

## QUANTUM-MECHANICAL DERIVATION OF AN EQUATION OF STATE OF IRON

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A quantum-mechanical method of deriving an equation of state of iron is developed. The energy bands in iron at  $T = 0$  are first considered. A detailed analysis is made of the change in the nature of the dependence of energy on quasi-momentum, and of the spacing of the bands, at various degrees of compression. A direct formula for the pressure in solid bodies is derived by use of the quantum-mechanical stress tensor and of the exchange-correlation forces that act between different cells of the crystal. Computed values of pressure for various degrees of compression  $\delta$ , and a comparison with experiment, are presented. In the final section, formulas are derived for the thermal pressure and thermal energy of the electrons; the methods of quantum field theory are used. The calculated values of the electronic specific heat agree with the anomalously large experimental value observed in iron.

## 1. INTRODUCTION

FOR calculation of the dependence of pressure on density in solids at high pressures, the statistical theory of Thomas and Fermi<sup>[1,2]</sup> and of Thomas, Fermi, and Dirac<sup>[1,3]</sup> is usually used; this is a quasi-classical approximation to the method of the self-consistent field. Kirzhnits<sup>[4,5]</sup> treated a Thomas-Fermi model with quantum and exchange corrections (the TFC model). Kalitkin<sup>[6]</sup> did similar calculations, based on the method of Kirzhnits, for a compressed material at temperature  $T = 0$ . His calculation of quantum corrections improved the agreement of the calculated values with experimental data of Al'tshuler et al.<sup>[7]</sup> At normal densities, and also at low compressions, the TFC model becomes in general inapplicable, because in this range it is not permissible to neglect the shell structure of the atom. Furthermore, in the derivation of the equations for the quantum corrections in the TFC model, it was assumed that the corrections were small; but the calculation gave a large value for the correction terms.

All of this indicates that it is important to remove the basic inaccuracy of the statistical methods, which consists in the fact that in them no account is taken of the separated bands in metals. In consequence, the statistical methods are unable to explain possible irregularities of the  $p(\rho)$  curve, phase transitions of electronic type<sup>1)</sup>, the

<sup>1)</sup>The idea of the possibility of phase transitions dependent on a redistribution of electrons among shells was proposed by Fermi and developed quantitatively by Sternheimer<sup>[8]</sup> for cesium. The occurrence of irregularities on the  $p(\rho)$  curve, was first noted by I. Lifshitz.<sup>[9]</sup>

anomalously large value of the electronic specific heat of transition metals, etc. A more accurate calculation of the  $p(\rho)$  curve, with attention to the individual filling up of the different bands, becomes indispensable.

In the present work, a band theory is used; it assumes that each electron may be considered as moving independently in a periodic potential field, which takes account, on the average, of the interaction of an electron with the rest of the crystal. The wave function of the system of electrons is expressed in terms of one-electron wave functions, for which the wave equations in the self-consistent periodic field are written in the form

$$\left\{ -\frac{\hbar^2}{2m} \Delta + V(\mathbf{k}, \mathbf{r}) \right\} \psi_n(\mathbf{k}, \mathbf{r}) = E_n(\mathbf{k}) \psi_n(\mathbf{k}, \mathbf{r}). \quad (1)$$

Here  $V(\mathbf{k}, \mathbf{r})$  is the potential acting on the electron;  $E_n(\mathbf{k})$  is the energy level of state  $n, \mathbf{k}$ ; the index  $n$  denotes the set of quantum numbers of the level to which the band goes over for relative density  $\delta \rightarrow 0$ , when we have to do in effect with a level of an isolated atom;  $\mathbf{k}$  is the quasi-momentum. The solutions of Eq. (1) must satisfy Bloch's periodicity condition

$$\psi_n(\mathbf{k}, \mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\mathbf{R}} \psi_n(\mathbf{k}, \mathbf{r}), \quad (2)$$

where  $\mathbf{R}$  is an arbitrary lattice vector. Because of the translational symmetry of the crystal, it is possible to limit oneself to the first Brillouin zone in  $\mathbf{k}$ -space. After the function  $E_n(\mathbf{k})$ , which determines the energy-band structure of the crystal, has been found, a filling up in energy space is carried out in accordance with the number of electrons in the crystal, and the Fermi energy  $E_F$  is found.

It must be recognized that the solution of (1) for various crystal structures presents a very difficult problem. There are many approximate methods that have been developed for this purpose (see, for example, the review by German<sup>[10]</sup>). These complicated methods of calculation, which require the expenditure of enormous computational labor, are justified for normal densities of metals by the facts that, first, in this case use is made of a quite reasonable potential, taken from the Hartree and Hartree-Fock calculations for isolated atoms; and, second, what is being investigated is the structure of the Fermi surface of metals and semiconductors for various directions of the quasi-momentum, as it depends on the specific form of the Brillouin zone for various types of crystal lattice. All this is necessary for the solution of detailed problems connected with the electrical properties of semiconductors and metals.

For highly compressed metals, the Hartree potentials of separated atoms cannot be used, because they are very different from the actual potential that acts on an electron in the compressed crystal. Furthermore, the pressure is a quantity that obviously depends little on the precise form of the cell in  $\mathbf{k}$ -space for crystals with a high degree of symmetry. Therefore it seemed to us to be expedient to use the method of spherical cells in the calculation of the pressure in a compressed crystal. It is expedient to use as the potential acting on an electron the Thomas-Fermi potential of compressed atoms.

## 2. ENERGY BANDS IN IRON

In the spherical-cell method of Wigner and Seitz<sup>[11]</sup>, each elementary polyhedron is replaced by a sphere of equal volume. We seek a solution of Eq. (1) in the form of a series in spherical harmonics (eight harmonics are used):

$$\psi = \sum_{l=0}^7 \sum_{m=-l}^l A_{lm}(k) f_l(E, r) Y_{lm}(\vartheta, \varphi). \quad (3)$$

The Schrödinger equation (1) for the case of a Thomas-Fermi potential has the form

$$\Delta\psi + \left[ 2\alpha^2 Z^{-2/3} E_n(k) + 2\alpha Z^{2/3} \frac{\Phi(x)}{x} \right] \psi = 0, \quad 0 < x < x_0. \quad (4)$$

Here  $\alpha = 1/2 (3\pi/4)^{2/3}$ ,  $x_0$  is the dimensionless radius of the cell,  $r = \alpha Z^{-1/3} a_0 x$ ,  $a_0$  is the Bohr radius, and  $\Phi(x)$  satisfies the Thomas-Fermi equation:

$$x^{1/2} \Phi''(x) = \Phi^{3/2}(x); \quad \Phi(0) = 1, \quad x_0 \Phi'(x_0) = \Phi(x_0).$$

The series (4) satisfies Eq. (5) if  $f_l(x)$  satisfies the equation

$$\frac{d^2}{dx^2}(xf') + \left[ 2\alpha^2 Z^{-2/3} E_n(k) + \frac{2\alpha Z^{2/3}}{x} \Phi(x) - \frac{l(l+1)}{x^2} \right] x f_l(x) = 0. \quad (5)$$

In the case being considered, the direction of the quasi-momentum  $\mathbf{k}$  is distinct; therefore the projection  $M$  of the moment is a conserved quantity. The whole moment is not conserved; therefore the solution of (4) is a sum (3) in which functions of different  $l$  are mixed. Nevertheless it is reasonable to assign to each definite band an index  $l$ , if we understand by this the value of  $l$  for the level to which the band goes over when  $\delta$  approaches zero (hereafter we use the band designations 4s, 3d, 3p, 3s, etc.). The boundary conditions (2), for our case of spherical cells, take the form

$$\begin{aligned} \psi(x_0, \vartheta, \varphi) e^{-ik \cos \vartheta} &= \psi(x_0, \pi - \vartheta, \varphi + \pi) e^{ik \cos \vartheta}, \\ \psi'_x(x_0, \vartheta, \varphi) e^{-ik \cos \vartheta} &= -\psi'_x(x_0, \pi - \vartheta, \varphi + \pi) e^{ik \cos \vartheta}. \end{aligned} \quad (6)$$

We multiply (6) by  $Y_{LM}^*(\vartheta, \varphi)$  and integrate over the angular variables. We get

$$\begin{aligned} \sum_{l,m} A_{lm} f'_l(x_0) a_{lLM}(k) &= 0 \quad \text{for even } L, \\ \sum_{l,m} A_{lm} f_l(x_0) a_{lLM}(k) &= 0 \quad \text{for odd } L, \end{aligned} \quad (7)$$

where

$$\int Y_{LM}^*(\vartheta, \varphi) Y_{lm}(\vartheta, \varphi) e^{-ik \cos \vartheta} d\Omega = a_{lLM}(k).$$

Since the integrals differ from zero only for  $M = m$ , the sum over  $m$  in the system (7) disappears, and for each value of  $M$  we get a separate system. An eigenvalue  $E_n(k)$  is found from the condition that the determinant of the system (7) must vanish, by numerical calculation on an electronic computer.

Equation (5) was also solved numerically, and the values of  $f_l(E, x_0)$  and  $f'_l(E, x_0)$  were obtained in the form of a table with  $E$  as parameter. After the branches  $E_n(k)$  have been found, the filling of the bands is carried out up to the Fermi energy  $E_F$ , on the basis of the normalization condition

$$\frac{8\pi \cdot 4\pi/3}{(2\pi)^3} \sum_n \kappa_n \int_{E_n(k) \leq E_F} k^2 dk = Z, \quad \kappa_n = \begin{cases} 1, & \text{if } M=0 \\ 2, & \text{if } M>0 \end{cases} \quad (8)$$

The Thomas-Fermi potential is different for every density of iron; the energy levels  $E_n(k)$  are also different. In the next section it will be shown that in the calculation of pressure, only the top bands 4s, 3d, 3s, and 3p play a role. Because of the  $M$ -

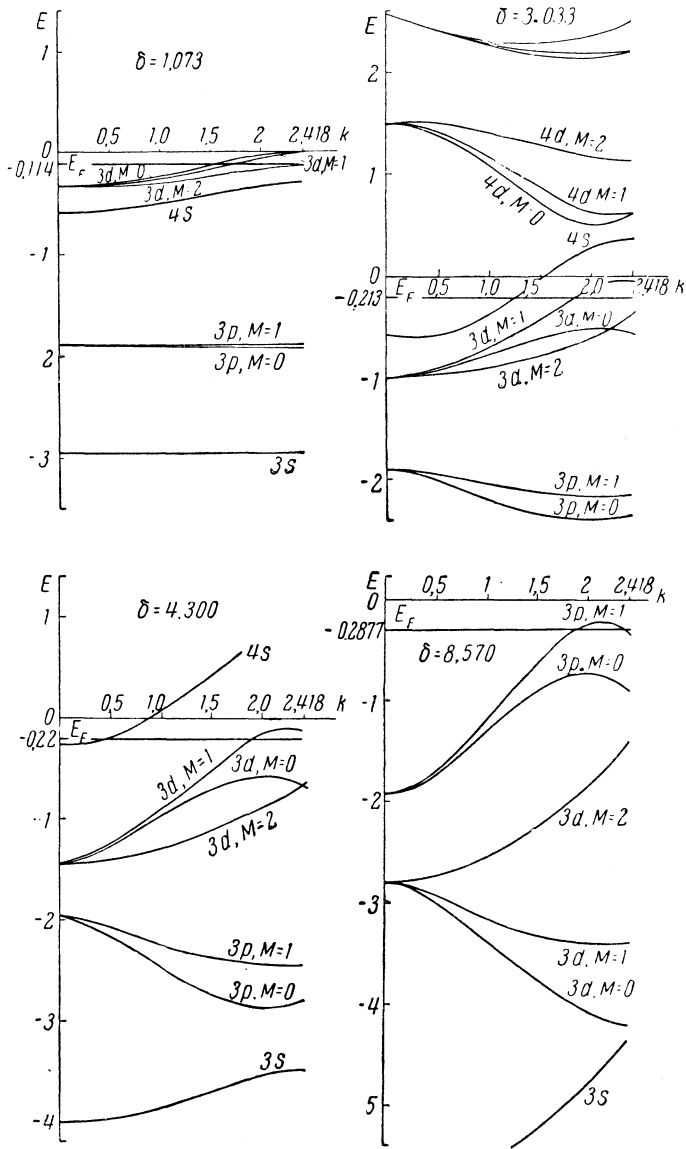


FIG. 1

splitting, the 3d band breaks up into three 3d subbands  $M = 0$ ,  $M = 1$ , and  $M = 2$ , and the 3p band into two 3p subbands  $M = 0$  and  $M = 1$ .

Figure 1 shows the  $E(k)$  curves up to a maximum  $k_0 = 2\pi(\frac{3}{4}\pi)^{2/3} = 2.418$  for relative compressions 1.07, 3.03, 4.3, and 8.57. Also shown is the Fermi energy  $E_F$  (each energy is expressed in atomic units  $e^2/a_0 = 27.23$  eV).

There is a significant change in the character of the filling up of bands with change of the degree of compression  $\delta$ . In the case of almost normal density ( $\delta = 1.073$ , Fig. 1), the 4s band is completely filled; the 3d subband  $M = 0$  is filled completely; but the 3d subbands  $M = 1$  and  $M = 2$  are filled only partly. At threefold compression, the 4s band as well as the 3d is only partly filled (cf. Fig. 1). The same is true at  $\delta = 4.3$ , though

in this case the 4s band is almost unoccupied. On further increase of density the 3d band is lowered and becomes filled, the 4s band is completely empty, and the 3p band is partly filled and contains four electrons instead of six. The fact that at large  $\delta$  the 3p band is not full in iron is very interesting in this connection: that in nickel, which has two electrons more, complete filling of the 3p band is to be expected. This means that nickel may lose its metallic properties under high compression. At present the corresponding calculation for nickel is being carried out in order to find the value of  $\delta$  at which this peculiar phenomenon can first occur.

Figure 2 shows, for iron, the variation of the minimum and maximum energies of the various bands with degree of compression  $\delta$ . The Fermi energy is plotted as a heavy line. At the points of intersection of the line  $E_F(\delta)$  with the band limits, various anomalies are possible; we will speak of these in the next section.

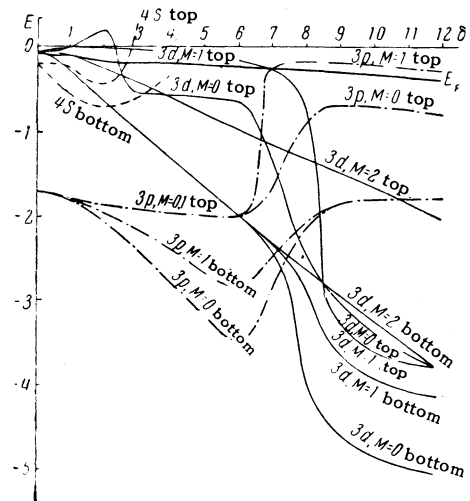


FIG. 2

### 3. DEPENDENCE OF PRESSURE ON DENSITY FOR IRON AT $T = 0$

To find the dependence of pressure on density in solid bodies, it is usual first to calculate the energy of the body, and then to find its change with a change of configuration of the body (for example, a change of the distance between the nuclei). Such a method requires knowledge of the energy of the body for two neighboring configurations. Since the change of energy, even at high compression, is insignificant in comparison with its absolute value, such a method of calculating the pressure requires a very high accuracy in the energy calculation.

Our aim is therefore to obtain a direct formula for the pressure in a solid body.

An expression for the force acting on a nucleus, in the form of an exchange integral in the wave functions of the configuration being considered, was obtained by Feynman<sup>[12]</sup> for the case of molecules. It turns out that for solids it is also possible to obtain an expression for the pressure in terms of wave functions of the system in the state being considered. Here one obtains a more complicated expression, containing an integral over the surface of an elementary cell of the crystal and the Coulomb (basically the exchange-correlation) interaction between electrons located in different cells; on the other hand, Coulomb interaction within a single cell is eliminated.

We use the general quantum-mechanical formula for the derivative of a current with respect to time<sup>[13]</sup>,

$$m_\alpha \frac{\partial j_{\alpha\mu}}{\partial t} = - \sum_{\lambda, \nu} \frac{\partial T_{\alpha\mu, \lambda\nu}}{\partial q_{\lambda\nu}} - \Psi^* \Psi \frac{\partial U}{\partial q_{\alpha\mu}},$$

$$T_{\alpha\mu, \lambda\nu} = \frac{\hbar^2}{4m_\lambda} \left( - \Psi^* \frac{\partial^2 \Psi}{\partial q_{\lambda\nu} \partial q_{\alpha\mu}} - \Psi \frac{\partial^2 \Psi^*}{\partial q_{\lambda\nu} \partial q_{\alpha\mu}} + \frac{\partial \Psi}{\partial q_{\alpha\mu}} \frac{\partial \Psi^*}{\partial q_{\lambda\nu}} + \frac{\partial \Psi}{\partial q_{\lambda\nu}} \frac{\partial \Psi^*}{\partial q_{\alpha\mu}} \right). \quad (9)$$

Here  $q_{\alpha\mu}$  means the  $\mu$ -th coordinate of an arbitrary particle  $\alpha$ . We integrate Eq. (9), written for the  $\mu$ -th coordinate of the  $n$ -th particle, over the configuration space of all the other particles,  $d\tau_n$ :

$$m_n \frac{\partial}{\partial t} \int j_{n\mu} d\tau_n = - \sum_{\lambda, \nu} \int \frac{\partial T_{n\mu, \lambda\nu}}{\partial q_{\lambda\nu}} d\tau_n - \int \frac{\partial U}{\partial q_{n\mu}} \Psi^* \Psi d\tau_n.$$

The first integral on the right side is equal to zero if the index does not refer to the  $n$ -th particle; the expression on the left is the  $\mu$ -projection of the force density  $f_n$ , acting on the  $n$ -th particle;

$$U = \frac{1}{2} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{r_{ij}}, \quad \frac{\partial U}{\partial q_{n\mu}} = \sum_{j \neq n} \frac{\partial}{\partial q_{n\mu}} \left( \frac{e^2 Z_j Z_n}{r_{jn}} \right).$$

We introduce the notation

$$\int |\Psi|^2 d\tau_{nm} = \Gamma_{n, m}(q, q'),$$

where  $d\tau_{nm}$  is the configuration space without the coordinates  $q = q_n$  and  $q' = q_m$  of two particles. We have for the complete force density  $f_\mu(q)$

$$f_\mu(q) = - \sum_\nu \frac{\partial T_{\mu\nu}(q)}{\partial q_\nu} - \sum_{n, j} e^2 Z_n Z_j \int_\Omega \Gamma_{nj}(q, q') \frac{\partial}{\partial q_\mu} \frac{1}{|q - q'|} dq',$$

$$T_{\mu\nu}(q) = \sum_n \left[ \int T_{n\mu, n\nu} d\tau_n \right]_{q_n=q},$$

where  $\Omega$  is the volume of the whole crystal. The whole force acting on any distinct volume  $\omega$ , for example on an elementary cell of the crystal, is

$$F_\mu = \int_\omega f_\mu(q) dq = - \oint_\omega \sum_\nu \Gamma_{\mu\nu}(q) n_\nu dS - \sum_{n, j} e^2 Z_n Z_j \int_\omega dq \int_\Omega dq' \Gamma_{nj}(q, q') \frac{\partial}{\partial q_\mu} \frac{1}{|q - q'|} dq. \quad (10)$$

$\Gamma_{nj}(q, q')$  is the probability that the  $n$ -th particle is at the point  $q$  and the  $j$ -th at the point  $q'$ ;  $\gamma_n(q) = \int |\Psi|^2 d\tau_n$  is the probability that the  $n$ -th particle is at the point  $q$ . The difference  $\Gamma_{nj}(q, q') - \gamma_n(q) \gamma_j(q') = -\Gamma'_{nj}(q, q')$  characterizes the phenomenon of exchange. The charge density is  $\rho(q) = \sum_n e Z_n \gamma_n(q)$ .

The whole force  $F_\mu = 0$ . But it is possible to separate from (10) the force  $F_\mu^{(gh)}$  that is exerted on the given cell  $g$  by an arbitrary other cell  $h$ , and also the surface forces. For this purpose it is useful to separate the electrostatic interaction into two parts—classical and exchange. Furthermore, we separate the integral over  $\Omega$  in (10) into two parts:

$$\int_\Omega dq' = \int_\omega dq' + \int_{\Omega-\omega} dq'.$$

The first gives zero, since on interchange of the designations of the variables  $q$  and  $q'$  the integral changes sign. We have

$$\sum_{n, j} e^2 Z_n Z_j \int_\omega dq \int_{\Omega-\omega} dq' \Gamma_{nj}(q, q') \frac{\partial}{\partial q_\mu} \frac{1}{|q - q'|} = \int_\omega \rho(q) dq \int_{\Omega-\omega} \rho(q') \frac{\partial}{\partial q_\mu} \frac{1}{|q - q'|} dq' - \int_\omega dq \int_{\Omega-\omega} dq' \frac{\partial}{\partial q_\mu} \frac{1}{|q - q'|} \sum_{n, j} e^2 Z_n Z_j \{ \Gamma'_{nj}(q, q') + \gamma_n(q) \gamma_j(q') \}. \quad (11)$$

We now go over to the approximation of immovable nuclei, attached to definite sites. Then the components of the tensor  $T_{\mu\nu}(q)$  that are due to nuclei may be neglected. The first, classical electrostatic term in (11), for neutral nuclei with sufficiently high symmetry, may also be neglected. Seitz<sup>[11]</sup> made an estimate of the contribution of the deviation from spherical symmetry in a charge distribution for a body-centered lattice of ions with a smoothed uniform distribution of negative charges; he obtained a very small correction to the energy.

Finally we obtain an expression for the force acting on the  $g$ -th nucleus:

$$F_{\mu}^{(g)} = \oint_{\omega_g} \sum_{\nu} T_{\mu\nu}(q) n_{\nu} dS + \sum_n F_{\mu}^{(gh)},$$

$$F_{\mu}^{(gh)} = e^2 \int_{\omega_g} dq \int_{\omega_h} dq' \{ \Gamma(q, q') - \gamma(q) \gamma(q') \} \frac{\partial}{\partial q_{\mu}} \frac{1}{|q - q'|}. \quad (12)$$

Here

$$\gamma(q) = \sum_n \gamma_n^e(q) = N \int |\Psi(q, q_2, \dots, q_N)|^2 d\tau_1,$$

where  $N$  is the total number of electrons;

$$\Gamma(q, q') = \sum_{n,j} \Gamma_{nj}^e(q, q')$$

$$= \frac{N(N-1)}{2} \int |\Psi(q, q', q_3, \dots, q_N)|^2 d\tau_{1,2}; \quad (13)$$

$$T_{\mu\nu}(q) = \frac{\hbar^2}{4m} \left[ -\frac{\partial^2 \gamma(q'|q)}{\partial q_{\mu} \partial q_{\nu}} - \frac{\partial^2 \gamma(q'|q)}{\partial q'_{\mu} \partial q'_{\nu}} + \frac{\partial^2 \gamma(q'|q)}{\partial q'_{\mu} \partial q_{\nu}} \right. \\ \left. + \frac{\partial^2 \gamma(q'|q)}{\partial q_{\mu} \partial q'_{\nu}} \right]_{q'=q},$$

$$\gamma(q'|q) = N \int \Psi^*(q', q_2, \dots, q_N) \Psi(q, q_2, \dots, q_N) d\tau_1. \quad (14)$$

To calculate the pressure, it is necessary to find the work by the forces between nuclei in a uniform dilatation of the body in all directions in the ratio  $(1+\epsilon)$ . The change  $\Delta E$  of the energy of the system, found in this way, must be divided by the change of volume  $\Delta V = 3\epsilon\omega$ .

The work by the Coulomb forces  $F^{(gh)}$  is expressible in the form  $\epsilon F^{(gh)} R_{gh}$ , where  $R_{gh}$  is the distance between centers of neighboring nuclei and may be different in different directions. The work by surface forces is equal simply to the mean of  $T_{\mu\nu}$  over the cell surface, multiplied by the change of volume. We get as the final formula for the pressure

$$p = p_{\text{kin}} + p_{\text{Coul}}; \quad (15)$$

$$p_{\text{kin}} = \int p_{\text{kin}}(q) \frac{d\Omega}{4\pi},$$

$$p_{\text{kin}}(q) = T_{\mu\nu}(q) n_{\mu} n_{\nu}$$

$$= \frac{\hbar^2}{4m} \left[ -\frac{\partial^2 \gamma(q'|q)}{\partial n^2} - \frac{\partial^2 \gamma(q'|q)}{\partial n'^2} + 2 \frac{\partial^2 \gamma(q'|q)}{\partial n' \partial n} \right]_{q'=q}; \quad (15a)$$

$$p_{\text{Coul}} = \frac{1}{6\omega} \sum_{h \neq 0} F^{(0h)} R_{(0h)}. \quad (15b)$$

The index zero designates the cell being considered;  $\mathbf{n}$  is the direction of the normal to the cell surface.

A paper by Dmitriev<sup>[14]</sup> contains a detailed derivation of the work by the forces between nuclei in uniform dilatation of the body. The results obtained are derived by another method, without use of the concept of the momentum of the system of particles, by calculating directly by perturba-

tion theory the infinitesimal change of energy in an infinitesimal dilatation.

All the calculations of the preceding section were carried out in the one-electron approximation, in which the wave function of the system is exhibited in the form of a determinant of one-electron functions  $\psi_j(q)$ . In this case

$$\gamma(q'|q) = \sum_{i=1}^N \psi_i^*(q') \psi_i(q), \quad \gamma(q) = \sum_{i=1}^N |\psi_i(q)|^2,$$

$$\Gamma(q, q') - \gamma(q) \gamma(q') = -|\gamma^+(q'|q)|^2 - |\gamma^-(q'|q)|^2, \quad (16)$$

where  $\gamma^+(q'|q)$  is the part of the density matrix corresponding to electrons with one spin direction and where  $\gamma^-(q'|q)$  is the part corresponding to electrons with the opposite spin direction. Then  $p_{\text{kin}}(q)$  takes the form

$$p_{\text{kin}} = \frac{\hbar^2}{4m} \sum_{i=1}^N \left[ -\psi_i^*(q) \frac{\partial^2 \psi_i(q)}{\partial n^2} \right. \\ \left. - \psi_i(q) \frac{\partial^2 \psi_i^*(q)}{\partial n^2} + 2 \left| \frac{\partial \psi_i(q)}{\partial n^2} \right|^2 \right]. \quad (17)$$

In the spherical-shell method that we have used, we get, after substitution of (3) in (17), the following formula for the kinetic pressure in atomic units ( $e^2/a_0^4 = 293 \times 10^6$  atm):

$$p_{\text{kin}} = \frac{1}{6\pi^2} \frac{1}{(\alpha Z^{-1/3})^5} \sum_n \kappa_n \int_{E_n(k) \leq E_F} k^2 dk \left( \sum_{l=M}^7 |A_{lM}^n(k)|^2 \right. \\ \left. \times \{ |f_l^n(k, x_0)|^2 - f_l^n(k, x_0) f_l^n(k, x_0) \} \right) \left[ \sum_{l=M}^7 |A_{lM}^n(k)|^2 \right]^{-1}. \quad (18)$$

Here  $n$  is the number of the band. For each band,  $M$  is given. It is evident from (18) that the contribution of the inner electrons to the pressure is insignificant, since the wave functions of these electrons on the cell surface are very small.

Calculation of the exchange pressure by formulas (15b), (12), and (16) is very complicated, because it requires a sixfold integration over two neighboring cells and also a further twofold integration over the quasimomentum. At present a procedure for such a calculation is being developed, but it is not yet complete. For the case of a free-electron gas, formula (15b) should lead to the known expression for the exchange pressure,

$$p_{\text{exch}} = -\frac{1}{4} \left( \frac{3}{\pi} \right)^{1/3} \frac{Z^{1/3}}{\alpha^4} \rho_e \frac{e^2}{a_0^4}. \quad (19)$$

Actually, (15b) and (12) lead to this result if the radius of the spherical shell shrinks to zero. Therefore as a first approximation for the exchange pressure it is expedient, especially at

large compression  $\delta$ , to use formula (19), substituting in it the calculated value of the electron density  $\rho_e$  on the cell boundary (in (19) the quantity  $\rho_e$  is dimensionless; to obtain the electron density in  $\text{cm}^{-3}$  it is necessary to divide  $\rho_e$  by  $[\alpha Z^{-1/3} a_0]^3$ ).

A correlation correction to the pressure was also made by Wigner's formula,

$$\rho_{\text{corr}} = -\frac{e^2}{a_0^4} \frac{0.288}{4\pi x_s^2 (x_s + 5.1)^2} = -\frac{6.72}{x_s^2 (x_s + 5.1)^2} [10^6 \text{atm}],$$

$$x_s = r_s/a_0, \quad 4/3\pi r_s^3 = (\alpha Z^{-1/3} a_0)^3 / \rho_e \quad (20)$$

Table I shows the results of the calculation of pressure in iron at various  $\delta$ 's (in  $10^6$  atm). For  $\delta > 2$  the correlation correction may be disregarded.

In Fig. 3 the calculated function  $p(\delta)$  is compared with the experimental curve of Al'tshuler et al.<sup>[7]</sup> and also with Kalitkin's<sup>[6]</sup> curve (the TFC model). The results obtained are closer to the experimental data than is the TFC curve. Although the TFC method is strictly inapplicable at small  $\delta$ , Kalitkin made an estimate of the density of uncompressed iron and obtained  $\rho_0 = 5.15$ . The quantum-mechanical method described gave  $\rho_0 = 6.44$ , which is appreciably closer to the normal density of iron, 7.8.

The method described in principle gives a region of negative pressure. However, in this range the role of the exchange and correlation effects is important, and a higher accuracy of calculation is required than is required for a compressed material.

For  $\delta \leq 2$  the contributions of the 4s and 3d

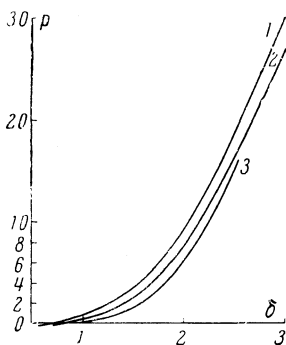


FIG. 3. The function  $p(\delta)$  according to data of various authors: curve 1, calculation of Kalitkin<sup>[6]</sup> by the TFC model; curve 2, present work; curve 3, experimental data.<sup>[7]</sup>

bands to the pressure are approximately equal, and therefore the contribution of the 3d band plays an important role. For  $\delta \geq 6$  the contribution of the 3p band is appreciable. The 3s band makes an insignificant negative contribution to the pressure.

In the previous section it was noted that at points of intersection of the  $E_F(\delta)$  line with band edges, anomalous properties are possible. One of these points is  $\delta_0 = 4.4$ , where an edge of the 4s band finally breaks away from the Fermi surface. I. Lifshitz<sup>[9]</sup> first called attention to the possibility of such anomalies. Formula (18) can be written in the form

$$p_{\text{kin}} = 33.6 \sum_n \alpha_n \int_{E_n(k) < E_F} f_n(k) \frac{3k^2 dk}{k_0^3} \text{ atomic units,}$$

The value of  $f_n(k)$  is different for the 4s and for the 3d bands. According to calculation in the neighborhood of  $\delta_0 = 4.4$ , the value of  $f(k)$  is 0.00920 for the 4s band near  $k = 0$ , and 0.00305 for the 3d band. When some of the electrons from the 3d band go over to the 4s band (upon decrease of the density from  $\delta_0 = 4.4$ ), the pressure changes by an amount  $\Delta p \sim k^3$ . But  $\Delta E \sim (\delta_0 - \delta) \sim k^2$ , so that  $\Delta p \sim (\delta_0 - \delta)^{3/2}$ . Calculation gave the result that near  $\delta_0 = 4.4$ , the pressure changes according to the law

$$p = 1.27\delta^{2.70} + 0.27 [(4.4 - \delta)/0.1]^{3/2} \text{ for } \delta < 4.4,$$

$$p = 1.27\delta^{2.70} \text{ for } \delta > 4.4. \quad (21)$$

The curve of the speed of sound,  $c^2 \sim dp/d\delta$ , has a vertical tangent at  $\delta_0 = 4.4$ . Figure 4 gives

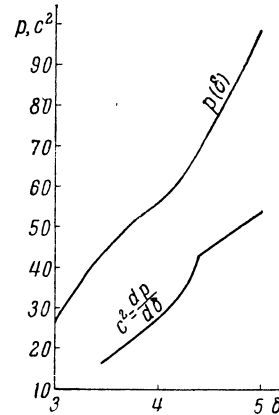


FIG. 4

Table I

| $\delta$ | $P_{\text{kin}}$ | $P_{\text{exch}}$ | $P_{\text{corr}}$ | $p$    | $\delta$ | $P_{\text{kin}}$ | $P_{\text{exch}}$ | $P_{\text{corr}}$ | $p$   |
|----------|------------------|-------------------|-------------------|--------|----------|------------------|-------------------|-------------------|-------|
| 0.7465   | 1.040            | -1.147            | -0.064            | -0.171 | 4.301    | 86.70            | -22               | —                 | 64.7  |
| 1.073    | 2.96             | -2.15             | -0.10             | 0.71   | 6.051    | 201.5            | -40.15            | —                 | 161.3 |
| 2.072    | 16.28            | -7.54             | —                 | 8.74   | 8.570    | 463              | -73.9             | —                 | 389   |
| 3.033    | 39.10            | -12.1             | —                 | 27     | 11.840   | 968              | -130              | —                 | 838   |

the calculated curve  $p(\delta)$  in the range  $3 < \delta < 5$ ; it has a characteristic kink, described by (21).

It must be mentioned that the sufficiency of eight spherical harmonics has been verified in the case of absence of a potential; then the dependence of pressure on density has the form  $p = A\rho^{5/3}$ , where  $A$  is the well known constant of a free Fermi gas. Pavlovskii and Tarasov (private communication) have shown that upon use of the method of spherical cells with eight harmonics, the calculated coefficient  $A$  agrees to within 5% with the exact value for a free electron gas. This result provides additional confirmation of the reliability at large  $\delta$  of the method used here. The sufficiency of eight harmonics also follows from the fact that in our calculations the coefficients  $A_{JM}(k)$  are small for large  $l$ .

We again emphasize that for accuracy of the pressure calculation, it is essential to be able to eliminate the Coulomb interaction within a cell and to reduce the exchange pressure to an interaction between neighboring cells (it is described at large  $\delta$  by the formula for a free electron gas).

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

The rigorous treatment of a many-particle system at nonvanishing temperatures must be carried out by the methods of quantum field theory, which were first developed in a form suitable for problems of statistics by Matsubara<sup>[5]</sup>. Further generalization and development of Matsubara's method is contained in the papers of Abrikosov, Gor'kov, and Dzyaloshinskii<sup>[16]</sup>, Fradkin<sup>[17]</sup>, Luttinger<sup>[18]</sup>, and others.

The thermodynamic potential  $\Omega$  of a system of electrons is expressed in the form

$$e^{-\beta(\Omega - \mu N)} = \langle S \rangle. \quad (22)$$

Here  $\langle \rangle$  denotes a thermal statistical mean in the sense of

$$\langle S \rangle = \text{Sp} \{ e^{-\beta(H_0 - \mu N)} S \} / \text{Sp} \{ e^{-\beta(H_0 - \mu N)} \}, \quad (23)$$

$$S = T_\tau \exp \left\{ - \int_0^\beta H_1 d\tau \right\} = T_\tau \mathfrak{C} \quad (24)$$

( $H_0$  is the free Hamiltonian,  $H_1$  is the interaction Hamiltonian, and  $T_\tau$  denotes the time-ordering operator in imaginary time  $\tau$ <sup>[16]</sup>;  $\beta$  is the inverse temperature;  $\Omega_0$  is the thermodynamic potential in the absence of interaction.

The complete Hamiltonian for a system of electrons for given potential  $U(x)$  of the nuclei is expressed in the form

$$\begin{aligned} H = & \int \psi^*(x) \left[ \frac{p^2}{2m} + U(x) \right] \psi(x) d^3x \\ & + \frac{1}{2} \int T [\psi^*(y) \psi(y) J(y-z) \psi^*(z) \psi(z)] dy dz \\ & - \frac{1}{2} J(0) \int \psi^*(y) \psi(y) dy, \\ & J(y-z) = v(y-z) \delta(y_0 - z_0), \end{aligned} \quad (25)$$

where  $v(\mathbf{y} - \mathbf{z})$  is the Coulomb interaction energy of two particles, and  $\psi(x)$  is the field operator. The first term in (25) is naturally regarded as a free Hamiltonian and the last two as an interaction Hamiltonian.

In the case of a free electron gas, when there is spatial homogeneity, one can successfully seek simplification through a calculation by perturbation theory, with use of a diagram technique. In the case of a crystal, there is an essential inhomogeneity, connected with accumulation of electrons near ionic residues. The free Hamiltonian in (25), which describes the behavior of the electrons in the absence of interaction, is very far from the actual first approximation of "independent particles," moving in some self-consistent field of the nuclei and of all the electrons of the crystal. Therefore it is very important to introduce the self-consistent field, with a change in the concept of the free Hamiltonian  $H_0$ .

We write  $H_0$  in the form

$$H_0 = \int \psi^*(y) \left[ \frac{p^2}{2m} + U \right] \psi(y) dy + \int \psi^*(y) \Phi(z, y) \psi(z) dy dz. \quad (26)$$

Then

$$\begin{aligned} H_1 = & \frac{1}{2} \int T [\psi^*(y) \psi(y) J(y-z) \psi^*(z) \psi(z)] dy dz \\ & - \frac{1}{2} J(0) \int \psi^*(y) \psi(y) dy - \int \psi^*(y) \Phi(z, y) \psi(z) dy dz. \end{aligned} \quad (27)$$

The field operator  $\psi(x)$  is represented in the form

$$\psi(x) = \sum a_i u_i(\mathbf{x}) e^{-E_i x_0}, \quad \psi^*(x) = \sum a_i^* u_i^*(\mathbf{x}) e^{E_i x_0}. \quad (28)$$

In the second-quantization representation, the free Hamiltonian  $H_0$  must have the usual form

$$H_0 = \sum_i E_i a_i^* a_i. \quad (29)$$

It is not hard to see that to satisfy (29) the functions  $u_i(\mathbf{x})$  must be eigenfunctions and the  $E_i$ 's eigenvalues of the equation<sup>2)</sup>

$$\left[ \frac{p^2}{2m} + U(x) \right] u_i(x) + \int \Phi(y, x) u_i(y) dy = E_i u_i(x). \quad (30)$$

<sup>2)</sup>Here  $u_i(\mathbf{x}) = u_i(\mathbf{x}) \exp \{-E_i x_0\}$ . Since even without homogeneity  $\Phi(y, x)$  is a function of the time difference  $(x_0 - y_0)$ , Eq. (30) does not depend on the time  $x_0$ .

It is easy to find the free Green's function  $G_0(x, x')$   
 $= \langle T[\psi^*(x)\psi(x')] \rangle$ :

$$\begin{aligned} G_0(x, x') &= \sum_i u_i^*(x) u_i(x') \exp\{E_i(x_0 - x'_0)\} \langle a_i^* a_i \rangle \\ &= \sum_i f_i u_i^*(x) u_i(x') \exp\{E_i(x_0 - x'_0)\} \text{ for } x_0 > x'_0, \\ G_0(x, x') &= -\sum_i u_i(x) u_i^*(x') \exp\{E_i(x_0 - x'_0)\} \langle a_i a_i^* \rangle \\ &= \sum_i (f_i - 1) u_i^*(x) u_i(x') \exp\{E_i(x_0 - x'_0)\}, \\ f_i &= \langle a_i^* a_i \rangle = [1 + \exp\{(E_i - \mu)\beta\}]^{-1}. \end{aligned} \quad (31)$$

The function  $\Phi(z, y)$  has not yet been defined. It is natural to define it by the condition that the Green's function  $G(x, x')$  of an electron, with allowance for the interaction  $H_1$ , shall coincide with the free Green's function  $G_0(x, x')$ . This condition  $G(x, x') = G_0(x, x')$  can be satisfied to a definite order in the Coulomb interaction constant  $e^2$ , since for  $G(x, x')$  we can get only a power series in  $e^2$ .

The equality  $G(x, x') = G_0(x, x')$  can be transformed on the basis of lemma (3.25) of Matsubara's<sup>[15]</sup> paper, and also of the commutation relation (5.5) of the same paper. Without presenting the calculations, we write the equation for the determination of  $\Phi(y, z)$ :

$$\begin{aligned} \int dz J(x-z) \frac{\langle T\{\psi(x')\psi^*(x)\psi^*(z)\psi(z)\mathcal{S}\rangle}{\langle \mathcal{S} \rangle} \\ + \frac{1}{2} J(0) G_0(x, x') = - \int dz \Phi(x, z) G_0(z, x'). \end{aligned} \quad (32)$$

The first approximation to  $\Phi(x, z)$  in terms of  $e^2$  is obtained by replacing  $\mathcal{S}$  by unity in (32). After some calculations that make use of Wick's theorem and with the notation

$$\begin{aligned} \langle \psi^*(y)\psi(y) \rangle &= \rho(y) = \sum_i f_i u_i^*(y) u_i(y), \\ \rho(y, z) &= \sum_i f_i u_i^*(y) u_i(z), \end{aligned} \quad (33)$$

we get for the first approximation

$$\Phi_1(x, z) = \delta(x-z) \int v(x-y) \rho(y) dy - J(x-z) \rho(x, z). \quad (34)$$

On substituting (34) in (30), we get an equation of Hartree-Fock type for the one-electron functions  $u_i(x)$  at arbitrary temperature:

$$\begin{aligned} \left[ \frac{p^2}{2m} + U(x) \right] u_i(x) + \int v(x-\xi) \rho(\xi) d\xi u_i(x) \\ - \int v(x-y) \rho(y, x) u_i(y) dy = E_i u_i(x). \end{aligned} \quad (35)$$

By solving Eq. (35) it is in principle possible to get complete information about the system of electrons at  $T \neq 0$ , with allowance for exchange

effects. In practice, however, the rigorous solution of Eq. (35) for a solid body is a task difficult to perform. It is desirable to restrict oneself to the simplest approximation. It seems most natural at the start to omit the exchange terms in (35) and to solve the resulting "hot" equation of Hartree type by a method of successive approximations, after taking as a first approximation the statistical potential at  $T \neq 0$ . With the aid of the wave functions  $u_i(x)$  and eigenvalues  $E_i$  thus found, one can then find the contribution of exchange terms to the thermal energy and thermal pressure of the electrons. The future carrying out of calculations of the equation of state of iron at  $T \neq 0$ , on the basis outlined above, is under consideration.

We pass on now to the derivation of a formula for the thermodynamic potential  $\Omega$  in the first approximation in  $\lambda = e^2$ . From (22) and (27) we get the exact equality

$$\begin{aligned} 3 \frac{\partial \Omega}{\partial \lambda} &= - \frac{\langle \partial S / \partial \lambda \rangle}{\langle \mathcal{S} \rangle} \\ &= \frac{1}{2\lambda} \left\langle \int dy dz T \{ \psi^*(y) \psi(y) J(y-z) \psi^*(z) \psi(z) \mathcal{S} \} \right\rangle \frac{1}{\langle \mathcal{S} \rangle} \\ &\quad - \frac{1}{2\lambda} J(0) \int \rho(y) dy - \frac{1}{\lambda} \int \Phi(z, y) G_0(y, z) dy dz. \end{aligned} \quad (36)$$

We get the first approximation  $\Omega_1$  by replacing  $\mathcal{S}$  by unity and  $\Phi$  by  $\Phi_1$  and using Wick's theorem. After slight transformations we get

$$\begin{aligned} \lambda \frac{\partial \Omega_1}{\partial \lambda} &= - \frac{1}{2} \int \rho(y) v(y-z) \rho(z) d^3y d^3z \\ &\quad + \frac{1}{2} \int \rho(y, z) v(y-z) d^3y d^3z. \end{aligned}$$

Since the Coulomb function  $v \sim \lambda$ , we finally get  $\Omega$  in first approximation:

$$\begin{aligned} \Omega_1 &= \Omega_{10} - \frac{1}{2} \int \rho(y) \rho(z) v(y-z) d^3y d^3z \\ &\quad + \frac{1}{2} \int \rho(y, z) \rho(z, y) v(y-z) d^3y d^3z. \end{aligned} \quad (37)$$

Here  $\Omega_{10} = -\beta^{-1} \sum_i \ln[1 + \exp\{(\mu - E_i)\beta\}]$  is the thermodynamic potential in the absence of interaction. (It must be recalled that  $E_i$  is an eigenvalue of the energy of an electron in a self-consistent field that contains within itself a part of the Coulomb interaction.) The chemical potential  $\mu$  is found from the condition

$$N = (\partial \Omega / \partial \mu)_{T, v}.$$

On differentiating (37), we get

$$\begin{aligned} N &= \sum_i f_i \left( 1 - \frac{\partial E_i}{\partial \mu} \right) + \int \frac{\partial \rho(y)}{\partial \mu} \rho(z) v(y-z) d^3y d^3z \\ &\quad - \frac{1}{2} \int \frac{\partial \rho(z, y)}{\partial \mu} \rho(y, z) v(y-z) d^3y d^3z. \end{aligned} \quad (38)$$



If we differentiate Eq. (30) with respect to  $\mu$ , we get after simple transformations the important equality

$$\sum_i f_i \frac{\partial E_i}{\partial \mu} = \int \frac{\partial \rho(y)}{\partial \mu} \rho(z) v(y-z) d^3 y d^3 z - \int \frac{\partial \rho(z, y)}{\partial \mu} \rho(y, z) v(y-z) d^3 y d^3 z. \quad (39)$$

Similarly, by differentiating with respect to  $\beta$  we have

$$\sum_i f_i \frac{\partial E_i}{\partial \beta} = \int \frac{\partial \rho(y)}{\partial \beta} \rho(z) v(y-z) d^3 y d^3 z - \int \frac{\partial \rho(z, y)}{\partial \beta} \rho(y, z) v(y-z) d^3 y d^3 z. \quad (40)$$

On substituting (39) in (38), we get an obvious equation, which serves to determine the chemical potential  $\mu$ :

$$N = \sum_i f_i. \quad (41)$$

The sum in (41) reduces to an integral over the quasimomentum within a band and a sum over all bands, if the eigenvalues  $E_i(\mathbf{k})$  are known.

The entropy  $s = -(\partial \Omega / \partial T)_{\mu, V} = \beta^2 (\partial \Omega / \partial \beta)_{\mu, V}$ . On differentiating with respect to  $\beta$  and using (40), we find

$$s = \sum_i \ln [1 + e^{(\mu - E_i)\beta}] + \beta \sum_i f_i (E_i - \mu). \quad (42)$$

The heat capacity at constant volume,  $C_V$ , is

$$C_V = T \left( \frac{\partial s}{\partial T} \right)_{N, V} = \sum_i E_i \left( \frac{\partial f_i}{\partial T} \right)_{N, V}. \quad (43)$$

Formula (43) permits calculation of the electronic heat capacity if the eigenvalues  $E_i$  and their variation with temperature are known. In addition it is necessary to find  $\mu$  and  $d\mu/dT$ .

A very important fact is that the eigenvalues and the value of the chemical potential  $\mu$  as functions of temperature are sufficient for finding the electronic thermal terms in the equation of state.

The thermal energy  $E_T$  and the thermal pressure  $p_T$  are found by the usual thermodynamic formulas

$$E_T = \int_0^T C_V dT, \quad p_T = T \int_0^T \frac{1}{T^2} \left( \frac{\partial E_T}{\partial V} \right)_T dT. \quad (44)$$

At low temperatures,  $T < 10000^\circ$  ( $\sim 0.03$  atomic units), the dependence of  $E_i$  on temperature may be neglected. In this case it follows from (43) that  $E_T = \sum f_i E_i |_0^T$ . The calculation of the heat capacity is of the same nature as for a free electron gas, but with one important difference. For densities close to the normal density, the top edge of the 3d,

$m = 2$  band is very close to the Fermi energy  $\mu_0$ . In connection with this, one needs an accurate carrying out of the Sommerfeld expansion at low temperatures, and in some cases simply an accurate numerical integration.

We give without derivation the formula for calculation of the thermal energy,

$$E_T = \sum_m \kappa_m \left\{ \int_{\mu_0}^{\mu} g_m(\epsilon) (\epsilon - \mu) d\epsilon + T^2 \int_0^{\infty} \frac{g_m(\mu + Tx) + g_m(\mu - Tx)}{1 + e^x} x dx \right\} + \kappa T^2 \int_0^{\infty} \frac{(x + \Delta + \Delta\mu/T) g(E_2 - Tx)}{1 + e^{\Delta + \Delta\mu/T + x}} dx. \quad (45)$$

The chemical potential  $\mu$  is found from the condition

$$\sum_m \kappa_m \left\{ \int_{\mu_0}^{\mu} g_m(\epsilon) d\epsilon + T \int_0^{\infty} \frac{g_m(\mu + Tx) - g_m(\mu - Tx)}{1 + e^x} dx \right\} = \kappa T \int_0^{\infty} \frac{g(E_2 - Tx)}{1 + e^{\Delta + \Delta\mu/T + x}} dx. \quad (46)$$

Here  $m$  is the index of the normal band;  $g_m(\epsilon) = (6k^2/k_0^3)(dk/d\epsilon)_m$  is the density of levels in band  $m$ ;  $E_2$  is the top edge of the anomalous 3d,  $m = 2$  band;  $\kappa = 2$  for bands 3d,  $m = 2$  and 3d,  $m = 1$ ;  $\kappa_m = 1$  for band 3d,  $m = 0$ ;  $\Delta\mu = \mu - \mu_0 = \alpha T$ ;  $\Delta = (\mu - E_2)/T$ .

At low temperatures, an expansion of the function  $g(\epsilon)$  as a series can be made in formulas (45) and (46). We get

$$\frac{E_T}{T^2} = \varphi(\delta, T) = \frac{\pi^2}{6} \sum_m \kappa_m g_m(\mu_0) \left[ 1 - \frac{3\alpha^2}{\pi^2} + \frac{6}{\pi^2} \kappa g(E_2) \left[ \sum_m \kappa_m g_m(\mu_0) \right]^{-1} \int_{\Delta + \alpha}^{\infty} \frac{y dy}{1 + e^y} \right], \quad (47)$$

$$\alpha \sum_m \kappa_m g_m(\mu_0) = \kappa g(E_2) \ln [1 + e^{-(\Delta + \alpha)}]. \quad (48)$$

We find that the thermal energy is proportional to the density of levels at the Fermi edge; the contribution of the anomalous band is important.

Table II gives the function  $\varphi$  for iron, at various densities and temperatures, calculated both by the exact formula (45) and by the approximate (47). A very important fact is the following: the large absolute values of  $\varphi(\delta, T)$  obtained at densities close to the normal are characteristic of the electronic heat capacity of the transition metals (to obtain  $\varphi/2$  in erg/g deg<sup>2</sup> it is necessary to multiply the table values by 4.7).

Table II

| $\delta = 0.7465$ |             |       | $\delta = 1.073$ |             |       | $\delta = 2.022$ |             |       |
|-------------------|-------------|-------|------------------|-------------|-------|------------------|-------------|-------|
| $T$               | $\varphi/2$ |       | $T$              | $\varphi/2$ |       | $T$              | $\varphi/2$ |       |
|                   | Approximate | Exact |                  | Approximate | Exact |                  | Approximate | Exact |
| 0.001             | 85.42       | 85.46 | 0.001            | 27.32       | 27.33 | 0.001            | —           | 13.37 |
| 0.003             | 82.08       | 81.24 | 0.003            | 31.77       | 31.84 | 0.003            | —           | 13.36 |
| 0.009             | 81.54       | 90.66 | 0.009            | 47.14       | 47.03 | 0.009            | 13.38       | 13.39 |
| 0.018             | 81.31       | 90.29 | 0.018            | 50.68       | 53.25 | 0.018            | 13.90       | 14.25 |
| 0.030             | 81.50       | 69.08 | 0.030            | 51.35       | 54.05 | 0.030            | 16.48       | 17.81 |
| 0.060             | 81.50       | 35.05 | 0.060            | 52.00       | 38.43 | 0.060            | 21.49       | 23.66 |
| 0.090             | 81.50       | 20.95 | 0.090            | 52.00       | 25.97 | 0.090            | 23.27       | 22.93 |

It is impossible to obtain correct values of the electronic heat capacity of the transition metals by any statistical method, because the anomalously large value of the heat capacity is connected with the large density of levels in the d band.

In closing, I express my sincere thanks to Ya. B. Zel'dovich and N. A. Dmitriev for interesting discussions and for their interest in the work, and also to V. A. Tarasov, who developed useful methods of calculation and who did much of the computational work.

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