ISSN 1027-5495. Functional Materials, 23, No.3 (2016), p. 364-369.
doi:http://dx.doi.org/10.15407/fm23.03.364

Electron gas pressure in pure metals and metal superconductors

V.F.Khirnyi

Institute for Single Crystals, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Nauky Ave., 61001 Kharkiv, Ukrane

Received March 10, 2016

The pressure of gas of non-interacting electrons P_0 at $T \cong 0$ K in metals and metal superconductors in the normal and superconducting states, is determined. Found are the dependences of the critical temperature of superconductors on such a pressure and the relation between P_0 and the energy of the ground state of the atoms in the Hartree-Fock approximation. The temperature dependences of P_0 and other parameters of metal superconductors in superconducting state, are studied. The possibility and conditions of emergence of superconductivity at room temperature are established on the base of the model of non-interacting electrons. Shown is the common nature of energy gap in superconductors and exchange energy of spin-orbital interactions between nucley of ions and "superconducting" electrons.

Keywords: internal pressure of free electron gas, common superconductors, energy Hartree-Fock, critical temperature, energy of spin-orbital interaction.

Определены значения давления газа невзаимодействующих электронов P_0 при температуре $T \cong 0$ К в металлах и металлических сверхпроводниках, находящихся в нормальном и сверхпроводящем состояниях. Обнаружены зависимость критической температуры сверхпроводников от этого давления и закономерность между значениями P_0 и энергией основного состояния атомов в приближении Хартри-Фока. Изучены зависимости P_0 и других параметров в металлических сверхпроводниках, находящихся в сверхпроводящем состоянии, от температуры. Определены возможность и условия достижения сверхпроводимости при комнатной температуре, согласно модели невзаимодействующих электронов. Показана общность природы энергетической щели сверхпроводников и обменной энергии спин-орбитального взаимодействия между ядрами ионов и "сверхпроводящими электронами".

Тиск електронного газу у чистих металах та металічних надпровідниках. *В.Ф.Хірний*.

Визначено значення тиску газу невзаємодіючих електронів P_0 при температурі $T \cong 0$ К в металах і металевих надпровідниках, які знаходяться у нормальному та надпровідному станах. Виявлено залежність критичної температури надпровідників від P_0 та закономірність між значеннями P_0 і енергією основного стану атомів у наближенні Хартри-Фока. Вивчено залежності P_0 та інших параметрів в металевих надпровідниках, які знаходяться у надпровідному стані, від температури. Визначено можливість та умови досягнення надпровідності при кімнатній температурі, згідно моделі невзаємодіючих електронів. Виявлено общність природи енергетичої щілини надпровідників та енергії взаємодії між ядрами іонів і надпровідними електронами.

1. Introduction

According to the model of non-interacting electrons, internal pressure of free electron gas P_0 in the ground state in normal pure metals at $T = 0$ K is on the order of 100000 atmospheres [1–3]. This pressure is balanced by the Coulomb attractive forces between the conduction electrons and ions located in the crystal lattice sites [1]. In normal (non-superconducting) metals the properties of the ground state of free and independent electrons are established by means of the Fermi-Dirac statistics while considering conduction electrons as Fermi gas. This statement is also correct for metal superconductors in the normal state. Naturally, the pressure within Fermi gas depends on the conductivity and superconductivity of metals and compounds [2, 3], since electron pairing which occurs in them changes the Coulomb interaction. The internal pressure influences the properties of normal metals and superconductors. For instance, as shown in our earlier papers [4, 5], for $YBa_2Cu_3O_{7-\delta}$ the critical temperature T_c and the concentration of mobile charge carriers depend on internal chemical pressure more strongly than on external pressure. Thereat, the change of the pressure was calculated by varying the number of oxygen ions, i.e. carriers of holes.

While investigating electronic properties of metals there was initially used the approximation of non-interacting electrons (the Drude-Sommerfeld model). Further interactions of electrons (in the frame of the Landau theory of Fermi liquid) were taken into account. During recent years there have been discussed deviations of the behaviour of electrons from the predictions of this theory in some compounds (including superconductors) which contain rare-earth metals. This is caused by a strong correlation interaction in such metals.

In the present work, an attempt was made to predict one of possible directions of search for new superconductors on the base of the (the Drude-Sommerfeld model of non-interacting electrons). For this purpose we studied the properties of internal pressure of non-interacting electrons gas in metals and ordinary low-temperature metal superconductors in the normal and superconducting state.

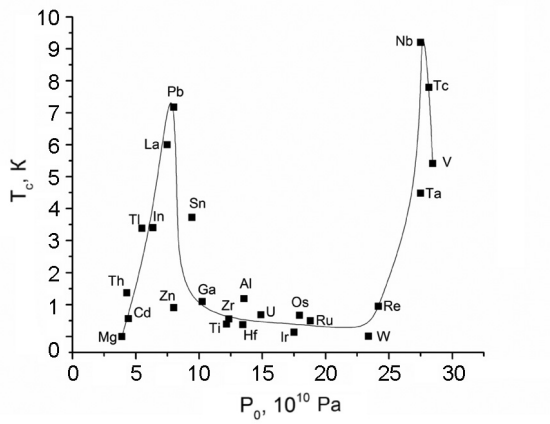

Fig. 1. Dependence of critical temperature of pure metal superconductors in the normal state on the pressure of gas of free electrons P_0.

2. Results and discussion

In the frames of the model of free electrons, the electron gas pressure P_0 in metals is determined from the formula [3]

$$P_0 = 0.4nE_F, \qquad (1)$$

where $n = Z(N/V)$ is the concentration of free electrons; Z, the valence of the given metal, (N/V), the number of atoms in 1 cm^3; $E_F = 0.284 \cdot 10^{-15} v_F^2$ (eV), the Fermi energy; $v_F = 1.157 \cdot k_F$ (cm/sec), the Fermi velocity, $k_F = (29.609\ N/V)^{1/3}$ is the Fermi wave vector for metals (cm^{-1}) [2], V, the sample volume, N, the number of electrons in the sample. The internal pressure in pure non-superconducting normal metals is determined from the relation $P_0 = (\partial E/\partial V)_N$ between the pressure and energy density E of electron gas in the ground state which is also valid at $T \neq 0$ K [3]. Based on the above-said, we studied the changes of T_c depending on P_0 under the condition that $T \cong T_c \cong 0$ K, i.e. using the Fermi-Dirac statistics for superconductors in the normal state. Moreover, we investigated the temperature dependences of E_F, P_0 and the density of the states of "normal" electrons at $T < T_c$.

Shown in Fig. 1 is the dependence $T_c(P_0)$. The graph contains the maxima with $T_c =$ 7.2 K for Pb and 9.4 K for Nb at low and high P_0 values. Between these maxima $T_c(P_0)$ decreases almost monotonously at P_0 changing from ~ $10 \cdot 10^{10}$ Pa for Ga ($T_c = 1.09$ K) to ~ $23 \cdot 10^{10}$ P for W ($T_c = 0.012$ K). While building the graph we assumed the valence of vanadium to be V^{4+}.

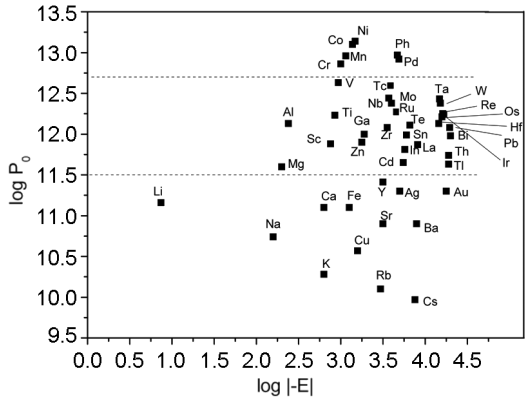

Fig. 2. Dependence of P_0 on the energy of the ground state of atoms $|-E|$ in the Hartree-Fock approximations [14].

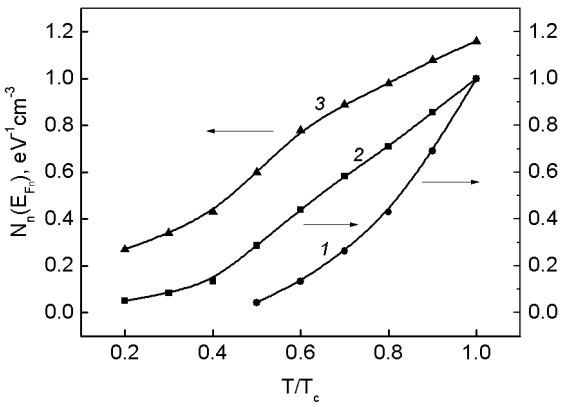

Fig. 3. Temperature dependences: *1* – $P_0(T)/P_0(T_c)$, *2* – $E_{Fn}(T)/E_F(T_c)$, *3* – $N_n(E_{Fn}) = 3n_n/4E_{Fn}$ obtained for Al.

Superconductivity and internal pressure experienced by atoms and electrons in metals vary with the changes in the form of atomic orbitals and in crystal structure. Initially their form is defined by the energy of the ground state of the atoms [2]. Superconductors are metals possessing special intrinsic properties. Therefore, it has been assumed that for superconducting metals there exists a peculiarity of the relation between the energy E of the ground state of the atoms and the value of internal pressure P_0. The interaction of electrons obtained in the Hartree-Fock approximation [6] has not been taken into account. This assumption is confirmed by Fig. 2 which shows the dependence of $\log P_0$ on $\log|-E|$. As is seen, the pressure P_0 of superconducting metals corresponds to a certain band marked by two dotted lines. The values of E (in atomic units) are taken from the paper [6] for free atoms, since electrons of atoms in crystals form chemical bonds, and their energy state differs from the one of non-interacting electrons.

According to Fig. 2, at temperatures up to $T = 0$ K the pressure P_0 for superconducting pure metals in the normal state changes from the lowest value $P_{0s1} = 3.9 \cdot 10^{10}$ Pa for Mg to the highest values $P_{0s2} = 28.5 \cdot 10^{10}$ Pa for V; k_F — from $k_{F1} \cong 1.4 \cdot 10^8$ to $k_{F2} \cong 2.0 \cdot 10^8$ (cm^{-1}); v_F — from $v_{F1} \cong 1.6 \cdot 10^8$ to $v_{F2} \cong 2.4 \cdot 10^8$ (cm/sec), whereas E_F ranges between $E_{F1} \cong 7.1$ and $E_{F2} \cong 15.4$ (eV), for superconducting magnesium and vanadium, respectively.

As seen from Fig. 2, the range of pressures of free electron gas characteristic of pure metal superconductors in the normal state is bounded from above and from below by P_0 value of normal metals. From below it is bounded by metals with one electron on the outer s-shell: alkali metals with body-centred cubic lattices such as Li:$1s^2 2s^1$, Na:[Ne]$3s^1$, K: [Ar]$4s^1$, Rb:[Kr]$5s^1$ and Cs:[Xe]$6s^1$; noble metals with face-centred cubic lattice such as Cu:[Ar]$3d^{10}4s^1$, Ag:[Kr]$4d^{10}5s^1$ and Au:[Xe]$4f^{14}5d^{10}6s^1$, as well as metals with two electrons on the s-shell such as Ca:[Ar]$4s^2$, Sr:[Kr]$5s^2$, Ba:[Xe]$6s^2$, Y:[Kr]$4d^15s^2$ and Fe:[Ar]$3d^64s^2$. From above this range is bounded by transition metals with one and two electrons on the s-shell, except for palladium, namely, Cr:[Ar]$3d^54s^1$, Mn:[Ar]$3d^54s^2$, Co:[Ar]$3d^74s^2$, Ni:[Ar]$3d^84s^2$, Rh:[Ar]$4d^85s^1$ and Pd:[Kr]$4d^{10}$.

The obtained result complies with the rule [7] to the effect that if the number of valence electrons satisfies the conditions $2 < Z$ and $Z > 8$, than superconductivity in a pure metal is absent.

From the relation for P_0 [3]:

$$P_0 = 0.6B, \qquad (2)$$

where B is the compression modulus, there has been established the region of the values of B characteristic of pure metal superconductors. It is located between those of compression moduli for magnesium and vanadium which change from $65 \cdot 10^{10}$ to $474.2 \cdot 10^{10}$ (dyn/cm^2). The values of the compression moduli calculated from the relation (2) differ from the ones measured experimentally (see [3]) by several fold. In the present work it is shown (see Fig. 2) that the pressure of free electron gas plays a significant role for superconductivity. Thereat, we have not taken into account the internal "stretching" pressure caused by thermal expansion of the lattice defined by

the relation $P_{0t} = \beta BT$, where β is the bulk thermal expansion coefficient [8]. The existence domain for superconductivity is bounded by the values of $T = T_c$ close to 0 K. Therefore, P_{0t} is less than P_0 by two orders.

Up to now there have been considered the values of P_0 at temperatures $T > T_c$, when the concentration of "normal" electrons n_n is equal to n, and the concentration of "superconducting" electrons n_s is zero. At $T < T_c$ the number of "normal" electrons N_N diminishes with the temperature, whereas the number of "superconducting" electrons N_S rises. The ratio N_N/N (where N is the total number of electrons equal to $N_S + N_N$) is proportional to $(T/T_c)^4$, and tends to zero when $T \cong 0$ K [9, 10]. As N_N diminishes, the ratios $E_{Fn}(T)/E_F(T_c)$ and $P_0(T)/P_0(T_c)$ change as $(T/T_c)^4$, see Fig. 3. Fig. 3 also contains the temperature dependence of the distribution density for "normal" electrons $N_n(E_{Fn}) = 3n_n/4E_{Fn}$. Here E_{Fn} is the total Fermi energy of "normal" electrons in metals in superconducting state, $E_{Fn} = E_F$ at $T > T_c$ and $E_F(T_c) = E_F$, when $T = T_c$ and $P_0(T_c) = P_0$, when $T = T_c$. The numerical values are obtained for aluminum.

Thus, in superconductors at $T = 0$ the values of E_{Fn} and the internal pressure P_0 created by "normal" electrons are equal to zero due to the absence of such electrons. As follows from the relation (1), $P_0 = 0$ not only at $N_N = 0$ and $E_F \neq 0$, but also at $E_F = 0$ and $N_N \neq 0$. According to [2] and Fig. 4, curve B, one can assume that $E_F \cong 0$ in metals with the concentration of "normal" electrons $n^* \cong 2.3 \cdot 10^{18}$ cm^{-3} and lower. This is seen from the graph of the dependence of the Fermi energy on the concentration of electrons Fig. 4.

Now, following the authors of [11] suppose that with diminution of the concentration of charge carriers the critical temperature rises. Then a rough estimation of T_c obtained by the linear extrapolation $T_c(n) \sim 1/n$ between Nb ($T_c \cong 10$ K, $n \cong 5 \cdot 10^{22}$ cm^{-3}), $YBa_2Cu_3O_{7-\delta}$ ($T_c \cong 90$ K, $n \cong 5 \cdot 10^{21}$ cm^{-3}) and $HgBa_{2-x}Sr_xCuO_{10-\delta}$ with $n \leq 10^{21}$ cm^{-3} gives $T_c \cong 310$ K, see Fig. 4, point 4 on curve A.

Thus, according to Fig. 3, at the transition of the samples into the superconducting state the internal pressure P_0 smoothly reduces to zero at $T \to 0$ K. However, the bulk compression modulus determined experimentally remains practically unchanged, and the samples do not break down. Therefore, we assume that P_0 changes into the pressure P' created by gas of spins of "superconducting" electrons from the Cooper pairs. As P_0 diminishes, the Coulomb interaction between free "normal" electrons and ions which compensates P_0, also decreases and vanishes at $T \cong 0$ K, since $N_N \to 0$. Therefore, the pressure P' is balanced by the interaction similar to the Coulomb interaction, between the ion nuclei spins and electrons from the Cooper pairs which form spin dipoles. Thereat, the electrons with the spin (or their projections) directions opposite to those of the nuclei of ions, are attracted by the latter and form local polarized spin clouds around them.

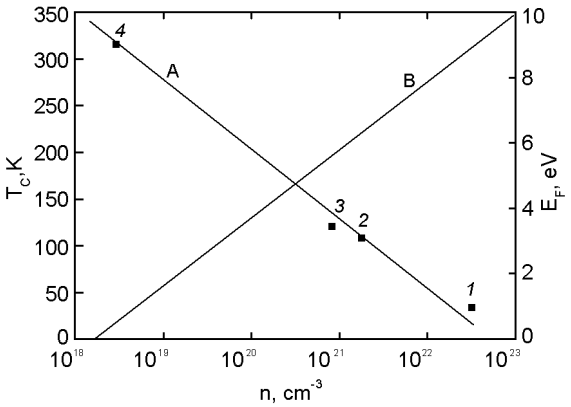

Fig. 4. Determination of T_c for metals with $n^* \cong 2.3 \cdot 10^{18}$ cm^{-3} (line A, point 4) and E_F depending on the concentration of electrons (line B [2]): 1) Nb, 2) $YBa_2Cu_3O_{7-\delta}$ and 3) $HgBa_{2-x}Sr_xCuO_{10-\delta}$.

In the rest of the superconductor volume the electrons with the spin directions similar to those of the ions, form spin gas. This gas creates the pressure P'. At T_c the spins electrons start encircling the ions. Attraction of "superconducting" electrons to nuclei ions is stronger than the one of other metals, and T_c is higher for those metals in which the nuclear spin I_p and the modulus of nuclear magnetic moment μ_p turn out to be higher than those of other metals. This assumption is indirectly confirmed by the data from [2] which are contained in Table. Were I_p is expressed in the units of $\hbar$, μp — in the units of $e\hbar/2M_pc$, where e is the charge of electron, $\hbar$, the Planck constant divided by 2π, M_p, the mass of proton, c, the velocity of light in vacuum. Minor deviations from this rule characteristic of

Table . Nuclear spins, nuclear magnetic moments and critical temperature of superconductors [2]

No. in Mendeleev's Table	Substance	$I_p(\hbar)$	μ_p $(e\hbar/2M_pc)$	T_c (K)
13	Al	5/2	3.639	1.2
22	Ti	5/2	0.787	0.39
23	V	7/2	5.139	5.38
30	Zn	5/2	0.874	0.875
31	Ga	3/2	2.011	1.091
40	Zr	5/2	1.298	0.546
41	Nb	9/2	6.144	9.2
42	Mo	5/2	0.910	0.92
44	Ru	5/2	−0.69	0.51
48	Cd	1/2	−0.592	0.56
49	In	9/2	5.507	3.40
50	Sn	1/2	−1.041	3.72
57	La	7/2	2.761	6.0
73	Ta	7/2	2.340	4.48
74	W	1/2	0.115	0.012
75	Re	5/2	3.176	1.7
76	Os	3/2	0.651	0.655
77	Ir	3/2	0.17	0.14
80	Hg	1/2	0,498	4.153
81	Tl	1/2	1.612	2.39
82	Pb	1/2	0.584	7.193

polyvalent metal superconductors can be explained on the base of the Drude-Sommerfeld model.

These "superconducting electrons" are located on the external ion orbitals occupied by electrons. Thereat, the energy necessary for breaking a Cooper pair and removing it from the nucleus by a thermal method, must be equal to the energy of spin-orbital interaction E' for N_S electrons. We suppose that the energy of such an interaction between the ion nuclei and "superconducting" electrons is to be equal to the one between the ion nuclei and internal electrons. Therefore, the temperature dependence of $E'(T)/E'(T = 0)$ is similar to that of $N_S(T)/N \sim 1 - (T/T_c)^4$ and nealy of $\varepsilon(T)/\varepsilon(T = 0)$, where ε is the value of energy gap of superconductors. Thus, in the Drude-Sommerfeld model E' plays the role similar to that of ε in superconductors. This is confirmed by the fact that the energies of spin-orbital (exchange) interaction E' and of the energy gap ε of pure metal superconductors are of the same order ($10^{-15} \div 10^{-16}$ erg) [12]. Note that magnetic coupling of the spins of metal ion nuclei and superconducting electrons to be broken, is very weak and can noticeably contribute to the energy only at low temperatures [12]. External magnetic fields also reduce E', similar to decrease of ε in superconductors. They make a contribution to H_{eff}, the local magnetic field of the nucleus bound up with the interaction of the magnetic moment of the nucleus with the electron shell of its ion. Such a consideration implies that nature of magnetism and superconductivity in the the Drude-Sommerfeld model have a common nature. This gives a criterion for search for new superconductors.

Superconducting state is not observed for the samples in which the energy of spin-orbital interaction is absent at all (e.g. due to complete screening of the nucleus). At the same time, for the superconductors with $E' \geq 10^{-13}$ erg $T_c \approx 300$ K maybe.

It should be noted that the value of energy gap in superconducting metals define their parameter of exchange interaction. For in-

stance, for Al it is equal to $3.4 \cdot 10^{-4}$ eV [2], for YBCO $3 \cdot 10^{-3}$ eV.

Superconductivity is an extremely complicate phenomenon which occurrence depends on many properties of metals. In the given study, by analogy with [11], we consider the influence of electron density on T_c in the frame of the model of non-interacting electrons. Thereat, a superconducting metal with $T_c \cong 310$ K must have the density $n^* \cong 10^{18}$ cm^{-3}, which is by three orders lower than the values characteristic of the metal state. Such a metal cannot exist in pure form. However, this state may be achieved for a semiconductor which transforms into a metal at the said (and lesser) electron density under the transition semiconductor-metal (or dielectric-metal), for instance, due to the Motta effect [13]. For semiconductors the conditions of emergence of superconductivity differ than those for pure metals, and the model of free electrons cannot be applied to them. In semiconductors the concentration of charge carriers ranges between 10^{17} and 10^{21} cm^{-3}. However, their T_c are very low. In particular, for $SrTiO_3$ the maximal $T_c = 0.38$ K at $n = 10^{20}$ cm^{-3} .

3. Conclusions

In the present work it is shown for the first time that internal pressure plays a significant role in the mechanism of emergence of superconductivity. For pure metal superconductors in the normal state there is established the relation between the internal pressure of gas of free non-interacting electrons and the energy of the ground state of atoms calculated in the Hartree-Fock approximation. The interaction of electrons has not been taken into account. The dependence of the critical temperature on the internal pressure is established. One of possible ways for raising the critical temperature of superconductors is predicted. Established is the common nature of energy gap in superconductors and exchange (magnetic) energy of spin-orbital interactions between nuclei of ions of metal superconductors and electrons from Cooper pairs.

References

1. S.Fluge, Practical Quantum Mechanics, Springer, Freiburg (1971).
2. C.Kittel, Introduction to Solid State Physics, John Wiley, New York (1978).
3. N.W.Ashcroft, N.D.Mermin, Solid State Physics, Holt, New York (1979).
4. V.F.Khirnyi, *Fiz. Nizk. Temp.*, **41**, 1126 (2015).
5. V.F.Khirnyi, *Functional Materials*, **21**, 399 (2014).
6. Modern Techniques in Computational Chemistry, MOTECC, 1991, ed. by E.Clementi, ESCOM-III, Leiden:North-Holland (1991), v.91.
7. B.T.Matthias, in: Prog. Low. Temp. Phys., Amsterdam. North-Holland **1**, 11 (1957).
8. B.I.Bertjaev, I.I.Reut, *Izvestija Samarskogo Nauchnogo Centra RAN*, **12**, 70 (2010).
9. A.Abrikosov, I.Khalatnikov, Fizika Nizkikh Temperatur. Prilozhenie., Moskow, Mir, 1964.
10. C.J.Gorter, in: Prog. Low. Temp. Phys., v.1, Amsterdam, North-Holland (1955).
11. J.G.Bednorz, K.A.Muller, *Z. Phys. B.* **64**, 189 (1986).
12. S.V.Vonsobskii, Magnetizm, Nauka, Moscow (1971) [in Russian[.
13. N.F.Mott, E.A.Devis, Electronic Process in Non-crystalline Materials, Clarendon, Oxford (1971).