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Abstract

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On the Theory of Superconductivity of Metals

1. In recent works on superconductivity ([1,3]), great success has been achieved in explaining the microscopic nature of this phenomenon. However, they consider the properties of weakly interacting gases of Fermi (electrons) and Bose (phonons) quasiparticles without connection with the structure of the metal. It is therefore of interest to use the many-electron model of a metal ([4]) for the investigation of the indicated problem.

Let us consider a system of ν interacting outer electrons of a crystal ($\nu < N-$ the number of lattice sites*) with Hamiltonian

$$H = \nu E_0 + \sum_{m,p,\sigma} \left(m \left| \sum_{\alpha \neq m} F_\alpha \right| p \right) a^+_{m\sigma} a_{p\sigma} +$$

$$+ \frac{1}{2} \sum_{m,l,p,r,\sigma,\sigma'} (m,l|G|p,r) a^+_{m\sigma} a^+_{l\sigma'} a_{r\sigma'} a_{p\sigma}, \tag{1}$$

where a^+ and a are Fermi operators of second quantization; E_0 is the energy of the one-electron state of a ν-electron; $\left(m \left| \sum_{\alpha \neq m} F_\alpha \right| p \right)$ and $(m,l|G|p,r)$ are, respectively, the matrix elements of the interaction energies $F_\alpha(x_m)$ of the m-th ν-electron with the atomic core α, and $G(x,x')$ of two electrons in the representation of the one-particle functions $\varphi_p(x)$; σ are spin indices; m, l, r, p are site numbers.

Retaining in (1) the terms containing no more than three different functions φ when they overlap ([4]), we obtain

$$H = \nu E_0 + \frac{1}{2} \sum_{\substack{m,l,\sigma,\sigma' \\ (m \neq l)}} B'_{ml} n_{m\sigma} n_{l\sigma'} -$$

$$- \frac{1}{2} \sum_{\substack{m,l,\sigma,\sigma' \\ (m \neq l)}} I_{ml} a^+_{m\sigma} a^+_{l\sigma'} a_{l\sigma} a_{m\sigma'} + \sum_{\substack{m,l,\sigma \\ (m \neq l)}} L_{ml} a^+_{m\sigma} a_{l\sigma}, \tag{2}$$

where $n_{m\sigma} = a^{+}_{m\sigma} a_{m\sigma}$ is the operator of the occupation numbers of the state (m, σ); B'_{ml} is the energy of the Coulomb repulsion of two electrons at sites m and l, screened by the attraction of electron m to the atomic core of site l (or conversely); I_{ml} is the exchange integral of the electrons of sites l and m;

$$L_{ml} = \sum_{\alpha(\neq m)} \int \varphi^{*}_{m}(x) F_{\alpha}(x) \varphi_{l}(x)\, dx + \sum_{\alpha,\sigma} n_{\alpha\sigma} \int |\varphi_{2}(x)|^{2} G(x, x') \varphi^{*}_{m}(x') \varphi_{l}(x')\, dx\, dx' \tag{3}$$

* For $\nu < N$, the neutrality of the metal may, for example, be ensured by "bound" electrons. The formation of excitations of the "pair" type ([2]) is assumed to be excluded because of the large value of the energy of Coulomb repulsion of two ν-electrons at one site. The case of "pairs" obeying approximately Bose statistics has been considered by us and will be published in another article. The case $\nu > N$, in the presence of Fermi excitations of the "triples" type, has also been considered by us by the method of the present article, and in this case essentially the same results are obtained.

the "transfer" integral of the γ-electron from site m to l*. When diagonalizing (2) we shall take into account that in I_{ml} there are two overlaps of the functions $\varphi_{m}(\mathbf{x})$, while B'_{ml} is small owing to screening, and therefore in (2) we shall retain only the term with E_0 and the "transfer" terms containing double products of Fermi operators.

Passing to the representation of wave vectors $\mathbf{k}$, we find from (2)

$$H = \sum_{\mathbf{k},\sigma} \mathcal{E}(\mathbf{k})\, a^{+}_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}, \tag{4}$$

where

$$\mathcal{E}(\mathbf{k}) = E_0 + \sum_{f} L(f) e^{i\mathbf{k}f}$$

(f is the distance between two lattice sites) is the dispersion relation of the system of γ-electrons.

Using the nearest-neighbor and effective-mass approximations, we obtain

$$\mathcal{E}(\mathbf{k}) \simeq E_0 + \sigma L - L(ka)^2, \qquad m_{eff} \simeq -\frac{\hbar^2}{2La^2}; \tag{5}$$

here a is the (cubic) lattice constant; L is the value (3) for nearest neighbors.

Applying the method of work ([5]), one can extract from (2) the perturbation due to the interaction with phonons:

$$H = \sum_{\mathbf{k},\sigma} \mathcal{E}(\mathbf{k})\, a^+_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} +$$

$$+ \sum_{\mathbf{q}} \hbar\omega(q) b^+_{\mathbf{q}} b_{\mathbf{q}} + g \sum_{\substack{\mathbf{k},\mathbf{q},\sigma \\ (\mathbf{k}'-\mathbf{k}=\mathbf{q})}} \left\{ i\sqrt{\frac{\hbar\omega(q)}{2Na^3}}\, a^+_{\mathbf{k}\sigma} a_{\mathbf{k}'\sigma} b^+_{\mathbf{q}} + \text{c. c.} \right\}, \qquad (6)$$

where $b_{\mathbf{q}}$ are Bose operators; $\omega(q)$ is the frequency; $\mathbf{q}$ is the phonon wave vector; the coupling constant

$$g = \frac{2\pi}{3} \frac{La^{7/2}}{u\sqrt{M}},$$

M is the ion mass and u the speed of sound.

Consideration of (6), according to ([2,3]), makes it possible to establish the presence of superconductivity in the system under consideration. In particular, for the critical temperature we find

$$T_\kappa = c \exp\left\{ -\frac{18Mu^2}{(3\nu/\pi N)^{1/3}|L|} \right\}, \qquad (7)$$

where c is a coefficient inversely proportional to $M^{1/2}$.

2. According to ([2,3]), the criterion for superconductivity is that the interaction with phonons prevail over the screened Coulomb interaction. In our treatment the latter is partially taken into account in the spectrum of the system itself (in L). The indicated criterion requires that the remaining part of the Coulomb energy (B'_{ml}) and the exchange energy (I_{ml}) be smaller than the term in (6) describing the coupling with phonons. Since the constant $g \sim L$, it follows from this that the condition is $|L| \gg B'_{ml}, I_{ml}$. The integrals I_{ml} contain two overlaps of the functions φ and are therefore small compared with L. The integrals B'_{ml}, however, will be the smaller the larger the effective charge of the atomic cores Z_{eff}, since in that case the screening of the interelectronic repulsion increases. The influence of a change in Z_{eff} on the magnitude of L depends on the sign of the latter.

In the case $L < 0$ ($m_{eff} > 0$) in (3) the first sum predominates, where

$$F_\alpha(\mathbf{x}) \simeq -\frac{Z_{eff}e^2}{|\mathbf{x} - \mathbf{R}_\alpha|},$$

so that an increase of Z_{eff} leads to an increase of $|L|$. Since in this case

Figure 1

Figure 1: Figure 1

* The structure of L_{ml} is analogous to ([4]), with the difference that in the second sum of (3) $|\varphi_2(\mathbf{x})|^2$ enters only for sites occupied by γ-electrons, so that L_{ml} depends on the distribution of γ-electrons over the sites. However, in the nearest-neighbor approximation one may assume that L_{ml} depends mainly only on the positions of the sites m and l.

simultaneously B'_{m1} decreases, then in this case the requirement of sufficiently large values of Z_{eff} is consistent with the criterion of superconductivity. In the case $L > 0$ ($m_{eff} < 0$), Z_{eff} must be sufficiently small for the second (positive) sum in (3) to predominate. But, together with the decrease of Z_{eff}, the screening in B'_{m1} worsens, and the condition $L \gg B'_{m1}$ may in this case fail to be satisfied. Therefore one may expect that superconductivity is favored by $L < 0$ and by large* values of Z_{eff}.

To check this conclusion we used Slater' s method ([6]) for calculating Z_{eff} and found (see Fig. 1) that for all superconductors, with the

Fig. 1. Effective charges of atomic cores for the outer electron, calculated by Slater' s method ([6]). *a*—superconductors; *b*—non-superconducting metals; *c*—ferromagnets; *g*—semiconductors; *d*—metalloids; *e*—elements for which it has not been determined whether they belong to metals or semiconductors. For Pt, Pu, and Am the upper points correspond to the data of ([8]), and the lower ones to ([9]). For Tb the upper point corresponds to ([9]); for Pd the lower point is taken according to ([9]) (p. 276).

exception of Nb ($Z_{eff} = 2.8$), the inequality $Z_{eff} > 3$ is satisfied. The largest value of Z_{eff} among the superconductors turned out to be for Bi ($Z_{eff} = 6.3$), and the upper limits of Z_{eff} for them in each period are determined by semiconductors. Within the indicated limits, the non-superconducting metals are the ferromagnets (Fe, Co, Ni), and also the elements: Mn (antiferromagnet), Cu, Rh, Pd, Ag, W, Ir, Pt, and Au. A number of metals with $Z_{eff} < 3$, entering into compounds with metalloids and other metals for which $Z_{eff} > 3$, form superconducting compounds. For example, the compound Mo ($Z_{eff} = 2.95$) with C ($Z_{eff} = 3.25$) is a superconductor with $T_k = 7.6$–8.3°K.

The compound of Mo with N ($Z_{eff} = 3.9$) raises T_k to 12°K ([7]). An analogous phenomenon is observed in intermetallic compounds. This effect is observed especially distinctly in compounds of alkali metals (with the lowest Z_{eff} in each period) with Bi.

These and analogous facts show that consideration of Z_{eff} and of ways of increasing it may prove to be a simple and useful means both for explaining existing experimental facts and in the search for new superconducting elements and compounds. In conclusion it is necessary to note that the approximations associated with the model itself, as well as the method of calculating Z_{eff}, of course limit the accuracy of the numerical estimates given above, leaving, however, as it seems to us, the validity of the qualitative conclusions in force.

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* The requirement of large Z_{eff} is in accordance with the empirical rule ([10]), according to which superconductivity appears when there is a large number of valence electrons per atom. Indeed, the larger this number, the less screened the nucleus and the larger Z_{eff}, and this, according to our interpretation, leads to a better coupling with the lattice.

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Note: Figure translations are in progress. See original paper for figures.