

*QUANTUM MECHANICAL THEORY OF THE EQUATION OF STATE FOR POTASSIUM,  
ALUMINUM, AND IRON*

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The change in the nature of the electron bands of K, Al and Fe upon variation of density is considered. Results of calculation of the cold pressure are analyzed in detail and are compared with the data of the statistical theory in which quantum corrections are taken into account. The values of the electron specific heat and of the Gruneisen coefficient  $\gamma_e$  are calculated for K, Al and Fe. A considerable rearrangement of the electron bands in Al due to compression is predicted, which should lead to the appearance of negative  $\gamma_e$ . Energy overlap of the 4s and 3d bands, due to compression and resulting in a first-order phase transition in the region of negative  $\gamma_e$ , is observed in potassium.

## INTRODUCTION

WE have presented earlier<sup>[1]</sup> the results of a quantum-mechanical investigation of the equation of state of Fe (reference<sup>[1]</sup> will henceforth be cited as I). It turned out that allowance for the concrete filling of different bands in metals makes it possible to calculate more accurately the  $p(\rho)$  curve than the statistical theory with quantum correction.<sup>[2, 3]</sup> We were able at the same time to explain the anomalously large electronic specific heat of Fe, something impossible in the framework of the statistical theory. Further calculations have made it possible to predict the transformation of metallic Ni compressed by a factor 6.5 into a dielectric<sup>[4]</sup> and the transformation of solid argon<sup>[5]</sup> compressed by a factor of 3 into a metal. The theory developed in I has now been noticeably improved and makes it possible to calculate with sufficient assurance the cold-pressure curve  $p(\rho)$  for many metals at a relative compression  $\delta > 2$ . This yields interesting data on the structure of the electronic energy bands at different  $\delta$ , shedding light on many properties of metals at high pressures and temperatures.

The purpose of the present work was to explain in detail recent results on Al, Fe, K, and solid Cl. In Sec. 2 we consider the change in the structure of the energy bands following change in density, in Sec. 3 we present results of calculations for the pressure, and in Sec. 4 we analyze in detail the electron specific heat and Gruneisen coefficient in a wide range of temperatures  $T$  and densities  $\rho$ .

The procedure described in I was improved in order to find solutions of the Hartree equation for

single-electron wave functions in a crystal in the Wigner-Seitz approximation. The influence of the exchange on the wave functions and the potential were not taken into account here. Subsequently exchange was taken into account approximately in the calculation of pressure.

To solve the Hartree equation, it is very important to use a successive-approximation procedure in which the first approximation is the Thomas-Fermi potential of the compressed atom. From the obtained first-approximation wave functions one finds the effective potential and the wave functions of the electron for the second approximation, etc. until the succeeding potential and wave functions do not differ from the preceding ones. We developed a procedure for improving the convergence of the successive approximation, making it possible to get along with four or five successive approximations.

## 1. ELECTRON BAND STRUCTURE AND ITS DENSITY DEPENDENCE

All the results on the dependence of the energy  $E$  on the quasimomentum  $k$  will be presented for the final solution of the Hartree equation. It must be noted that even in the first approximation the character of the bands  $E(k)$  is qualitatively the same as in the final solution. This quantitative difference, however, greatly influences the absolute value of the pressure.

Henceforth the relative compression  $\delta = \rho/\rho_0$  will always be given relative to the normal experimental density of the substance.

We start the description of the band structure

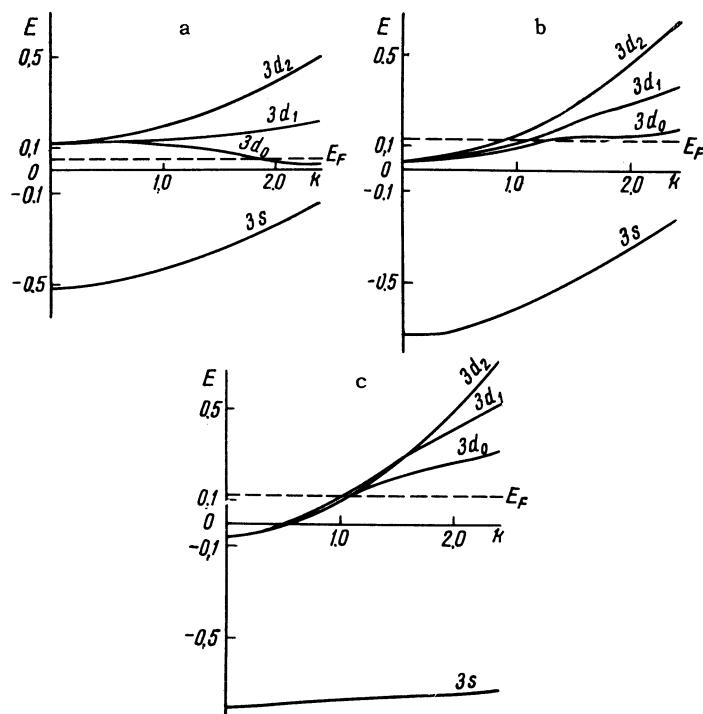


FIG. 1. Plot of  $E(k)$  for aluminum at different densities:  
a)  $\delta = 1.48$ , b)  $\delta = 2.95$ , c)  $\delta = 4.18$ .

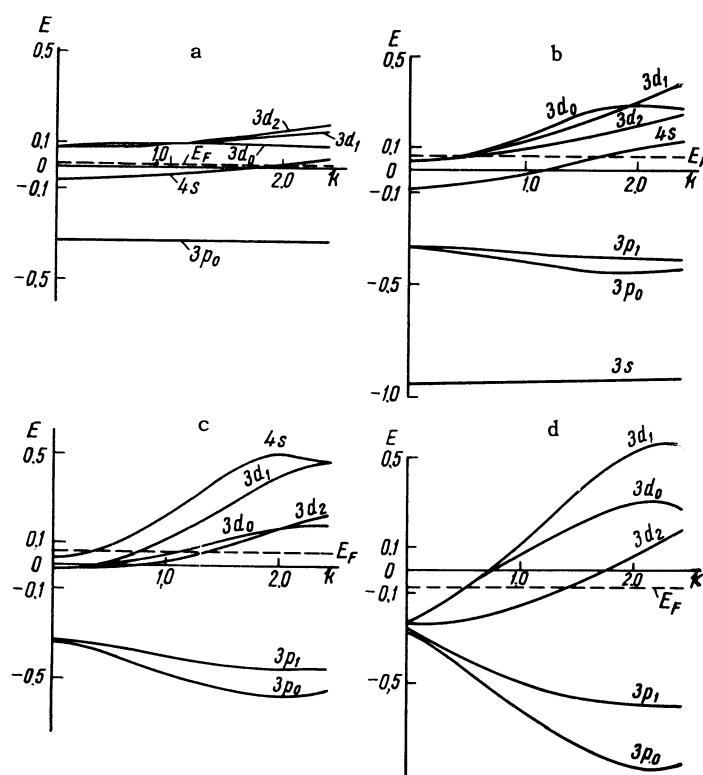


FIG. 2. Energy bands in K at different degrees of compression: a)  $\delta = 1$ , b)  $\delta = 3$ , c)  $\delta = 5$ , d)  $\delta = 10$ .

with aluminum. The configuration in the aluminum atom is  $1s^2 2s^2 2p^6 3s^2 3p$ , and the 3d level lies 0.148 at. un. above the 3p level.<sup>1)</sup> In the aluminum metal, however, the last electron is at 3d and not

3p. To be sure, the sub-band  $3d_0$ , at which the last electron is located, is directed downward, i.e., the energy  $E$  decreases with  $k$ , and in the case of large  $k$  the wave function of the electron contains a large admixture of p-states. Figures 1a-c show  $E(k)$  curves for aluminum at  $\delta$  equal to 1.48, 2.95,

<sup>1)</sup>One atomic unit = 27.23 eV =  $3.16 \times 10^5$  °K.

Table I. Dependence of pressure (in  $10^6$  atm) on the density at  $T = 0$

Fe, $\rho_0 = 7.8 \text{ g/cm}^3$			Al, $\rho_0 = 2.7 \text{ g/cm}^3$			$K, \rho_0 = 0.862 \text{ g/cm}^3$			Solid Cl, $\rho_0 = 1.65 \text{ g/cm}^3$		
$\delta$	$p$	$p_{\text{stat}}$	$\delta$	$p$	$p_{\text{stat}}$	$\delta$	$p$	$p_{\text{stat}}$	$\delta$	$p$	$p_{\text{stat}}$
0.746	-0,072	0.35	1.01	0.551	0.10	0.75	-0.001		0.75	-0,040	
1.073	0.958	1.00	1.480	1.660	0.30	1.00	0.006		1.00	0.021	
2.005	7.434	9.20	1.961	3.510	1.10	2.00	0.087		2.00	0.565	-0.070
3.00	21.130	28.50	2.950	7.240	4.50	3.00	0.200	-0.155	3.00	2.130	0.325
4.00	41.00	60.50	3.500	11.08	7.40	4.00	0.193				
5.00	77.42	115.8	4.180	17.95	12.30	5.00	0.134	0.067			
6.00	127.50	175.60	5.500	35.60	25.70	6.50	0.400				
8.00	279.00	339.00	7.000	60.35	46.00	8.50	0.960				
						10.00	1.750	3.00			
						20.00	22.53	23.10			

and 4.18. We see clearly that at  $\delta = 2.95$  the  $3d_0$  band has reversed direction and goes upward. This greatly influences the level density near the Fermi surface and the electronic specific heat of aluminum.

Figures 2a-d show the energy bands in K for  $\delta$  equal to 1, 3, 5, and 10. In the normal state (Fig. 2a,  $\rho_0 = 0.862 \text{ g/cm}^3$ ) of solid K, the outer electron is at the 4s band. At a compression corresponding to  $\delta = 3$ , the important overlap of the 4s and 3d bands already takes place and exerts a great influence on the external properties of the electrons; it will be considered in greater detail in Sec. 4.

Subsequently, at  $\delta = 5$ , the 4s band is very little filled, and at  $\delta = 10$  only the 3d band is filled. This lowering of the d bands and the rising of the s bands upon compression is very characteristic of many metals, and takes place in particular in iron.

The same effect, the approach of the 3d band, but now to the 3p band, is observed in solid Cl. (It must be borne in mind that normal molecular  $\text{Cl}_2$  is not described by our theory.) At  $\rho = 1.9 \text{ g/cm}^3$  and  $k = 0$ , the 3p band has an energy  $-0.115 \text{ at.un.}$  and the 3d band an energy  $+0.084 \text{ at.un.}$  At  $\rho = 3.8 \text{ g/cm}^3$  and  $k = 0$ , the energy of the 3p band is  $0.044 \text{ at.un.}$  and that of the 3d band  $0.015 \text{ at.un.}$  At  $\rho = 5.7 \text{ g/cm}^3$  and  $k = 0$ , however, the 3p band is  $0.127 \text{ at.un.}$  above the 3d band.

## 2. DEPENDENCE OF THE PRESSURE ON THE DENSITY AT $T = 0$

It was shown in I that the pressure consists of two parts: kinetic, containing an integral over the unit-cell surface, and Coulomb, of the exchange-correlation type, which contains the interaction between electrons in different cells. The latter part of the pressure,  $p_{\text{exch}}$ , is very difficult to calculate and is evaluated for the time being by the free-electron-gas formula:

$$p_{\text{exch}} = \frac{1}{3\pi^3} \frac{e^2}{a_0^4} W^2 = 3.15 W^2 \cdot 10^6 \text{ atm},$$

where  $W$  is the difference between the Fermi energy  $E_F$  and the potential at the boundary of the cell (in atomic units).

Calculation of the kinetic pressure shows that the method of successive approximation improves the results noticeably. For example, in Fe at  $\delta = 2$ ,  $p_{\text{kin}} = 15.1 \times 10^6 \text{ atm}$  in first approximation, and the final value is  $p_{\text{kin}} = 10.4 \times 10^6 \text{ atm}$ ; at  $\delta = 3$ , we have  $p_{\text{kin}} = 27.5 \times 10^6 \text{ atm}$  in first approximation and  $21.1 \times 10^6 \text{ atm}$  ultimately. In the case of aluminum the first approximation calculations are closer to the final calculations than for iron.

Table I presents the results of the calculation of the pressure at different compressions for Fe, Al, K, and solid Cl, as well as a comparison with the data of the statistical theory with quantum corrections.<sup>[3]</sup> We see that the results differ markedly. In aluminum the statistical theory gives too low a pressure, but in iron, to the contrary, the pressure is too high.

However, at large  $\delta \sim 10-12$ , for all metals there is naturally agreement between our results and the data of the statistical theory.<sup>[3]</sup> This was verified on Fe and Al.

Figure 3 shows a comparison of the calculated pressure with the data of the statistical theory for Fe. Starting with  $\delta > 2.5$ , our calculated data are in fair agreement with the experimental ones<sup>[6]</sup> in almost all metals.

In the low density region ( $\delta \sim 1$ ), the foregoing method gives both positive and negative pressure, and makes it possible to determine the calculated density of the substance at  $p = 0$ . Oscillations of the normal density  $\rho_0$  with variation of  $Z$  are also obtained. For example, the calculated normal density of K is found to be  $0.68 \text{ g/cm}^3$ , as against the  $3.95 \text{ g/cm}^3$  obtained from the data of the statistical

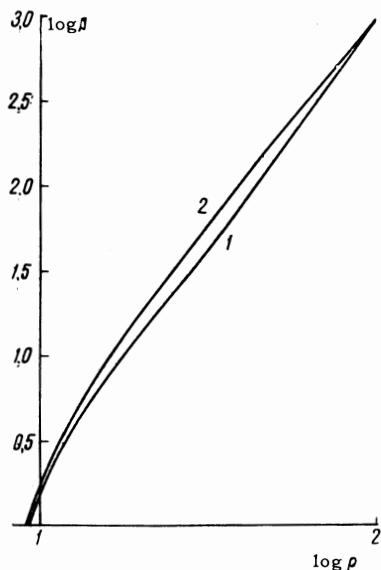


FIG. 3. Plot of pressure vs density: curve 1—out data, curve 2—calculation by statistical theory ( $\log p = 1$  denotes  $p = 10^6$  atm).

theory in the calculation of Kalitkin.<sup>[3]</sup>

For iron, the error in the determination of the normal density reaches 20%. Further progress in this direction calls unconditionally for a more accurate calculation of the exchange pressure. At the present time much effort is expended on developing a procedure for calculating the exchange pressure from the obtained electronic wave functions. The next step forward is to take into account the influence of the exchange on the wave functions themselves. It is proposed for this purpose to find methods of solving the Hartree-Fock equation in crystals. This work is presently also under way.

Inasmuch as the employed quantum mechanical procedure does not describe the Van der Waals forces, the calculation should give a small positive pressure for the close-packed solid Ar at all densities ( $\rho_0 = 1.9$  g/cm<sup>3</sup>—experimental density of solid Ar), as is indeed the case.

Figure 4 shows the calculated curve of cold pressure in K, the abscissas representing  $1/\delta$ , which is proportional to the volume. We see on the curve a clearly pronounced minimum at  $1/\delta = 0.21$  and a maximum at  $1/\delta = 0.29$ . Such a behavior is distinct proof of the presence of a first-order phase transition, and in reality a jump of density at constant pressure will be observed. This constant-pressure line is shown in Fig. 4. The bounded areas above and below this line should be equal. The transition pressure is here 180,000 atm and a large jump in density, almost by a factor of 2, is obtained. The feasibility

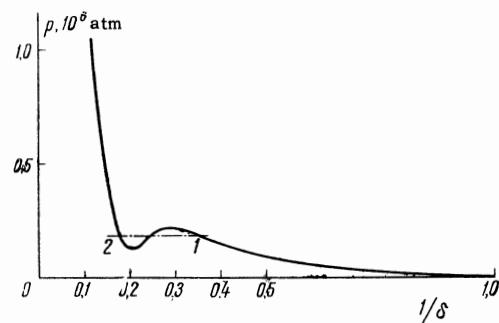


FIG. 4. Plot of  $p(1/\delta)$  for K. Line 1-2 is the constant-pressure line of the phase transition.

of a first-order phase transition in alkaline metals was considered qualitatively by Arkhipov.<sup>[9]</sup> The accuracy of the calculation of  $p(\delta)$  in K is still insufficient to guarantee the accuracy of these figures, but since this phenomenon is connected with rearrangement of the electron band in K, which we have already mentioned, there is no doubt that such a phase transition in K is possible. It would be very desirable to investigate this question experimentally. The reliability of the electronic phase transition is confirmed also by the fact that the predicted region of negative and small positive Gruneisen coefficient of the electrons, connected with the rearrangement of the band upon compression, was confirmed experimentally, as will be related in detail in the next section.

### 3. THERMAL ENERGY AND THERMAL PRESSURE OF ELECTRONS

At relatively low temperatures, knowledge of the electronic bands  $E(k)$  is sufficient to find the thermal energy and thermal pressure of the electrons. We shall find first the chemical potential  $\mu$  as a function of the temperature, after which we shall calculate the thermal energy  $E_T$  and the thermal pressure  $P_T$ .

We introduce the notation

$$E_T = \frac{1}{2}\beta T^2, \quad \gamma_e = p_T V / E_T.$$

The quantity  $\gamma_e$  is called the electron Gruneisen coefficient. Using the thermodynamic relation

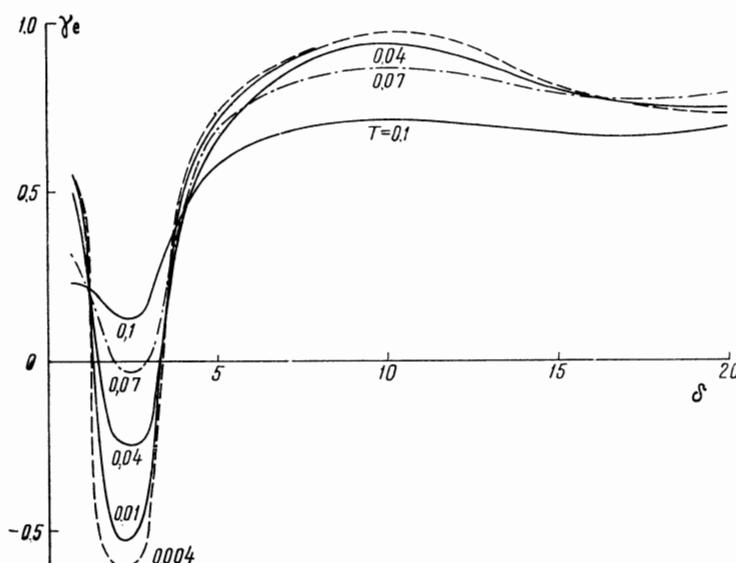
$$p_T = T \int_0^T \frac{1}{T^2} \left( \frac{\partial E_T}{\partial V} \right)_T dT,$$

we obtain

$$\gamma_e = - \frac{\partial \ln \bar{\beta}}{\partial \ln \delta} \bar{\beta}, \quad \bar{\beta} = \frac{1}{T} \int_0^T \beta dT.$$

At very low temperatures  $\bar{\beta} = \beta$  and  $\gamma_e = -\partial \ln \beta / \partial \ln \delta$ .

At very low temperatures the calculated value

FIG. 5. Plot of  $\gamma_e(\delta)$  for K at different temperatures.

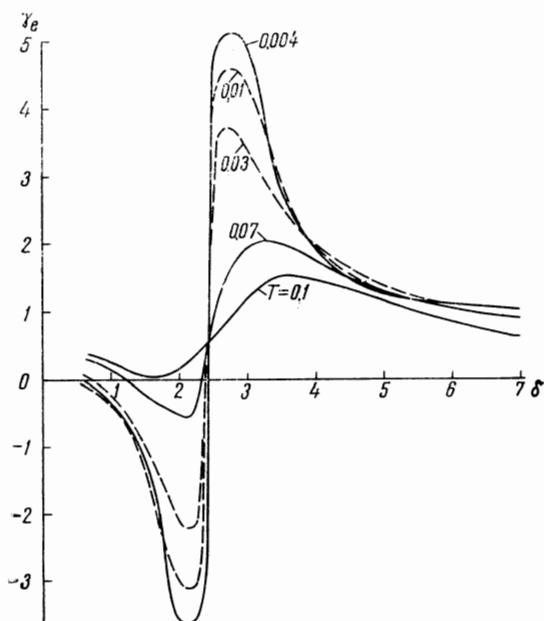
of  $\beta$  is in fair agreement with the experimental data; for example, for aluminum we have  $\beta = 517$  and  $\beta_{\text{exp}} = 500$ ; for potassium  $\beta = 456$  and  $\beta_{\text{exp}} = 560$  ( $\beta$  is in erg/g-deg<sup>2</sup>).

Thus, the Gruneisen coefficient is connected with the character of variation of the density of the electronic states on the Fermi surface, since the value of  $\beta$  is proportional to the density of the electronic states. Usually with increasing density the electronic bands broaden and  $\beta$  decreases, which leads to positive  $\gamma_e$ . A typical example of such a case is Fe (see Table II). The calculated values of  $\gamma_e$  at  $\delta = 1-2$  for iron are close to unity, in good agreement with the experimental data. The anomalously large value of  $\beta$  of transition metals is connected with the large density of the electronic states on the Fermi surface for the 3d bands.

In some cases the density of the electronic levels on the Fermi surface can increase upon compression, which leads to a negative  $\gamma_e$ . Such a region of negative  $\gamma_e$  was found in K, as can be seen from Fig. 5. The reason for the appearance of negative  $\gamma_e$  is connected with the fact that at a relative compression 2-3 the hitherto-unfilled 3d

band begins to overlap energetically the 4s band, which leads to an increase of  $\beta$  upon compression, although the width of the fundamental 4s band increases at the same time.

When the temperature increases to (20-30)  $\times 10^3$  deg, the calculated value of  $\gamma_e$  reverses sign and becomes approximately equal to 0.15 in the same density interval  $2.5 < \delta < 3.5$ . The Hugoniot adiabat calculated from this value of  $\gamma_e$  and from the extrapolated section of the cold curve is in reasonable agreement with experiment. At the same time, the large statistical values of  $\gamma_e$  did not permit a noncontradictory interpretation of the

FIG. 6. Plot of  $\gamma_e(\delta)$  for aluminum at different temperatures.Table II.  $\gamma_e(\delta)$  for Fe at different temperatures

T	$\delta$					
	0.746	1.073	2.005	3.00	4.00	5.00
0.004	1.434	1.439	0.953	0.572	0.509	0.397
0.007	1.483	1.387	1.013	0.571	0.507	0.395
0.010	1.607	1.369	1.068	0.566	0.497	0.378
0.020	1.810	1.379	1.032	0.550	0.400	0.240
0.040	1.716	1.386	1.004	0.660	0.388	0.192
0.070	1.462	1.282	1.040	0.810	0.605	0.308
0.100	1.278	1.169	1.189	0.923	0.764	0.449

dynamic experiments (experiments with shock waves). All this shows that knowledge of the changes in the structure of the energy bands of metals with change in density is very important in the reduction of dynamic-experiment data.

As seen from Fig. 6, a clearly pronounced region of negative  $\gamma_e$  is obtained theoretically in aluminum. This phenomenon is connected in this case with the rearrangement of the character of the electronic bands upon compression. At normal density and near it, the sub-band  $3d_0$ , on which the last electron of aluminum is located, is directed downward and at large  $k$  on the Fermi surface the wave function of the electron contains a large admixture of p-states. Following a compression with  $\delta \sim 2$ , the sub-band  $3d_0$  already has a maximum, and the level density on the Fermi surface is larger than at normal density.

As a result of such rearrangement, the cold-compression curve has a noticeable inflection at  $\delta = 2$ . It is important here that as a result of the rearrangement the value of  $\beta$  increases with increasing density, in some region, reaching a maximum at  $\delta \sim 2.4$ . Subsequently the sub-bands  $3d_0$ ,  $3d_1$ , and  $3d_2$  move upward simultaneously, their width increases with increasing  $\delta$ , and  $\beta$  begins to decrease. This means that there is a region of negative  $\gamma_e$  at  $1 < \delta < 2.4$ , after which  $\gamma_e$  rapidly passes through zero, becomes positive; the  $\gamma_e(\delta)$  curve has two extrema, in both the negative and the positive regions. The presence of a region of negative  $\gamma_e$  and of an inflection in the cold-pressure curve should lead to a turning of the shock adiabat of Al to the right at  $\delta = 2$ . The experimental data obtained in [7, 8] show that apparently such a turning of the adiabat does indeed take place near  $\delta \sim 2$ .

Subsequently, on going into the region of large positive  $\gamma_e$ , one should expect a sharp turning of the shock adiabat of Al to the left. These theoreti-

cal premises are presently undergoing a thorough experimental study.

Summarizing the foregoing, we can see that the developed quantum-mechanical theory makes it possible to predict a large set of properties of metals in the compressed state. The developed method makes it possible even now to calculate the electronic rearrangement upon compression, the loss of metallic properties in a definite density interval, and thermal energy and thermal pressure of the electrons.

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