SOVIET PHYSICS JETP VOLUME 21, NUMBER 4 OCTOBER, 1965

Letters to the Editor1)

A POSSIBLE MECHANISM FOR SUPERCONDUCTIVITY IN ALLOYS

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J. Exptl. Theoret. Phys. (U.S.S.R.) 48, 1194-1197 (April, 1965)

A recent paper by Little [1] put forward the interesting suggestion that superconductivity with a high critical temperature might occur in one-dimensional systems. It was shown that an attraction may occur between the electrons of the central chain of a polymer owing to the mutual interactions of the electrons of the central and side chains. Below we investigate an analogous mechanism for superconductivity in ordinary three-dimensional systems.

Consider first a pure metal of the transition group with two overlapping unfilled bands (s and d or s and f), or an ordered bimetallic alloy (compound) which possesses the same type of electronic spectrum.

If we take the one-electron wave functions to be Bloch functions $\psi_k = \exp(ik\cdot\mathbf{r})u_k(\mathbf{r})$, the Hamiltonian of the system will have the form

$$H = H_a{}^0 + H_b{}^0 + H_{ab};$$

$$H_a{}^0 = \Sigma\varepsilon_k{}^a a_k{}^+ a_k + {}^1/{}_2\Sigma A^{aa}_{k_1k_2;\,k_3k_4}\,a_{k_1}{}^+a_{k_2}{}^+a_{k_3}a_{k_4};$$

$$H_b{}^0 = \Sigma\varepsilon_f{}^b a_f{}^+ a_f + {}^1/{}_2\Sigma A^{bb}_{f_1f_2;\,f_3f_4}\,b_{f_1}{}^+b_{f_2}{}^+b_{f_3}b_{f_4};$$

$$H_{ab} = \Sigma A^{ab}_{k_1f_1;\,k_2f_2}\,a_{k_1}{}^+b_{f_1}{}^+a_{k_2}b_{f_2} + H_{ab}{}'; \qquad (1)$$

where $k = \{p^a, \sigma^a\}$; $f = \{p^b, \sigma^b\}$; $\sigma_1 = \sigma_2$; $\sigma_3 = \sigma_4$; $p_1 + p_2 = p_3 + p_4 + 2\pi b$; b is an integral multiple of the reciprocal lattice vector; the index a refers to the outer s-electrons, the index b to the inner d- or f-electrons. If we neglect screening, the exchange integral A_{ab} has the form

$$A^{ab}_{k_1f_1;\,k_2f_2} = \int \frac{e^2}{r_{12}}\psi_{k_1}{}^*(\mathbf{r}_1)\psi_{f_1}{}^*(\mathbf{r}_2)\psi_{k_2}(\mathbf{r}_1)\psi_{f_2}(\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2.$$

A^{aa} and A^{bb} have similar forms. In what follows we shall assume that in the expressions for A^{aa}, A^{bb} and A^{ab} we have included a factor corresponding to screening with a Debye radius

$$1/\varkappa_D \approx (r_B/k_0)^{1/2}; \qquad r_B = \hbar^2/me^2.$$

Then the exchange integrals A will be of order $e^2\varkappa_D$. H'_{ab} contains terms of the types

a^+a^+bb, b^+b^+aa, a^+a^+ab, a^+b^+aa, b^+b^+ba, a^+b^+bb.

We shall neglect these terms, since the corresponding matrix elements for transitions near the Fermi surface will be of order $(k_0 r_B)^{-1}$ times less than those of A^{ab} and H^{ab}, if we assume that

$$\psi_k{}^a \approx V^{-1/2}\exp(i\mathbf{kr}), \qquad \psi_f{}^b = N^{-1/2}\sum_{\mathbf{n}}\exp(i\mathbf{fR_n})\,\psi_0(\mathbf{r}-\mathbf{R_n})$$

(where $\psi_0(\mathbf{r})$ is the electron wave function for an isolated atom; cf. below). If we neglect the overlap of the wave functions $\psi_0(\mathbf{r})$ for neighboring atoms, we have

$$A^{ab}_{0k_1f_1;\,k_2f_2} = 4\pi e^2 V^{-1}|\mathbf{k}_2-\mathbf{k}_1|^{-2}\int|\psi_0(\mathbf{r})|^2\exp[i(\mathbf{k}_2-\mathbf{k}_1,\mathbf{r})]\,d\mathbf{r}$$

(where A_0 denotes the value of A if we neglect screening); that is, $A_{q_1q_2:q_3q_4}$ depends only on the momentum transfer $q = q_3 - q_1$, as in the case of free electrons.

It is easy to see that H_{ab} induces an extra interaction between the a-electrons via the b-electrons and vice versa. By carrying out a canonical transformation (cf. [2]) or by restricting ourselves, for simplicity, to second-order perturbation theory, we find the Hamiltonian of the a-electrons after elimination of the b-electrons:

$$H_a = H_a{}^0 + H_a{}';$$

$$H_a{}' = (2V)^{-1}\Sigma g^a_{k_1k_2k_3k_4}\,a_{k_1}{}^+a_{k_2}{}^+a_{k_3}a_{k_4};$$

$$g^a_{k_1k_2k_3k_4} = 2V\sum_{ff'}A^{ab}_{k_1f;\,k_3f'}A^{ab}_{f'k_2;\,fk_4}\,n_{f'}{}^b(1-n_f{}^b)$$

$$\times[(\varepsilon_{k_3}{}^a - \varepsilon_{k_1}{}^a - \varepsilon_f{}^b + \varepsilon_{f'}{}^b)^{-1} + (\varepsilon_{k_4}{}^a - \varepsilon_{k_2}{}^a - \varepsilon_f{}^b + \varepsilon_{f'}{}^b)^{-1}]. \qquad (2)$$

(Here $\epsilon^a_{k_1} + \epsilon^a_{k_2} = \epsilon^a_{k_3} + \epsilon^a_{k_4}$; $f' = f + k_1 - k_3 + 2\pi b$.) The Hamiltonian of the b-electrons after elimination of the a-electrons has a similar form. Because of the factor $n^b_{f'}(1 - n^b_f)$, the quantity $\epsilon^b_f - \epsilon^b_{f'}$ is positive, and so for small $\epsilon^a_{k_3} - \epsilon^a_{k_1}$ we have $g^a < 0$, i.e., H'_a corresponds to an attraction. A more exact calculation shows that the vertex part $\tilde\Gamma_{aa}$ which is irreducible with respect to two a-arrows with the same direction will satisfy the operator equation

$$\tilde\Gamma_{aa} = [A_0{}^{aa} + A_0{}^{ab}\Pi_b(1 - A_0{}^{bb}\Pi_b)^{-1}A_0{}^{ba}](1 + \Pi_a\tilde\Gamma_{aa}).$$

where Π is the polarization operator. This is the most self-consistent way of incorporating the effects of screening in $\tilde\Gamma_{aa}$. Hence we can calculate the complete vertex part for small total momentum (cf. [3]). It is easily seen that g^a depends only weakly on $k_1, \ldots k_4$ for $\epsilon^a_{k_3} - \epsilon^a_{k_1} < \Delta E_b$, where $\Delta E_b \sim (\epsilon^b_f - \epsilon^b_{f'})_{av}$ is the width of the b-electron band. For $\epsilon^a_{k_3} - \epsilon^a_{k_1} > \Delta E_b$ we get $g^a \to 0$. The quantity g^b behaves similarly. The

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1) In connection with the publication of a special supplement to JETP, the «Letters» will no longer be published in the main journal. – The Editors.

order of magnitude of $|g^a|_{av}$ is

$$|g^a|_{av} \sim k_0^3 e^4 / (\varkappa_D \Delta E_b).$$

Since $|q|_{av} \sim m\Delta E_b/(\hbar^2 k_0) < \kappa_D$, we have (cf.[4])

$$V(A_{eff}{}^{aa})_{av} \sim e^2 \varkappa_D{}^{-2}[1 + 2e^2 m k_0 (\varkappa_D{}^2 \Pi \hbar^2)^{-1} \ln (\Delta E_a / \Delta E_b)]; \quad \Delta E_b \ll \Delta E_a. \tag{3}$$

The interaction constant associated with the neglected terms H'_{ab} is easily seen to be of order $(k_0 r_B)^{-2} \Delta E_a/\Delta E_b$ times less than g^a. If we have

$$g_0{}^a = |g^a|_{av} - V(A^{aa}_{eff})_{av} > 0,$$

then the system of a-electrons will be superconducting. It is clear from Eq. (3) that this condition may be fulfilled for sufficiently small ΔE_b. Replacing H_a by an equivalent BCS-type Hamiltonian, we get the usual expression for the critical temperature:

$$T_c{}^a \approx \Delta E_b \exp(-1/\rho); \quad \rho = g_0{}^a m k_0 / (2\pi^2 \hbar^2). \tag{4}$$

We see that in general $\rho \gtrsim 1$, so that for $\Delta E_b \sim 0.3 - 1$ eV, $T_c^a \sim 10^2 - 10^3$ °K.

Obviously, however, the condition $g_0^a > 0$ is not satisfied for pure metals of the transition group—none of them are superconductors with critical temperatures of the order of 10^2 °K. The condition may be satisfied in the case of ordered alloys with comparable concentrations of the two components and with an electronic spectrum of the appropriate type. For disordered alloys with comparable concentrations of the components it is impossible to base the treatment on Bloch functions; however our results are evidently still qualitatively valid in this case.

The inner d- and f-electrons in ferromagnetic substances are generally taken to be described by the electronic wave functions for an isolated atom rather than by Bloch functions. Using an s-d exchange model of this type, Vonsovskiĭ and Svirskiĭ[5] have considered the additional attraction between the s-electrons due to their interaction with the d-electrons in the case where there are two d-electrons per atom so that they can form either a singlet or a triplet state. However, Vonsovskiĭ and Svirskiĭ took this additional attraction to be a small correction to the attraction due to phonon exchange, and therefore it was assumed that the critical temperature was, as usual, mainly determined by the Debye frequency ω_D.

Consider now an ordered alloy of a metal with a non-metal (C, N, Si, or S) where the latter has an upper unfilled shell whose electrons are sufficiently strongly bound to the atom not to be "collectivized" in the alloy. In this case, again, we should describe the electrons of the non-metallic component by atomic rather than Bloch wave functions. Then we can use the Hamiltonian (1) as above, but now the quantities f_i referring to the electrons of the non-metal (the b-electrons) will represent $\{n_i, \lambda_i\}$ where λ_i are the quantum numbers of an electron in the non-metallic atom. Obviously the most important processes now are the transitions of an electron within a single non-metallic atom. Thus we must replace $\epsilon_f^b - \epsilon_{f'}^b$ in expression (2) by $\epsilon_{n\lambda}^b - \epsilon_{n\lambda'}^b$. The order of magnitude of $|g^a|_{av}$ is now given by:

$$|g^a|_{av} \sim k_0^3 e_{eff}^4 / (\kappa_D{}^4 \Delta E_b); \quad e_{eff} \lesssim e;$$

$$A^{ab}_{0k_1 n\lambda;\, k_2 n\lambda'} \approx \frac{4\pi e^2}{V} \frac{\exp\{i(\mathbf{k}_2 - \mathbf{k}_1, \mathbf{R}_n)\}}{|\mathbf{k}_2 - \mathbf{k}_1|^2} \times \int d\mathbf{r} \exp\{i(\mathbf{k}_2 - \mathbf{k}_1, \mathbf{r})\} \psi_{0\lambda}^*(\mathbf{r}) \psi_{0\lambda'}(\mathbf{r}).$$

ΔE_b will now be of the order of the spacing between the ground state and lowest excited level in the non-metallic atom. The order-of-magnitude expression for T_c given by (4) with ΔE_b of this order will obviously also be valid for disordered alloys of a metal with a non-metal, and for a metal containing impurities (an alloy with a low concentration of one component); in the latter case the energy levels of the impurity atom, even if it is metallic, will have a local character. In this latter case the quantity must be multiplied by the impurity concentration, $C_i \ll 1$; this fact appears to be responsible for the high transition temperatures of some alloys. In the case of an alloy of a metal with a non-metal (or of a metal with impurities), if ΔE_b is to be sufficiently small there must occur close to the ground state some level due either to the fine structure or to the splitting due to the Stark effect in the crystalline electric field. In such a case ΔE_b may again be of order 0.1—1 eV. In conclusion we note that to get an alloy with high critical temperature we must optimize the value of ΔE_b, since as we increase ΔE_b the pre-exponential factor in the expression (4) increases but at the same time the magnitude of the negative exponent $1/\rho$ increases too. A more detailed discussion of the mechanism of superconductivity will be given elsewhere.

I am grateful to V. Z. Kresin for interesting discussions.

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Translated by A. J. Leggett
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CAPTURE OF NEGATIVE MUONS BY ATOMS IN A CHEMICAL COMPOUND

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Submitted to JETP editor December 26, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 48, 1197-1199 (April, 1965)

An investigation of the relative probabilities of capture of negative muons by atoms in a chemical compound is of independent interest, and also yields information needed for the interpretation of other experiments with muons, which by virtue of various circumstances, are carried out with targets that are chemical compounds. In this connection we have carried out measurements with several compounds, data on which are listed in Table I.

It is seen from the table that in our cases the Fermi-Teller Z-law[1] does not describe satisfactorily the experiment, as was noted in many earlier papers[2-8]. If we assume the results of the experiments in which the deviations from the Z-law exceed one mean-square error to be in disagreement with the law, then at the present the experimental situation, taking our data into account, is represented by Table II.

Table I

Compound	Ratio	Experiment	Z-law
LiCl	Cl/Li	7,2±1.1	5.12
CsCl	Cl/Cs	0,57±0.03	0.34
ZnO	O/Zn	0,450±0.013	0.28
ZnS	O/S	0,55±0.11	0.54
AlCu	Cu/Al	1.20±0.05	0.26

Table II

Character of compound	Number of experiments	Z-law satisfied	Z-law not satisfied
Alloys	6	2	4
Insulators	21	5	16
Carbon compounds	4	0	4
Total:	31	7	24

An analysis of the available data shows that, compared with the prediction of the Z-law, mesic atoms of the elements which have a relatively large electron-affinity energy are produced with some preference. This tendency is illustrated by Table III, which shows the experimental results systematized on the basis of electron affinity. In

Table III

Character of compound	Data from	Compound	Ratio	φ	Tendency
Alloys	[5]	AgZn	Ag/Zn	1.40±0,44	0
	[7]	CuAl	Cu/Al	1,58±0.16	+
		CuAl	Cu/Al	1,89±0.23	+
	[8]	CuAu	Cu/Au	1,45±0.14	+
	Our data	AgLi	Ag/Li	1,29±0,36	0
		CuAl	Cu/Al	4.55±0.20	+
Insulators	[3]	Al_2O_3	O/Al	1,63±0.22	+
		CaS	S/Ca	1,00±0.25	0
	[4]	P_2O_5	O/P	2.03±0.22	+
		SiO_2	O/Si	2.26±0.15	+
		Al_2O_3	O/Al	2.50±0.22	+
		KOH	O/K	5.23±0.96	+
		KHF_2	F/K	1,79±0.25	+
	[5]	LiI	I/Li	0,89±0.11	0
	[6]	PbF_2	F/Pb	0.95±0.14	0
	[7]	BiF_3	F/Bi	1,95±0.19	+
		UF_4	F/U	1.68±0.17	+
	[8]	CuS	Cu/S	1.04±0.10	0
		Sb_2S_3	S/Sb	1.30±0.08	+
		PbS	S/Pb	1,79±0.22	+
		CuO	Cu/O	1,70±0.14	+
		Sb_2O_3	Sb/O	0,44±0.02	—
		PbO	O/Pb	2,24±0.25	+
	Our data	LiCl	Cl/Li	1.41±0.22	+
		CsCl	Cl/Cs	1.68±0.09	+
		ZnO	O/Zn	1,51±0,05	+
		ZnS	O/S	1.02±0.20	0
Carbon compounds		$C_2O_2H_8$	O/C	0,49±0.06	—
	[2]	$C_6H_4Cl_2$—I	Cl/C	0.47±0,04	—
		$C_6H_4Cl_2$—II	Cl/C	0.57±0.05	—
	[4]	CCl_4	Cl/C	0,36±0.07	—