$$

Considering the secular equation near the point p and retaining only the terms quadratic in $\Delta k = k - p$, we reduce it to the form

$$\lambda^3 - [3 + (\Delta k/W)^2]\lambda + 2 = 0. \tag{10}$$

The parameter λ is connected with the energy:

$$\varepsilon(k) = \tfrac{1}{2}[\,|p|^2 + (\Delta k)^2] + \lambda W. \tag{11}$$

Equation (10) has three roots at $\Delta k = 0$, the lower band corresponds to $\lambda_1 = -2$, and the two upper ones to $\lambda_2 = \lambda_3 = 0$. Expanding (10) in a series at small Δk, we obtain the energy $\varepsilon_1'(k)$ of the first band near the point p in the reduced band:

$$\varepsilon_1'(\Delta k) = \varepsilon_c' - (\Delta k)^2/2m^*, \tag{12}$$

where $\varepsilon_c' = \tfrac{2}{3} - 2W$ is the energy at the critical point, and the effective mass $m^* = 9W/4$.

Equation (12) contains the energy corrections linear in W at $\Delta k \ll W$, and the contribution of the remaining planes is quadratic in W. This point corresponds to a singularity of type M_2 (the band energy has a minimum in the direction of the z axis and a maximum in the perpendicular direction), and at energy higher than ε_c it corresponds to a nonanalytic increment to the state density per unit volume:

$$\Delta\nu(\varepsilon) = -2\pi^{-2} m^* [2(\varepsilon - \varepsilon_c)]^{1/2}. \tag{13}$$

The factor 2 stems from the fact that the first Brillouin zone has singularity of the considered type simultaneously at two nonequivalent points of the reciprocal lattice.

At sufficiently high values of the parameter W, the points 2 and 3, which correspond to singularities on the state-density curve, can change places: The Fermi surface is tangent to the point p, and the filling of the second band has not yet started. Expression (13) for the increment is also valid. The increment (13) to the state density makes it possible, in addition, to calculate, given the chemical potential μ, the increments $\Delta n(\mu)$ to the density and $\Delta E(\mu)$ to the energy per unit volume

$$\Delta n(\mu) = -\tfrac{2}{3} m^* \pi^{-2} [2(\mu - \varepsilon_c)]^{3/2}, \tag{14}$$

$$\Delta E = \varepsilon_c \Delta n(\mu). \tag{15}$$

In these equations $\mu' - \varepsilon_c' \ll W$ and the terms $o(W^{5/2})$ have been discarded. Within the same accuracy, the
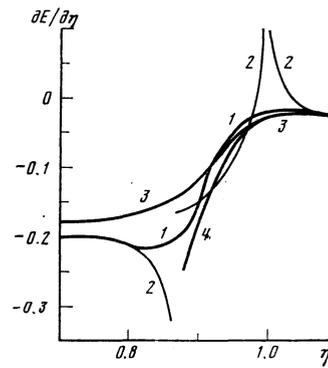
FIG. 2. Dependence of the derivative $\partial E/\partial\eta$ on the parameter η, ($q = 1$, $W = 0.1$): 1—numerical integration; 2—simple perturbation theory, third order; 3—second-order perturbation theory after Harrison; 4—the same, but correction for the tangency of the corner of the zone.

increment to the thermodynamic potential $\Omega = E - \mu n$ at a fixed chemical potential μ vanishes. This increment $\Delta\Omega(\mu)$ is equal also to the increment to the total energy ΔE, but at a fixed density n, and therefore the improved perturbation theory contains no increment of order $W^{5/2}$ in the energy at a given density, even if the Fermi surface intersects an edge of the Brillouin zone. But this increment remains nevertheless in the calculation of the derivative of the energy with respect to the parameter γ or η, by virtue of Eq. (5).

Figure 2 shows the dependence of the derivative $(\partial E/\partial\eta)_W$ as a function of the parameter η. Curve 1 was obtained by numerical integration: the eigenvalues (9) are determined numerically, and the contribution of the remaining planes to the energy is determined by usual perturbation theory in third order in W. Double numerical integration yields $E(\mu)$ and $n(\mu)$, and hence η as a function of μ. The derivative is calculated from Eq. (5). Curve 2 is the result of the usual perturbation theory in third order in W: the derivative becomes infinite at $\eta = 1$ (tangency of the zone face to the Fermi sphere) and at $\eta = 0.8660$ (tangency of the edge of the Brillouin zone of the SH lattice). Curve 3a was calculated in second order perturbation theory, and the intersection with the face is accounted for by Harrison's method.[1] Curve 4 is the same, but with account taking of the intersection with the edge of the zone in accord with (14). Both curves 3 and 4 are plotted in accord with the following scheme: the chemical potential μ is given and the density $n(\mu)$ calculated, Eq. (6) yields the value of γ, after which, calculating the energy by Eq. (5) in ordinary perturbation theory, we obtain the derivative.

As already noted, the expression for the correction (14) is no longer valid if $\mu' - \varepsilon_c'$ is of the order of W. In the limiting case of large μ (small η), just as in the other limiting case of small μ, ordinary perturbation theory holds. In this case the filling of the upper energy bands compensates for the splitting; for example the sum of three eigenvalues of the matrix (9) is equal to its trace, i.e., to the sum in the absence of perturbations.

Since the investigation of the stability of the structure

calls for explicit (or implicit) calculation of the deriva-
tives, the use of the simple perturbation theory can
lead to the appearance of fictitious metastable states.
For example, at sufficiently high densities (small r_s
and W) the main contribution to the structure-dependent
part of the energy is made by the energy of the ion lat-
tice. For an SH structure this energy has a minimum
at $\gamma = 0.928$ ($\eta = 1.090$), its derivative is therefore
negative at lower values of γ.

If the correction due to the band energy is calculated
by perturbation theory, it becomes infinite near $\eta = 1$
($\gamma = 0.716$) and consequently goes through zero on the
right and on the left of this point, i.e., a fictitious
minimum of the total energy with respect to η appears.
The exact theory[1] yields in the same case, at fixed μ,
a finite increment of the order of $W^2 \ln W$ to the density;
consequently, by virtue of (5) the increment to the deri-
vative is of the same order. Whether the parameter W
suffices to stabilize the structure can be determined in
this case only by numerically comparing the derivative
of the energy of the ion lattice, which contributes to
formation of the isotropic structure, with the derivative
of the contribution of the band energy, which tends to
distort the structure.

A similar situation, but at sufficiently low density,
takes place near $\eta = 0.8660$ ($\gamma = 0.465$). Assume that
the interaction favors the formation of an anisotropic
structure with $\eta < 0.8660$, i.e., the correctly calculated
derivative of this energy is positive at $\eta = 0.8660$. The
fictitious infinite negative increment (curve 2 of Fig. 2)
again yields a fictitious minimum of the total energy
near this point. Consequently, the investigation of the
question of the stabilization of the structure when the
Fermi surface is tangent to the face or edge of the zone
cannot be carried out within the framework of simple
perturbation theory.

2. ANALYSIS OF THE STABILITY OF METALLIC HYDROGEN

The results are applicable to the analysis of the ani-
sotropic simple hexagonal structure of metallic hydro-
gen. We are interested in the possibility of stabilizing
this structure when the Fermi surface is tangent to an
edge of the Brillouin zone, i.e., the behavior of the en-
ergy when γ is close to 0.465. This value of γ corre-
sponds to tangency of the edge of the zone to the Fermi
surface. We write down with the aid of the simple the-
ory the structure-dependent part of the energy in the
form of a series in r_s. For the energy per atom we
have

$$E = E_0(r_s) - \alpha_M(\gamma)/2r_s + a_2(\gamma) + r_s a_3(\gamma). \qquad (16)$$

We confine ourselves to third-order perturbation theory
or to terms linear in r_s. The Madelung constant $\alpha_M(\gamma)$
and the coefficients a_2 and a_3 depend only on the aniso-
tropy parameter. The energy $E_0(r_s)$ of the free elec-
tron gas does not depend on γ, and an expansion in pow-
ers of r_s accurate to terms of order of r_s inclusive is
given in Ref. 9.

Figure 3 shows the perturbation-theory diagrams.
The coefficient $a_2(\gamma)$ is the contribution of diagram a,
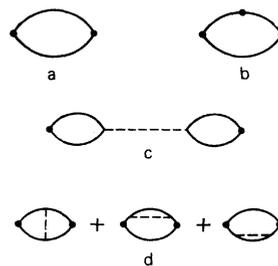
FIG. 3. Perturbation-
theory diagrams for the
structure-dependent
contributions.

and $a_3(\gamma)$ is the contribution of diagrams b, c, and d.
An analytic expression is known for diagrams a, b, and
c; the contribution of diagrams d is calculated and tab-
ulated in Ref. 10. For each fixed r_s we obtain the
structure with the minimum energy by varying the pa-
rameter γ. Diagrams a and b correspond to summation
of the band energy, so that to calculate the derivative
with respect to γ the contribution of the nearest sites of
the reciprocal lattice from the coefficients a_2 and a_3 and
add to (16) the band energy due only to these nearest
sites. The procedure of calculating the contribution of
the nearest sites to the energy was described above.
To increase the accuracy we calculate this energy by
numerical integration over states with energy lower
than μ using Eq. (1) directly: the band energy was cal-
culated in third-order perturbation theory and the ei-
genvalues of the matrix (9) were sought near the degen-
eracy points. The energy calculated in this manner in-
cludes also the kinetic energy of the free gas, which
must be excluded from $E_0(r_s)$.

The derivatives with respect to γ of all the contribu-
tions to the total energy are calculated by simple per-
turbation theory. An exception is the partial derivative
$(\partial E/\partial \gamma)_W$, which was calculated from Eq. (5). We note
that Eq. (5) corresponds formally to summation of an
infinite sequence of diagram and depends simultaneous-
ly on r_s and γ.

Table I lists, for different γ, the values of r_s that
causes vanishing of the derivative with respect to γ
and corresponds to the minimum of the total energy as
a function of γ. The table lists also the total energy
reckoned from the energy -0.5 at. un. of the free atom,
and the pressure P (in megabars) needed to keep the
structure together. It is seen that the parameter γ de-
creases monotonically with increasing r_s. The singular
value $\gamma = 0.465$ at which simple perturbation theory has
predicted a metastable structure is now absent, and
pressure must be applied to retain this phase.

Table I gives also the values of the parameter W for
equilibrium structures. We note that near $\gamma = 0.465$
the parameter W is large enough, so that the Van Hove
singular point change places on Fig. 1b. This means

TABLE I.

$\gamma = c/a$	r_S	E/N	P, Mbar	W
0.600	1.2172	0.0039	5.8058	0.0852
0.560	1.3409	−0.0310	2.8996	0.1029
0.520	1.4534	−0.0509	1.6054	0.1231
0.500	1.5023	−0.0573	1.2752	0.1341
0.460	1.5837	−0.0661	0.9483	0.1580
0.420	1.6399	−0.0716	0.8996	0.1847
0.400	1.6589	−0.0736	0.9485	0.1994
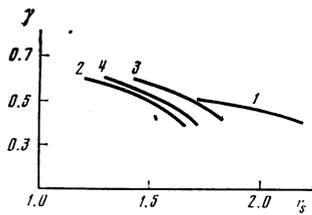
FIG. 4. Anisotropy parameter $\gamma = c/a$ as a function of r_S in metallic hydrogen: 1—unrestricted Hartree-Fock method; 2—perturbation theory and the Geldart-Taylor equation; 3—perturbation theory and the Hubbard-Geldart-Vosco equation; 4—perturbation theory and the Toigo-Woodruff equation.

that the Fermi surface differs strongly from a sphere: the occupied states lie entirely in the first Brillouin zone. This picture corresponds more to the treatment of a crystal lattice, in the low-density limit, as a system of interacting linear chains of atoms.[11] This treatment predicts also the absence of a metastable structure at zero pressure.

The uncertainty in the calculation of the correlation energy by the different formulas makes it impossible to compare the perturbation-theory results, which are accurate in the limit of small r_S, with the results of a variational calculation,[11] which is accurate in the limit of large r_S but is also subject to some energy uncertainty because of the use of trial functions in the form of combinations of Gaussian orbitals. We note, however, that the dependence of γ on r_S is calculated in perturbation theory without allowance for the correlation energy. Figure 4 shows this dependence: curve 1 is the result of the variational calculation,[11] curve 2 was calculated by the modified perturbation theory as described in the present article; curve 3 is also a result of perturbation theory, but the contribution of diagrams d of Fig. 3 was calculated, to permit comparison with other calculations, in the Hubbard-Geldart-Vosco approximation.[12] We note that for strongly distorted structures this approximation greatly underestimates the contribution of diagrams d of Fig. 3.[10] Curve 4 is the same but with the Toigo-Woodruff approximation.[13]

There is also another possibility of taking into account the electron-electron interaction, the so-called local-field approximation.[14,15] Figure 5 shows the corresponding diagrams; the shaded vertex corresponds to replacement of the pure Coulomb potential of the electron-ion interaction by some effective local potential. The Fourier components of this potential differ from those of the Coulomb potential by the factor $T(K) = = 1/\varepsilon_{eff}(K)$, and it is assumed that this factor depends only on the momentum transfer K. The diagrams of Fig. 5 differ from those of Fig. 3 only in terms of
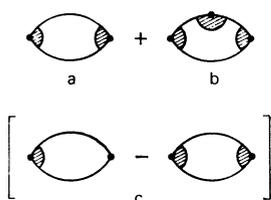
FIG. 5. Perturbation-theory diagrams in the local-field approximation.

TABLE II.

$\gamma = c/a$	r_S	E/N	P, Mbar	W	$T(K)$
0.6000	1.17615	0.01397	7.600	0.0917	1.1148
0.5600	1.32483	−0.03538	3.331	0.1133	1.1152
0.5200	1.46918	−0.06249	1.567	0.1378	1.1076
0.5000	1.53715	−0.07102	1.123	0.1510	1.1006
0.4600	1.66468	−0.08264	0.646	0.1794	1.0804
0.4200	1.78344	−0.09044	0.444	0.2112	1.0517

fourth-order perturbation theory, i.e., by contributions of order r_S^2 to the energy. Although each shaded vertex corresponds to taking an infinite ladder into account, there are still a number of fourth-order perturbation-theory diagrams whose contribution is likewise not taken into account in this scheme.

The difference between the results of these two calculation schemes characterizes the contribution of the discarded higher orders of perturbation theory. Table II gives the results of calculations using the diagrams of Fig. 5; the Geldart-Taylor approximation is used for the effective-screening function $T(K)$. Recognizing that the difference between $T(K)$ and unity is small, is maximal at the nearest site of the reciprocal lattice, and decreases rapidly with increasing K, the factor $T(K)$ is assumed to differ from unity only at these nearest sites in the calculation of the contribution of diagram b of Fig. 5.

We note that the two-pole diagram of Fig. 5 should have only one shaded vertex. Since numerical integration yields only the combined contribution of diagrams a and b, it is necessary to add diagrams c. The contribution of the latter is calculated by simple perturbation theory.

We see that the results of the calculations by both schemes are close both quantitatively and qualitatively. The difference lies in the fact that with increasing anisotropy less dense structure are realized for the diagrams in Fig. 5, and a somewhat lower pressure is needed to hold together the metallic hydrogen.

The last column of Table II gives the coefficient $T(K)$ for the K corresponding to the nearest sites of the reciprocal lattice. The deviation of $T(K)$ from unity characterizes the effective screening of the external field and serves as a measure of the electron-electron interaction. We see that this difference is small and is comparable with the electron-ion interaction constant W. Consequently, using third-order perturbation in W, there is no advantage in calculating the contribution of the fourth and higher orders of perturbation theory in the electron-electron interaction.

Figure 6 shows a plot of the pressure in metallic hydrogen against the atomic volume $V_0 = 4\pi r_S^3/3$. Curves 1 and 2 were calculated in the Toigo-Woodruff approximation, using the diagrams of Figs. 3 and 5, respectively. The pressure in the Geldart-Taylor approximation is given in the tables. We see that with increasing volume V_0 the pressure decreases but remains positive. Starting with r_S on the order of 1.6, the scatter of the pressures calculated from different formulas becomes comparable with the pressure itself. This means that, at least at $r_S < 1.6$ there is no metastable

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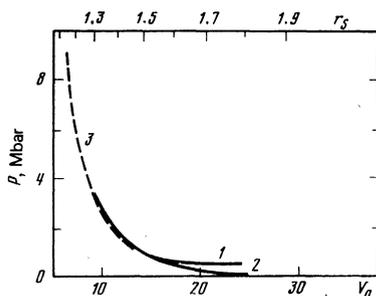
FIG. 6. Pressure as a function of the atomic volume V_0: 1—using the diagrams of Fig. 3; 2—using the diagrams of Fig. 5; 3—result of Ref. 6.

phase of metallic hydrogen at zero pressure. To advance into the region of larger r_s it is necessary to take into account higher orders of perturbation theory and in the limit of large r_s the perturbation theory series of the free electron gas stop converging altogether. To approach metallic hydrogen from the low-density side it is necessary to use other method, such as the unrestricted Hartree-Fock method[11] or an approximation similar to the Hubbard model.[16]

It is also of interest to trace the connection between the results of the present paper and the existing calculations for metallic hydrogen in the magabar region. Curve 3 of Fig. 6 was taken from the paper of Kagan et al.[6] where simple perturbation theory is used, and account was taken of the contribution of the diagrams of Fig. 5 and the contribution of the zero-point vibrations of the ion lattice. We see that with increasing V_0 curve 3 goes over smoothly into curves 1 and 2.

The situation is more complicated in the calculation of the dependence of the anisotropy parameter γ on r_s. As already noted, an infinite derivative of the total energy with respect to the parameter γ appears in perturbation theory also when the Fermi surface is tangent to a face of the Brillouin zone. In the case of a primitive hexagonal lattice this infinite derivative corresponds to $\eta_c = 1$ ($\gamma_c = 0.716$). A result of this fictitious infinity is that even in the limiting case of small r_s when the structure is determined by the minimum of only the ion energy (this minimum corresponds in the SH structure to $\gamma = 0.928$) a fictitious metastable state with γ close to 0.716 appears within the framework of perturbation theory. Consequently, a search for a minimum of the energy with respect to γ with fixed r_s is legitimate if $|\gamma - \gamma_c| \gtrsim W$. It is therefore necessary to review the

results of the calculations of the anisotropy parameter in metallic hydrogen in the megabar region, and not in the SH structure alone.

In the present paper the infinity was eliminated in the diagrams corresponding to the interaction of the electrons with the field produced by the nearest reciprocal-lattice sites. This infinity remains, however, if account is taken of diagrams $3c$ and $3d$ in the calculation in the calculation of the effective vertex, as well as in the calculation of a three-pole diagram in which one or two vertices correspond to a nearest site. This is why the region $\gamma > 0.6$ is not considered in the present paper.

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